
Welcome

Welcome to Camerino!

The conference organizers, together with the University of Camerino and all the institutional sponsors of the international XAFS 14 conference are proud to have you all again in Italy, site of the first international conference on EXAFS and Near Edge structure held in Frascati, 1982, after the initial weekend meeting taking place at Daresbury in 1981.

After more than three decades, the world, and science of course, changed very much. The x-ray absorption spectroscopy (XAS) transformed from a “new” and sometimes misused technique to a more mature tool for deeper and deeper investigations of structural and electronic properties of matter. The potential of this technique remains now particularly high and new perspectives are opened by advances in experimental and theoretical methods and by new radiation sources.

The continuous interest in developing and using XAS is clearly shown by the success of the XAFS conference series and by this conference in particular, with about 500 participants from all over the world regularly registered, probably the largest participation ever recorded for this event. An innovative format of the conference containing symposia on specific topics of large interest, the presence of numerous excellent invited speakers, and the extremely high number of first-class contributed abstracts, guarantee a truly interesting scientific program which we are proud of.

The choice of Camerino as a XAFS conference site deserves also a few lines of comments. Camerino is a quiet “hidden” historical town, outside of the usual touristic routes in Italy, which certainly deserves the journey, as you may soon appreciate. Being one of the oldest Universities in Italy and Europe, it hosted also, since the 70s, several researchers working around the exploitation of synchrotron radiation of the ADONE storage ring in Frascati. The XAS group in Camerino, in charge of organizing this conference, grew about 20 years ago around this original seed. In recent times, the University of Camerino followed the general negative trend related to the decrease of resources devoted to basic research and to the educational system, but both a high-level scientific and teaching activities still stand with about 10000 students attending various courses in different fields. You will see, looking at the good University infrastructures and experienced personnel, at the wonderful landscapes and old monuments, tasting the genuine food and meeting this wonderful people that it is worthwhile to keep a strong scientific tradition in this place.

The Marche region around Camerino offers a variety of opportunities for tourism ranging from the seaside to the hills and mountains of the interior, with many nice historical towns. This is a lively region that has developed a system of small to medium enterprises featuring a particularly high capacity for creativity in fashion and manufacturing ranging from clothing to home appliances, without forgetting the need of a high-level educational system.

We are confident that you will appreciate the nice and friendly environment of this conference, that can stimulate many occasions of fruitful meeting and conversations among scientists all day long and while attending pleasant and interesting social events.

We hereby welcome you to an exciting conference that we hope you will all remember at the same time as fruitful and pleasant.

On behalf of the Organizing Committee

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Chairman of the Conference

Chairman of the conference

Andrea Di Cicco

Co-chair

Adriano Filipponi

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MONDAY 27

Location: Benedetto XIII

8.30 Conference opening

9.00/10.30 Plenary session M1

9.00 Sarma D. D.

EXAFS and NEXAFS studies of strongly correlated electron systems

9.45 Kotani Akio

Theoretical and experimental study of high-magnetic-field XMCD spectra at the $L_{2,3}$ absorption edges of mixed-valence rare-earth compounds

11.00/13.00 Symposium S1

Electronic correlations, corehole interaction and relaxation effects in x-ray absorption spectra

11.00 Kruger Peter

Multiplet couplings and band structure in $L_{2,3}$ -edge absorption through multi-channel multiple scattering theory

11.25 Taranukhina Anna

Multichannel Green's function multiple scattering calculations of x-ray absorption

11.50 Ebert Hubert

Theoretical description of X-ray absorption in correlated magnetic solids

12.15 Ikeno Hidekazu

Ab-initio CI calculations for 3d transition metal $L_{2,3}$ x-ray absorption spectra

12.40 Shirley Eric

Exotic effects in near-edge spectra

11.30/13.30 Poster Session PS1

15.30/17.30 Location: Ducal Palace

■ P1.1 Material Science I Sala La Muta

15.30 Wei Shiqiang

Experimental and theoretical investigations on ferromagnetic nature of dilute magnetic semiconductors

15.50 Lawniczak-Jablonska Krystyna

The influence of high temperature annealing procedures on the location of Mn inside the GaAs matrix

16.10 Ruffoni Matthew

Measuring strain at the atomic-scale with Differential X-ray Absorption Spectroscopy

16.30 Yalovega Galina

Fluorinated single-walled carbon nanotubes: X-ray absorption and DFT analysis

16.45 Pedio Maddalena

Investigation of C K-edge of differently sp-hybridized systems

17.00 Ouvrard Guy

In operando characterization of lithium battery materials

17.15 Arcon Iztok

In situ XAS studies of new cathode materials for high energy Li-ion batteries

■ P1.2 Disordered Systems Allara e Grosso

15.30 Ferlat Guillaume

MD-XAS studies of glasses and liquids: from weakly to highly disordered cases

15.50 Schnohr Claudia

Amorphous phase structure and vibrational anisotropy in the III-V semiconductor InP

16.10 Coppari Federica

Combined EXAFS and Raman high-pressure studies of amorphous Ge and SiGe alloys

16.30 Lahiri Debduitta

Structural understanding of the preferential glass-formation-ability in multi-component bulk metallic glass, using XAFS

16.45 Kolobov Alex

EXAFS study of the local structure of liquid

Ge₂Sb₂Te₅ (GST)

17.00 Spezia Riccardo

Molecular dynamics to rationalize EXAFS experiments: a dynamical model explaining hydration behaviour across the lanthanoids(III) series

17.15 Migliorati Valentina

Ion hydration in high-density water

■ P1.3 Instrumentation Aula Aranjo Ruiz

15.30 Frenkel Anatoly

Combined XAFS/XRD instrument at the X18A beamline at NSLS for in situ, time-resolved catalysis research

15.50 Fonda Emiliano

First results at SAMBA the SOLEIL hard x-ray beamline for EXAFS and QEXAFS experiments

16.10 Kleimenov Evgueni

HERFD XAS / RIXS spectrometer

16.30 Rocca Francesco

Nano-scale X-ray absorption spectroscopy using XEOL-SNOM detection mode

16.45 Silversmit Geert

Polycapillary based π -XAS and confocal π -XANES at a bending magnet source of the ESRF

17.00 Marcelli Augusto

Time-resolved simultaneous spectroscopies as a probe of physical-chemical processes

17.15 Zhang Ke

Very sensitive X-ray fluorescence analyzer detector

■ P1.4 Theory I Aula Betti

15.30 Fujikawa Takashi

Relativistic many-body XMCD theory including core degenerate effects

15.50 Harada Isao

Theory of XAS and XMCD for field-controlled valence mixed states in RE compounds

16.10 Hatada Keisuke

Full potential multiple scattering for core electron spectroscopies

16.30 Joly Yves

Self-consistency, Hubbard, spin-orbit and other advances in the FDMNES code to simulate XANES and RXD experiments

16.50 Sébilleau Didier

On the convergence of the multiple scattering series

17.10 Gougoussis Christos

Parameter free calculations of K-edge XAS in solids: theory and applications

18.00/20.00 Location: Ducal Palace

■ P2.1 Nano structures I Sala La Muta

18.00 Bianconi Antonio

Probing fast quantum lattice and charge critical fluctuations by XANES and EXAFS

18.30 Soo Yun-Liang

Studies of long-range-order and short-range-order structures in zirconia nanocrystals using TEM, XRD, and EXAFS

18.45 Carta Daniela

An X-ray absorption study of the inversion degree in ferrite nanocrystals

MFe₂O₄ (M = Mn, Co, Ni)

19.00 Dubiel Manfred

Temperature dependence of EXAFS cumulants of Ag nanoparticles in glasses

19.15 Requejo Felix

Structural and electronic characterization of Fe₂O₃ capped Au nanoparticles

Charge effects on Au core induced by the Fe-oxide shell.

19.30 Bitter Harry

Structure performance relations in nano-sized Ti-doped sodium-alanate for hydrogen storage

19.45 Maurizio Chiara

Ag-for-Na ion-exchanged waveguides:

correlation between the Ag site and the photoluminescence emission.

■ P2.2 Extreme conditions Allara e Grosso

18.00 Itié Jean-Paul

High pressure x-ray absorption spectroscopy: energy dispersive versus classical set-up

18.20 Baudalet François

Magnetism and structure under extreme condition

18.40 Pellicer-Porres Julio

X-ray absorption study of CuGaO₂ and CuAlO₂ delafossites under high pressure

19.00 Aquilanti Giuliana

Melting in the diamond anvil cell using energy dispersive XAS

19.15 Ramos Aline

Pressure induced metal-insulator transition in LaMnO₃

19.30 Pylkkänen Tuomas

High-pressure ices VI-VIII studied with x-ray Raman scattering

19.45 Peyrusse Olivier

K-edge absorption spectra in Warm Dense Matter

■ P2.3 Chemistry Aula Aranjo Ruiz

18.00 Frank Patrick

The XAS model of dissolved Cu(II) and its significance to biological electron transfer

18.30 Giorgetti Marco

EXAFS and XANES Simulations of Fe/Co hexacyanoferrate spectra by GNXAS and MXAN

18.45 Tenderholt Adam

Sulfur K-edge x-ray absorption spectroscopy and density functional theory calculations on molybdenum tris(dithiolene) complexes: XAS as a probe of electronic and geometric structures

19.00 Provost Karine

Coupling CP-MD simulations and x-ray absorption spectroscopy: exploring the structure of oxaliplatin in aqueous solution.

19.15 Jalilehvand Farideh

Cadmium(II) complex formation with cysteine, penicillamine and glutathione in aqueous solution and solid state

19.30 Miedema Piter

2p x-ray absorption of iron and cobalt-phthalocyanines

19.45 Alonso Mori Roberto

Electronic structure of sulfur studied by x-ray absorption and emission spectroscopy

■ P2.4 Theory II Aula Betti

18.00 Bordage Amélie

V³⁺ incorporation in garnet: experiments and calculations

18.20 Benfatto Maurizio

The MXAN analysis of the sulphur K-edge XANES of cysteine

18.40 Cabaret Delphine

The use of band structure pseudopotential DFT codes for the calculation of XANES spectra: recent applications in biological materials, minerals and glasses

19.00 Juhin Amélie

From local to itinerant model of X-ray Absorption: application to the calculation of X-ray Natural Linear Dichroism

19.20 Mijovilovich Ana

Relaxed final state DFT simulations of sulfur K-edge XANES and microXANES for catalysis.

19.40 Vedrinskii Rostislav

A new interpretation of $L_{2,3}$ X-ray absorption in rutile TiO₂

TUESDAY 28

Location: Benedetto XIII

8.30/10.30 Plenary session M2

8.30 Wernet Philippe

X-ray absorption spectroscopy for probing bonding, structure and ultrafast dynamics in water

9.00 Bergmann Uwe

Advanced hard X-ray spectroscopy - recent results on water and 3d transition metal systems

9.30 Falcone Roger

Time-Resolved X-Ray Absorption in materials in extreme conditions

10.00 Lee Richard

Perspective for High Energy Density Studies using X-ray Free Electron Lasers

11.00/13.00 Symposium S2

Advances in ultrafast spectroscopy using present and next generation x-ray sources

11.00 Chergui Majed

Ultrafast X-ray absorption spectroscopy of molecular systems in solution

11.25 Aziz Emad

Probing ultra-fast dynamics in aqueous solutions using soft x-ray techniques

11.50 Milne Chris

Ultrafast time-resolved x-ray absorption spectroscopy: watching atoms dance

12.15 Huse Nils

Direct observation of transient ligand-field changes in transition metal complexes via time-resolved soft x-ray spectroscopy

12.40 Young Linda

Laser-induced x-ray transparency in free atoms and molecules

11.30/13.30 Poster Session (continuation) PS1

15.30/17.30 Location: Ducal Palace

■ P3.1 Nano structures II Sala La Muta

15.30 d'Acapito Francesco

The Mn site in Mn-doped-As nanowires: an EXAFS study

15.50 Saintavit Philippe

Magnetic memory of a single-molecule quantum magnet wired to a gold surface

16.10 Holub-Krappe Elizabeta

Correlation of magnetism and structure for ultra thin Au/Co/Au films: evidence for magnetoelastic effects

16.30 Erenburg Simon

Microstructure of quantum dots ensembles by EXAFS spectroscopy

16.45 Heigl Franziskus

XANES and photoluminescence studies of crystalline Ge and GeO₂ nanowires

17.00 Persson Andreas

On the spin reorientation of ordered magnetic nano-dot arrays: Pt/Co/Pt versus Au/Co/Au

17.15 Miyanaga Takafumi

Local structural change under antiferro and ferromagnetic transition in FeRh alloy

■ P3.2 Surface and Magnetism Allara e Grosso

15.30 Amemiya Kenta

Depth profiling of magnetic and atomic structures of ultrathin films by depth-resolved XMCD and XAFS techniques with a sub-nm depth resolution

16.00 Matsui Fumihiko

Resolving subsurface magnetism at atomic scale by diffraction spectroscopy

16.15 Abe Hitoshi

Surface antiferromagnetic coupling of Fe/Cu(001) induced by NO adsorption studied by means of depth-resolved XMCD method

16.30 Robert Frahm

In-situ investigation of Bi thin film condensation by surface sensitive X-ray absorption spectroscopy at cryogenic temperatures

16.45 López-Flores Víctor

Development of ReflEXAFS data analysis for deeper surface structure studies

17.00 Jiang De-Tong

Structural and electronic properties of tetracene thin films

17.15 Nefedov Alexei

NEXAFS characterization of the self-limiting monolayer growth of terephthalic acid on rutile TiO₂ (110)

■ P3.3 Time-resolved studies Aula Arango Ruiz

15.30 Allen Patrick

Application of single shot dispersive XAFS to study picosecond materials dynamics

15.50 Stern Edward

Picosecond time resolved response of the Ge lattice after femtosecond pulsed laser excitation

16.10 Fons Paul

Sub-nanosecond XAFS-based observations of optical switching in the phase-change alloy Ge₂Sb₂Te₅

16.30 Dau Holger

Photosynthetic water oxidation driven by Laser flashes and tracked by x-ray spectroscopy

16.50 Singh Jagdeep

In situ space and time resolved x-ray absorption spectroscopy: dynamic structure of platinum during kinetic oscillations of CO oxidation

17.10 van der Veen Renske

Retrieving photochemically active structures by time-resolved EXAFS spectroscopy

■ P3.4 Theory III Aula Betti

15.30 Da Pieve Fabiana

Spin polarized resonant photoemission from Fe

15.50 Di Matteo Sergio

Orbital and charge ordering detected by resonant x-ray scattering in strongly correlated electron systems.

16.10 Soininen Juha

X-ray Raman scattering: role of first-principles theory in the analysis

16.30 Suljoti Edlira

Subtleties of electron correlation in La 4d resonances

16.50 Rehr John

Calculation of optical constants and related quantities from optical to x-ray frequencies

17.10 Gordon Robert

Natural dichroism in the near-edge of cubic systems

18.00/20.00 Location: Ducal Palace

■ P4.1 Material Science II Sala La Muta

18.00 Azevedo Gustavo

Local structure study of RM_{1-x}O₃ R=Bi, Gd, Pr multiferroics with EXAFS

18.20 Meneghini Carlo

The local nature of 'disorder' in r₂FeMoO₆ double perovskites

18.40 Woick Joseph

Effect of strain on the local atomic structure of LaSrCoO₃

19.00 Menushenkov Alexey

Double-well potential for oxygen ion vibrations in Nd_{1-x}Ce_xCuO_{4-δ}

19.15 Nakajima Nobuo

A UV-induced uniaxial motion of body-centered titanium ions in perovskite titanates

19.30 Andreasson Pererik

Localizing oxygen vacancies in SrTiO₃ by 3d-impurities

19.45 Jiménez-Villacorta Félix

Local environment and electronic structure of Fe at the interface in magnetic granular iron-silicon nitride systems

■ P4.2 Biology I Allara e Grosso

18.00 Arcovito Alessandro

Structure and dynamics of hemeprotein using x-ray absorption spectroscopy

18.20 Hedman Britt

X-ray Absorption Spectroscopy edge studies of biological models and enzymes

18.40 Meyer-Klaucke Wolfram

Geometric and electronic structure of [Fe]-hydrogenase active site

19.00 Feiters Martin

Anion binding in biological systems

19.15 Giachini Lisa

Synergic approach to xafs analysis for the identification of unknown metal-sites in proteins

19.30 Stellato Francesco

Zinc binding effect on Cu coordination mode in prion protein octa-repeat subdomain

19.45 Nazarenko Elena

Regulatory site structure of Fe-metallated R protein: Quantitative XANES analysis

■ P4.3 Data analysis I Aula Arango Ruiz

18.00 Newville Matthew

Improvements in modeling EXAFS with many-pole self-energy and Feff8.5

18.20 Kuzmin Alexei

Quantum Mechanics-Classical Molecular Dynamics approach to EXAFS

18.40 D'Angelo Paola

Combined techniques in the structural investigation of ions in solution: the symbiosis XAS-Molecular Dynamics

19.00 Krayzman Victor

Simultaneous RMC fit of the total scattering and EXAFS data

19.20 Lenoir Thomas

Determining the number of species from multi-component XAFS data

19.40 Booth Corwin

Conventional error analysis in conventional EXAFS analysis: lessons from Nyquist and Fourier

■ P4.4 Related Phenomena Aula Betti

18.00 Glatzel Pieter

Chemical information in hard X-ray photon-in photon-out spectroscopy

18.20 Subias Gloria

Resonant x-ray scattering in 3d-transition-metal oxides: anisotropy and charge orderings

18.40 Ishii Masashi

Study of double-photon interaction for a single atom x-ray absorption spectroscopy

19.00 Schlappa Justine

Collective spin-excitations in a quantum spin ladder probed by high-resolution Resonant Inelastic X-ray Scattering

19.15 Herrero-Martin Javier

RXS to study the charge/orbital ordering in mixed valence transition metal oxides far from half doping

19.30 Zhou Kejin

The Metal-Insulator-Transition in VO₂ investigated by Resonant Inelastic X-ray Scattering

19.45 Vanko Gyorgy

Novel insights to cobalt 1s pre-edges with resonant X-ray emission spectroscopy

WEDNESDAY 29

Location: Benedetto XIII

8.30/10.30

Plenary session M3

8.30

Baberschke Klaus

Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces: an XAFS and XMCD study

9.15

Hodgson Keith

Current and next generation synchrotron light sources enabling discovery in structural biology

Robert Pettifer memorial

10.00

Collins Steve

Borrmann Spectroscopy

11.00/13.00

Symposium S3

Complementarity of XAS and diffraction techniques

11.00

Billinge Simon

Total scattering and the atomic pair distribution function: an alternative route to the local and intermediate structure

11.25

Bowron Daniel

Comprehensive three dimensional models of structurally disordered systems capturing the local and bulk structure in an experimentally consistent manner

11.50

Renevier Hubert

Strain and composition of semiconductor nanostructures by grazing incidence Diffraction Anomalous Fine Structure spectroscopy

12.15

Strange Richard

Crystallography with online optical and X-ray absorption spectroscopies demonstrates an ordered mechanism in copper nitrite reductase

12.40

Streltsov Victor

Structural studies (XAS, DFT, XRD) of Amyloid-beta metal binding and oligomer formation in Alzheimer's Disease

11.30/13.30

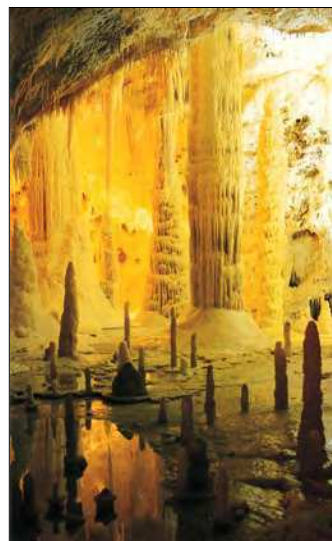
Poster Session PS2

14.30

Social events

Conference Excursion:

- Option A:
Frasassi caves, experience an incredible upside down world
- Option B:
Assisi, a journey through art and spirituality



THURSDAY 30

Location: Benedetto XIII

8.30/10.30 Plenary session M4

8.30 Iwasawa Yasuhiro

Real time XAFS for structural kinetics/dynamics of 2D and nanoparticle catalyses

9.15 van Bokhoven Jeroen

Studying functioning catalysts with X-rays

10.00 Grunwaldt Jan-Dierk

Shining X-rays on catalysts at work

11.00/13.00 Special session S4

Catalysis and Energy Sciences: From EXAFS to QEXAFS and Beyond

11.00 Frahm Ronald

QEXAFS: Technique, science, future

11.25 Asakura Kiyotaka

Combined in situ analysis of

Ni₂P/MCM-41 under

hydrodesulfurization conditions: simultaneous observation of QXAFS and FTIR

11.50 Lillerud Karl Petter

Combined EXAFS and XRPD in understanding the structure and the reactivity of metal organic frameworks (MOFs) upon solvent removal and molecule coordination

12.15 Segre Carlo

Removal of oxygen adsorbates on Pt/C and PtNi(1:1)/C alloy nanoparticle catalysts for the oxygen reduction reaction in PEMFCs

12.40 Witkowska Agnieszka

Nano-structured Pt-based catalysts for fuel cell applications probed by in situ XAFS

11.30/13.30 Poster Session (continuation) PS2

15.30/17.30 Location: Ducal Palace

■ P5.1 Catalysis I Sala La Muta

15.30 Bauer Matthias

Iron-catalysis through the XAS-eye: structures, mechanisms and beyond

15.50 Stötzel Jan

Reduction and re-oxidation of Cu/Al₂O₃ catalysts investigated with quick scanning XANES and EXAFS

16.10 Mettu Anilkumar

In situ X-ray absorption study of CuO-CeO₂/Al₂O₃ catalysts in the total oxidation of propane

16.30 La Fontaine Camille

When SOLEIL sheds light on catalysis: methods and results

16.45 Ronning Magnus

Complimentary in situ characterisation techniques at realistic working conditions for the Fischer-Tropsch synthesis

17.00 Lamberti Carlo

Local structure of CPO-27-Ni metallorganic framework upon dehydration and coordination of ligand molecules (NO, CO and N₂): comparison between experiments and ab initio periodic calculations

17.15 Nchari Luanga

Towards a deeper mechanistic understanding of the Soai reaction: XAS studies of diisopropylzinc as a function of solution environment

■ P5.2 Magnetic dichroism (XMCD) Allara e Gr.

15.30 Antoniak Carolin

Correlation of magnetic moments and local structure of FePt nanoparticles

15.50 Frank De Groot

The accuracy of the XMCD effective spin sum rule

16.10 Sipr Ondrej

Influence of the magnetic dipole T₂ term on the XMCD spectra of clusters

16.30 Matsuda Yasuhiro

XMCD spectroscopy on valence fluctuating and

heavy fermion compounds in very high magnetic fields up to 40 T

16.50 Yokoyama Toshihiko

Self-assembled Co nanorods grown on Cu(110)-(2x3)N studied by XMCD

17.10 Kawamura Naomi

X-ray magnetic circular dichroism at Os L-edge under multiple extreme conditions in SmOs₂Sb₁₂

■ P5.3 Environmental studies Aula A. Ruiz

15.30 Ravel Bruce

EXAFS studies of catalytic DNA sensors for mercury contamination of water

15.50 Flank Anne-Marie

Experimental evidence of six-fold oxygen coordination for phosphorus

16.10 Cibin Giannantonio

A combined XANES and SR-XRF study of the airborne dust preserved in Antarctic deep ice cores across a climate transition

16.30 Noren Katarina

Speciation of zinc in ash from combustion of biomass and municipal solid waste

16.50 Giuli Gabriele

Tektites and microtektites Fe oxidation state

17.10 Testemale Denis

The use of x-ray absorption spectroscopy in hydrothermal geochemistry: transport and speciation of dissolved metals

■ P5.4 Gas phase systems Aula Betti

15.30 Lau Tobias

X-ray spectroscopy in a linear ion trap: size-selected transition metal, doped silicon, and protonated water clusters

15.50 Mazza Tommaso

Structure and hydrogen uptake of free titanium clusters in a supersonic beam probed by combined XAS and multicoincidence technique

16.10 Kivimäki Antti

UV-visible emission as a probe of core excitations applied to small molecules

16.30 Piseri Paolo

NEXAFS characterization of sp-rich carbon clusters in the gas phase

16.50 Zhong Jun

Interaction mechanism of gas-SWNTs probed by XANES

17.10 Kodre Alojz

Atomic absorption background: K edge of iodine and L edges of cesium

18.00/20.00 Location: Ducal Palace

■ P6.1 Catalysis II Sala La Muta

18.00 Kimura Masao

In situ observation of redox reactions of Pd/Sr-Fe-O for exhaust emission catalyst

18.20 Tromp Moniek

Development of X-ray emission spectroscopy in single site catalysis

18.40 Tew Min Wei

Distinguishing interstitial and surface hydrogen in and on nano-sized palladium catalysts using Pd K and L_{2,3} edges X-ray absorption spectroscopy

19.00 Piovano Andrea

In situ electrochemical oxygen intercalation inside SrFeO_{2.5} investigated by time resolved EXAFS and XANES: a comparison with the SrCoO_{2.5} system

19.15 Alayon Evalyn Mae

In situ XAS probes partially oxidized platinum generating high activity for CO oxidation

19.30 Matsumura Daiju

Dynamic structural change of Pd/LaFeO₃ nanoparticles under redox atmosphere and CO-NO catalytic reaction studied by dispersive XAFS

19.45 Agostini Giovanni

Combining EXAFS, TEM, and chemisorption in determining the particle size and dispersion of

fcc-metal nanoparticles deposited on high surface area supports: a general model

■ P6.2 Biology II Allara e Grosso

18.00 Lay Peter

Biomedical applications of X-ray absorption and vibrational spectroscopic microscopies in bioinorganic chemistry

18.20 Bunker Bruce

XAFS study of gold adsorption to Bacillus subtilis and Pseudomonas putida bacterial cells

18.40 Sarangi Ritimukta

Geometric and electronic structures of Ni(II) and methyl-Ni(III) intermediates of methyl-CoM reductase

19.00 Soldatov Mikhail

Local atomic and electronic structure of novel experimental anticancer drugs

19.15 Ko Jun Young

Synchrotron X-ray microscopy and spectroscopy analysis of Iron in hemochromatosis liver and intestines

19.30 Quinn Paul

X-ray absorption studies of tissue surrounding cobalt-chromium-molybdenum orthopedic implants

19.45 Barrea Raul

X-ray imaging and Zn K edge microXANES shows Clotiquinol and Disulfiram activity in prostate cancer in vivo

■ P6.3 Data analysis II Aula Arango Ruiz

18.00 Purans Juris

EXAFS measurements with femtometer accuracy: isotopic effect in the first, second, and third coordination shells of germanium

18.20 Fornasini Paolo

Negative thermal expansion and local dynamics

18.40 Chantler Christopher

Accurate measurement and physical insight: latest results of the x-ray extended range technique for high accuracy absolute XAFS

19.00 Babanov Yuri

Variable angle XAFS study of multilayer nanoheterostructures: Determination of selective concentration profile and depth-dependent partial atomic distributions

19.15 Yamamoto Takashi

Unified concept on the chemical variation of pre-edge structure

19.30 Smolentsev Grigory

Structure of reaction intermediates refined by quantitative analysis of time-resolved XANES spectra

19.45 Rodolakis Fanny

Mott transition in V₂O₅: a high resolution X-ray absorption spectroscopy study

■ P6.4 Actinides and nuclear waste Aula Betti

18.00 Hennig Christoph

Double-electron excitation in absorption spectra of actinides

18.20 Reich Tobias

EXAFS study of Np(V) sorption onto gibbsite (γ-Al(OH)₃)

18.40 Denecke Melissa

Spatially resolved XRF, XAFS, XRD, STXM and IR investigation of U-rich natural analogue clay

19.00 Rothe Jörg

A combined XAFS, LIBD and ESI TOF-MS study on the formation of polynuclear An(IV) complexes and colloids

19.20 Badaut Vivien

Selenite retention by siderite: In situ and ex situ XAFS experiments

19.40 Brendebach Boris

Sulfur incorporation in high level nuclear waste glasses: a S K-edge XAFS investigation

20.30/22.30 Social Dinner

FRIDAY 31

Location: Benedetto XIII

8.30/10.30

Plenary session M5

8.30

Manceau Alain

X-ray views of the defect structure and chemistry of environmental nanoparticles

9.15

Wogelius Roy

X-ray absorption spectroscopy and environmental mineralogy

10.00

Den Auwer Christophe

The diversity of actinide polyhedra from aqueous to complex molecular systems

11.00/11.45

IXAS Award session

11.00

IXAS Young Scientist Awards

(Dale Sayers and Farrel Lytle Prizes)

11.15

IXAS Outstanding Scientist Award

(Ed Stern Prize)

11.45/12.30

IXAS session and conclusion

11.45

International X-ray Absorption Society affairs

12.00

Concluding remarks

12.15

Presentation of XAFS15, 2012

- City of Camerino -

UNICAM University Campus/Bus stop ~ 0.7 km

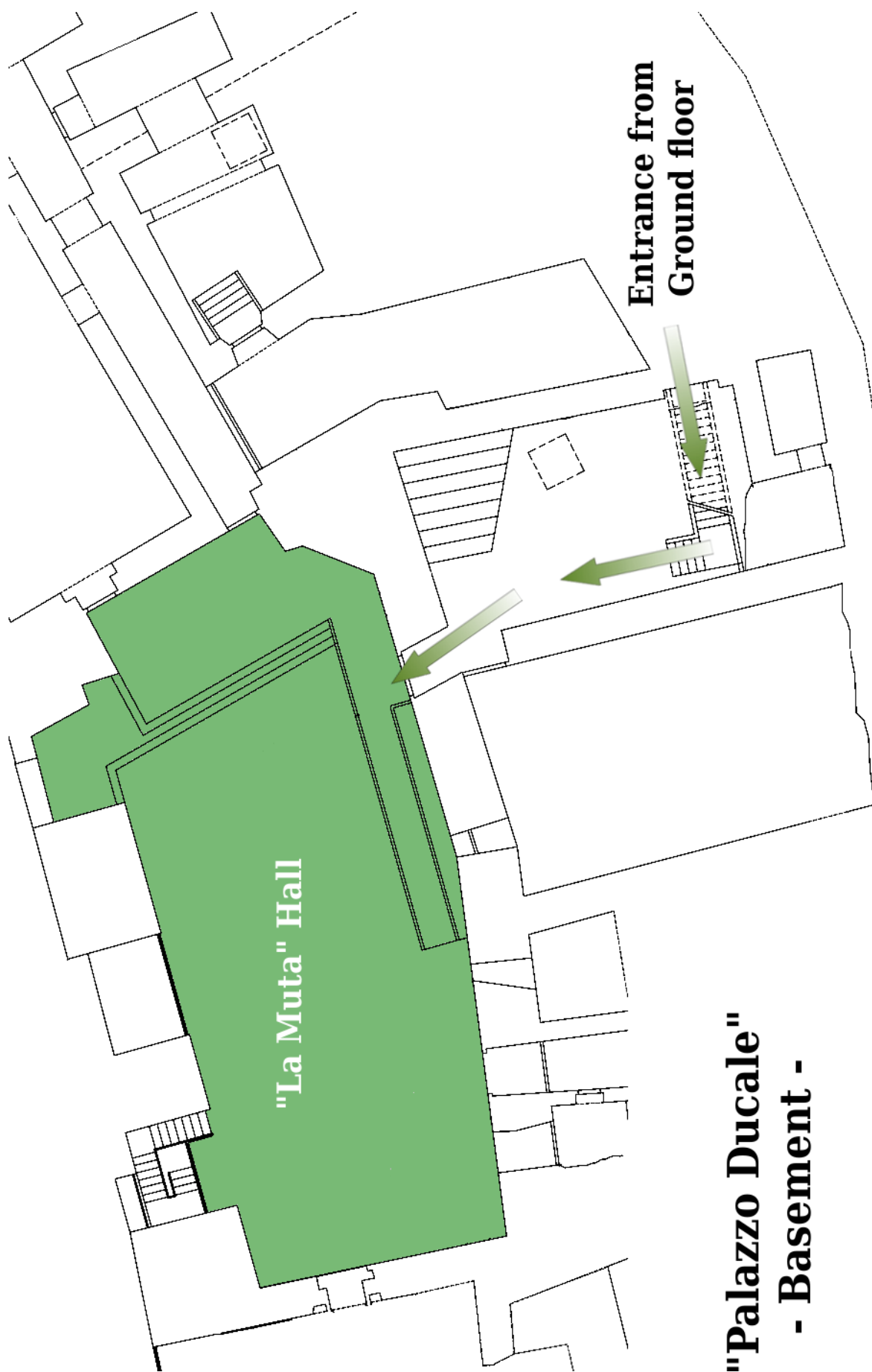
B&B Colle Ridente/Bus stop ~ 1.2 km

200 m



- 1 Canteen
- 2 "Mattei 2" college
- 3 Bus stop
- 4 "Fazzini" college
- 5 "D'Avack" college
- 6 Bus stop/Central Parking/Escalator for Piazza Cavour
- 7 Escalator for Central Parking/Bus Stop
- 8 Hotel Roma
- 9 Hotel I Duchi

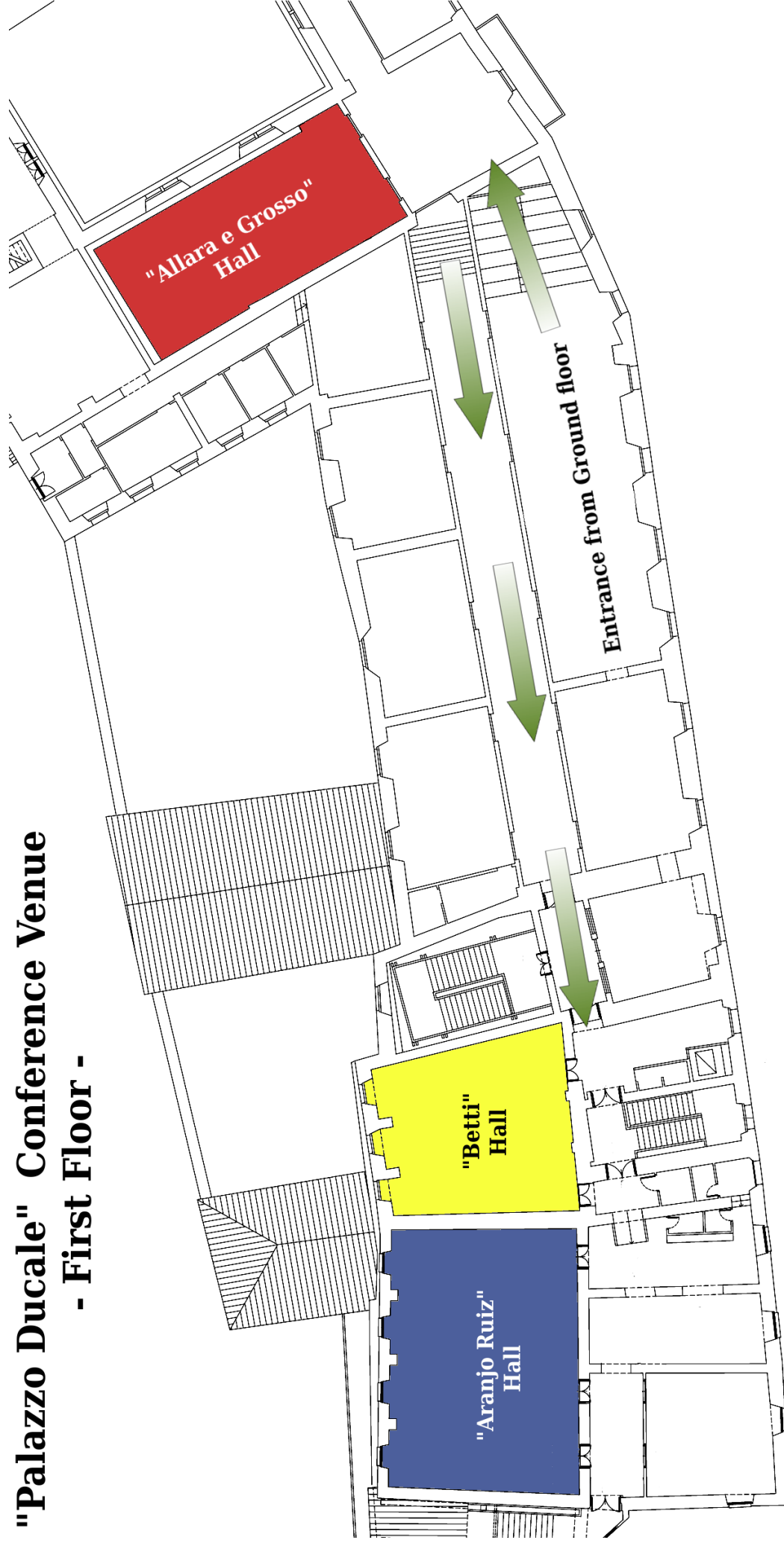
- A Benedetto XIII (Conference Venue)
- B Palazzo Ducale (Conference Venue)



"Palazzo Ducale"
- Basement -

"Palazzo Ducale" Conference Venue

- First Floor -



Conference venue and information

The plenary morning sessions and symposia will take place in the “Benedetto XIII” hall located in a wide area just near the cafeteria and some of the student accommodations. Parallel afternoon sessions will take place in historical halls (sala La Muta, Allara e Grosso, Arango Ruiz and Betti) in the old University buildings (Palazzo Ducale). Lecture halls are easily identified by a system of pathway signs and color coding. Useful maps are contained in this book.

Registration Desk

The registration desk will be located at the entrance of “Benedetto XIII” hall, and will be open on Sunday 13:00-23:00 and Monday to Friday 8:30-13:00.

An information desk will be available at the “Palazzo Ducale” at the entrance of the “La Muta” hall Monday to Friday 15:30-18:00.

Emergency phone number: (+39)-320-4278470

Guideline for speakers

For your presentations you have to use computer-based projection **only**, using PDF (Portable Document Format, preferred) or Powerpoint 2007 formats.

Overhead projections will be **not** available.

Files containing the presentations must be stored in the computers of the XAFS14 organization (running a Windows operating systems), used for projections, and use of your own laptop (or MAC) connected to the projector will be **not possible**.

It will be possible to transfer your files using common media (like USB memory sticks or CDROMs). Files have to be uploaded in our computers well before the beginning of the session.

Poster Sessions

The Poster Sessions will take place in the Benedetto XIII area, near the main hall for morning sessions and the canteen.

There will be two sessions:

- the first (PS1) from 11:30 to 13:30 (presence of authors required from 12:45 to 13:30) on Monday and Tuesday;
- the second (PS2) on Wednesday and Thursday from 11:30 am to 13:30 (presence of authors required from 12:45 to 13:30).

Posters have to be installed on Monday 10:30-11:30 (PS1) and on Wednesday 10:30-11:30 (PS2), removed by authors before Wednesday 10:30 (PS1) and before Friday 10:30 (PS2).

Posters not removed in due time by authors may be removed and destroyed by organization without prior notice.

Local Transportation

There is a regular bus service (Contram) which connects the main locations in Camerino area. A dedicated bus service will be available connecting the area of the University cafeteria (“Benedetto XIII”) with the city centre (“Palazzo Ducale”). This service will be running after lunch and dinner and will allow to reach University colleges where most of the participants are accommodated. Details about this service will be provided at the Conference desk.

Meals

Lunches and dinners for attendees will be served in the University cafeteria. Many good restaurants, pubs, bars, b&b and country-houses offering a fine selection of meals are available in the area. The canteen will be open:

-
- Monday-Friday 12:30-14:30,
 - Monday-Thursday 20:00-22:00.

Coffee breaks will be available 10:30-11:00 and 17:30-18:00 on the dates specified on the program. Breakfast for attendees hosted in Mattei, Fazzini and Campus colleges will be served in the University cafeteria. Attendees hosted at D'Avack have breakfast in the D'Avack cafeteria.

Social Events

Monday, 27 July 2009, 21:00

Concert at "Filippo Marchetti" historical theatre: "Nicola Piovani in Quintetto". Concert of Nicola Piovani, oscar-winning composer of the music to Roberto Benigni's Life is Beautiful.

Wednesday, 29 July 2009, 14:00

Conference Excursion:

- Frasassi caves, experience an incredible upside down world;
- Assisi, a journey through art and spirituality.

Wednesday, 29 July 2009, 21:30

Unicam Jazz Band concert. Free admission.

Thursday, 30 July 2009, 20:00

Social Dinner at "Palazzo Ducale": the social dinner will be held in the suggestive courtyard of Palazzo Ducale.

Saturday, 1 August 2009, 21:30

Concert at "Chiostro San Domenico": Esperanza Spalding World Tour 2009 concert.

Information about other events and concerts will be available at the Conference desk.

Exhibition

You are welcome to visit the exhibition stands during these days. Commercial exhibitors will be:

- Saint-Gobain Crystals;
- XIA - X-Ray Instrumentation Associates.

Starting from Monday, 27th, commercial and cultural heritage stands will be open at the Benedetto XIII entrance hall (morning sessions) and near the Sala La Muta (afternoon) at the Ducal Palace.

City Guide

Restaurants

- Ristorante I Duchi, Via V. Favorino 72, Tel. 0737-630440
- Ristorante Roma, Piazza Garibaldi 6, Tel. 0737-632592
- Ristorante La Rocca del Borgia, Piazzale G. Marconi 1, Tel. 0737-630338
- Ristorante-pub Noè, Largo Boccati, Tel. 0737-630874
- Ristorante-bar Dada Zen, Via XX Settembre, tel. 338-9631601

Pizzerias

- Pizzeria Apogeo, Via E. Corvino 11, Tel. 0737-636728
- Pizzeria Maga Magò, Via E. Betti 2, Tel. 0737-630827
- Pizzeria-ristorante Etoile (next to Mattei College), Via Le Mosse 68, Tel. 0737-630041

-
- Pizzeria-rosticceria La Saporita, Corso V. Emanuele, Tel. 0737-633080
 - Pizzeria Al solito posto (pizza take away), Corso V. Emanuele, Tel. 334-1848023
 - Pizzeria da Pasquale (pizza take away), Via Pieragostino 25, Tel. 0737-630183
 - Pizzeria Le Margherite (not far from Mattei College-Pizza take away), Tel. 0737-633092
 - Pizzeria Re, Via C. Lili 27, Tel. 0737-637133
 - Pizzeria Romana (pizza take away), Tel. 347-1968413

Kebabs

- Doner Kebab, Via C. Lili 36, Tel. 334-1487656
- Kebab, piazza Garibaldi

Pubs and Coffee Bars

- Pub Asterix, Piazza G. Garibaldi 20, Tel. 0737-630554
- Bar Caffè concerto, Corso V. Emanuele, Tel. 0737-630157
- Bar Centrale, Piazza Cavour 24, Tel. 0737-633044
- Bar Diana, Corso V.- Emanuele 55, Tel. 0737-632460
- Bar K2, Piazza Garibaldi 23, Tel. 0737 632505
- Bar Lili, Via Lili 22, Tel. 0737-630350
- Bar I duchi, Via V. Favorino 72, Tel. 0737-630440
- Bar D'Avack (ground floor D'Avack College), Via M. Muzio
- Caffè Ateneo (next to Mattei College), Via Le Mosse, Località Colle Paradiso

Useful Numbers

Post Office

- P.zza Umberto I, Tel. 0737-634811

Pharmacies

- Farmacia Cappello, Via Ridolfini 16, Tel. 0737 633016 - 633312
- Farmacia Centrale, Corso V. Emanuele 40, Tel. 0737-632511
- Farmacia Comunale, P. zza Umberto 16, Tel. 0737-633568

Hospital

- Asur n. 10, Loc. Caselle, Tel. 0737 6091(Switchboard), <http://www.asurzona10.marche.it/home.asp>

Health Emergency Number 118

Doctor in Duty free call 800-118013

C.R.I. Italian Red Cross

Via G. Leopardi 35, Tel. 0737-632838/632245

POLICE - Emergency number 113.

HIGHWAY POLICE - Via Le Mosse, Tel. 0737-630773.

CARABINIERI - Emergency number 112.

FIRE BRIGADE - Vigili del Fuoco - Emergency number 115, Loc. Caselle 1, Tel. 0737-632322.

Invited Speakers

Plenary sessions

Baberschke Klaus	Bergmann Uwe
Collins Steve	Den Auwer Christophe
Falcone Roger	Grunwaldt Jan-Dierk
Hodgson Keith	Iwasawa Yasuhiro
Kotani Akio	Lee Richard
Manceau Alain	Sarma D. D.
van Bokhoven Jeroen	Wernet Philippe
Wogelius Roy	

Symposia and special sessions

Aziz Emad	Billinge Simon
Bowron Daniel	Chergui Majed
Ebert Hubert	Ikeno Hidekazu
Kruger Peter	Lillerud Karl Petter
Milne Chris	Shirley Eric
Strange Richard	Witkowska Agnieszka
Young Linda	Frahm Ronald
Renevier Hubert	

Parallel sessions

Amemiya Kenta	Antoniak Carolin
Arcovito Alessandro	Azevedo Gustavo
Bianconi Antonio	Cabaret Delphine
Di Matteo Sergio	Ferlat Guillaume
Subias Gloria	Frank Patrick
Fujikawa Takashi	Hatada Keisuke
d'Acapito Francesco	Itié Jean-Paul
Joly Yves	Lau Tobias
Pellicer-Porres Julio	Rehr John
Wei Shiqiang	Sarangi Ritimukta
Sébilleau Didier	Soininen Juha
Fabiana Da Pieve	Glatzel Pieter
Schnohr Claudia	

Monday 27th July

M1: Plenary session M1

Location: “Benedetto XIII” Hall
Time: 9:00

EXAFS and NEXAFS studies of strongly correlated electron systems

D. D. Sarma¹

(1) Solid State and Structural Chemistry Unit Indian Institute of Science Bangalore 560012 India

Strongly correlated electron systems exhibit a wide spectrum of exciting properties including various electronic and magnetic phase transitions as a function of temperature, pressure and composition. Typically, such systems contain an element whose electronically/magnetically active orbitals have electron-electron interaction strengths sizable compared to the hopping interaction strengths with neighbouring sites. Over the last couple of decades, interest in such systems containing transition metal elements, particularly the 3d elements, has been renewed in view of all the diverse properties these exhibit, such as colossal and other types of magnetoresistivity, unusual superconductivity, multi-functionality including multi-ferroic properties. All such properties are largely controlled by competing energy scales of electron-electron Coulomb interactions leading to a tendency towards electron localization and hopping interaction strengths giving rise to delocalization; in several cases, the lattice degree of freedom is also believed to play an important role in determining the properties.

Various forms of high energy electron spectroscopy in general, and NEXAFS in particular, have contributed significantly to our understanding of such systems over the years. NEXAFS has been particularly useful in obtaining the local electronic structure information in conjunction with single impurity cluster calculations that incorporate many-body effects arising from the electron-electron interactions as well as local hopping effects. However, such analysis may prove to be limited in explaining spectral features in a class of strongly correlated systems. I shall discuss some of these issues in this talk.

EXAFS also has been relatively less utilised in the study of strongly correlated systems, though local structural effects are known to play important roles in controlling the physical properties of many such systems. I shall discuss applications of EXAFS in understanding the properties of such fascinating systems, such as colossal magnetoresistive systems and systems exhibiting metal-insulator transitions as a function of composition.

Location: “Benedetto XIII” Hall
Time: 9:45

Theoretical and experimental study of high-magnetic-field XMCD spectra at the $L_{2,3}$ absorption edges of mixed-valence rare-earth compounds

Akio Kotani^{1,2}, Yasuhiro H. Matsuda³, and Hiroyuki Nojiri⁴

(1) Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

(2) RIKEN Harima Institute, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

(3) Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan

(4) Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

XMCD spectra at the $L_{2,3}$ edges of mixed-valence Ce and Yb compounds in high magnetic fields and at zero temperature are calculated with a new theoretical framework proposed recently by Kotani[1,2]. The Zeeman splitting of 4f states, the mixed-valence character of 4f states, and the 4f-5d exchange interaction are incorporated into a single impurity Anderson model.

New XMCD experiments in high magnetic fields up to “40 T” are carried out for mixed-valence Eu and Yb compounds by using a miniature pulsed magnet, which was developed recently by Matsuda et al.[3] The XMCD data are taken at 5 K by the transmission measurements for right and left circularly polarized X-rays at BL39XU in SPring-8.

After presenting some typical results of calculated and measured XMCD spectra, we direct our attention to the XMCD spectra at the field-induced valence transition of YbInCu_4 around 32 T, and compare the theoretical and experimental results.

In the present talk, more weight is laid on theoretical aspects than on experimental ones, but more details on experiments are also reported in this conference[4].

[1] A. Kotani, Phys. Rev. B 78, 195115 (2008) .

[2] A. Kotani, presented at 21st International Conference on X-Ray and Inner-Shell Processes, 2008 (to be published in Eur. Phys. J. ST).

[3] Y. H. Matsuda et al., J. Phys. Soc. Jpn. 76, 034702 (2007).

[4] Y. H. Matsuda et al., presented in this conference.

S1: Electronic correlations, core-hole interaction and relaxation effects in x-ray absorption spectra

Location: “Benedetto XIII” Hall
Time: 11:00

Multiplet couplings and band structure in $L_{2,3}$ -edge absorption through multi-channel multiple scattering theory

Peter Krüger¹

(1) ICB, UMR 5209 Université de Bourgogne - CNRS, BP 47870, F-21078 Dijon, France

Using the recently developed multi-channel multiple scattering (MCMS) method [1] we have calculated the x-ray absorption spectra (XAS) at the $L_{2,3}$ -edge of transition metal compounds. The MCMS method is a fully ab initio approach which combines an accurate description of the band structure of the material with a correlated particle-hole wave function on the absorber atom. The latter allows one to take account of the strong configuration mixing that takes place in the absorption final state wave function. Good agreement with experiment is achieved for all $3d^0$ compounds. In the case of titanium oxides, the differences observed in the $L_{2,3}$ -edge XAS between the various crystallographic phases (perovskite SrTiO_3 , rutile TiO_2 , anatase TiO_2) are commonly attributed to changes in local properties such as point symmetry or metal-ligand bonding. We challenge this local picture by showing that the differences are due to long range band structure effects [2] which are impossible to reproduce with metal-ligand (TiO_6) cluster models. Finally we study the x-ray magnetic dichroism in the transition metal $L_{2,3}$ -edge absorption using MCMS theory for the photo-electron-hole interaction while treating the exchange interaction between photo- and valence electrons on a mean field level. The results are compared with one-electron band structure and atomic multiplet calculations.

[1] P. Krüger and C. R. Natoli, Phys. Rev. B 70, 245120 (2004).

[2] P. Krüger, to be submitted.

Location: “Benedetto XIII” Hall
Time: 11:25

Multichannel Green’s function multiple scattering calculations of x-ray absorption

Anna Taranukhina¹, Alexander Novakovich¹, and Rostislav Vedrinskii¹

(1) *Institute of Physics, Southern Federal University, 194 Stachky Ave., Rostov-on-Don 344090, Russia*

We report on the interface (MCGFXL) of the earlier developed code GFCC, realizing the multichannel formulation of the multiple scattering (MS) Green’s function (GF) method [1], and the code XKDQ [2], based on the traditional MS method. The proposed method enables us to describe simultaneously one-particle effects of photoelectron multiple scattering from the ionized atom (IA) environment, many-particle effects of the photoelectron interaction with IA, and the spin-orbit (SO) interaction. Our approach assumes a localized-hole model, which means that the electron-hole (EH) and (SO) interactions influence only the primary electron waves outgoing from IA and the secondary waves scattering on it. This concept is similar to that of the theory developed by Natoli *et al.* [3], however, the practical implementation of the latter [4] is quite different. Our technique provides a way of combining singlechannel GFs into the multichannel GF via the Dyson equation. The EH and SO interactions within IA are treated in terms of the multichannel *t*-matrix defined in the close-coupling approximation. Sample calculations of $L_{2,3}$ edge spectra for potassium in compounds show reasonable agreement with experiment. The work is supported in part by Ministry of Education and Science of the Russian Federation Grant 2.1.1/3690.1.

[1]. R.V. Vedrinskii, Gegusin I.I., and A.I. Taranukhina, in Abstracts of the 6th International Conference on X-ray Absorption Fine Structure, York, UK, 1990, p.A13.

[2]. V. Krayzman, I. Maznichenko, A. Novakovich, and R. Vedrinskii, in Proceedings of the 13th International Conference on X-Ray Absorption Fine Structure, Stanford, California, 2006, Vol. 882, p.p. 431-433.

[3]. C.R. Natoli, M. Benfatto, C. Brouder, M. F. Ruiz Lopez, and D.L. Foulis, Phys. Rev. B 42, 1944 (1990).

[4]. P. Krüger, and C.R. Natoli, Phys. Rev. B 70, 245120 (2004).

Location: “Benedetto XIII” Hall
Time: 11:50

Theoretical description of X-ray absorption in correlated magnetic solids

Hubert Ebert¹, J. Minar¹, and O. Sipr²

(1) *University Munich, Dept. of Chemistry Butenandtstr. 5-13 81377 Munich Germany*

(2) *Institute of Physics AS CR, Prague, Czech Republic*

During the last years, great progress has been made in dealing with correlation effects in magnetic solids. Among the various theoretical approaches available now, the LSDA+DMFT (local spin density approximation + dynamical mean field theory) plays a prominent role, as it accounts for dynamical correlations when dealing with the ground state of a magnetic solid. We present a description of x-ray absorption spectra based on combining the LSDA+DMFT and a the multiple scattering formalism. Working with a fully relativistic formulation, this approach gives access to a corresponding treatment of x-ray magnetic circular dichroism (XMCD). By applying the XMCD sum rules, we can demonstrate that the enhancement of orbital magnetism in ferromagnetic 3d-transition metals, which results from using the LSDA+DMFT formalism instead of plain LSDA, is indeed reflected by the XMCD spectra. Comparing the LSDA+DMFT-based XAS and XMCD spectra with experiment, however, some discrepancies remain that are ascribed to dynamical effects connected with the absorption process itself. To account for these effects we extended the sketched approach by including the presence of a core hole within the XAS and XMCD calculations. In addition, a combination of the LSDA+DMFT-based approach with a calculation of the x-ray response function along the lines of TD-DFT (time-dependent density functional theory) has been worked out.

Location: “Benedetto XIII” Hall
Time: 12:15

Ab-initio CI calculations for 3d transition metal $L_{2,3}$ x-ray absorption spectra

Hidekazu Ikeno¹, Frank M.F. de Groot², and Isao Tanaka¹

(1) Department of Materials Science and Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-ku 606-8501 Kyoto Japan

(2) Department of Inorganic Chemistry and Catalysis, Utrecht University, Sorbonnelaan 16 3584 CA Utrecht, Netherlands

The shape of a x-ray absorption spectrum (XAS) at the $L_{2,3}$ -edge of 3d transition metal (TM) elements is dominated by the multiplet structures because of the strong electronic correlations among spatially localized 3d electrons, the 2p core-hole and the excited electron. In order to calculate the multiplet structures from first principles, we have developed an *ab-initio* configuration interaction (CI) program for XAS. In this method, the molecular orbitals (MOs) obtained by relativistic density functional theory are used as basis functions for the CI calculations. The one-electron integrals, which describe the ligand field splitting and the hopping integrals among MOs, and the two-electron integrals, which denote the inter-electron interaction energies, are directly evaluated over MOs. All ligand field effects including the crystal field and the covalent bonding between a TM ion and the ligand atoms are automatically included by using MOs. This technique has been successfully used to quantitatively predict TM- $L_{2,3}$ spectra for a range of actual oxide geometries, without any adjustable parameters[1-4]. The charge transfer multiplet calculations were also made in the *ab-initio* manner by taking the CI among two or more electronic configurations, e.g., $(\phi_{3d})^n + (\phi_{3d})^{n+1}(\phi_{\text{ligand}})^{-1}$, where ϕ_{3d} (ϕ_{ligand}) denotes the MO mainly composed TM-3d (ligand) AOs[5].

In this talk, the *ab-initio* CI approach is briefly introduced. Then, the effects of the covalent bonding and the charge transfer on the multiplet structures will be discussed.

[1] H. Ikeno, et al., Phys. Rev. B 72, 75123 (2005).

[2] H. Ikeno, et al., Ultramicroscopy 106, 970 (2006).

[3] K. Ogasawara et al., Phys. Rev. B 64 115413 (2001).

[4] Y. Kumagai et al., Phys. Rev. B 77, 155124 (2008).

[5] H. Ikeno et al., J. Phys.: Condens. Matter 21, 104208 (2009).

Location: “Benedetto XIII” Hall
Time: 12:40

Exotic effects in near-edge spectra

Eric L. Shirley¹

(1) NIST, Optical Tech. Div. 100 Bureau Dr., MS 8441 20899-8441 Gaithersburg Maryland USA

Near-edge spectra can reveal a rich structure because of several effects. The electron-core hole attraction enhances near-edge features, so that they have large oscillator strength. This attraction can also localize the electron in bound states that are very sensitive to the local environment. For this reason, peaks such as those resulting from electron-quadrupole transitions such as 1s-to-3d and multiplet features such as resulting from 2p-to-3d excitation reflect (1.) atomic multiplet effects, (2.) ligand-field effects and local atomic geometry, (3.) electronic-vibrational coupling and, (4.) other electronic degrees of freedom such as charge-transfer satellites.

It is not difficult to understand and simulate each of these effects to some degree. To incorporate all of them into the calculation of an excitation spectrum, however, is more difficult. This is because of the very large space of states that one must consider, in which to solve the excited-state Hamiltonian. Methods like real-space multiple scattering address several issues with some special key advantages, whereas effective-Hamiltonian-based methods (like the Bethe-Salpeter equation) constitute an intrinsic framework into which one can incorporate additional degrees of freedom at the cost of a larger Hilbert space of states.

In this presentation, I wish to address each of the above 4 numbered points, using a first-principles Bethe-Salpeter treatment. Simple perovskites such as strontium and lead titanate will be used as prototype examples. This cautious approach might delay attacking exotic systems, yet this approach is a deliberate attempt to advance the frontier of at least highly quantitative calculations. Finally, while only periodic systems are to be studied in this work, the physical effects considered should have analogies in all systems.

P1.1: Material Science I

Location: “La Muta” Hall
Time: 15:30

Experimental and theoretical investigations on ferromagnetic nature of dilute magnetic semiconductors

Shiqiang Wei¹, Wensheng Yan¹, Zhihu Sun¹, Qinghua Liu¹, Zhiyun Pan¹, Tao Yao¹, Jian Ye¹, Yong Jiang¹, Fengchun Hu¹, Guobin Zhang¹, Pengshou Xu¹, and Ziyu Wu¹

(1) National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, People’s Republic of China

X-ray absorption fine structure (XAFS) technique and first-principles calculations are effectively combined to establish correlations of preparations, local as well as electronic structures and ferromagnetism, and to shed light on the magnetism origin for a variety of ZnO-, GaN-, and Si-based dilute magnetic semiconductors (DMSs). The results of Mn:ZnO and (Mn,N):ZnO thin films reveal that either the existence of Zn vacancy or N substitution of O sites can stabilize the ferromagnetic interactions between neighboring Mn-Mn pairs, and enhance the magnetic moment per Mn. For Co:ZnO thin films, the substitutional Co ions gather together via intervening oxygen atoms, rather than distribute themselves randomly in the lattice. In a 2.5at.% Mn-doped GaN film, a part of substantial Mn ions is found to locate at the interstitial sites near the substitutional Mn ions and forms Mn-Mn dimers that possess unique electronic and magnetic properties. Similar phenomena have also been predicted by our first-principles calculations for the Mn-doped Si system in which the interstitial Mn atoms intend to assemble together via an intervening substitutional Mn ion. In summary, we have proposed a pathway to understand the microscopic origin of ferromagnetism in the DMS materials from the viewpoint of experimental determination and theoretical calculations.

Authors to whom correspondence should be addressed
E-mail: sqwei@ustc.edu.cn, wuzy@ustc.edu.cn

Location: “La Muta” Hall
Time: 15:50

The influence of high temperature annealing procedures on the location of Mn inside the GaAs matrix

Krystyna Lawniczak-Jablonska¹, Joanna Libera¹, Anna Wolska¹, Marcin T.Klepka¹, and Janusz Sadowski^{1,2}

(1) Institute of Physics, Polish Academy of Science A; Lotnikow 32/46 02 668 Warsaw Poland
(2) MAX-Lab, Lund University, SE-221 00 Lund, Sweden

Recently, the interest in formation of hybrid ferromagnetic-semiconductor structures increases because of the interesting physics involved and possible application in spintronics. One example of such systems is GaAs with MnAs nanoinclusions. If GaMnAs ferromagnetic semiconductor is subjected to the high temperature annealing then the ternary alloy decomposes to the material implying inclusions of binary MnAs phase inside the GaAs matrix. MnAs is a ferromagnetic metal and in form of small clusters inside GaAs it can exist in two phases – zinc-blende or hexagonal, depending on the high temperature annealing procedure. We used the EXAFS technique to estimate the fraction of Mn atoms located in different structures after high temperature post-growth annealing of GaMnAs layers. Investigated layers with different Mn content were grown by MBE and were obtained in two steps. First GaMnAs layers with different Mn content were grown on GaAs(001) substrates at 230 °C, then self-organized MnAs nanoclusters were formed due to annealing of GaMnAs layers. Post-growth annealing was performed in the MBE growth chamber for 30 min under Arsen flux at temperatures 500 °C and 600 °C. TEM and XRD studies confirmed that after such treatment cubic and hexagonal MnAs inclusions were formed but the amount of Mn bounded in each kind of inclusions couldn’t be determined. The EXAFS technique is element specific and probes the local atomic structure, therefore, it is a perfect tool to find the proportion of Mn atom located in each kind of inclusion. The systematic EXAFS studies allowed to define correlation between Mn content and location in as grown structures and to determine how this influences the proportion of Mn atoms located in both types of MnAs inclusions after annealing. This work was supported by national grant of Ministry of Science and High Education N202-052-32/1189 as well as by DESY/HASYLAB and the European Community under Contract RII3-CT-2004-506008 (IA-SFS).

Location: “La Muta” Hall
Time: 16:10

Measuring strain at the atomic-scale with Differential X-ray Absorption Spectroscopy

Matthew Ruffoni¹, and Sakura Pascarelli¹

(1) ESRF 6 rue Jules Horowitz 38043 Grenoble France

The development of smart materials for use in transducer devices has driven considerable research in recent decades. In this field, phenomena such as magnetostriction underpin the operation of sensors and actuators, and energy harvesting devices. Thus, knowledge of their origin and mechanics, and how they manifest themselves in different materials, enables the development of new devices and optimisation of existing technologies. Yet this research is not without its limitations.

Theoretical studies naturally describe material properties at a fundamental, atomic-scale. But experimental work struggles to verify such models at a similarly microscopic level. Saturation strains from typical magnetostrictive materials induce displacements between neighbouring atoms of only a few femtometres. On such a scale, even commonly employed local probes, such as x-ray absorption spectroscopy (XAS), lack the resolution to observe this motion by some two orders of magnitude. As a result, experiments typically employ strain gauges on large, macroscopic samples, where the strain is easier to detect, but where atomic information is lost.

However, the recent development of differential XAS (DiffXAS) at the ESRF presents a unique opportunity to bridge this gap between macro-scale experimental work, and fundamental theoretical models [1].

This talk will study the development of DiffXAS via the most significant results obtained to date. These include studies of the important Fe-Ga and Fe-Pt systems, where DiffXAS analysis procedures have allowed chemically-selective, atomic magnetostriction coefficients to be quantified [2][3]; and an investigation of the magneto-elastic coupling of FeCo through measurements under applied hydrostatic pressure [4].

[1] R.F. Pettifer et al., Nature 435, 79 (2005)

[2] M. P. Ruffoni et al., Phys. Rev. Lett. 101, 147202 (2008)

[3] S. Pascarelli et al., Phys. Rev. B 77, 184406 (2008)

[4] S. Pascarelli et al., Phys. Rev. Lett. 99, 237204 (2007)

Location: “La Muta” Hall
Time: 16:30

Fluorinated single-walled carbon nanotubes: X-ray absorption and DFT analysis

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In this work, the high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy was used to elucidate the nature of chemical bonding between carbon and fluorine atoms on the surface and inside fluorinated single-walled carbon nanotubes (F-SWCNTs). The experimental and theoretical investigations were done.

SWCNTs (D=1.4-1.6 nm) were synthesized by an electro-arc method using Ni-Y catalyst. The direct fluorination was carried out at 222° C. The F-SWCNTs had 35-40 wt.% fluorine. Measurements were performed at the Russian-German beamline at the BESSY II.

C 1s NEXAFS spectra of F-SWCNTs show drastic changes in a spectral shape as compared to those of pristine SWCNTs. New absorption structures are similar for all the samples and reflect unoccupied electron states which are formed owing to a C-F bonding in F-SWCNTs. It was found that these F-SWCNTs are characterized by a nondestructive side-wall covalent attachment of the F atoms and a formation of σ (C2pz -F2p) bonds.

At the same time, the models of F-SWCNTs with 1.4 and 1.6 nm diameters were generated. Theoretical C K-edge has been analyzed using non-muffin-tin approach, the finite difference method (FDMNES 2008). Sensitivity of NEXAFS spectra to changes chirality value of CNTs has been shown.

In order to obtain the optimized geometry for the F atoms/molecule included in CNTs and detailed understanding origin of the chemical bond between C and F atoms we have carried out first-principles total energy pseudopotential calculations for F-SWCNTs using density functional theory (DFT, GGA).

The several models of C-F chemical bond, were considered. X-ray absorption theoretical analysis at the C K-edge was carried out for all these models and shown an inconsistency of (“substitution model”).

This work was supported by the Russian Foundation for Basic Research (project 09-02-01278) and the bilateral (“Program Russian-German Laboratory”) at BESSY.

Location: “La Muta” Hall
Time: 16:45

Investigation of C Kedge of differently sp-hybridized systems

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Near Edge X ray Absorption Fine Structure (NEXAFS) from C K edge is a precious tool to understand the basic properties of high interest systems as Self assembled Molecular films or nanostructures. Meantime it provides the cross section of the C 1s-p* transitions of the C containing systems, giving for example in molecule adsorbed on surfaces the average molecular orientation and hints on the evolution of molecular states. The existence of allotropic form of carbon characterized by sp hybridization (carbynoid species) is a challenging problem for the science of carbonaceous materials [1] and in nanostructured carbon films [2] or in liquid C [3] NEXAFS was used as a tool for quantitative evaluation of the presence of sp-hybridized species and the sp/sp² ratios. The sp, sp² and sp³ hybridizations [4] as well as the C rings [5] show characteristic features in C K edge NEXAFS. We present here a systematic study of C K edge of differently sp-hybridized C compound presenting different sp hybridization: acetylene (sp), graphite, ethylene sp², fullerenes (sp³), ethane, diamond (sp³). In order to enlighten the quantitative determination of the sp/sp² ratio in NEXAFS spectra the experimental spectra are compared with theoretical simulations obtained from Multiple Scattering formalism (MXAN) and also from density-functional theory calculations (STOBE) where electronic final-state relaxation is accounted. The comparison between the simulation methods will be discussed.

[1] F Cataldo, ed. Polyynes. Synthesis, properties and applications. Boca Raton: CRC Taylor & Francis; 2005; RB Heimann, SE Evsyukov, L Kavan, eds. Carbyne and carbynoid structures. Dordrecht: Kluwer Academic Press; 1999

[2] L. Ravagnan et al. Carbon 44, 1518 (2006)

[3] S L. Johnson et al. Phys. Rev. Lett. 94, 057407 (2005)

[4] V. Carravetta et al Chem Physics Letters 288, 37 (1998)

[5] C. Kolczewski et al, J. Chem. Phys. 124, 034302 (2006)

Location: “La Muta” Hall
Time: 17:00

In operando characterization of lithium battery materials

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The functioning of lithium batteries implies the reversible accommodation of extra lithium ions and electrons, which induces structural transformations and redox processes. The nature and extent of these reactions have a very large influence on the battery performances: voltage, capacity, reversibility, polarisation, cycle life. For the characterization of the battery materials at different levels of lithiation, XAFS is very efficient to precisely determine changes occurring in both the atomic environment of acting species (EXAFS) and their electronic state (XANES). Very often, the results can be nicely correlated to theoretical calculations [1].

XAFS allows in situ characterization of the materials, with a dedicated electrochemical cell, as close as possible to a “true” battery and allowing X-rays transmission experiments. Beyond the experiments at equilibrium, we started recently a complete series of experiments using time resolution of Dispersive XAFS, in order to characterize the battery materials during the battery functioning (in operando mode). Such a step is very important because the good or bad performances of a battery are evidently observed during its cycling.

We will first present typical cases for XAFS determination of changes occurring in battery materials. It will include clear reversible changes in both coordination and oxidation states of active transition elements. The results will be fruitfully compared with simulations obtained in DFT calculations.

In the second part we will present very recent results obtained during the functioning of the batteries, containing two promising electrode materials, LiFePO₄ and LiV₃O₈. We were able to spot the presence of metastable phases during the battery cycling, phases which do not exist at the equilibrium, and important delays in phase transformations.

[1] F. Boucher, N. Bourgeon, K. Delbé, P. Moreau, D. Guyomard, and G. Ouvrard, J. Phys. Chem. Solids 67, 1238 (2006)

Location: "La Muta" Hall
Time: 17:15

In situ XAS studies of new cathode materials for high energy Li-ion batteries

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Lithium ion batteries are entering the large scale applications like transportation, emergency power and dispersed electric-power storage, driving the research and development of new active cathode materials. Promising candidates are Li_2MSiO_4 and Li_2MTiO_4 based compounds ($M = \text{Mn}, \text{Fe}$), exploiting the oxidation potential of Fe(II)/Fe(III) and Mn(II)/Mn(IV) redox couple, which, at least in theory, can deliver much higher capacities than currently used $\text{Li}(\text{Co},\text{Ni})\text{O}_2$ materials. In addition, these materials are cheaper, thermally more stable, and more "green" [1].

We use in situ XANES and EXAFS analysis to study the mechanism of charge transfer and structural changes in the local environment of transition metals during lithium exchange. Fe and Mn K-edge XAS spectra of the Li_2MSiO_4 and Li_2MTiO_4 samples prepared in the form of half-batteries were measured continuously during the first cycle of charging and discharging of the battery at XAFS beamline of ELETTRA, Trieste, and at beamline C of HASYLAB, Hamburg (EU contract RII3-CT-2004-506008 (IA-SFS)).

In XANES analysis the gradual changes in relative ratio of Mn(III)/Mn(II) and Fe(III)/Fe(II) in the intermediate states of charge/discharge process are monitored with high precision (0.2 %), exploiting the linear combination fit with the XANES spectrum of the starting (as prepared) compound and the spectrum at the highest oxidation state in charging period. EXAFS results clearly demonstrate that the change of valence state of the transition metal on individual crystallographic site is accompanied by the deformation of the nearest oxygen coordination shell. The process is reversible in the process of battery discharging.

The obtained information is essential in developing new synthesis routes for high energy density cathode materials with optimal electrochemical properties for large batteries.

[1] R. Dominko et al., J. Power Sources (2009) on line.

P1.2: Disordered Systems

Location: "Allara e Grosso" Hall
Time: 15:30

MD-XAS studies of glasses and liquids: from weakly to highly disordered cases

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Molecular dynamics (MD) or Monte-Carlo (MC) simulations are valuable tools for the interpretation of XAS data, especially in the case of disordered systems and/or complex chemical compositions. They provide energetically-constrained structural models and a rigorous way to account for the configurational average. They are also useful to identify the dominant contributions to the XAS signal and are in many cases essential for a structural analysis beyond the first coordination shell. In return, the experimental information can sometimes be used to refine the simulated model or ideally the simulation potentials.

We shall illustrate these aspects from examples taken from our past studies [1] with particular focus on recent works in oxide glasses [2,3]. These will include a detailed MD-EXAFS study of the environment of a transition element, Zr, in a borosilicate glassy matrix [2]. In this moderately disordered but rather chemically complex amorphous network, a site analysis (*i.e.* a statistical analysis of a large number of clusters extracted from the MD configurations) allowed to characterize the most likely preferred environment of Zr. Another example will be taken from our on-going study of B_2O_3 glass at high pressure [3]. In this chemically simple but significantly distorted matrix, we show how a MD-XANES combination can be used to assess the fractions of boron atoms in n -fold coordinations as the pressure is increased. Finally, we shall evoke briefly current directions to circumvent the main drawback of numerical simulations, *i.e.* their computational cost.

[1] G. Ferlat *et al.* J. Phys.: Condens. Matter, 17, S145 (2005); G. Ferlat *et al.* Phys. Rev. B, 69, 155202 (2004); G. Ferlat *et al.* Phys. Rev. B, 63, 134202 (2001).

[2] G. Ferlat *et al.* Phys. Rev. B, 73, 214207 (2006).

[3] G. Ferlat *et al.* in preparation

Location: “Allara e Grosso” Hall
Time: 15:50

Amorphous phase structure and vibrational anisotropy in the III-V semiconductor InP

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InP is an important III-V semiconductor used in the fabrication of both electronic and photonic devices. The amorphous phase (a-InP) not only lacks the long-range order characteristic of crystalline material (c-InP) but contains a significant fraction of homopolar In-In bonding, the latter forbidden in the c-InP zincblende structure yet apparently necessary to stabilise the disordered amorphous phase. We have produced amorphous InP by ion irradiation with either low or very high ion energies where elastic (ballistic displacement) or inelastic (excitation and ionization) processes, respectively, govern the energy dissipation. EXAFS measurements at 20K demonstrate the atomic-scale structure of the amorphous phase is similar for the two regimes despite the fundamentally different interaction processes, indicative of a common amorphisation mechanism identified as a quench from the melt.

Comparing temperature-dependent EXAFS measurements from 20-295K with x-ray diffraction studies, we have differentiated between vibrations parallel and perpendicular to the bond direction and evaluated the correlation of absorber-backscatterer motion. Significant vibrational anisotropy is observed in c-InP with first nearest neighbour relative vibrations considerably smaller along the bond direction compared to the perpendicular direction indicative of in-phase motion in the former and uncorrelated vibration in the latter. Our findings are consistent with bond bending being energetically-favoured over bond stretching as characteristic for four-fold tetrahedrally-coordinated semiconductors. As anticipated, the structural disorder of a-InP exceeds that of c-InP yet the thermally-induced disorder is very similar for the two phases pointing to a comparable degree of correlated first nearest neighbour motion. The Einstein temperature of a-InP is slightly less than that of c-InP, consistent with the presence of floppier, looser bonding in the disordered amorphous phase.

Location: “Allara e Grosso” Hall
Time: 16:10

Combined EXAFS and Raman high-pressure studies of amorphous Ge and SiGe alloys

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Amorphous covalent systems show a complex behavior upon application of an external pressure. At ambient conditions they are characterized by an open structure which is likely to rearrange upon pressurization, resulting in phase transitions and metallization. In particular simple amorphous systems like a-Ge, a-Si, a-SiGe can show polyamorphism, that is the existence of different phases characterized by different values of some thermodynamic parameters. a-Si and a-Ge are known to undergo polyamorphic transition between a low-density (LDA) and a high-density (HDA) amorphous phase [1,2,3]. The combination of Raman and EXAFS spectroscopy, together with the use of diamond anvil cells as high-pressure device, represents a powerful tool for the investigation of such transformations, providing complementary information on phonon vibrations and local structure. In this contribution we present the results of our high-pressure Raman and EXAFS experiments on a-Ge and a-SiGe sample. Depending on the density of defects characterizing the sample, a-Ge is seen to undergo a transition to a HDA metallic phase around 8 GPa and to a crystalline metastable structure (ST12-Ge) around 7 GPa upon depressurization (for low density of defects)[4]. Presently available data on a-SiGe are limited to ambient pressure. Here we will present the first Raman and EXAFS spectra of the amorphous alloy in high-pressure condition (up to 30 GPa) collected in diamond anvil cell and exploiting the performances of the new energy dispersive EXAFS beamline (ODE) at Soleil Synchrotron Radiation Facilities.

[1]Hedler *et al.* Nature Materials **3**, 804 (2004)

[2]McMillan *et al.* Nature Materials **4**, 680 (2005)

[3]Bath *et al.* Nature **448**, 787 (2007)

[4]Di Cicco *et al.* Phys. Rev. B **78**, 033309 (2008)

Location: "Allara e Grosso" Hall
Time: 16:30

Structural understanding of the preferential glass-formation-ability in multi-component bulk metallic glass, using XAFS.

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Understanding the causes of preferential glass-formation-ability in certain alloys is important for the wide scale synthesis of bulk metallic glass and is speculated to be correlated with the short range order in the parent (glass) and daughter (quasi-crystalline / crystalline) phases. The short-range-order is usually in the form of icosahedral clusters. We have, for the first time, determined the cluster size in the glass (Zr_{69.5}Al_{7.5}Cu₁₂Ni₁₁) and the details of disorder within and demonstrated their direct effect on glass-formation-ability. The cluster size was determined assuming icosahedral structure and fitting the coordination of the first shell at Ni, Cu, Zr edges. The cluster around Ni and Cu sites was found to be 55-atom (stoichiometric) and of diameter 1.2 nm, while the cluster around Zr was found to be 13-atom of diameter 0.6 nm. These sizes can be compared with the 10-20 nm size of binary alloys with lower glass-formation-ability, directly establishing the role of cluster size on the latter and confirming the classical nucleation theory. A remarkable observation with annealing at 400-500 °C is that, while binary alloys already crystallize, the change in the multi-component alloy is marked only by the expansion of first shell bond-length and a dramatic improvement in order (Debye-Waller factor) of the higher shells of the cluster. There is no growth in cluster size or phase transition. The implications of this observation are significant: the entire thermal energy induced by annealing is utilized in ordering the atoms which leaves little energy for diffusion. In absence of diffusion, the cluster does not grow in size and remains below the critical size of nucleation, which explains their preferential glass formation ability. A key role in the preferential glass-formation-ability of these multi-component glasses is, thus, played by static disorder which originate from the "confusion principle" or the multi-component nature in such systems.

Location: "Allara e Grosso" Hall
Time: 16:45

EXAFS study of the local structure of liquid Ge₂Sb₂Te₅ (GST)

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GST is broadly used in optical memory devices is also a leading candidate for future non-volatile memory devices. The phenomenology of the phase change is very simple - an intense laser or electrical pulse melts the crystalline material that is subsequently quenched into the amorphous phase. Based on XAFS studies it was suggested by some of the present authors that the phase transition primarily involves a switch of Ge atom between octahedral and tetrahedral sites within the Te fcc lattice [1].

As far as the liquid phase is concerned, almost nothing is known. In a recent paper [2], it has been claimed based on neutron diffraction that liquid GST possesses octahedral bonding geometry. However, neutron diffraction is not site selective and the conclusion about the structure has been drawn from rather qualitative arguments. Considering the importance of the phase change, precise knowledge of the structure of the liquid phase is badly required.

We have designed a special cell which was filled with fine GST powder mixed with BN in ratios optimized for individual edges, that has allowed us to create and study the liquid phase. The EXAFS measurements were performed in transmission mode at BL01B1 at SPring8 over a temperature range from room temperature to 750 °C (the melting point of GST is 615 °C at the K-edges of all three constituent elements. Special care was taken to check that the spectra before and after melting were identical, i.e. we reversibly melt and subsequently solidify the material. Clear differences were observed in both XANES and EXAFS spectra between the solid and liquid states.

In this talk we present the results of the data analysis in comparison with those for the amorphous phase. Applications of the obtained results for device performance are also discussed.

[1] A.V. Kolobov et al., Nature Materials, 3 (2004) 703

[2] C. Steiner et al., Adv. Mater., 20 (2008) 4535

Location: “Allara e Grosso” Hall
Time: 17:00

Molecular dynamics to rationalize EXAFS experiments: a dynamical model explaining hydration behaviour across the lanthanoids(III) series

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Understanding molecular organization around heavy metal cations – like transition metals, lanthanoids or actinoids – is of fundamental importance to address their chemical reactivity. For aqueous solutions, the first step is to understand solvation properties. Molecular dynamics simulations can provide a real help in understanding the molecular structure of hydrated ions as a tool to better interpret X-ray absorption experiments. This is particularly useful for lanthanoids(III) that change their coordination number across the series from 9 to 8.

We have developed a classical interaction potential with explicit polarizability that was parameterized and tested on the first atom of the series, La^{3+} [1] that can be used in classical molecular dynamics simulations in explicit water. The classical potential developed for La^{3+} was thus extended to the whole series [2,3]. We were able to reproduce and rationalize different experimental results. Further, we can construct the EXAFS signal using the full information statistically averaged provided by the radial distribution functions as naturally obtained from our simulations. The theoretically reconstructed signal is in good agreement with new EXAFS data performed on the whole series in solution [4].

Our microscopic picture, in agreement with recent EXAFS results, is that the changing in coordination number from 9 to 8 across the series does not occur via the so-called gadolinium break model but in a continuous shape regulated by changing the self-exchange dynamical behavior across the series.

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- [1] M.Duvail, M.Souaille, R.Spezia, T.Cartailier and P.Vitorge. J.Chem.Phys. 127, 034504 (2007).
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- [3] M.Duvail, P.Vitorge and R.Spezia. J.Chem.Phys. 130, 104501 (2009).
- [4] I.Persson, P.D’Angelo, S.D.Panfilis, M.Sandstrom and L.Eriksson. Chem-Eur.J. 14, 3056 (2008)

Location: “Allara e Grosso” Hall
Time: 17:15

Ion hydration in high-density water

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The properties of aqueous solutions under pressure are fundamentally important for a wide range of scientific disciplines, such as geoscience, environmental sciences and planetary modeling. Despite this broad interest our present knowledge of their structure is mostly restricted to “ambient temperature and pressure conditions”, as a result of the considerable experimental challenges faced when trying to measure the behaviour of aqueous solution at high pressure. We present here an extensive study of the hydration properties of $\text{Zn}(2+)$ ion in conditions of very high pressure, combining X-ray absorption spectroscopy and Quantum Mechanics/Molecular Dynamics simulations. This combined procedure allowed us, on one hand, to unveil the structural transformations occurring to water from the low- to the high- density conditions, and, on the other hand, to investigate the pressure effects on the hydration structure and dynamics of the $\text{Zn}(2+)$ ion in aqueous solution.

P1.3: Instrumentation

Location: "Aranjo Ruiz" Hall
Time: 15:30

Combined XAFS/XRD instrument at the X18A beamline at NSLS for in situ, time-resolved catalysis research

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XAFS and XRD techniques give complementary information about the structure of catalytic materials. XRD is effective in systems with medium to long range order, while XAFS provides short range information. To analyze catalysts in situ, fast and synchronous collection of the XRD and XAFS data is required, in order to measure the changes in the actual structure of catalysts, substrates and/or templates at multiple length scales. The first in US dedicated instrument for combined XAFS/XRD studies was built at the beamline X18A of NSLS. This beamline uses Rh-coated mirror to focus the x-ray beam to 1 mm² spot at the sample and has energy range from 5 to 30 keV. The setup includes transmission and fluorescence XAFS detectors, position-sensitive linear XRD detector, residual gas analyzer and the automated gas mixing system. The first application of this instrument was aimed at the investigation of the mechanism of reduction of CuFe₂O₄ with CO. Its structural transformation upon reduction cannot be fully studied by XRD alone, due to the likelihood of forming disordered metastable phases accompanying its reduction. Such phases may be invisible to diffraction but detectable by XAFS. Fe and Cu K-edge EXAFS data demonstrate that the sample reduced at 200 C and cooled down to room temperature is a linear combination of the fresh sample and the fully reduced (at 300 C) sample. XRD data shows presence of the same two phases. We present our self-consistent interpretation of these two techniques. High temperature XAFS and XRD data feature multiple phases that can be deconvoluted by processing multi-edge XAFS and XRD data self-consistently. Future upgrades include Quick EXAFS (QEXAFS) with sub-second time resolution and Diffraction Anomalous Fine-Structure (DAFS) measurements.

Location: “Aranjo Ruiz” Hall
Time: 15:50

First results at SAMBA the SOLEIL hard x-ray beamline for EXAFS and QEXAFS experiments

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SAMBA (Spectroscopies Applied to Materials Based on Absorption) is an X-ray spectrometer dedicated to EXAFS experiments which spans the X-ray spectrum from 4 to 43 keV. The beamline, installed on a SOLEIL dipole, opened to first users in January 2008.

The design of the optics fulfills the needs of a wide community of users belonging to condensed matter physics, chemistry, biology or surface science. Two bendable mirrors are located before and after three monochromators for beam collimation and vertical focusing, respectively. In its “high flux mode” configuration, the double crystal monochromator Si(220) or Si(111) dynamically focuses the beam in the horizontal plane and keeps its size constant during energy scans. In May 2009 one of the two QEXAFS monochromators will be installed for time-resolved experiments at frequencies as high as 50Hz. This monochromator is a modified version of that built by the group of Prof. R. Frahm [1] and the energy range can be modified automatically in a few seconds without breaking the vacuum. Data collection system gives an access to real time recording of encoder and detectors values.

The beamline is equipped for surface science studies and in situ EXAFS measurements in a dedicated UHV environments as well as computer controlled ovens and gas flow systems for catalysis. When necessary, Raman and UV-Vis spectrometers can be used to obtain consistent data sets from in situ time-resolved experiments [2]. A setup for fluorescence yield grazing incidence measurements has been tested and it will be available in the next future.

We will illustrate selected results in surface science and those obtained in time-resolved mode, in soft chemistry, operando catalysis and charging and discharging of Lithium-based batteries.

[1] Stotzel J., Lutzenkirchen-Hecht D., Fonda E., De-Oliveira N., Briois V. and Frahm R., Review Of Scientific Instruments 79 (8) (2008) 38-41

[2] Briois V. et al.. Physica Scripta T115 (2005), 38-44.

Location: “Aranjo Ruiz” Hall
Time: 16:10

HERFD XAS / RIXS spectrometer

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An X-ray spectrometer for HERFD XAS and RIXS studies is designed and constructed at the superXAS beamline of the Swiss Light Source (SLS). The spectrometer consists of three key elements: a sample holder, an X-ray dispersive element (spherically bent silicon or germanium crystal in Johann geometry) and a one-dimensional-array X-ray detector (MYTHEN II detector, developed at the Paul Scherrer Institut). The detected X-ray fluorescence energy is scanned by changing the angle between the sample, crystal and detector. The energy resolution of the spectrometer is estimated to range from sub-eV to several eV, depending on the crystal type and fluorescence energy detected. The main purpose of the construction of the spectrometer is the investigation of catalytic materials at reaction conditions, although general-purpose spectroscopic investigations are planned as well. First results on the Pt L-edge HERFD XAS of platinum-nanoparticle catalysts at reaction conditions will be presented.

Location: "Aranjo Ruiz" Hall
Time: 16:30

Nano-scale X-ray absorption spectroscopy using XEOL-SNOM detection mode

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The knowledge of the local structure of nanocrystalline thin films is crucial for understanding and optimizing their functional properties. The volume averaging can hide local level deviations, because the properties of individual grains may deviate from the average ones. Therefore, special local sensitive methods, having nanoscale resolution, are required for adequate investigation of nanocrystalline thin films.

The "X-TIP" STRP project supported by the European Commission under the 6th Framework Programme strove to address these needs through the combination of x-ray absorption spectroscopy (XAS) using synchrotron radiation microbeams with scanning near-field optical microscopy (SNOM) detection of the x-ray excited optical luminescence (XEOL) signal. The new instrumentation developed within this project offers the possibility to carry out a selective structural analysis of the sample surface with the subwavelength spatial resolution determined by the SNOM probe aperture. In addition, the apex of the optical fibre plays the role of a topographic probe, and chemical and topographic mappings can be simultaneously recorded. In this contribution, we will present the state of art and the experimental results obtained with the XAS-SNOM prototype at ESRF (Grenoble, F). We will illustrate the possibility to obtain an element-specific contrast and to perform nano-XAS experiments by detecting the Zn *K* and W *L*₃ absorption edges in luminescent ZnO and ZnWO₄ nanostructured thin films. The presence of ZnO phase is unambiguously detected only at the nano-scale by XAS-SNOM method. The analysis of the Zn *K*-edge XANES shows that ZnO nanocrystals exist in both wurtzite-type and high-pressure rock-salt-type phases.

S. Larcheri, F. Rocca et al.: Superlattices and Microstructures 39, 267, 2006; Review of Scientific Instruments 79, 017302, 2008; Micron 40, 61, 2009.

Location: "Aranjo Ruiz" Hall
Time: 16:45

Polycapillary based μ -XAS and confocal μ -XANES at a bending magnet source of the ESRF

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Glass polycapillary optics are shown to be easy to use alternative focusing optics for bending magnet XAS stations, compared to e.g. Kirkpatrick-Baez mirror systems. Their acceptance is several mm horizontally and vertically, while the angular acceptance can be matched to the source divergence by the design of the polycapillary. Polycapillaries consist of a bundle of hundreds of thousand of small bent glass fibres all oriented towards the same focal point. Due to repeated total reflections the incoming X-rays are guided towards that focal point, resulting in an achromatic optic.

A polycapillary half-lens based focusing system was successfully tested for transmission and fluorescence μ -XAS at DUBBLE (BM26A, ESRF). This beamline is equipped with a non-fixed exit Si(111) monochromator, the resulting vertical positional variations of the X-ray beam during an EXAFS scan are essentially cancelled by the focusing effect of the polycapillary. Beam sizes of 10-20 μ m, transmission efficiencies of 25-45% and intensity gain factors of about 2000 were obtained in the 7-14 keV energy range. Although the polycapillary optic has a smoothly changing energy dependent transmission efficiency, the amplitude and shape of the EXAFS oscillations are not influenced by this. An EXAFS spectrum on a probed mass of 3 pg of Zn was achieved on a biological sample in fluorescence mode.

In addition, by mounting a second polycapillary half-lens in front of an energy dispersive detector, a confocal set-up is obtained, which restricts the part of the sample seen by the detector to a microscopic volume of about 15x20x20 μ m³ at the Fe K absorption edge.

The applicability of the polycapillary μ -XAS set-up and the confocal μ -XANES is illustrated within the field of environmental science and geology.

Location: “Aranjo Ruiz” Hall
Time: 17:00

Time-resolved simultaneous spectroscopies as a probe of physical-chemical processes

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The continuously increasing demand of advanced techniques characterized by time-resolution and simultaneous analytical capabilities continuously stimulates scientists to look for new experimental methods. The availability of brilliant synchrotron radiation sources offers new and incredible opportunities and allow performing many different spectroscopic techniques providing answers to complex problems in term both of spatial and time resolution. Nevertheless, the lack of experimental methods based on concurrent and possibly simultaneous time-resolved experimental techniques exist.

Pioneering time resolved experiments combining X-ray and IR radiation with a conventional source have been performed more than a decade ago but now many beamlines at third generation synchrotron radiation facilities are equipped with conventional sources to allow complementary techniques and the strategy of a concurrent analysis is mandatory in frontier multi-disciplinary researches.

Actually, the combination of an IR and X-ray simultaneous spectroscopic analysis may return unique information in materials science. As an example metal endohedral fullerenes, large clusters composed by carbon atoms are characterized by properties whose understanding is relevant for both fundamental studies and technological applications. Among the isomers of the C₈₂ fullerene: C_{2v} and C_s isomers were synthesized and investigated. We will present and discuss both vibrational and structural properties of M@C₈₂ (M=Y, La and Gd) compounds by means of temperature dependent FTIR and XANES spectroscopy. Looking at both synchronous and asynchronous correlations we will show how 2D-correlation analysis of combined X-ray and IR data may support the identification of different isomers.

The example illustrates the potential advantage of the simultaneous combination of x-ray spectroscopy with FTIR spectroscopy when applied to materials science researches or to dynamic phenomena such as phase transitions.

Location: “Aranjo Ruiz” Hall
Time: 17:15

Very sensitive X-ray fluorescence analyzer detector

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The primary goal of our second generation wavelength dispersive X-ray fluorescence analyzer detector development is to largely improve the sensitivity of the first generation system[1], while maintain its tunability over a large energy region. A prototype analyzer detector system was designed using a novel analyzer configuration too boost the background rejection rate. Evaluated at synchrotron beamlines, the analyzer system has demonstrated superb background rejection rate of 10,000 times when measuring systems with two fluorescence lines close to each other. Such detectors should benefit x-ray spectroscopy and x-ray fluorescence analysis research community when working on dilute metal systems at the third generation synchrotron beamlines.

[1] K. Zhang, G. Rosenbaum, R. Liu, C. Liu C. Carmeli, G. Bunker, and D. Fischer, the American Institute of Physics series of conference proceedings, Eighth International Conference on Synchrotron Radiation Instrumentation, (edit. T. Warwick et al.) 957, 2004.

P1.4: Theory I

Location: “Betti” Hall
Time: 15:30

Relativistic many-body XMCD theory including core degenerate effects

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A many-body relativistic theory to analyze X-ray Magnetic Circular Dichroism (XMCD) spectra has been developed on the basis of relativistic quantum electrodynamics (QED) Keldysh Green's function approach. This theoretical framework enables us to handle relativistic many-body effects in terms of nonrelativistic Green's function and relativistic correction operator Q , which naturally incorporates radiation field screening and other optical field effects in addition to electron-electron interactions. The former can describe the intensity ratio of L_2/L_3 which deviates from the statistical weight $1/2$.

In addition to these effects, we consider the degenerate or nearly degenerate effects of core levels from which photoelectrons are excited. In XPS spectra, for example Rh 3d sub level excitations, their peak shapes are quite different: This interesting behavior is explained by core-hole moving [1]. We discuss similar problems in X-ray absorption spectra in particular excitation from deep 2p, 3d sub levels which are degenerate in each sub levels and nearly degenerate to each other: The hole left behind is not frozen there. Some numerical calculations demonstrate their importance.

[1] C-O. Almbladh, M. Bergersson, J. Elect. Spect. Relat. Phenom. 137-140 (2004) 393.

Location: “Betti” Hall
Time: 15:50

Theory of XAS and XMCD for field-controlled valence mixed states in RE compounds

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It is well known that some Rare-Earth (RE) compounds exhibit a valence fluctuating phenomenon, which is one of the most interesting subjects in condensed matter physics. Recently, the valence mixed state in $\text{EuNi}_2(\text{Si}_{0.18}\text{Ge}_{0.82})$ has been in fact controlled by extremely high magnetic fields: the magnetic field-induced valence transition from a non-magnetic $4f^6$ state ($J = 0$) to a magnetic $4f^7\bar{L}$ state, where \bar{L} denotes a hole in a valence band, ($J = 7/2$) has been observed by means of X-ray Absorption Spectroscopy (XAS) at Eu L -edges [1] and their X-ray Magnetic Circular Dichroism (XMCD) at around 40 T. In order to understand the phenomenon, we calculate XAS and XMCD spectra based on an effective model, in which the hybridization between the $4f^6$ state and the $4f^7\bar{L}$ state is taken into account. For XMCD, we need more detailed information on the Eu-5d band, which is polarized by the 4f electrons. Especially, the polarization of the 5d band associated with the $4f^6$ state is crucial to reproduce XMCD spectra observed. We discuss the mechanism of XMCD in connection with a possible origin of the polarization of the $4f^6$ state with a channel, for instance, the Van Vleck term. Then, the model is extended to the valence fluctuating phenomenon in Sm compounds, revealing similar natures of the valence mixed states to those in Eu compounds and different natures from those in Ce and Yb compounds. Finally, we demonstrate how effective XAS and XMCD are for studying such mixed valence phenomena.

[1] Y. H. Matsuda *et al.*, J. Phys. Soc. Jpn 77 (2008) 054713.

Location: “Betti” Hall
Time: 16:10

Full potential multiple scattering for core electron spectroscopies

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We present a rigorous derivation of a real space Full-Potential Multiple-Scattering-Theory (FP-MST), valid both for continuum and bound states, that is free from the drawbacks that up to now have impaired its development, in particular the need to use cell shape functions and rectangular matrices. In this connection we give a new scheme to generate local basis functions for the truncated potential cells that is simple, fast, efficient, valid for any shape of the cell and reduces to the minimum the number of spherical harmonics in the expansion of the scattering wave function. This approach provides a straightforward extension of MST in the Muffin-Tin (MT) approximation, with only one truncation parameter given by the classical relation $l_{\max} = kR_b$, where k is the photo-electron wave vector and R_b the radius of the bounding sphere of the scattering cell. Significant applications of the theory are presented, both for continuum and bound states.

Location: “Betti” Hall
Time: 16:30

Self-consistency, Hubbard, spin-orbit and other advances in the FDMNES code to simulate XANES and RXD experiments

Yves Joly¹, and Oana Bunau¹

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A user friendly tool allowing the simulation of x-ray absorption near edge structure (XANES) spectra and Resonant X-ray Diffraction (RXD) peak intensity is necessary for many purposes. We present the actual developments of the FDMNES code which realizes this task in a monoelectronic approach. The code uses both the multiple-scattering theory and the finite different method in a fully relativistic frame including thus the spin-orbit interaction. Special care on the multipole analysis permits the interpretation in physical term of the spectra. In diffraction the resonant and non-resonant, magnetic and non-magnetic, components are all included, allowing an easy use, by the non experts, of the code. In the same idea, the automatic analysis of the unit cell (or molecule) symmetry greatly simplifies the user’s work. Summation on and energy shift between the different absorption sites are automatically included. Comparison with experiment in order to fit parameters is also possible. The last advances with the self-consistent calculations are discussed. It is shown that within the multiple-scattering theory, using the muffin-tin approximation on the shape of the potential, the improvement is not high and limited in the pre-edge region. The improvements coming from the non-muffin-tin corrections are notably higher. Various examples in oxides and metal in RXD and XANES are given showing the potentiality of the code.

Location: “Betti” Hall
Time: 16:50

On the convergence of the multiple scattering series

Didier Sébilleau¹, Calogero Renzo Natoli²

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(2) *Theory Group, LNF-INFN, via Enrico Fermi 40, 00044 Frascati, Italy*

Among the various algorithms used to compute multiple scattering, series expansion is a widespread one. It is known to diverge at low energies, but the energy domain where convergence breaks down depends strongly on the material. We present here a systematic study of the convergence of this multiple scattering expansion based on the variations of the spectral radius (which is the largest of the moduli of the eigenvalues of the multiple scattering matrix) as a function of many different parameters. In particular, we find that these variations are not monotone but exhibit strong oscillations. A direct consequence is that divergence can occur in energy domains higher than some domains where there is convergence. We try to understand these oscillations and to reproduce them using simple models. Although standard formulas for estimating eigenvalues of a matrix do not work in this case, we nevertheless derive a fast algorithm that allows to compute the spectral radius without having to find all the eigenvalues. This allows us to know in advance whether multiple scattering series expansion will converge or not.

Location: “Betti” Hall
Time: 17:10

Parameter free calculations of K-edge XAS in solids : theory and applications

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We present a first principles method to calculate K-edge XAS and XMCD in materials. The method relies on plane-wave expansion, pseudopotentials and the continued fraction approach [1]. Core-hole effects are included and correlation is treated in the DFT+U approximation where the value of U is calculated from first principles [2]. The use of ultrasoft pseudopotentials [3] is allowed to substantially reduce the computational time. The code is freely distributed under the gnu licence [5].

We apply the method to XAS spectra of transition metal oxides as NiO, CuO, CoO [4] and to cuprates, La₂CuO₄ and CuCa₂O₂Cl₂. These systems are traditionally considered real challenges for density functional theory. We demonstrate that the use of a U parameter is mandatory to achieve a good agreement with experiments in the pre-edge region. We show that pre-edge features due to intersite 3d-4p hybridisation occurs in NiO. Furthermore, through a detailed comparison with 1s core-hole photoemission data, we point out the systematic appearance of manybody excitations in the near-edge region.

[1] M. Taillefumier et al, Phys. Rev. B **66**, 195107 (2002)

[2] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005)

[3] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)

[4] C. Gougoussis, M. Calandra, A. Seitsonen, Ch. Brouder, A. Shukla and F. Mauri, Phys. Rev. B **79**, 045118 (2009)

[5] P. Giannozzi et al., <http://www.quantum-espresso.org>

P2.1: Nano structures I

Location: “La Muta” Hall
Time: 18:00

Probing fast quantum lattice and charge critical fluctuations by XANES and EXAFS

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We present a review on the key contributions of XANES and EXAFS spectroscopy to detect lattice and charge fluctuations in high T_c superconductors, from cuprates and diborides to the recently discovered iron pnictides, and in complex systems where quantum critical fluctuations in the time scale of 10^{-13} sec determine the functional properties. The basic physical processes in the high energy core excitations can be fully exploited to unveil unique fast dynamical phenomena in complex systems

Location: “La Muta” Hall
Time: 18:30

Studies of long-range-order and short-range-order structures in zirconia nanocrystals using TEM, XRD, and EXAFS

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Cubic zirconia is an important material system for wear-reduction applications in the biomedical industry. However, the cubic phase of bulk zirconia is only stable at high temperatures or when mixed with chemical stabilizers. Recently, nanocrystals of cubic zirconia have been found to be stable at room temperatures without chemical stabilizers and therefore provide new possibilities for important technological applications. In this work, structural variations of zirconia nanocrystals were probed in different length scales by using transmission electron micrograph (TEM), x-ray powder diffraction (XRD), and extended x-ray absorption fine structure (EXAFS) techniques, respectively. These samples were prepared by a sol-gel method and thermally annealed at different temperatures. The as-grown ZrO_2 powders exhibit nanosized particles in TEM and cubic-zirconia-like crystal structure in the XRD pattern. However, the local structures around Zr probed by EXAFS indicate that Zr atoms in the sample form cubic sublattice while O atoms are residing on one of the two tetragonal sites with respect to the central Zr atom. As the annealing temperature increases and larger particles are formed, substantial change of local structure is observed while the crystal structure progressively evolves from cubic to tetragonal and then to monoclinic. This work serves as a typical example for the complementary application of EXAFS and XRD techniques in the studies of structural variations for nanocrystal materials.

Location: "La Muta" Hall
Time: 18:45

An X-ray absorption study of the inversion degree in ferrite nanocrystals MFe_2O_4 (M = Mn, Co, Ni)

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Nanocrystalline ferrite spinels, MFe_2O_4 (where M = Co, Ni, Mn) have been of great interest in recent years for their remarkable magnetic, optical and electrical properties. In the structure of ferrites, bivalent and trivalent cations reside on tetrahedral and octahedral interstitial sites available in the close packing of oxygen anions. An accurate estimation of the the cations distribution in octahedral and tetrahedral sites is essential in order to understand the properties of ferrites.

X-ray Absorption spectroscopy has been found to be a useful tool to determine the cation distribution in ferrite spinels.¹⁻³ In particular, the combined use of X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) at both the Fe^{3+} and M^{2+} edges seems to have superior capabilities with respect to other probes used to the same end, such as X-ray and neutron diffraction and Mössbauer spectroscopy. In fact, XRD cannot distinguish Fe from Mn/Co/Ni due to their similar scattering factors. Mössbauer spectroscopy is effective in determining the environment of Fe^{3+} ions but does not provide information on the M^{2+} cations.

In this work, we have prepared via sol-gel technique, nanocrystalline Mn, Co and Ni spinel ferrites dispersed in a highly porous SiO_2 aerogel matrix. We have used EXAFS and XANES at the Fe, Mn, Ni and Co K-edge in order to study the cation site distribution of manganese, cobalt and nickel ferrite nanoparticles dispersed in the amorphous matrix. The analysis indicates that the degree of inversion of the spinel structure increases in the series Mn (0.20), Co (0.68) and Ni spinel (1.00).

1) Carta, D.; Mountjoy, G.; Navarra, G.; Casula, M. F.; Loche, D.; Marras, S.; Corrias A. J. Phys. Chem. C 2007, 111, 6308.

2) Carta, D.; Casula, M. F.; Mountjoy, G.; Corrias, A. Phys. Chem. Chem. Phys. 2008, 10, 3108.

3) Carta, D.; Loche, D.; Mountjoy, G.; Navarra, G.; Corrias, A. J. Phys. Chem. C 2008, 112, 15623

Location: "La Muta" Hall
Time: 19:00

Temperature dependence of EXAFS cumulants of Ag nanoparticles in glasses

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In the present work, Ag nanoparticles of sizes from 1.5 to 7 nm were produced by ion exchange of soda-lime glasses in a mixed nitrate melt for different times. In HASYLAB/Hamburg the Ag K-spectra (25.514 keV) were recorded in transmission mode in the temperature range of 10 – 300 K by means of a liquid-helium vapor flow cryostat, whereas a self-constructed oven was utilized for situ heating experiments. Ratio method and EXAFS fitting procedure were applied to reveal the temperature dependence using the cumulant-expansion method up to third order ones. The temperature dependence of the nearest neighbor Ag-Ag distance exhibit differences to that of polycrystalline Ag foil for temperatures below 400 K. This effect can be explained by a thermoelastic model describing the mismatch of thermal expansion coefficients of Ag particles and the glass matrix. Furthermore, the absolute value of Ag-Ag separation of different nanoparticles is shifted due to the existence of silver oxide-like clusters as predecessors in the formation of crystalline Ag nanoparticles. The data of the second cumulant, the Debye-Waller factor (DWF), represent a higher static disorder, especially for nanoparticles of 1.5 – 3 nm size, caused by the increasing portion of surface or interface atoms. From the temperature dependent part of DWF we estimated the Einstein temperature. This parameter increases with decreasing size of particles reflecting the interface influence between the metal particles and the surrounding glass matrix.

Location: "La Muta" Hall
Time: 19:15

Structural and electronic characterization of Fe_xO_y capped Au nanoparticles. Charge effects on Au core induced by the Fe-oxide shell.

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Core@shell nanoparticles (NP) comprise a core of one material and a coating shell of another material. Since the size and material properties of both the core and the shell can be manipulated at will, a vast range of particles can be made with myriad properties, useful in many areas, such as nano-sensors for cellular imaging, gap controlled semiconductor, etc.[1,2] Samples were synthesized through a two-step procedure: Au (core) NP were firstly obtained and then used as seeds to incubate an emulsion containing the monomers and initiators that synthesize the Fe_xO_y shell.[3]

The morphology and size of the NP was investigated by Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS). One sample contained 5 nm diameter Au seeds, the other contained the 15 nm diameter Au@ Fe_xO_y NP. By modeling of the SAXS curves we determined the presence of a core@shell interface containing S, as well as the radial electronic density distribution. The structural parameters of the Fe_xO_y shell were determined by X-Ray Absorption Fine Structure (XAFS) analysis at the Fe K-edge, while XAFS studies at Au L-edges evidence an increment of Au5d empty states due to the presence of the Fe_xO_y shell.

This work was partially supported by grants ANPCYT PICT-00038 and CONICET PIP 03079, Argentina; project XAS 6609/07 (LNLS, Brazil) and the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

[1] M.-C. Daniel, D. Astruc. Chem. Rev. 104 (1), 293 (2004).

[2] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chem. Rev. 105 (4), 1025 (2005).

[3] E. V. Shevchenko et al. Adv. Mater. 20 (22), 9999 (2008).

Location: "La Muta" Hall
Time: 19:30

Structure performance relations in nano-sized Ti-doped sodium-alanate for hydrogen storage

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Hydrogen is regarded as a future energy carrier. Light-weight metal hydrides such as sodium-alanate (NaAlH_4) are potential candidates for hydrogen storage. Here we will report on the use of Ti-doped nano-sized (< 30 nm) sodium-alanate for hydrogen storage. The optimal material released hydrogen close room temperature (max desorption rate 99 °C) while reloading started at an unprecedented low pressure of 10 bar. Moreover, the followed approach allowed us to establish a structure-performance relation for Ti-doped sodium alanates. To obtain nano-sized alanates the use of an inert support, carbon nanofibers (CNF) were used for that purpose, was essential. For a detailed characterization of these materials X-Ray based techniques are indispensable. In the current study we used mainly EXAFS, in situ XRD and XPS. The order of Ti and NaAlH_4 deposition turned out to have a significant influence on the sorption characteristics of the materials. When NaAlH_4 was deposited first, Ti acted mainly as a catalyst and decreased the temperature of the maximum H_2 desorption rate from above 160 °C (without Ti) to 132 °C. However, when Ti was deposited first the desorption properties were further improved (max desorption at 99 °C; Fig 1). This was the results of a better mixing between Ti and Al as inferred from exafs and a smaller alanate particle size in that sample. The latter was the result of the synthesis procedure. Moreover, the presence of Ti also lowered the initial uptake pressure of hydrogen from 20 (without Ti) to 10 bar H_2 pressure at 115 °C for 30 nm NaAlH_4 particles (fig. 2). It is speculated based on an in-situ XRD study that the favorable hydrogen desorption properties of nano-alanates might be the result of the coupling of the two partial desorption/decomposition steps, which occur in bulk materials, i.e., NaAlH_4 to Na_3AlH_6 , Al and H_2 followed by Na_3AlH_6 to NaH, Al and H_2 , to one direct decomposition step from NaAlH_4 to NaH, Al and H_2 .

Location: "La Muta" Hall
Time: 19:45

Ag-for-Na ion-exchanged waveguides: correlation between the Ag site and the photoluminescence emission.

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The Ag site in Ag-for-Na ion-exchanged borosilicate and germanate waveguides has been investigated by the EXAFS spectroscopy. In contrast with the results generally reported in literature, it is shown that for both silicate and germanate waveguides the Ag site is strongly dependent on the Ag content, being the Ag-O distance longer for higher doping level. It is demonstrated that this trend is related to a structural rearrangement of the Ag site in the whole doped layer; the EXAFS results on the samples that underwent the ion-exchange at higher temperatures and the comparison with literature data suggest that the sites with shorter distances are more stable. The correlation between local structure around Ag and the photoluminescence properties of the borosilicate waveguides is established: in particular, the red-shift of the blue band observed in the absorption and excitation spectra by increasing the Ag concentration has been univocally related to the increase of the Ag-O bond length.

P2.2: Extreme conditions

Location: "Allara e Grosso" Hall
Time: 18:00

High pressure x-ray absorption spectroscopy: energy dispersive versus classical set-up

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Until recently, most of high pressure X-ray Absorption Spectroscopy (XAS) experiments were performed using energy dispersive set-up (EDXAS), mainly because this technique was well-suited to overcome the specific drawbacks due to the use of diamond anvil cells (size of the sample, Bragg peaks of the diamond, stability of the beam) but with the limitations due to the technique (no simultaneous I0 measurement, experiments in transmission with no access to dilute samples, correlation between energy resolution and energy range, no EXAFS range for the low energy edges). Now with highly focused classical XAS beamlines operating in third generation synchrotron, the majority of drawbacks due to the high pressure set-up can be overcome. Therefore the choice between scanning or energy dispersive set-ups will strongly depend on the specificity of the planned experiments. The EDXAS is well adapted to measurements of small differences between two signals, like for XMCD or small pressure induced modifications. The energy range available for the EXAFS measurement remains limited for both technique by the Bragg peaks of the diamond except for low energy edges (<6 keV) where the EDXAS is obviously limited because of the possible size of the polychromator. An advantage of the classical set-up is the possibility to combine a large energy range with locally a high resolution, which is not possible for EDXAS where resolution and energy range are correlated. Classical XAS technique offers also the possibility to perform different edges simultaneously during the same experiment. Although fluorescence measurements can be performed using both techniques (through Turbo-EXAFS for EDXAS), the flux is larger in the case of classical EXAFS which is therefore more adapted for measurements on diluted samples. All these points will be illustrated by recent experiments performed on different materials like rare earth compounds, transition metal oxides and semiconductors.

Location: “Allara e Grosso” Hall
Time: 18:20

Magnetism and structure under extreme condition

Baudelet François¹, A. Congeduti¹, Q. Kong¹, A. Monza¹, S. Chagnot¹, J.P. Itié¹, O. Mathon², S.Pascarelli², A.Polian³, M. d’Astuto³, and J.C. Chervin³

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The X-ray Magnetic Circular Dichroism (XMCD) under pressure is a technique of probing microscopic magnetic properties. XMCD is a selective probe, which can access to a large variety of elements. The dispersive EXAFS station at SOLEIL (ODE-beam-line) gives the possibility to perform numerous pressure XAS and XMCD experiments with an excellent statistic. The main advantages of Dispersive XAFS are the focusing optics, the short acquisition time (few ms) and the great stability during the measurements due to the absence of any mechanical movement. These advantages allow the study of small samples, 80 microns at SOLEIL, which is mandatory in the case of high pressure studies.

The modification of the inter-atomic distances may lead to a large variety of magnetic transitions. Nevertheless, pressure can also induce more subtle changes in crystallographic structures like bond angle variations or in electronic structures like in the electronic density at the Fermi level, leading to dramatic changes in magnetic properties.

We measured XMCD signals under hydrostatic high pressure, with a non-magnetic high-pressure anvil-cell small enough to be inserted between the polar pieces of a magnetic dipole. This allows to study the fundamental aspect of magnetism of conduction bands, but also opens the possibility of studying directly the magnetic properties of geological materials.

We will present the new ODE beam line at SOLEIL and the sample environments combination: high magnetic fields, high pressure and low temperature. First high pressure XMCD results on magnetite will be commented.

Location: “Allara e Grosso” Hall
Time: 18:40

X-ray absorption study of $CuGaO_2$ and $CuAlO_2$ delafossites under high pressure

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The $CuGaO_2$ and $CuAlO_2$ delafossite compounds have been studied by x-ray absorption under high pressure at the Cu and Ga K -edges. We have obtained the compressibility of the $Cu - O$ and $Ga - O$ bonds. The structural consequences of our measurements are discussed in connection with complementary x-ray diffraction experiments. We have observed in both compounds the transition to high pressure polymorphs. XANES reveals that GaO_6 octahedra remain essentially undistorted after the phase transition, whereas the Cu environment is considerably transformed. In particular, single crystal measurements at the Cu K -edge show a considerably decrease in the linear dichroism. These observations will be related to Raman measurements.

Location: “Allara e Grosso” Hall
Time: 19:00

Melting in the diamond anvil cell using energy dispersive XAS

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Science at extreme pressure conditions in diamond anvil cells (DAC) historically represents one of the main applications of energy dispersive x-ray absorption spectroscopy (EDXAS) and is well documented in the literature. However, applying pressure is not sufficient for studying chemical properties of matter or to have access to its different states: solid and liquid. Laser-heating in the diamond anvil cell has shown to be applicable for many fields of research ranging from mineral physics, to material synthesis through the study of basic physical and chemical properties in the high P-T regime. In this contribution we show the first melting XAS data in a laser heated DAC recorded at the beamline ID24 of the ESRF.

The specific advantages of EDXAS for melting in the DAC using the laser heating techniques will be highlighted. Two examples will be shown: molten iron and germanium at Megabar pressures.

Location: “Allara e Grosso” Hall
Time: 19:15

Pressure induced metal-insulator transition in LaMnO₃

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The physics leading to the remarkable properties of the manganese perovskites involves a delicate balance between delocalization and carriers trapping. At the local scale, it is strongly related to minor changes in the octahedral distortions (as the Jahn Teller splitting within the Mn³⁺O₆ octahedra), bond lengths shortening, and tilt or buckling of the Mn-O-Mn angle among octahedra. In these systems external pressure is a clean and straightforward way to driven a given system towards ferromagnetism and/or metallization.

We use in situ high pressure XAS to investigate the actual path followed by the Jahn-Teller (JT) distorted LaMnO₃, across the pressure-induced insulator to metal transition, at around 32 GPa [1]. The high pressure Mn K edge experiments were performed at the LUCIA beamline at SLS [2], using a perforated diamond anvil cell. From the edge shift, simulations of the XANES features and EXAFS analysis, we describe successive steps towards the pressure-induced abrupt changes in the resistivity. These steps are associated to local processes such as the opening of the inter-octahedra tilt angles and the average symmetrization of the Mn local environment [3]. The total edge shift, of about 1.4 eV as measured by the maximum of the first derivative at the rising edge, is lower than the expected value if the JT distortion were totally suppressed across the transition. All modifications present a hysteretic behavior when the pressure is released, pointing to the coexistence of two phases and a percolation process over a large pressure range, which leads to metallization.

[1] I. Loa et al., Phys. Rev. Lett. 87, 125501 (2001)

[2] A.M. Flank et al., NIM B, 246, 269 (2006)

[3] A.Y. Ramos et al., Phys. Rev. B 75, 052103 (2007)

Location: “Allara e Grosso” Hall
Time: 19:30

High-pressure ices VI-VIII studied with x-ray Raman scattering

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We present measurements of the oxygen *K*-edge x-ray absorption near-edge structure (XANES) of the high-pressure ices VI–VIII using x-ray Raman scattering (XRS). XRS, *i.e.* non-resonant inelastic x-ray scattering from core electrons, is rapidly emerging as a valuable alternative and a complementary method to x-ray absorption spectroscopy. XRS allows the measurement of soft x-ray absorption edges with hard x-rays, eliminating surface sensitivity and providing access to high pressure cells.

Local coordination influences the XANES of water considerably, as witnessed by the large spectral changes between different phases [1–3]. Intriguingly, XANES appears to be more sensitive than diffraction to distortions in the first-shell structures of liquid water. To fully understand the effect of hydrogen bonds on XANES beyond simple spectral fingerprint arguments, detailed comparisons with electronic structure calculations are essential. In this context, high-pressure ices are important benchmarks as structurally well-characterized model systems of hydrogen bonding. We present experimental studies of ices Ih and VI–VIII, which span a large range of densities and local structures, as well as the proton-ordering transition between ices VII and VIII.

Comparisons with spectral calculations using density functional theory reveal that previous assignments of near, main and post-edge intensities with either broken or strong hydrogen bonds are too simplistic to account for the XANES of these high-pressure ices. A proper analysis of these features is also important for reassessing the controversial interpretation of liquid water XANES.

- [1] Ph. Wernet *et al.* *Science* 304, 995 (2004)
- [2] Y. Q. Cai *et al.* *Phys. Rev. Lett.* 94, 025502 (2005)
- [3] J. S. Tse *et al.* *Phys. Rev. Lett.* 100, 095502 (2008)

Location: “Allara e Grosso” Hall
Time: 19:45

K-edge absorption spectra in Warm Dense Matter

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The recent development of compact, short (ps or subps) X-ray sources [1] gives access to the structural aspect of short time-scale phenomena and to the study of very transient systems such as warm dense materials. Among the structural tools used for the study of static (solid) materials, X-ray Absorption Fine Structure (XAFS) has proven to provide useful information on the local structure (atomic arrangement) and on the electronic Density of States. In a context where the matter is disordered but highly correlated, we present K-edge absorption studies of Warm Dense aluminum. The range of temperature starts from the ambient temperature to a few eV while the density remains close to the solid density, *i.e.* a regime starting from the solid to the strongly correlated plasma. We describe here two theoretical approaches for the calculation of K-edge absorption features. The first one involves a (Modified) HyperNetted Chain – Density Functional Theory (MHNC-DFT) model of dense matter coupled with a specific modeling of the XAFS features [2]. The second one is based on *ab initio* Quantum Molecular Dynamics (QMD) simulations from which a Kubo-Greenwood formulation combined with the Projector Augmented Wave (PAW) formalism gives a direct access to X-ray absorption spectra [3]. These spectra are compared with recent K-edge absorption measurements in aluminum targets isochorically heated by laser-created protons and probed by a short X-ray backlighting source.

- [1] F. Dorchie, M. Harmand, D. Descamps, C. Fourment, S. Hulin, S. Petit, O. Peyrusse, and J. J. Santos, *Appl. Phys. Lett.* 93, 121113 (2008).
- [2] O. Peyrusse, *J. Phys.: Condens. Matter* 20 195211(2008).
- [3] S. Mazevet and G. Zérah, *Phys. Rev. Lett.* 101, 155001 (2008)

P2.3: Chemistry

Location: "Aranjo Ruiz" Hall
Time: 18:00

The XAS model of dissolved Cu(II) and its significance to biological electron transfer

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The standard model for dissolved Cu(II) portrays this ion as an axially elongated octahedron. Using EXAFS and MXAN analyses of copper K-edge XAS spectra, new structural models for dissolved $[\text{Cu}(\text{aq})]^{2+}$, $[\text{Cu}(\text{amm})]^{2+}$, and $[\text{Cu}(\text{ImH})_4]^{2+}$ have been determined. These structures uniformly depart from the octahedral model, in favor of an axially elongated square pyramidal core. Further structural elements also include a -z axially localized scatterer at comparatively greater distance. More removed second shell scatterers further imply organized solvent molecules. The distant structural shells can vary with the solvent medium. MXAN results also indicate that the equatorial ligands need not be coplanar with copper. Preliminary results from new extended, $k = 18 \text{ \AA}^{-1}$, higher resolution copper K-edge XAS data sets are also reported. The low symmetry of dissolved Cu(II) ion contradicts the central thesis of the rack-induced bonding hypothesis in copper electron transfer proteins. The asymmetry of biological copper is not a frozen excited state enforced by a rigid protein scaffold, but is entirely in harmony with the structural flexibility of ground state Cu(II) ion.

Location: "Aranjo Ruiz" Hall
Time: 18:30

EXAFS and XANES Simulations of Fe/Co hexacyanoferrate spectra by GNXAS and MXAN

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Renewed attention to metal hexacyanoferrate is based on their use as magnetic devices, and in particular, on the discovery of the photoinduced magnetization effects in some of these compounds [1,2]. From the structural viewpoint these complexes are characterized by a rigid three dimensional cubic network (although other crystal symmetry are found in few other hexacyanoferrates) of repeating $-\text{NC}-\text{M}_a-\text{CN}-\text{M}_b-\text{NC}-$ units where M_a is Fe and M_b Co and/or Ni. Iron and cobalt sites are typically octahedral, and the sites at the cube centre are occupied by water as well as countercations as necessary to achieve charge neutrality.

In the present paper Full Multiple Scattering (FMS) theory has been applied to analyse Fe/Co hexacyanoferrate XANES spectra: the structural parameters are determined using the MXAN program [3,4] to calculate and fit experimental data. A previously reported EXAFS analysis was performed [5] via the GNXAS package [6], by a Multiple Edge approach of three contiguous edges (Fe, Co, and Ni K-edges) the structural parameters of which are entirely correlated, and the use of a four-body MS calculations. The XANES data of Fe and Co K-edges are independently analysed here. An excellent reproduction of the XANES spectra, and a good agreement with the previous EXAFS results is obtained. The CN bond length has been determined with a statistical error of few thousandths of Å, whereas the Co-Fe distance is also determined with a 0.2 Å accuracy.

- [1] S. Ferlay et al., Science 271, 49 (1996).
[2] O. Sato et al., Science 272, 704 (1996)
[3] M. Benfatto and S. Della Longa, J. Synchrotron Rad. 8, 1087 (2001)
[4] K. Hayakawa et al. J. Am. Chem. Soc. 126, 15618, (2004).
[5] M. Giorgetti and M. Berrettoni, Inorg. Chem. 47, 6001 (2008).
[6] A. Filipponi and A. Di Cicco, Phys. Rev. B 52, 15135 (1995).

Location: “Aranjo Ruiz” Hall
Time: 18:45

Sulfur K-edge x-ray absorption spectroscopy and density functional theory calculations on molybdenum tris(dithiolene) complexes: XAS as a probe of electronic and geometric structures

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The electronic structures of a series of Mo tris(alkyl-dithiolene) complexes, $[\text{Mo}(\text{mdt})_3]^z$ (where mdt = 1,2-dimethylethene-1,2-dithiolate(2-) and $z = 2-, 1-, 0$), with near trigonal prismatic geometries have been determined using S K-edge x-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculations. Additional experimentally-calibrated DFT calculations and comparisons with S K-edge data of Mo tris(aryl-dithiolene) complexes demonstrate that XAS is not only a good probe of ligand- vs. metal-based oxidation, but can also be used to determine whether a metal tris(dithiolene) complex is trigonal prismatic or is distorted towards octahedral symmetry because of the electronic control of the “Bailar twist”. This work was funded at SSRL by DOE-BES, NIH NCCR, and DOE BER.

Location: “Aranjo Ruiz” Hall
Time: 19:00

Coupling CP-MD simulations and x-ray absorption spectroscopy: exploring the structure of oxaliplatin in aqueous solution.

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We present a joint experimental and theoretical XAS study of oxaliplatin in aqueous solution. Oxaliplatin is an anticancer drug of the cisplatin family currently used in the treatment of colorectal cancer. It presents a Pt(II) coordinated to two bidentate ligands: oxalate and diaminocyclohexane. EXAFS and XANES spectra of oxaliplatin are re-examined for a combined molecular dynamic (CP-MD) - experimental analysis. One important purpose under this work is to avoid the use of effective Debye-Waller factors in EXAFS modeling.

FEFF EXAFS and XANES spectra of oxaliplatin are obtained using structural configurations extracted from a CP-MD simulation of a truncated form of oxaliplatin: EDO-Pt. This compound proves to be a good model to mimic the XAS spectroscopic behavior of oxaliplatin. The resulting theoretical spectra are in good agreement with experiment. The analysis of the theoretical EXAFS spectrum allows the assignment of features in the experimental spectra to specific structural motifs, not only in R-space but also in k-space, especially for the contribution from the outer oxygen atoms of oxalate.

In order to get further insight into the combination of theoretical and experimental XAS techniques, standard analysis of EXAFS data is performed on both experimental and theoretical spectra. For the theoretical spectrum issued from the CP-MD simulation, the microscopic description of the system is known. Thus, we can estimate the systematic error associated to the fitting procedure. On the basis of this systematic error, we can estimate the structural parameters of oxaliplatin in aqueous solution, and thus, the accuracy of the theoretical methodology.

Location: "Aranjo Ruiz" Hall
Time: 19:15

Cadmium(II) complex formation with cysteine, penicillamine and glutathione in aqueous solution and solid state

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Cadmium(II) is generally known as a non-essential, highly toxic metal ion that acts as a carcinogen in mammals and inhibits growth of plants. However, cadmium(II) cysteinate compounds have been recently recognized to provide an environmentally friendly route for the production of CdS nanoparticles, used in semiconductors.

We have investigated the complex formation between cadmium(II) and the ligands cysteine (H₂Cys), penicillamine (H₂Pen = dimethylcysteine) and glutathione in aqueous solution (pH = 7.5 and 11.0) and solid state, by means of vibrational, ¹¹³Cd NMR, Cd K- and L₃-edge X-ray absorption spectroscopy. Cadmium(II) ions form a highly insoluble precipitate with cysteine at low pH, Cd(HCys)₂·H₂O, for which we have proposed a "cage/ cyclic" type of structure, composed of mainly CdS₃O and CdS₄ units with single thiolate (Cd-S-Cd) bridges and average Cd-S and Cd-O distances of 2.52(2) and 2.27(4) Å.

In aqueous solutions containing $C_{Cd(II)} = 0.1 \text{ mol dm}^{-3}$ and L/ M ratio of 2.0, both cysteine and penicillamine form complexes with CdS₂N(N/O) coordination, while with glutathione complexes with different types of coordination, e.g. CdS₄, CdS₂(N/O)_x and CdS(N/O)_y are formed. With a large excess of ligand ($C_{H_2L} / C_{Cd(II)} > 10$), cadmium(II)-cysteine and glutathione complexes with CdS₄ coordination geometry dominate. However, in corresponding penicillamine solutions, [Cd(penicillamate)₃]ⁿ⁻ complexes with chelating CdS₃(N/O) coordination dominate already at pH 7.5, and become mixed with CdS₂N(N/O) complexes at pH 11.0.

The present study reveals differences between cysteine and penicillamine that can explain why cysteine-rich metallothionines are capable of capturing cadmium(II) ions, while penicillamine, clinically useful for treating the toxic effects of mercury(II) and lead(II) exposure, is not efficient against cadmium(II) poisoning.

Location: "Aranjo Ruiz" Hall
Time: 19:30

2p x-ray absorption of iron- and cobalt-phthalocyanines

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3d transition metal ions in a planar organic environment, for example phthalocyanines (Pc's), are model systems for proteins [1,2]. In addition, they have potential applications in catalysis and in magnetization control [3,4]. The details of the ligand coordination give rise to different 3d-orbital splitting in the planar D_{4h} environment, usually approximated with crystal field parameters. In our study the 3d-orbital splitting of Fe(II) ($3d^6$) and Co(II) ($3d^7$) in D_{4h} were calculated using the charge transfer multiplet program [5,6]. By variation of the 10Dq, Ds and Dt crystal field parameters, different spin states can be reached for Fe(II) and Co(II). The relative occupations of the 3d-orbitals yield a range of ground states. Although several theoretical and experimental studies have been performed on the electronic ground state of the Fe(II)- and Co(II)-Pc, there is no agreement in these studies with regard to the ground state symmetry.

The Fe and Co L edge X-ray absorption spectra (XAS), X-ray magnetic circular dichroism (XMCD) and X-ray magnetic linear dichroism (XMLD) spectra of Fe(II)- and Co(II)-Pc systems have been measured, where the bulk data are compared with single layers on a gold surface. The spectra have been simulated for these different possible ground states, yielding the optimized ground state(s) for the Pc systems (on a support). In addition, detailed Fe(II) phase diagrams have been created as a function of 10Dq, Ds and Dt.

1. Phthalocyanines: Properties and Applications, ed. C.C. Leznoff and A.B. Lever, Vol. 4. 1996, New York: VCH Publishers
2. H. Eicher and A. Trautwein, J. Chem. Phys., 1969, 50(6), p. 2540
3. M. Bernien et al., PRL, 2009, 102(047202)
4. P. Gambardella et al., Nature Materials, 2009, 8, 189
5. F.M.F. de Groot, Coord. Chem. Rev., 2005 249(1-2), p.31-63
6. Core Level Spectroscopy of Solids, F. de Groot and A. Kotani, 2008, CRC Press

Location: “Aranjo Ruiz” Hall
Time: 19:45

Electronic structure of sulfur studied by x-ray absorption and emission spectroscopy

Roberto Alonso Mori^{1,2}, Pieter Glatzel¹, Eleonora Paris², and Gabriele Giuli²

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Due to its wide range of oxidation states sulfur forms chemical bonds with atoms with very different electronegativities. The metal sulfide minerals are a major source of the world’s metals, whereas disulfide minerals also have interesting solid state properties. Understanding the fundamental chemistry of sulfur provides the key to explaining fundamental mechanisms ranging from volcano climatic interactions to the genesis of ore and its environmental issues related with the reactions of the sulfides with surface and ground waters to form acid sulfate compounds.

The electronic structure of sulfur in minerals and glasses was widely investigated via x-ray Absorption Near Edge Structure (XANES) spectroscopy. However, the XANES spectral shape is influenced by various effects, namely the local symmetry, the ligand type, even up to high coordination spheres, and the valence electron occupation, making it in some cases difficult to determine quantitatively the oxidation state. Therefore we used X-ray Emission Spectroscopy (XES) as a complementary technique to avoid some of the inherent difficulties of XANES, and to extract additional information on the electronic structure. Since the K_α spectral shape is almost independent of the ligand environment, its energy position can be accurately correlated with the valence-shell electron population as it is shown by means of quantum chemical calculations. A considerably better agreement is achieved for the K_α lines than for XANES. Furthermore, the simple K_α spectral shape allows for a robust spectral deconvolution in mixed-valence systems. The electronic structure of sulfur in the various sulfur-bearing minerals is also investigated by means of K_β XES. The spectra are discussed in the framework of ab-initio ground state DFT calculations. S K_β spectroscopy proved to be a reliable complementary technique to XANES to get information on the sulfur ligand environment.

P2.4: Theory II

Location: “Betti” Hall
Time: 18:00

V^{3+} incorporation in garnet : experiments and calculations

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The features in K-edge X-ray absorption spectra of transition metals provide useful information about their crystallographic environment and electronic structure. In particular, the energy and relative intensities of the pre-edge features depend on the valence state and site symmetry of the absorbing atom. Compared with conventional XANES measurements in fluorescence mode, recording fluorescence at a selected emission energy, while scanning the incident energy range, leads to a significant sharpening of the pre-edge features. This High Energy Resolution Fluorescence Detection X-ray Absorption Spectroscopy leads to better resolved spectra, which facilitates the separation of the pre-edge from the main edge and thus allows a more detailed study of the pre-edge features.

Here, we performed HERFD-XAS measurements (on ID26@ESRF) at the V K-edge on an orientated single-crystal of tsavorite, a V^{3+} -bearing garnet ($Ca_3Al_2(SiO_4)_3:V^{3+}$). We investigated the angular dependence of the pre-edge features to assess the importance of electric quadrupole transitions. Indeed, in a cubic compound, the angular dependence is only related to electric quadrupole transitions.

To better ascribe the origin of these transitions, the theoretical X-ray absorption spectrum was determined by monoelectronic and multielectronic calculations, based respectively on the Density Functional Theory and the Ligand Field Multiplet Theory. The combination of these two theoretical approaches gives a full understanding of the electronic structure of V^{3+} in garnet. The comparison with the experimental spectra also provides quantitative information about the relaxation of the crystal structure around the impurity and on site-distorsion.

The proper understanding of the spectral signature of this valence of vanadium (+III) is crucial to study natural samples, where V occurs under different valences, as in titanomagnetites ($Fe_{3-x}Ti_xO_4:V^{3+}, V^{4+}$).

Location: "Betti" Hall
Time: 18:20

The MXAN analysis of the sulphur K-edge XANES of cysteine

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The cysteine molecule can be considered as a prototype of sulphur-containing peptides. Contrary to what happens to other sulphur-containing compounds the XANES data of cysteine has a very simple shape displaying two main peaks followed by a quite flat behavior. In spite of this simple structure an accurate simulation of the experimental data turns out to be quite hard and so far not well achieved [1]. In this paper we present a complete analysis of the XANES energy region employing MXAN [2] method combined with ab-initio molecular dynamics simulations of the Car-Parrinello type [3] and DFT calculations. The experimental edge has been reproduced with good accuracy. The effect of specific water-cysteine interactions as well the influence of effective charge of the atomic species on the near-edge simulations have been explored.

[1] Y. Mochizuki et al., Chemical Physical Letter 309, 241 (1999).

[2] M. Benfatto, and S. Della Longa, J. Synchrotron Rad. 8, 1087 (2001)

[3] P. Giannozzi P, F. De Angelis, and R.J. Car, Chem. Phys. 120, 5903 (2004)

Location: "Betti" Hall
Time: 18:40

Origin of the pre-edge feature at Al K-edge : the role of atomic vibrations

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Band structure DFT codes can be used for the calculation and the analysis of XANES spectra in a wide variety of materials (minerals, strongly correlated oxides, organo-metallic complexes, glasses ...). The method proposed by Taillefumier et al. (Phys. Rev. B 66 195107, 2002) for expressing the cross-section in a plane-wave pseudopotential formalism has been recently implemented in the open-source Quantum-espresso suite of codes under the name XSpectra. In this talk, after a brief recall of the method, I would like to present different applications that have been carried out using XSpectra.

The first application concerns the Fe K pre-edge in myoglobin (Mb) with two axial ligands, CO and CN, that provides different valence and spin states for Fe. A precise analysis of the pre-edge will be given in terms of molecular orbital hybridizations, thanks to complementary local and partial density of states (lpDOS) calculations.

The second application deals with minerals, at the K-edge of Al and Mg for instance, where the coordination of the absorbing site varies. Again the features (in the first 10 eV) will be analysed by lpDOS calculations and relations between the spectral features and the geometry of the absorbing site will be addressed. The role of atomic vibrations will be investigated, enlightening the participation of s empty states in the pre-edge region.

The last example is related to glass systems such as B₂O₃ and K₂O-MgO-2SiO₂. The XANES spectra are calculated from structural models obtained by molecular dynamics (MD). The combination of MD and XANES calculations is a useful tool to probe the local environment of the absorbing atom in amorphous materials.

Location: “Betti” Hall
Time: 19:00

From local to itinerant model of X-ray Absorption: application to the calculation of X-ray Natural Linear Dichroism

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The angular dependence (x-ray linear dichroism) of the Cr K pre-edge in $\text{MgAl}_2\text{O}_4\text{:Cr}^{3+}$ spinel is measured by means of x-ray absorption near-edge structure spectroscopy and compared to calculations based on density functional theory (DFT) and ligand field multiplet (LFM) theory. We also present an efficient method, based on symmetry considerations, to compute the dichroism of the cubic crystal starting from the dichroism of a single substitutional site. DFT shows that the electric dipole transitions do not contribute to the features visible in the pre-edge and provides a clear vision of the assignment of the $1s \rightarrow 3d$ transitions. However, DFT is unable to reproduce quantitatively the angular dependence of the pre-edge, which is, on the other side, well reproduced by LFM calculations. The most relevant factors determining the dichroism of Cr K pre-edge are identified as the site distortion and $3d$ - $3d$ electronic repulsion.

From this combined DFT, LFM approach is concluded that when the pre-edge features are more intense than 4 % of the edge jump, pure quadrupole transitions cannot explain alone the origin of the pre-edge. Finally, the shape of the dichroic signal is more sensitive than the isotropic spectrum to the trigonal distortion of the substitutional site. This suggests the possibility to obtain quantitative information on site distortion from the x-ray linear dichroism by performing angular dependent measurements on single crystals.

Location: “Betti” Hall
Time: 19:20

Relaxed final state DFT simulations of sulfur K-edge XANES and microXANES for catalysis.

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(1) *Inorganic Chemistry and Catalysis. University of Utrecht. The Netherlands.* (2) *Fysikum. University of Stockholm. Sweden.*

X-ray Near Edge Structure (XANES) and the space-resolved microXANES can provide qualitative and quantitative information on the fate of Sulfur in diverse environments. The DFT used in the works presented here (1), allows calculating the experimental spectrum, that is, with the excited core hole (after the excitation of the $1s$ electron during the “X-ray absorption” process) and the subsequent relaxation and with the calculation of the transition matrix, instead of extrapolating the XANES from the densities of states in the ground state. It has proven to be very successful in solutions and amino acids (2). Here examples are shown for the analysis of the differences between aliphatic and thiophenic sulfur compounds, usually found in oils and coals (3). The questions that can be answered range from identification and quantification of sulfur compounds for speciation analysis, to the analysis of the electronic structure of the sulfur, like the sulfur hybridization, protonation of the compound, as well as differentiation of aliphatic and aromatic sulfur. The advantages and limitations of the techniques are explained. Study cases: 1) Understanding Sulfur compounds speciation in detail: a) Thiophenic and aliphatic sulfur (3); b) Sulfide-disulfide (4). DFT simulations treating the core hole as half core hole give the best approximation to the XANES. Including the relaxation of the first excited states and taking the non-orthogonal transition moments gives almost a perfect match many eV above the edge. This unusual result is due to the use of the diffuse basis set, which allows a good description of both the delocalized states as well as bound states, in the near edge region. The first LUMO transitions and their relation to the spectral features are discussed. 2) Theory in action: microspectroscopy of the oligomerization reactions on zeolite crystals (5). We focus on XANES simulations to understand the fate of thiophene deposited on zeolite crystals, thermally treated.

A new interpretation of $L_{2,3}$ X-ray absorption in rutile TiO_2

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The Ti $L_{2,3}$ edge XAS of rutile has thoroughly been studied, theoretically and experimentally. At present, the main features of the spectrum are considered to be dominated by the first-neighbor surrounding of the ionized Ti atom and multiplet effects in the crystal field. In particular, the splitting of the second (e_g) peak was shown to be related to the distortion of the Ti environment from octahedron to a lower symmetry [1].

We calculated the Ti $L_{2,3}$ spectrum in the different approaches [2]: i) within the usual one-electron multiple scattering (MS) method (XKDQ code) and ii) using the multichannel version of the MS method (MCGFXL code). Analysis of the one-electron calculations reveals that the real distortion of the TiO_6 octahedron to D_{2h} is too small to account for the above splitting. It is found that this effect is due to peculiarities of the formation of unoccupied electron states in rutile with the x-ray hole located at the Ti atom. This result shows that the atomic multiplet theory including the crystal field misses some one-electron effects essential for a satisfactory description of Ti $L_{2,3}$ XAS in rutile; on the other hand, the adjustable parameters of the theory provide good agreement with experiment, which leads to incorrect interpretation of the spectrum. Our calculations within the multichannel MS method that allows for both multiplet-like effects without introducing free parameters and one-electron multiple scattering are in reasonable agreement with experiment. Remaining discrepancies are caused by employing the muffin-tin approximation. The work is supported in part by Ministry of Education and Science of the Russian Federation Grant 2.1.1/3690.

[1]. F.M.F. De Groot, J.C. Fuggle, B.T. Thole, and G.A. Sawatzky, Phys.Rev. B 41, 928 (1990).

[2]. A.I. Taranukhina, A.A. Novakovich, and R.V. Vedrinskii, submitted to XAFS 14 Conference (2009).

Tuesday 28th July

M2: Plenary session M2

Location:	“Benedetto XIII” Hall
Time:	8:30

X-ray absorption spectroscopy for probing bonding, structure and ultrafast dynamics in water

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X-ray absorption spectroscopy at the oxygen K edge will be discussed as a probe of bonding, structure and ultrafast dynamics in water. Various systems such as liquid water, ice and small clusters will be compared and discussed. Various methods such as soft x-ray absorption spectroscopy, x-ray Raman scattering, and time-resolved x-ray absorption spectroscopy are used to infer information on the hydrogen bond network in water (both from NEXAFS/XANES and EXAFS).

One focus will be on our recent efforts on time-resolved infrared pump - x-ray probe studies of the structural dynamics of liquid water. Femtosecond infrared excitation via the O-H stretching band induces an ultrafast temperature jump that gives rise to changes in the hydrogen bond network. For the first time, such changes are probed via the transient x-ray absorption at the oxygen K edge. The O-H stretching vibration displays a population relaxation with a 200 fs time constant by vibrational redistribution through the intramolecular bending and intermolecular librational and hydrogen-bond vibrational modes. Full equilibration into a heated water sample is reached within a few picoseconds. The related ultrafast temperature jump and the associated structural changes are characterized in detail with the transient x-ray absorption spectrum at the oxygen K edge.

Our work establishes a direct link between femtosecond vibrational spectroscopy and structural information. It allows for unraveling the ultrafast structural changes of the hydrogen bond network on their intrinsic time scales during and immediately after the disposal of excess energy.

Location: “Benedetto XIII” Hall
Time: 9:00

Advanced hard X-ray spectroscopy – recent results on water and 3d transition metal systems

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High-resolution energy analysis of the photon-out channel is a powerful advancement to hard x-ray spectroscopy experiments. For applications in the 6-10 keV range instruments with a resolution of 0.3 – 1 eV and a large solid angle are now available at several synchrotron facilities. The techniques performed at such instruments include non-resonant x-ray Raman scattering (XRS), resonant inelastic x-ray scattering (RIXS), x-ray emission spectroscopy (XES) and selective x-ray absorption spectroscopy (S-XAS). All of these techniques are bulk probes of the local electronic and geometric structure and provide unique information that is complimentary to that of traditional x-ray absorption spectroscopy. At SSRL beam line 6-2 we are now operating a multi-crystal analyzer setup in combination with either a Si (111) monochromator (~ 1 eV resolution) or a Si (311) monochromator (~ 0.2 eV resolution).

Examples of the latest results will be presented in this talk. They include a) new high-resolution XRS studies of the oxygen K edge of liquid water under various conditions and their impact on structural models, b) the first XES studies of ligand to metal transitions in the oxygen evolving complex of photosystem II, c) XES based ligand characterization of Fe-Mo nitrogenases and the d) the application of 1s3p RIXS as a core hole clock in the attosecond range.

An outlook of how these techniques can be used in future pump-probe experiments at X-ray free electron lasers will conclude the presentation.

Location: “Benedetto XIII” Hall
Time: 9:30

Time-Resolved X-Ray Absorption in materials in extreme conditions

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(2) *Lawrence Berkeley National Laboratory, One Cyclotron Road, MS 80R0114, Berkeley CA 94720 US*

I will discuss recent dynamic measurements on K-shell absorption in laser-heated, amorphous carbon and diamond thin films. Techniques for the study of materials under the extreme conditions of temperature and pressure, using soon-to-be-available, advanced x-ray free electron laser sources, will also be discussed.

Location: “Benedetto XIII” Hall
Time: 10:00

Perspective for High Energy Density Studies using X-ray Free Electron Lasers

Richard W. Lee¹, B. Nagler², U. Zastrau³, R. Fäustlin⁴, S. M. Vinko², T. Whitcher², R. Sobierajski⁵, J. Krzywinski⁶, L. Juha⁷, A. J. Nelson¹, S. Bajt⁴, T. Bornath⁸, T. Burian⁷, J. Chalupsky², H. Chapman⁴, J. Cihelka⁷, T. Döppner¹, T. Dzelzainis⁹, S. Düsterer⁴, M. Fajardo¹⁰, E. Förster³, C. Fortmann⁸, S. H. Glenzer¹, S. Göde⁸, G. Gregori², V. Hajkova⁷, P. Heimann¹¹, M. Jurek⁵, F. Y. Khattak¹², A. R. Khorsand¹³, D. Klinger⁵, M. Kozlova¹⁰, T. Laarmann⁴, H.-J. Lee¹⁴, K.-H. Meiwes-Broer⁸, P. Mercere¹⁵, W. J. Murphy², A. Przystawik⁸, R. Redmer⁸, H. Reinholz⁸, D. Riley⁹, G. Röpke⁸, K. Saksl¹⁶, R. Thiele⁸, J. Tiggesbäumker⁸, Toleikis⁴, T. Tschentscher⁴, I. Uschmann³, and J. S. Wark²

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(12) Department of Physics, Kohat University of Science and Technology, Kohat-26000, NWFP, Pakistan

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(14) Department of Physics, University of California, Berkeley CA 94720

(15) SOLEIL, L'Ormedes Merisiers Saint-Aubin, BP 48 91192 Gif-sur-Yvette, France

(16) Slovak Academy of Sciences, Watsonova 47, 04001 Kosice, Slovak Republic

A general overview of the potential for both warm and hot dense matter research for the future will be presented. First, a discussion of the regime defined as relevant to warm dense matter will be attempted in terms of the underlying physical phenomena that define the field. Next a categorization of the facilities to be included in the perspective will be given. With this as background a series of schematic experiments will be discussed with respect to the facilities where they will be pursued. Comments on the interaction amongst the various experiments and between the various facilities will be outlined.

Finally, a report will be given of the x-ray absorption of Warm Dense Matter experiment at the FLASH Free Electron Laser (FEL) facility at DESY. The FEL beam is used to produce Warm Dense Matter with soft x-ray absorption as the probe of electronic structure. A multilayer-coated parabolic mirror focuses the FEL radiation, to spot sizes as small as $0.3\mu\text{m}$ in a $\sim 15\text{fs}$ pulse of containing $\geq 10^{12}$ photons at 13.5 nm wavelength, onto a thin sample. Silicon photodiodes measure the transmitted and reflected beams, while spectroscopy provides detailed measurement of the temperature of the sample. The goal is to measure over a range of intensities approaching $10^{18}\text{W}/\text{cm}^2$. Experimental results will be presented along with theoretical calculations.

S2: Advances in ultrafast spectroscopy using present and next generation x-ray sources

Location: "Benedetto XIII" Hall
Time: 11:00

Ultrafast X-ray absorption spectroscopy of molecular systems in solution

M. Chergui¹

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We will present our results on the study of the photoinduced dynamics of molecular systems in liquids using ultrafast (picosecond and femtosecond) X-ray absorption spectroscopy. We will present examples on the spin and structural dynamics in Fe(II)-based molecular complexes [1,2] on the dynamics of electronic solvation [3,4] and on the bond formation in bimetallic complexes [5].

[1] W. Gawelda et al. "Structural determination of a short-lived Iron(II) Complex by Picosecond X-ray Absorption Spectroscopy" *Phys. Rev. Lett.* 98 (2007) 057401

[2] C. Bressler et al. "Femtosecond XANES of the light-induced spin crossover dynamics in an Iron(II)-complex" *Science* 323 (2009) 489

[3] V. T. Pham et al. "Observation of the solvent shell reorganisation around electronically excited atomic solutes by picosecond X-ray absorption spectroscopy" *J. Am. Chem. Soc.* 129 (2007) 1530

[4] C. Bressler et al. "Exploiting EXAFS and XANES for Time-Resolved Molecular Structures in Liquids" *Z. für Kristall.* 223 (2008) 307

[5] R. M. van der Veen et al. "Structural determination of photochemically active diplatinum molecule by time-resolved EXAFS spectroscopy" *Ang. Chem. Int. Ed.* 48 (2009) 2711

Location: "Benedetto XIII" Hall
Time: 11:25

Probing ultra-fast dynamics in aqueous solutions using soft x-ray techniques

Emad Flear Aziz¹, Niklas Ottosson², Manfred Faubel³, Ingolf V. Hertel⁴, and Bernd Winter¹

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Why the diffusion of OH⁻ in water faster than the halides? To understand this question, Charge-transfer-to-solvent (CTTS) excited states of aqueous chloride are studied by resonant inner-shell photoexcitation. Cl-aq 2p → e(i), i = 1-4, denotes a series of excitations to lowest and higher CTTS states.(1) These states are clearly identified through the occurrence of characteristic spectator Auger decays to double Cl 3p valence-hole states, where the CTTS states can be more stabilized and are more definitely visible than those in single Cl-aq 2p core excitations and in optical valence excitations. We were expecting to find a similar behavior for OH-aq. CTTS states correspond to a situation in which immediately after excitation the electron is bound in a potential well due to the pre-existing polarization of oriented solvent dipoles around the ion.(2) In sharp contrast, and quite unexpected, we observed that Auger decay is not operative for OH-aq, although the excited states of OH-aq are of CTTS nature (according to our X-ray absorption measurement), and also the experiment is fully analogous to the halide study. Instead, a new, competitive (on an ultrafast timescale) and unique relaxation mechanism, Inter Columbic-molecular Decay (ICD), opens up. This must be inherently related to hydroxide's hydrogen atom, which in a favorable transient hydration topology can act as a donor bond, and explain the extra fast diffusion of OH⁻ compare to other negatively charged ions in solution.

[1] B. Winter, E. F. Aziz, N. Ottosson, et al., *Journal of the American Chemical Society* 130, 7130 (2008).

[2] E. F. Aziz, N. Ottosson, M. Faubel, et al., *Nature* 455, 89 (2008).

Location: “Benedetto XIII” Hall
Time: 11:50

Ultrafast time-resolved x-ray absorption spectroscopy: watching atoms dance

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X-ray absorption spectroscopy has the ability to achieve structural resolution down to the sub-Å level in the condensed phase. By using XAS to probe laser-excited samples we can obtain excited-state structural and electronic dynamical information not available through other techniques.[1] Recent advances in femtosecond hard x-ray generation[2] have allowed us to extend our ultrafast XAS techniques into the sub-picosecond time domain which is the fundamental time scale of molecular motion. By combining ultrafast laser spectroscopic techniques[3] with picosecond[4] and femtosecond[5] XAS measurements we have completely resolved the photocycle of an Fe(II)-based molecular spin-crossover system in solution. Recent femtosecond XAS results and the prospect of these types of measurements at next-generation x-ray free electron lasers[6] will also be discussed.

[1] Ch. Bressler, R. Abela, and M. Chergui, *Z. Kristallogr.* **223** (Jan, 2008) 307–321.

[2] P. Beaud, S. L. Johnson, A. Streun, R. Abela, D. Abramsohn, D. Grolimund, F. Krasniqi, T. Schmidt, V. Schlott, and G. Ingold, *Phys. Rev. Lett.* **99** (Jan, 2007) 174801.

[3] W. Gawelda, A. Cannizzo, V.-T. Pham, F. van Mourik, Ch. Bressler, and M. Chergui, *J. Am. Chem. Soc.* **129** (Jan, 2007) 8199–8206.

[4] W. Gawelda, V.-T. Pham, M. Benfatto, Y. Zaushtsyn, M. Kaiser, D. Grolimund, S. L. Johnson, R. Abela, A. Hauser, Ch. Bressler, and M. Chergui, *Phys. Rev. Lett.* **98** (Feb, 2007) 4.

[5] Ch. Bressler, C. Milne, V.-T. Pham, A. El Nahhas, R. M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser, C. N. Borca, G. Ingold, R. Abela, and M. Chergui, *Science* **323** (Jan, 2009) 489–492.

[6] <http://www.xfel.eu/>; <http://lcls.slac.stanford.edu/>; <http://fel.web.psi.ch/>

Location: “Benedetto XIII” Hall
Time: 12:15

Directo observation of transient ligand-field changes in transition metal complexes via time-resolved soft x-ray spectroscopy

Nils Huse¹, Nils Huse¹, Tae Kyu Kim², Lindsey Jamula³, James K. McCusker³, and Robert W. Schoenlein¹

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Time-resolved laser spectroscopy and established x-ray methods have recently been combined to probe the local electronic and molecular structure in time and energy. Soft X-rays are sensitive to valence-charge distributions and hold tremendous potential for following chemical bonding and the formation of new molecular species in real time. This is particularly powerful for understanding molecular dynamics in solution, where important chemistry occurs.

Solvated transition-metal complexes are of fundamental interest due to strong interactions between electronic and molecular structure. In particular, octahedral ligands in Fe(II) complexes effectively couple optical charge-transfer excitations [1–3] to changes of the molecular structure, leading to rapid spin-state interconversion.

We have measured the absorption at the Fe L-edges of the low- and the transient high-spin states after the photo-induced metal-to-ligand charge transfer at the ALS Beamline 6.0.2. Critical to such liquid-phase studies has been the development of a liquid sample cell that allows to control the liquid film thickness with sub-200 nm accuracy.

These are to our knowledge the first picosecond spectra of solvated molecules ever recorded in the soft x-ray region. They reveal a red-shift of the Fe L-edges of the high-spin state, which corresponds to a reduction in ligand-field splitting of the Fe(II) d-orbitals. The delay scans track the decrease of the low-spin state absorption and the increase of the high-spin state absorption. These delay scans reflect the 70 ps width of the x-ray probe pulses demonstrating the formation of the meta-stable high-spin state within the probe pulse duration.

Our experimental approach opens the door to femtosecond soft x-ray investigations of liquid phase chemistry that have previously been inaccessible.

[1] Monat JE and McCusker JM, *JACS* **122**, 4092

[2] Khalil M et al., *JPCA* **111**, 38

[3] Bressler Ch et al., *Science* **323**, 489

Location: "Benedetto XIII" Hall
Time: 12:40

Laser-induced x-ray transparency in free atoms and molecules

Linda Young¹, R. W. Dunford¹, E. P. Kanter¹, B. Krässig¹, R. Santra^{1,2}, S. H. Southworth¹, T. Allison³, A. Belkacem³, T. E. Glover³, M. Hertlein³, and J. van Tilborg³

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Control of x-ray processes using intense optical lasers represents an emerging scientific frontier—one which combines x-ray physics with strong-field laser control. While the past decade has produced many examples where phase- and amplitude-controlled lasers at optical wavelengths are used to manipulate molecular motions, the extension to control of ultrafast, intraatomic, inner-shell processes is quite new. Gas phase systems are particularly suitable for illustrating the basic principles underlying combined x-ray and laser interactions. I will discuss three scenarios by which strong electromagnetic fields can be used to modify resonant x-ray absorption in a controlled manner: (1) Ultrafast field ionization of atoms at laser intensities in the range $10^{14} - 10^{15}$ W/cm² [1]; (2) laser-induced x-ray transparency of inner-shell resonances by laser dressing at $10^{12} - 10^{13}$ W/cm² [2]; and (3) control of resonant x-ray absorption by molecules through laser-induced alignment at 10^{12} W/cm² [3]. We have demonstrated these phenomena recently by probing the micron-scale intense field volume with microfocused hard and soft x rays from the Advanced Photon Source and the Advanced Light Source. Due to the rapid and controllable response of electrons in free atoms and molecules, one can envision interesting technologies – such as femtosecond x-ray switches and modulators.

[1] L. Young, D. A. Arms, E. M. Dufresne, R. W. Dunford, D. L. Ederer, C. Höhr, E. P. Kanter, B. Krässig, E. C. Landahl, E. R. Peterson, J. Rudati, R. Santra, S. H. Southworth, Phys. Rev. Lett. **97**, 083601 (2006).

[2] C. Buth, R. Santra, L. Young, Phys. Rev. Lett. **98**, 253001 (2007).

[3] E. R. Peterson, C. Buth, D. A. Arms, R. W. Dunford, E. P. Kanter, B. Krässig, E. C. Landahl, S. T. Pratt, R. Santra, S. H. Southworth, L. Young, Appl. Phys. Lett. **92**, 094106 (2008).

P3.1: Nano structures II

Location: "La Muta" Hall
Time: 15:30

The Mn site in Mn-doped iii-As nanowires: an EXAFS study

Francesco d'Acapito¹, M. Rovezzi¹, F. Boscherini², F. Jabeen³, M. Piccin³, L. Felisari³, V. Grillo³, G. Bais³, S. Rubini³, and F. Martelli³

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We present an EXAFS study of the Mn atomic environment of Mn-doped GaAs and InAs nanowires. Mn doping has been obtained either via the diffusion of the Mn used as catalyst for the nanowire growth or by providing Mn during the growth of Au-catalyzed wires. As a general finding we observe that Mn forms chemical bonds with As but is not predominantly incorporated in a substitutional site. In Mn-catalysed GaAs wires, Mn is mostly found bonded to As in a rather disordered environment and with a stretched bond length, reminiscent of that exhibited by MnAs phases. In Mn-catalysed InAs wires, the Mn site is similar but significantly more ordered, hinting at the presence of a more extended hexagonal MnAs phase. Finally, in Au-catalysed and Mn-doped GaAs nanowires, along with stretched Mn-As coordination we have found the presence of Mn in a Mn-Au intermetallic compound, which is presumably formed in the nanoparticle at the tip of the nanowire.

Location: “La Muta” Hall
Time: 15:50

Magnetic memory of a single-molecule quantum magnet wired to a gold surface

Philippe Saintavrit^{1,2}, Matteo Mannini^{3,4}, Francesco Pineider³, Chiara Danieli⁵, Edwige Otero², Corrado Sciancalepore⁵, Anna Maria Talarico⁵, Marie-Anne Arrio¹, Andrea Cornia⁵, Dante Gatteschi³, and Roberta Sessoli³

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In the field of molecular spintronics the use of magnetic molecules for information technology is a main target and the observation of magnetic hysteresis on individual molecules organized on surfaces is a necessary step to develop molecular memory arrays. Information storage at the molecular level requires molecules exhibiting an intrinsic remnant magnetization, like the so-called single-molecule magnets[1] (SMMs). These have been intensively investigated for their rich quantum behaviour[2] but no magnetic hysteresis had been so far reported for monolayers of SMMs on various non-magnetic substrates, most probably owing to the chemical instability of clusters on surfaces[3]. Using X-ray absorption spectroscopy and X-ray magnetic circular dichroism synchrotron-based techniques, pushed to the limits in sensitivity and operated at sub-kelvin temperatures (400 mK), we have now found that robust, tailor-made Fe₄ complexes retain magnetic hysteresis at gold surfaces [4,5]. Our results demonstrate that isolated SMMs can be used for storing information. The road is now open to address individual molecules wired to a conducting surface in their blocked magnetization state, thereby enabling investigation of the elementary interactions between electron transport and magnetism degrees of freedom at the molecular scale.

[1] R. Sessoli et al. Nature 365, 141–143 (1993).

[2] D. Gatteschi et al. Molecular Nanomagnets (Oxford Univ. Press, 2006).

[3] M. Mannini, Ph. Saintavrit et al. XAS and XMCD investigation of Mn₁₂ monolayers on gold. Chemistry : a European Journal 14, 7530–7535 (2008).

[4] M. Mannini, F. Pineider, Ph. Saintavrit et al. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. Nature Materials 8, 194 - 197 (2009).

[5] M. Mannini, F. Pineider, Ph. Saintavrit et al. X-ray magnetic circular dichroism picks out single-molecule magnets suitable for nanodevices. Advanced Materials 21, 167–171 (2009).

Location: "La Muta" Hall
Time: 16:10

Correlation of magnetism and structure for ultra thin Au/Co/Au films: evidence for magnetoelastic effects

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The Spin Reorientation Transition (SRT) of thin Au/Co/Au films, grown both, ex- and in-situ on W(110), are studied by means of soft X-ray based X-ray Magnetic Circular Dichroism (XMCD), Resonant Reflectivity, Photoemission and EXAFS experiments. We characterize and correlate the magnetic, electronic and structural properties of these films as a function of the Au and Co film thickness, as well as the temperature of the system. This set of systematic data brings new insight into the complexity of the SRT phenomena. We correlate the variations of the Co spin and orbital moments determined by XMCD measurements with the occurrence of the spin reorientation and the structural changes at the atomic level as measured by EXAFS. At 300 K, for in-situ grown Co on a Au(111) film, which was grown on a W(110) single crystal, no out-of-plane magnetization is found for these bare Co/Au bilayers. Such a novel observation, in terms of easy magnetization direction for low thickness Co on Au, is an intrinsic property of the particular interface as prepared here, and not due to surface contamination. After capping with Au an out-of-plane magnetization is observed below a thickness of four atomic Co layers. We obtain a new SRT phase diagram, which differs from the one for ex-situ grown films. Our recent findings based on the XMCD results establish that, contrary to the widely accepted picture, there is no increase of the Co perpendicular orbital moment, which accompanies the in- to out-of-plane SRT. Such an unexpected finding is linked with the large spin-orbit interaction within the Au caps. When the SRT upon Au capping occurs, a 5 Å thin Co layer undergoes structural changes of lattice parameters of $\Delta a/a = -1.2\%$ and $\Delta c/c = +6.6\%$. Observing structural variations as the SRT occurs, differs from previous work on Co/Au(111), and allows for the first time to quantify the magnetoelastic energy contribution related with the presence of the Co/Au interface.

Location: "La Muta" Hall
Time: 16:30

Microstructure of quantum dots ensembles by EXAFS spectroscopy

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Multilayered quantum dots containing systems are important for many practical applications. In a simplified model of weak tunneling and strong quantization, the electronic coupling between QDs brought close together appears as the formation of bonding and antibonding molecular type orbitals from the single dot states by an analogy with covalent bonds in natural molecules. Interpretation of QDs ensembles energy spectra must take into account the peculiarities of local structure of such formation, due to the strain field near the interfaces.

EXAFS spectroscopy provides a unique possibility to determine local structural changes in systems with thin layers and nanoclusters [1-2]. EXAFS spectra of the GeK- and GaK- edges were measured at the VEPP-3 storage ring of the Budker Institute of Nuclear Physics (Novosibirsk) and at the DUBBLE beamline of the ESRF (Grenoble).

It was established an influence of blocking layers (Si, AlN) effective thickness, number of Ge and GaN layers in sandwich and annealing temperature on the microstructure parameters of systems with QDs. It was determined, that N(Ge) and N(Ga)-coordination numbers and sizes of Ge- and GaN- islands increase with decreasing of blocking Si- and GaN- layers thickness. The origin of such growth of Ge- islands sizes is attributed to the better condition for preferential nucleation for samples with thin blocking Si layers due to an inhomogeneous strain field induced by buried dots. Some decrease of N(Ga)- coordination number on going from samples with small number of layers in sandwich to multi-layer samples is very likely determined by interface diffusion during multiple heating during preparation.

Financial support from the RAS Program N27 (grant 9) is greatly appreciated.

[1] Simon Erenburg, Nikolai Bausk, Lev Mazalov et al, J Synchrotron Rad. 10, 380 (2003)

[2] S.B.Erenburg, N.V.Bausk, L.N.Mazalov et al, Nucl. Instr. & Meth. Phys. Res A 543, 188 (2005)

Location: “La Muta” Hall
Time: 16:45

XANES and photoluminescence studies of crystalline Ge and GeO₂ nanowires

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The electronic and optical properties of materials used for the design of electronic circuits strongly depend on their characteristic size and dimensionality. There is renewed interest in germanium due to the relatively high electron and hole mobility, which becomes important as characteristic sizes are scaled down to the sub-100 nm range [1]. In this range, quantum confinement effects start becoming significant because of the exciton radius of Ge which is quite large (24.3 nm) [2]. Although Ge and GeO₂ nanostructures are both light emitters [2-4], studies of germanium nanowires (GeNW) have been scarce.

In this work we report a synchrotron study of Ge and GeO₂ nanowires prepared by a vapor-liquid-solid (VLS) method [5, 6]. The nanowires were grown using Au nanoparticles as a catalyst to take advantage of the low eutectic temperature (360 °C) of Ge-Au alloy. The electronic and local structure of Ge and GeO₂ nanowires were studied by X-ray Absorption Near-Edge Structure (XANES) at the O K- and Ge L3-edges. X-ray Excited Optical Luminescence (static and time resolved) were used to monitor the optical emission upon X-ray absorption with the excitation energy tuned across absorption edges of interest. With this method one obtains site specific insight into the chemical origin of luminescence.

[1] S. M. Sze, Physics of Semiconductor Devices (Wiley, New York, 1981)

[2] Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, and Y. Masumoto, Appl. Phys. Lett. 59, 3168 (1991)

[3] X.C. Wu, W.H. Song, B. Zhao, Y.P. Sun, and J.J. Du, Chem. Phys. Lett. 349, 210 (2001)

[4] P. Hidalgo, B. Mendoz, and J. Piqueras, Nanotechnology 16, 2521 (2005)

[5] R.S. Wagner and W.C. Ellis, Appl. Phys. Lett. 4, 89 (1964)

[6] X.H. Sun, C. Didychuk, T.K. Sham, and N.B. Wong, Nanotechnology 17, 2925 (2006)

Location: “La Muta” Hall
Time: 17:00

On the spin reorientation of ordered magnetic nano-dot arrays: Pt/Co/Pt versus Au/Co/Au

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We present in situ Co L-edge X-ray Magnetic Circular Dichroism (XMCD) spectroscopy measurements, in combination with XMCD-Photo-Electron Emission Microscopy (PEEM) results on self-organized, ordered, Co based nano dot arrays, shadow deposited, on nano structured $Si_{0.5}Ge_{0.5}$. The XMCD-PEEM micrographs reveal that the individual dots, of lateral size 200nm by 25nm, are magnetic at 300K.[1] The magnetic domain structure is recorded as a function of Co coverage. Both measurements prove the occurrence of a perpendicular Co dot magnetization and a macroscopic out of plane magnetic remanence. We characterize the spin reorientation of these dot arrays between the temperatures of 300K and 100K as a function of Co and Pt or Au cap layer thickness. The in- versus out-of-plane orbital moment anisotropy, is not always related with an out-of-plane magnetization and the occurrence of a spin reorientation. The out of plane phase is more stable in the Co/Au case, compared to Co/Pt. The typical magnetic domain size appears to be smaller in the Co/Pt case. The local atomic structure of the Co atoms is characterized by means of Co K-edge EXAFS measurements. For Co/Au dots two distinct nearest neighbor Co shells are resolved, in contrast with the Pt case where only one is found. Our structural and magnetic characterization of the spin reorientation transition in these nano magnet arrays by means of XMCD-PEEM and angle dependent XMCD measurements reveals that the spin reorientation takes place over a much broader thickness range than in two-dimensional thin films or multilayers. The EXAFS data indicate that for Co/Au dot arrays, on nano structured $Si_{0.5}Ge_{0.5}$, a magneto-elastic contribution to the magnetic energy influences the occurrence of the spin reorientation, in contrast to the case for Co/Pt dot arrays, where only a bulk like Co-Co distance is found.

[1] L. Gridneva, A. Persson, M. Á. Niño et al., Phys. Rev. B 77, 104425 (2008).

Location: “La Muta” Hall
Time: 17:15

Local structural change under antiferro- and ferromagnetic transition in FeRh alloy

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The local structural change in FeRh alloy has been investigated under antiferro (AFM)- and ferromagnetic (FM) transition by temperature dependent EXAFS analyses. In the process of the transition, the thermal expansion was observed as same time as the magnetic transition. This is so called “egg and chicken problem”, which is prominent structure transition or magnetic one. First nearest neighbor atomic pair, Fe-Rh or Rh-Fe, shows the thermal expansion from 250K (T1) and it was finished at 345K (T2). On the other hand, the second nearest atomic pair, Fe-Fe or Rh-Rh, shows the expansion from T1 to 390K (T3). The interatomic distance of Fe-Fe (or Rh-Rh) is longer than that of Fe-Rh. These discrepancies are overcome by introduce the idea of distorted ferromagnetic phase model.

P3.2: Surface and Magnetism

Location: “Allara e Grosso” Hall
Time: 15:30

Depth profiling of magnetic and atomic structures of ultrathin films by depth-resolved XMCD and XAFS techniques with a sub-nm depth resolution

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(2) *Japan Science and Technology Agency, CREST*

The depth profile of magnetic ultrathin films has attracted much interest because the surface and interface play important roles for the magnetic property of the whole film. Moreover, even the inner layers often exhibit some prominent depth dependence. In order to investigate the depth profile of ultrathin films, we have recently developed a depth-resolved technique based on XMCD and XAFS spectroscopies [1]. In this contribution, the depth profiling of the magnetic and atomic structures of ultrathin films is presented after a brief introduction to the depth-resolved technique.

The depth-resolved XMCD/XAFS is based on the electron-yield measurement, where the probing depth of the spectrum is determined by the effective escape depth of the electrons, which depends on the electron emission angle. A series of XMCD/XAFS spectra with different probing depths are obtained by separately collecting the electrons at different detection angles, by using an imaging-type microchannel plate detector. One can investigate the depth profile of the magnetic and atomic structures of ultrathin films with a sub-nm resolution, by analyzing the XMCD/XAFS spectra recorded at different probing depths.

We have studied magnetic and atomic structures of 3d transition metal films grown in-situ on Cu(100), as well as the effects of gas adsorption on the films [2,3]. Moreover, the depth-resolved technique has been applied to magnetic thin films covered with a protection layer such as Au [4], to which the in-situ measurements are not necessary.

[1] K. Amemiya et al., Appl. Phys. Lett. 84, 936 (2004).

[2] K. Amemiya et al., Phys. Rev. B 70, 195405 (2004).

[3] H. Abe et al., Phys. Rev. B 77, 054409 (2008).

[4] M. Sakamaki et al., Acta Phys. Pol. A 115, 309 (2009).

Location: “Allara e Grosso” Hall
Time: 16:00

Resolving subsurface magnetism at atomic scale by diffraction spectroscopy

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There was no direct method up to now for detecting the electronic and magnetic structure of each atomic layer at subsurface. For this purpose, we have developed a new method, DIFFRACTION SPECTROSCOPY, by combining two existing techniques: XAFS and Auger electron diffraction (AED). X-ray absorption near edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) measurements by Auger electron yield detection are powerful analysis tools for the electronic and magnetic structures of surfaces. However, all the signal from atoms within the electron mean-free-path range is summed into the obtained spectra. From a series of measured thickness dependent AED patterns, we deduced atomic-layer-specific AED patterns and succeeded in disentangling spectra from different atomic layers.

The spin reorientation transitions (SRT) of the magnetic epitaxial film from in-plane to perpendicular direction are intriguing phenomena. A Ni ultra thin film on a Cu(001) surface is regarded as a basic starting point for nanoscale magnetism. We applied diffraction spectroscopy and obtained atomic-layer resolved XANES and XMCD spectra in a non-destructive way. Surface and interior core-level shifts and magnetic moments are determined for each atomic layer [Phys. Rev. Lett. 100 (2008) 207201].

The orbital magnetic moments are more enhanced at the surface layers compared to the spin magnetic moments in the case of 8 ML (in-plane), while variations of the moments are rather small in the case of 15 ML (perpendicular). Atomic orbital is sensitive to the local bonding configuration, while spin reflects the long range magnetic ordering. At a thickness beyond SRT, the magnetic moment orients perpendicularly owing to the spin magnetic moment in the interior layers. At the region below SRT, where the spin magnetic moment is small, the orbital magnetic moment at the surface layers determines the orientation to be in-plane. SRT at 10 ML is based on such a subtle balance of magnetic moments.

Location: "Allara e Grosso" Hall
Time: 16:15

Surface antiferromagnetic coupling of Fe/Cu(001) induced by NO adsorption studied by means of depth-resolved XMCD method

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Fe(<4 ML)/Cu(001) films exhibit a perpendicular ferromagnetic coupling among a whole film. We have reported the CO adsorption effects on the films [1]. The surface layers of Fe/Cu(001) lose the effective spin magnetic moment, m_s^{eff} , upon CO adsorption. This disappearance of surface magnetization is due to a surface reconstruction and/or electron interaction between CO and the films. NO molecule, having one more electron than CO, is expected to interact more firmly with the films. We present here the effects of NO adsorption on the magnetism of Fe/Cu(001) films [2]. An antiferromagnetic coupling between the topmost layer and the other layers was obviously observed in NO/Fe(3 and 4 ML)/Cu(001).

Our experiments were performed at BL-7A of the Photon Factory. Conventional and depth-resolved XMCD measurements were carried out at 120 K.

XMCD spectra were measured for Fe(4 ML)/Cu(001) before and after NO adsorption. The bare 4 ML Fe film was magnetized perpendicularly, and m_s^{eff} was $2.5 \mu_B$. However, the NO adsorbed 4 ML Fe film exhibited in-plane magnetization. The NO adsorbed 4 ML Fe film showed m_s^{eff} of $1.2 \mu_B$, which is about a half of m_s^{eff} of the bare film.

The apparent fifty percent reduction of m_s^{eff} can be attributed to ideas that m_s^{eff} of 2 ML of the whole 4 ML film disappeared, or that m_s^{eff} of 1 ML aligns in the opposite direction to the other 3 ML. The latter case is confirmed by the careful analyses of the depth resolved XMCD spectra taken with different probing depths. In other words, an antiferromagnetic coupling is induced at the surface of Fe/Cu(001) by NO adsorption. We would also like to present the EXAFS study of NO/Fe/Cu(001) and compare it with that of CO/Fe/Cu(001).

[1] H. Abe *et al.* PRB 77, 054409 (2008).

[2] H. Abe *et al.* PRL *submitted*.

Location: "Allara e Grosso" Hall
Time: 16:30

In-situ investigation of Bi thin film condensation by surface sensitive X-ray absorption spectroscopy at cryogenic temperatures

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Thin Bi films quench-condensed (QC) on glass substrates at low temperatures around 20-50 K show several unique physical properties. For example, while bulk Bi has a positive temperature coefficient of resistivity (TCR), negative TCR values are usually reported for thin Bi films, and QC-Bi films are superconducting with a critical temperature of about 10 K, while bulk Bi is a semimetal revealing no superconductivity down to the mK regime on the other hand. However, these outstanding properties are transformed into the bulk-like behaviour of bismuth if the films are heated above a certain critical temperature T_C , which is accompanied by a structural transition to the well-known rhombohedral structure. T_C is known to depend on the film deposition rate, the vacuum conditions and especially on the Bi film thickness, with typical values in the range from about 10 K to more than 50 K. While films with a thickness of 60 nm are spontaneously transformed into rhombohedral structures even for temperatures below 4 K, the critical temperature may reach 70 K for a film thickness below 10 nm. We have therefore studied the metastable Bi phases in thin films which are deposited on float glass substrates held at temperatures of 20 K under ultrahigh vacuum conditions using a combination of simultaneous X-ray reflectometry, electrical resistivity measurements and especially surface sensitive grazing incidence X-ray absorption spectroscopy. The EXAFS measurements gave clear evidence for the presence of an amorphous Bi phase at low temperatures which is not stabilized by incorporated traces of residual gas. For a Bi film thickness of 6 nm, a subsequent annealing process of this amorphous material induces an irreversible transformation to a nano-crystalline structure above ca. 40 K, which is accompanied by an irreversible increase of the film's electrical resistivity. Our experiments also revealed the influence on film thickness on the formed structures.

Location: “Allara e Grosso” Hall
Time: 16:45

Development of RefEXAFS data analysis for deeper surface structure studies

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In this work, a method to analyse RefEXAFS spectra (EXAFS recorded in reflection mode) for the study of the structure of surfaces is presented. Its novelty lies in that it applies to data collected at incidence angles both below and above the critical angle.

Until now, the applicability range of the technique was restricted by the approximations involved in the data analysis process, as most of them try to extract the fine structure from a reflectivity spectrum of an specific incidence angle. In contrast, the method here presented aims to obtain all the EXAFS contributions of the absorbing element present in the sample from the simultaneous analysis of the whole set of spectra recorded at different incidence angles. The key point is that the structural information is obtained for each layer.

To this aim, in a first stage, the free atom reflectivity spectrum (without the fine structure) is simulated and fit. This is done for a complete set of reflectivity spectra recorded at different incidence angles. Secondly, an EXAFS function is proposed for each of the local environments present in the sample. Thirdly, the RefEXAFS signal corresponding to each reflectivity spectrum is calculated from the proposed EXAFS, making use of the information obtained from the reflectivity fit. Finally, the proposed EXAFS functions are varied so as to fit the experimental RefEXAFS signals for the whole set of the reflectivity spectra. Hence, the analysis gives robust results because of the redundancy in the collection of data at several different angles. With this method, it is possible to extract EXAFS information of the absorbing element from buried layers. Furthermore, multiple EXAFS signals corresponding to different coordination environments at different depths can be extracted.

To illustrate these capabilities, an example of a multilayer analysed by this method is presented together with the usual total reflection RefEXAFS analysis, and the results are compared.

Location: “Allara e Grosso” Hall
Time: 17:00

Structural and electronic properties of tetracene thin films

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The structures of tetracene thin films prepared by vacuum vapor deposition on hydrogenated silicon substrates [1] and silicon dioxide substrates [2] were studied as a function of the film thickness, using AFM, NEXAFS and X-ray diffraction, respectively. Using in situ NEXAFS, the growth of tetracene on hydrogenated silicon was studied in a coverage range from 0.06 ML to 20 ML and the evolution of the tetracene molecule tilting angle was deduced. Selected films were also studied using X-ray diffraction to characterize both the in-plane polycrystalline state and out-plane lattice spacing; and by AFM for the surface morphology. The difference between the growth on the two different weakly-interacting substrates and their implications will be discussed. The growth on the silicon dioxide was used to fabricate tetracene OFETs of various thicknesses. The transport properties and their relationship with the structural characterizations will be discussed.

[1] A. Tersigni, J. Shi, D.T. Jiang, and X.R. Qin, Phys. Rev. B 74, 205326 (2006).

[2] J. Shi and X.R. Qin, Phys. Rev. B 78, 115412 (2008).

Location: "Allara e Grosso" Hall
Time: 17:15

NEXAFS characterization of the self-limiting monolayer growth of terephthalic acid on rutile $\text{TiO}_2(110)$

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Chemically functionalized surfaces play an important role in many nanotechnological applications. However, not too many attempts have been made so far to create a chemically functionalized metal oxide surface by adsorption of organic molecules, even though metal oxide surfaces provide anisotropy and special adsorption sites that lead to well-ordered monolayers. Terephthalic acid (TPA) is a versatile molecular linker and has, consequently, received considerable attention in designing of two-dimensional supramolecular architectures at surfaces.

A systematic investigation on the orientation of the TPA molecules on a rutile $\text{TiO}_2(110)$ substrate has been carried out using near-edge x-ray absorption spectroscopy (NEXAFS) at HESGM beamline of BESSY. In order to determine the dependence of monolayer coverage on deposition time we deposited the TPA molecule in several steps, each lasting 5 - 15 s. The deposition rate was adjusted to 0.07 Å/sec. After each deposition step the measurement of the NEXAFS spectra for the C K as well as Ti $L_{2,3}$ and O K adsorption edges at a different incidence angles and at different azimuthal orientations of the TiO_2 crystal were performed. A saturation effect after about 70 sec of deposition was clearly observed, which we assign to 1 ML of TPA. Based on the saturation behavior we can conclude that a second layer of TPA cannot be grown or, at least, is very unstable. From angular dependencies of the NEXAFS spectra we find a planar adsorption geometry of TPA molecules at low coverages (up to approximately 0.3 ML), while when saturation coverage is reached the TPA molecules are adsorbed in an upright position. The latter adsorption geometry implies that one of the carboxyl groups binds to the surface as a bidentate carboxylate. We gratefully acknowledge travelling grants for measurements at BESSY from BMBF (Grant. Nr. 05ESXBA/5).

P3.3: Time-resolved studies

Location: "Aranjo Ruiz" Hall
Time: 15:30

Application of single shot dispersive XAFS to study picosecond materials dynamics

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Monitoring and elucidating the nature of chemical and materials transformations by direct structural probes in real time remains an important challenge across many scientific disciplines. Regarding XAFS measurements, in particular, numerous experimental approaches have been developed for achieving time resolution. Amongst these approaches, dispersive XAFS has the ability to acquire a complete structural signature in a "single shot" and at a time resolution dictated directly by the source brightness. With the advent of brighter sources such as 4th generation light sources (i.e., LCLS) or laser driven sources, it is now possible to achieve single shot, subnanosecond resolution using a dispersive XAFS configuration. Applications of this methodology using a laser-imploded target radiation source will be discussed, including examples of shock driven material compression and phase transformation.

[1] Yaakobi, B., Boehly, T. R., Meyerhofer, D. D., Collins, T.B., Remington, B. A., Allen, P. G., Pollaine, S. M., Lorenzana, Eggert, J.H. Phys. Rev. Lett. 95, 075501 (2005).

[2] Remington, B.A., Allen, P.G., et al. Mater. Sci. and Tech. 22, 474 (2006).

[3] Yaakobi, B., Boehly, T. R., Sangster, T. C., Meyerhofer, D. D., Remington, B. A., Allen, P. G., Pollaine, S. M., Lorenzana, H. E., Lorenz, K. T., Hawreliak, J. A. Physics Of Plasmas 15, Art: 062703 (2008).

Location: “Aranjo Ruiz” Hall
Time: 15:50

Picosecond time resolved response of the Ge lattice after femtosecond pulsed laser excitation

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A high-efficiency femtosecond pulse laser pump/x-ray pulse probe facility at Sector 20 of the Advance Photon Source (APS) is used to measure by XAFS the time dependence of the lattice response of Ge. The first and second neighbors' mean-squared relative vibration amplitudes (msd) changes are monitored as a function of the delay time between the laser and x-ray pulses. The laser excites the lattice by two separate mechanisms: (a) a direct excitation of coherent long-wavelength optical phonons and (b) indirectly exciting incoherent phonons through the interaction with excited electrons/holes. Since the diamond structure of Ge has a basis of two atoms, the first neighbor shell contains the basis atoms and the second neighbor shell atoms are on the FCC lattice sites; only the 1st shell is excited by mechanism (a) while the both the 1st and 2nd shells are excited by mechanism (b). Thus XAFS has the unique property to monitor simultaneously the time response of these two mechanisms. Our measurements find ~ 10 picosecond (ps) time delay between the responses of the 1st and 2nd shells. Since the coherent optical phonons are essentially instantly excited by the laser pulse, the incoherent phonons excitation is delayed by ~ 10 ps after laser excitation.

A presentation of the high-efficiency pump/probe facility which utilizes 100% of the x-rays emitted from a single pulse in the x-ray ring will be given. The results of the measurements as a function of laser power will be presented with their interpretation.

Location: “Aranjo Ruiz” Hall
Time: 16:10

Sub-nanosecond XAFS-based observations of optical switching in the phase-change alloy $\text{Ge}_2\text{Sb}_2\text{Te}_5$

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Chalcogenide-based phase-change memory (PCM) alloys are in widespread commercial use in the form of rewriteable optical disks and are a leading candidate for the next generation of non-volatile phase-change random access memory. In PCM optical (electrical) data is encoded via the anomalously large change in reflectivity (resistivity) between the amorphous and crystalline states. Among the various PCM alloys, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is prototypical in that it is being used both for the current generation of optical and the next generation of electrical based data storage.

We have taken advantage of the reversible nature of the recording process to develop a pump-probe technique to study the crystalline to amorphous phase transition in GST representative of the recording process. By locking the phase of the pump laser to the synchrotron x-ray pulses, structural snapshots of the laser induced changes have been recorded. The extremely fast nature of XAFS, leads to the ability to time-resolve structural changes in principle to the ~ 50 ps duration of the x-ray probe pulses, although in the current experiment the time resolution is limited by ~ 150 ps jitter in the pump laser. In the current experiment, a fast pump laser induced amorphization of a within a rotating GST sample, while a delayed focused $\sim 2 \mu\text{m}$ x-ray pulse was used to probe structural changes in the same region before and after the pump pulse. A second CW laser focused at a different position on the same rotation locus recrystallized the GST sample before it rotated back to the probe position allowing measurements each rotation cycle. In a series of experiments, we have used the above procedure to directly observe short-range structural transitions occurring in GST during the optical recording process at the Ge-edge and more recently the Sb and Te edges. The implications of these changes will be discussed.

Location: "Aranjo Ruiz" Hall
Time: 16:30

Photosynthetic water oxidation driven by Laser flashes and tracked by x-ray spectroscopy

Holger Dau¹, Michael Haumann¹, Ivelina Zaharieva¹, Marcel Risch¹, Alexander Grundmeier¹, Lazlo Gerencser¹, Petko Chernev¹, Magnus Anderlund², and Gustav Berggren²

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(2) Uppsala University, Dept. of Photochemistry and Molecular Science, Lägerhyddsvägen 1, 75237 Uppsala, Sweden

Photosynthetic water oxidation and dioxygen formation is facilitated by a Mn₄Ca complex bound to the proteins of Photosystem II (PSII) [1]. In our experiments, the Mn complex in PSII is synchronously driven through its reaction cycle by sequences of ns-Laser flashes; changes in electronic structure (especially oxidation states) and coordination geometry are followed by X-ray spectroscopy with (i) high (10 micro s) or (ii) low (100 ms) time resolution. The following is addressed:

(i) To study transient formation of reaction intermediates in PSII water oxidation, Mn oxidation-state changes have been monitored with micro-s resolution after Laser-flash excitation [2] (i) at O₂ partial pressures up to 100 times the atmospheric value (O₂ backpressure) [3] and (ii) for PSII dissolved in deuterated water (kinetic isotope effect).

(ii) To study changes in coordination geometry and electronic structure, we and others are working towards a comprehensive X-ray spectroscopy approach involving measurement and combined analysis of XANES spectra, K-alpha and K-beta emission lines, and 1s-3d RIXS data. Spectra were collected for relevant synthetic Mn complexes. For functional PSII at room temperature, advancement in the reaction cycle was induced by Laser-flash excitation at the beamline and changes in K-alpha and K-beta lines have been detected.

Results are discussed with focus on relevance for the mechanism of photosynthetic water oxidation.

Data has been collected at the beamline ID26 of the ESRF (Grenoble), in cooperation with Pieter Glatzel and his team. XAFS spectra were also collected at the KMC-1 of the BESSY (Berlin; with F. Schafers and M. Mertin).

[1] Dau, H.; Haumann, M., *Coord. Chem. Rev.* 2008, 252, 273-295.

[2] Haumann, M.; Liebisch, P.; Muller, C.; Barra, M.; Grabolle, M.; Dau, H., *Science* 2005, 310, (5750), 1019-21.

[3] Haumann, M.; Grundmeier, A.; Zaharieva, I.; Dau, H., *Proc Natl Acad Sci U S A* 2008, 105, (45), 17384-9.

Location: "Aranjo Ruiz" Hall
Time: 16:50

In situ space and time resolved x-ray absorption spectroscopy: dynamic structure of platinum during kinetic oscillations of CO oxidation

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CO oxidation is one of the most intensively studied reactions in the field of catalysis. On single crystals of platinum under low-pressure conditions, kinetic oscillations are related to varying reconstruction of surface, which occurs after adsorption of CO, leads to CO-rich and O₂-rich domains that have different reaction rates [1]. To translate results from single crystal studies and understand catalysis under real conditions, we have bridged both the pressure and materials gaps by determining the structure of a supported platinum catalyst during CO oxidation under real conditions. The structural changes during the kinetic oscillations are elucidated by combining in situ space and time resolved x-ray absorption spectroscopy (QEXAFS), [2] infrared spectroscopy, and kinetic measurements. We observed a high- and a low-activity regime, which have high and low reaction rates resp. (Fig. 1). The low activity state is characterized by the adsorbed CO that poisons the active surface [3,4]. In contrast to single crystals, the high activity state is characterized by presence of a surface oxide [5,6]. During ignition, Pt L3 spectra recorded with a time resolution of 0.5 sec showed increasing amounts of platinum oxide which autocatalytically increased the conversion. The catalyst structure and the reactivity were strongly related and both changed with position in the reactor. The kinetic oscillations during CO oxidation paralleled the reduction and re-oxidation of the surface of the catalyst (Fig. 2). The white line intensity of Pt L3 edge spectra recorded using QEXAFS, representative of the extent of oxidation of the surface, decreased with the decrease in CO₂ signal suggesting the reduction of the surface. The sudden increase in CO₂ production was paralleled by jump in white line intensity, which is oxygen adsorption and re-oxidation of the surface. Complimentary results from infrared study showed increasing amount of linearly and bridged CO with decreasing CO₂ production.

Location: "Aranjo Ruiz" Hall
Time: 17:10

Retrieving photochemically active structures by time-resolved EXAFS spectroscopy

Renske Marjan van der Veen^{1,2}, Chris J. Milne¹, Amal El Nahhas¹, Frederico A. Lima¹, Van-Thai Pham¹, Jonathan Best³, Julia A. Weinstein³, Camelia N. Borca², R. Abela², Christian Bressler¹, and Majed Chergui¹

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(2) *Swiss Light Source, Paul Scherrer Institut, Switzerland*

(3) *Department of Chemistry The University of Sheffield United Kingdom*

Observation of the making and transforming of chemical bonds in the course of a chemical reaction is the dream of every chemist. The recent implementation of x-ray absorption spectroscopy in the ultrafast time domain allows studying the electronic and structural dynamics of photochemically active molecules in solutions. In this study we present the structural determination of a photoexcited diplatinum molecule, [Pt₂(P₂O₅H₂)₄]⁴⁻. This molecule plays an important role in photocatalytic chemical conversions and its photochemical properties are a manifestation of the newly formed Pt-Pt bond in its excited triplet state. X-ray pulses of 70 ps width from the Swiss Light Source are used to probe the transient structure after excitation with a femtosecond laser pulse tuned to the excited state absorption at 380 nm. A rigorous model-based statistical analysis of the difference (excited – unexcited) EXAFS spectrum at the Pt L3 edge has been performed. This recently developed analysis has proven capable of not only unambiguously resolving excited-state structures but also of precise determination of the excited state population, traditionally a difficult parameter to determine accurately. [1] The resulting fit indicates a large contraction of 0.31(5) Å of the Pt atoms and a ligand expansion of 0.010(6) Å, with a fitted excited state population of 7±2%. [2] The ligand expansion is assigned to a weakening of the coordination bonds upon formation of the Pt-Pt bond in the excited state, and has been observed for the first time.

[1] W. Gawelda, V.-T. Pham, R. M. van der Veen, D. Grolimund, R. Abela, M. Chergui and C. Bressler. J. Chem. Phys (in press, 2009)

[2] R. M. van der Veen, C. J. Milne, A. El Nahhas, F. A. Lima, V.-T. Pham, J. Best, J. A. Weinstein, C. N. Borca, R. Abela, C. Bressler, and M. Chergui, Angew. Chem. Int. Ed., DOI:10.1002/anie.200805946 (2009)

P3.4: Theory III

Location: “Betti” Hall
Time: 15:30

Spin polarized resonant photoemission from Fe

Fabiana Da Pieve¹, and Peter Kruger²

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Ascertaining the nanoscale structure and magnetic properties of a surface, ultrathin films or interfaces remains a formidable but potentially extraordinary rewarding task. To properly study such aspects, a probe which combines elemental specificity with sensitivity to local order, both geometric and magnetic, is essential. Spin resolved resonant photoemission is potentially an ideal candidate for studying magnetic nanoscale systems. Resonant photoemission is the process of absorption followed by coulomb decay involving the excited electron. This process is degenerate with usual valence band photoemission, and often gives rise to strong interference effects. At present, there is no ab-initio implementation of this kind of spectroscopy: there have been only numerical studies performed using the multiplets approach on small clusters, neglecting the solid state band structure. Here we present an alternative scheme based on the multiple scattering approach which provides an ab initio description of the band structure. The autoionization process is treated in the independent particle picture. We discuss first results on spin resolved resonant photoemission from bulk Fe.

Location: “Betti” Hall
Time: 15:50

Orbital and charge ordering detected by resonant x-ray scattering in strongly correlated electron systems.

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The present work is devoted to a brief and basic review of the concepts of orbital and charge ordering (OO and CO, respectively) and to their detection by means of resonant x-ray diffraction. I described and compared more recent calculations that I performed on magnetite and MgTi_2O_4 with different theoretical methods and found that in the most of the analyzed cases the experimental data can be explained as well with or without OO, with or without CO. My conclusion is that several claims of detection of OO and/or CO by x-ray diffraction in the literature should be revisited in the light of the theoretical model adopted to explain the results.

Location: “Betti” Hall
Time: 16:10

X-ray Raman scattering: role of first-principles theory in the analysis

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In recent years non-resonant x-ray Raman scattering (XRS) [1] has become an important new tool for studying x-ray edges of samples ranging from crystalline solids to liquids. As an experimental method XRS can provide information very similar to x-ray absorption spectroscopy (XAS). Since XRS experiments are done using hard x-rays it has a definite advantage in studying the soft x-ray edges of liquids and systems in high-pressure environment. Another reason for the increased interest in XRS has been the significant advances in experimental techniques that make the method more accessible. However, the unique properties of XRS also require the development of new first-principles modeling capabilities and ideas how to apply them.

In this talk I discuss our first-principles approaches to XRS and how they have been used to obtain more detailed information from XRS experiments. I give examples both of our earlier work based on the Bethe-Salpeter equation [2], and on the real-space multiple-scattering method [3]. I also discuss our recent work on molecular systems that employs the Slater transition state method and Gaussian basis functions [4]. As examples of on-going projects I show results for doping dependent changes in the local density of states of MgB₂, and briefly touch on our work on water. Finally I describe our recent efforts to analyze the different components contributing to the XRS signal using symmetry based arguments.

Support from the Academy of Finland and DOE BES Computational Materials Science Network is gratefully acknowledged.

[1] Early work on the theory of XRS: S. Doniach, P. M. Platzman, and J. T. Yue, Phys. Rev. B **4**, 3345 (1971).

[2] J. A. Soininen et al., J. Phys.: Condens. Matt. **13**, 8039 (2001)

[3] J. A. Soininen, A. L. Ankudinov, and J. J. Rehr, Phys. Rev. B. **72**, 045136 (2005).

[4] A. Sakko et al., Phys. Rev. B **76**, 205115 (2007).

Location: “Betti” Hall
Time: 16:30

Subtleties of electron correlation in La 4d resonances

Edlira Suljoti^{1,2}, Frank M.F. de Groot¹, Mitsuru Nagasono², Wilfried Wurth² and Alexander Föhlisch²

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In this work I will discuss correlation effects arising from mixed- and symmetry entangled-discrete states, disclosed in lanthanides N_{IV,V} XAS edges [1].

Due to strong localization of the 4f valence shell, the tightly bound excited states are symmetry entangled states that involve a degree of correlation. Very notable for these systems, the highly intense giant resonance introduces a further mixing with the localized quantum entangled states. At excitation energies of the pre-edges, coherent decays of similar amplitudes from mixed states result in strong interference effects which are visualized in the asymmetrical profiles of the total electron yield (TEY) detected spectra. Controversially, the fluorescence yield measurements revealed a symmetrical Lorentzian profile. In order to investigate the subtleties of electron correlation in lanthanides we carried out resonant inelastic X-ray scattering (RIXS) experiments at the N_{IV,V}-edges of light lanthanide ions (La, Ce, Pr) accompanied with theoretical calculations. We found that symmetry aspects of the dipole transition cause breaking of coherence in some of the decay channels and modify the spectral profiles of the fluorescence yield.

[1] E. Suljoti, F.M.F. de Groot, P. Glatzel, F. Hennies, M. Deppe, A. Pietzsch, B. Sonntag, W. Wurth, and A. Föhlisch, *Entanglement and coherence in La 4d resonances, to be published.*

Location: “Betti” Hall
Time: 16:50

Calculation of optical constants and related quantities from optical to x-ray frequencies

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We discuss an efficient approach for the calculation of optical response based on a single-particle density matrix formalism [1]. This formalism avoids the need to compute wave-functions explicitly, and is applicable to arbitrary, aperiodic systems. The approach is implemented in an extension to the real-space Green's function code FEFF. The code yields linear optical constants including the complex dielectric constant $\epsilon(\omega)$, complex index of refraction $n(\omega)$, energy-loss spectra $-\text{Im } \epsilon^{-1}(\omega)$, photoabsorption coefficient $\mu(\omega)$, and optical reflectivity $R(\omega)$ over a very broad spectral range, from the visible to hard x-rays. Examples are presented for a number of materials. These results provide a theoretical complement to standard tables and are useful in a variety of applications including *ab initio* calculations self-energy shifts, inelastic losses, mean-free paths, and stopping powers [2,3]. For example, a many-pole self-energy model based on these results makes possible improved, parameter free calculations of various photon- and electron-spectra (XAS, NRIXS, EELS, etc.) [4]. This work was supported by the US DOE BES Grant DE-FG02-97ER45623 and facilitated by the DOE CMSN.

[1] M. P. Prange, J. J. Rehr, G. Rivas, J. J. Kas, and John W. Lawson, UW Preprint (2008); arXiv:0810.3271.

[2] A. P. Sorini, J. J. Kas, J. J. Rehr, M. P. Prange and Z. H. Levine, Phys. Rev. B **74**, 165111 (2006).

[3] J.J. Kas, A. P. Sorini, M. P. Prange, L. W. Cambell, and J. A. Soininen, and J. J. Rehr, Phys. Rev. B **76**, 195116 (2007).

[4] John J. Rehr, Joshua J. Kas, Micah P. Prange, Adam P. Sorini, Yoshinari Takimoto, Fernando Vila, Comptes Rendus Physique, doi:10.1016/j.crhy.2008.08.004.

Location: “Betti” Hall
Time: 17:10

Natural dichroism in the near-edge of cubic systems

Robert A. Gordon¹, Maurits W. Haverkort,² Subhra Sen Gupta,³ and George A. Sawatzky³

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Information on valence orbitals and electronic interactions in single crystal systems can be obtained through orientation-dependent x-ray measurements, but this can be problematic for a cubic system. Polarisation-dependent x-ray absorption measurements are common, but are dominated by dipole transitions which, for a cubic system, are isotropic even though a cubic system is not. Many edges, particularly for transition metals, do have electric quadrupole features that could lead to dichroism but proximity to the dipole transition can make interpretation challenging. X-ray Raman Spectroscopy (XRS) can also be used to perform orientation-dependent near-edge measurements - not only dependent on the direction of the momentum transfer but also its magnitude, q . Previous XRS measurements on polycrystalline materials revealed that multipole (higher order than dipole) transitions are readily observable in the pre-threshold region of rare earth $N_{4,5}$ edges, actually replacing the dipole at high- q . We have extended these studies to examine orientation-dependent XRS for CeO_2 and MnO single crystals, as prototype systems for theoretical treatment. Dichroism is observed at both the Ce $N_{4,5}$ and Mn $M_{2,3}$ edges in these cubic materials.

P4.1: Material Science II

Location: “La Muta” Hall
Time: 18:00

Local structure study of RMn_2O_5 ($R = \text{Bi, Gd, Pr}$) multiferroics with EXAFS

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The RMn_2O_5 family displays a complex interplay between lattice and magnetic degree of freedom, manifested as vibrational anomalies below 120K [1,2] and simultaneous magnetic and ferroelectric ordering (multiferroicity) below 40K [3]. It has been suggested that multiferroicity occurs due to local structural distortions associated with atomic displacements of Mn^{+3} , but conclusive experimental evidence to confirm such hypothesis is still missing.

Temperature-dependent EXAFS measurements were utilized to investigate the local structure and vibrational properties of RMn_2O_5 compounds ($R = \text{Bi, Pr, Gd}$) between 20K and 300K. Mn K-Edge results reveal that MnO coordination polyhedra are essentially rigid, in agreement with literature [4]. Bi L_3 edge spectra present clear anomalies in the first coordination shell above 125 K, related to vibrational disorder for different Bi-O bonds. Similar observations were made for $TbMn_2O_5$ by Tyson et al.[4], which have been interpreted as a result of the buckling of rigid Mn-O coordination polyhedra.

Our EXAFS results and synchrotron radiation XRD analysis by Granado [2] suggest that low energy vibrational modes associated with rigid rotations of the Mn-O polyhedra are operative at low temperatures, which might explain the low temperature linear expansion coefficient verified for this material [1]. Local structural distortions associated with the multiferroic transition could not be identified, indicating that any local structural distortion occurs below our resolution. A qualitative analysis of the R edge results for other members of the RMn_2O_5 family (Gd and Pr) is in agreement with the analysis proposed for $BiMn_2O_5$.

[1]García Flores et al., PRB 73, 104411 (2006)

[2]Granado et al., PRB 77, 134101 (2008)

[3]Cheong and Mostovoy, Nat. Mat. 6, 13 (2007)

[4]Tyson et al., PRB 75, 174413 (2007)

Location: “La Muta” Hall
Time: 18:20

The local nature of “disorder” in Sr_2FeMoO_6 double perovskites

Carlo Meneghini^{1,2}, F. Liscio³, F. Bardelli², S. Mobilio^{1,2,4}, Sugata Ray^{5,6,7}, and D. D. Sarma^{5,7}

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The degree of Fe/Mo alternate cation order (chemical order) is known to heavily influence the magnetic properties of Sr_2FeMoO_6 double perovskites although the nature of such disorder has never been critically studied.

We present here detailed X-Ray Absorption Fine Structure (XAFS) and synchrotron radiation X-ray Diffraction (XRD) studies on polycrystalline Sr_2FeMoO_6 with various degrees of crystallographic disorder. We found that a very high degree of short range cation order (SRO) is preserved even in samples with highly reduced long range chemical order (LRO).

Based on experimental results and with the help of detailed structural simulations, we have been able to model the nature of the disorder in this important class of materials. In particular we found that the chemical short (SRO) and long range order (LRO) features in Sr_2FeMoO_6 can be understood in terms of locally ordered regions. The combined results of XAFS, XRD and structural simulations, establish the presence of nanosized antiphase domains in the system which eventually controls the magnetic properties of these compounds.

Location: “La Muta” Hall
Time: 18:40

Effect of strain on the local atomic structure of LaSrCoO₃

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We have examined the effect of epitaxial mismatch strain; i.e., the strain that is imposed on the lattice of a thin film when it is grown epitaxially on a substrate with a different lattice constant, on the local atomic structure of thin (~ 220 Å) films of LaSrCoO₃ grown on SrTiO₃ and LaAlO₃ substrates. Growth on these substrates leads to films with both in-plane tensile and in-plane compressive strain, respectively. It is found that the strain imposed on the thin-film lattice is accommodated by both changes in the first-shell octahedral Co-O bond lengths and O-Co-O bond angles. Second shell tetrahedral Co-La and Co-Sr distances are found to behave similarly to distortions found previously in the tetrahedral semiconductors; i.e., they are contracted in layers with in-plane compressive strain and expanded in layers with in-plane tensile strain. Changes in their tetrahedral bond angles account for either the expansion or contraction of the lattice constant perpendicular to the thin film interface.

Location: “La Muta” Hall
Time: 19:00

Double-well potential for oxygen ion vibrations in Nd_{2-x}Ce_xCuO_{4-δ}

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Local structure peculiarities of the electron-doped high temperature superconductor Nd_{2-x}Ce_xCuO_{4-δ} (NCCO) of layer-like type were investigated by means of X-ray absorption spectroscopy above the Cu K, Nd L₃ and Ce L₃ absorption edges. XANES spectra analysis demonstrates that cerium in NCCO is in the tetravalent state, while Nd stays trivalent. It is shown that oxygen ions in superconductive CuO₂ plane move in a double-well potential similarly to the anomalous oxygen vibrations discovered earlier in hole-doped superconductive systems with perovskite-like cubical structure Ba_{1-x}K_xBiO₃ (BKBO) and La_{2-x}Sr_xCuO_{4-δ} (LSCO). Similar results reported elsewhere for other copper oxide superconductors indicate that double-well potential of oxygen vibrations is an inherent and general property of such superconductive materials irrespective to the type of doping (electron or hole) and type of structure (cubical or layer-like). We proposed a model of relationship between the local electronic and local crystalline structure explaining the metal-insulator transition and the superconducting state that occur in NCCO and LSCO as dopant concentration increases. Obtained results led us to the conclusion about the direct connection of local dynamical structure nonuniformity with local dynamical charge ordering observed in superconductive CuO₂ plane. Role of the dynamical charge ordering in the HTSC mechanism is discussed.

This work was supported by RFBR grant 08-02-00759a.

Location: “La Muta” Hall
Time: 19:15

A UV-induced uniaxial motion of body-centered titanium ions in perovskite titanates

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A photoinduced effect in perovskite titanates is one of the key issues in the field of dielectric materials; SrTiO₃ (STO) in a quantum paraelectric phase undergoes transition to a ferroelectric one under UV-irradiation, which gives insight into the nature of ferroelectricity in the oxides[1]. The defect-doped STO also shows a promising property as a candidate for a surface-emitting device[2]. Recently we have reported a XAFS study on the UV-induced visible-light-emitting phenomena common in STO-based materials, concluding that the uniaxial motion of body-centered titanium ions serves as energy absorbers[3]. However, the energy transfer process from titanium ions to color centers was unclear; UV light transfer electrons from the oxygen 2p valence band to the titanium 3d conduction one, which should be followed by some light-emitting processes. In the present study, another XAFS study using monochromatic UV light was performed for an STO-based red phosphor. The UV energy dependence of a characteristic feature appeared in UV (on - off) spectra is directly proportional to the photoluminescence excitation spectra. This result gives a deeper insight into the light-emitting process; an energy overlap between titanium 3d conduction band and defect levels is essential. In addition, we have performed x-ray diffraction measurements under UV irradiation and succeeded in visualizing the uniaxial motion of body-centered titanium ions, which will be written elsewhere.

[1] M. Takesada *et al.*, J. Phys. Soc. Jpn. **72**, 37 (2003); T. Hasegawa *et al.*, *ibid.* **72**, 41 (2003).

[2] D. Kan *et al.*, Appl. Phys. Lett. **88**, 191916 (2006); D. Kan *et al.*, Nature Mater. **4**, 816 (2005).

[3] M. Deguchi, N. Nakajima *et al.*, Phys. Rev. B **78**, 073103 (2008).

Location: “La Muta” Hall
Time: 19:30

Localizing oxygen vacancies in SrTiO₃ by 3d-impurities

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The distribution of oxygen vacancies in dilutely doped SrTiO₃ after annealing in a reducing atmosphere has been studied with X-ray absorption spectroscopy (XAS) and *ab initio* calculations. Samples were prepared by doping SrTiO₃ with 0.2 mol% of other 3d-transition metal (TM) ions (Sc – Zn). Our XAS results on oxidized samples show that 3d-TM impurities are indeed incorporated at the Ti site in SrTiO₃[1]. After reducing the single crystals, they become metallic and the spectra of all the 3d-TM impurities change significantly, whereas no change of the Ti spectrum could be detected. This observation was reproduced using real space multiple scattering calculations utilizing a model with an oxygen vacancy in the first shell of the impurity. Density functional theory calculations showed that the energy of removing an oxygen ion from the octahedron surrounding the 3d-TM is largest in the case of Ti.

This indicates that oxygen vacancies preferentially are created at the first shell surrounding impurities in SrTiO₃. Therefore, XAS on 3d-transition metal impurities can be used as a tool in several interesting scientific cases where the importance or even presence of oxygen vacancies is not yet clarified.

In addition, Cr impurities were used to study the evolution of oxygen vacancies during an electric-field-driven insulator-to-metal transition in resistive memory devices[2,3]. Recent results will be presented where the influence of the surrounding atmosphere, during this insulator-to-metal transition, is investigated.

[1] B. P. Andreasson, M. Janousch, U. Staub, G. I. Meijer, and B. Delley, Mater. Sci. Eng. B **144**, 60 (2007)

[2] M. Janousch, G. I. Meijer, U. Staub, B. Delley, S. F. Karg, and B. P. Andreasson, Adv. Mater. **19**, 2232 (2007).

[3] B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer, Appl. Phys. Lett. **94**, 013513 (2009).

Location: "La Muta" Hall
Time: 19:45

Local environment and electronic structure of Fe at the interface in magnetic granular iron-silicon nitride systems

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Fe/Si₃N₄ multilayers have been prepared by sequential magnetron sputtering. For every set of samples, the Fe layer thickness has been varied from 5 to 0.7 nm, focusing the attention in the samples which present magnetic particle behaviour. X-ray absorption spectroscopy measurements have been performed at the Fe K-edge in the fluorescence yield mode at the Spanish CRG Beamline (SpLine-BM25). EXAFS results show a reduction of the Fe-Fe coordination number as the nominal Fe layer thickness decreases, in agreement with the decrease of the average particle size. Furthermore, a new contribution, attributed to Fe-N bond at around 1.9 Å, appears. This Fe-N coordination increases as the Fe layer thickness decreases, so it can be deduced that this phase is located at the metal-ceramic interface, resulting in the formation of core-shell Fe-FeN nanoparticle system embedded in a Si₃N₄ matrix.

Near-edge spectra follow an analogue evolution. XANES calculations, performed with the FEFF code (version FEFF8), have been achieved accounting for the reduced size of the particles and the interface phase. The presence of a new FeN phase in the zinc-blende structure reproduces the new spectral features appeared in the experimental XANES spectra as the nominal Fe layer thickness is reduced. Finally, the electronic structure obtained during the XANES calculations, in terms of local-projected density of states (l-DOS) determine that hybridization between the Fe-4p, Fe-3d and O-2p levels, resulting in the existence of an intense pre-edge peak in the experimental spectra, is responsible of a broadening of the Fe-3d band, and a drastic reduction of the d-DOS at the Fermi level. From this reduction, and according to the Stoner criteria for ferromagnetism, it can be concluded that the formation of a non-magnetic intermediate FeN phase between magnetic particles and the insulating matrix is the responsible of the decrease in the magnetization while reducing the nominal Fe layer thickness.

P4.2: Biology I

Location: "Allara e Grosso" Hall
Time: 18:00

Structure and dynamics of hemeprotein using x-ray absorption spectroscopy

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Experimental investigations on protein dynamics are usually carried out in solution; however, in most cases, the determination of protein structure is carried out by crystallography that relies on the diffraction properties of the same protein arranged in a three-dimensional lattice. X-ray Absorption Spectroscopy (XAS) is an ideal tool to investigate the deep relationship between structure and dynamics at the same time, on a wide class of metal containing protein, such as hemeprotein. In fact, this technique can be used as a structural refinement of X-ray diffraction on the same crystal [1] or, as an independent tool to study structural dynamic properties of the hemeprotein under investigation both in crystal [2] or solution [3,4]. In this talk different examples will be presented and discussed, with particular emphasis onto the original contribution due to the application of the MXAN [5] software package to the analysis of XAS spectra in the low energy range.

[1] Arcovito, A., et al., X-ray structure analysis of a metalloprotein with enhanced active-site resolution using in situ x-ray absorption near edge structure spectroscopy. *Proc Natl Acad Sci U S A*, 2007. 104(15): p. 6211-6.

[2] Della Longa, S., et al., Quantitative analysis of x-ray absorption near edge structure data by a full multiple scattering procedure: the Fe-CO geometry in photolyzed carbonmonoxy-myoglobin single crystal. *Phys Rev Lett*, 2001. 87(15): p. 155501.

[3] Arcovito, A., et al., Light-induced relaxation of photolyzed carbonmonoxy myoglobin: a temperature-dependent x-ray absorption near-edge structure (XANES) study. *Biophys J*, 2005. 88(4): p. 2954-64.

[4] Arcovito, A., et al., An X-ray diffraction and X-ray absorption spectroscopy joint study of neuroglobin. *Arch Biochem Biophys*, 2008. 475(1): p. 7-13.

[5] Benfatto, M., et al., MXAN: a new software procedure to perform geometrical fitting of experimental XANES spectra. *J Synchrotron Radiat*, 2001. 8(Pt 2): p. 267-9.

Location: “Allara e Grosso” Hall
Time: 18:20

X-ray Absorption Spectroscopy edge studies of biological models and enzymes

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X-ray absorption near-edge structure is sensitive to the electronic structure and geometric arrangement around an absorbing atom site. This is particularly so for lower energy absorption edges (below 3 keV), where the energy resolution is enhanced due to high monochromator resolution and reduced core-hole life time broadening effects. The K edges of two important ligand elements, sulfur and chlorine, lie within the 2-3 keV range, as do the second-row transition metal L edges. We have developed methodology and instrumentation that make feasible studies of dilute samples, and applied these to, in particular, Fe-S model complexes and enzyme active sites of varying cluster size. The experimental and analysis approaches will be described, and the results of biological applications described.

This work was funded at SSRL by DOE-BES, NIH NCRR and DOE BER.

Location: “Allara e Grosso” Hall
Time: 18:40

Geometric and electronic structure of [Fe]-hydrogenase active site

Wolfram Meyer-Klaucke¹, Marco Salamone Stagni¹, Francesco Stellato², Sonja Vogt³, Eberhard Warkentin⁴, Gerd Wellenreuther¹, Silvia Morante², Ulrich Ermler⁴, Thomas B. Rauchfuss⁵, Rudolf Thauer³, and Seigo Shima³

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Hydrogenases are enzymes that catalyze the reversible oxidation of molecular hydrogen. Their structure and catalytic mechanism are of considerable applied interest as models for the development of efficient catalysts for hydrogen fueled processes. Despite intensive efforts, however, the understanding of how hydrogenases react with H₂ is only in its infancy. Two of the three known types of hydrogenases are iron-sulfur proteins that contain a dinuclear metal center, either [NiFe] or [FeFe]. In contrast [Fe]-hydrogenase is the only mononuclear hydrogenase and thus a perfect system for studying the structural and electronic determinants of these enzymes [1-3].

Here we analyze by EXAFS the geometric and by XANES the electronic structure of this metalloenzyme in as isolated, mutated and inhibited form. In the EXAFS the multiple scattering analysis by Excurve identifies two CO ligands and the protein bound cysteinic sulfur originating from the protein plus several light atoms. Here, incorporation of additional information is required to identify the type of the light atoms yielding an almost perfect fit to the data. The XANES pattern is in contrast by far more sensitive to the ligand types and thus only the final model resembles the position of the measured resonances well. This is in line with the analysis of model systems, for which we obtain excellent agreement between measurement and simulation.

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[2] Shima, S., Pilak, O., Vogt, S., Schick, M., Stagni, M.S., Meyer-Klaucke, W., Warkentin, E., Thauer, R.K., and Ermler, U., Science, 2008. 321: p. 572-575.

[3] Hiromoto, T., Ataka, K., Pilak, O., Vogt, S., Salamone. Stagni, M., Meyer-Klaucke, W., Warkentin, E., Thauer, R.K., Shima, S., and Ermler, U., FEBS Letter, 2009, accepted

Anion binding in biological systems

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(6) *Delft University of Technology, The Netherlands*

(7) *ETH Zurich, Switzerland*

Brown algae such as *Laminaria digitata* (oarweed) are effective accumulators of iodine from seawater, with tissue concentrations exceeding 50 mM. We have addressed the question of the chemical state of iodine and its biological role in *Laminaria* by XAS [1]. We have also studied the enzyme haloperoxidase, which is implicated in the accumulation of halides in brown algae and contains vanadate in its active site, from *Ascophyllum nodosum* (knotted wrack) with XAS [2] at various edges (V, I, Br) and under various circumstances, and compared the results to the crystal structure. Molybdenum is essential for many forms of life, tungsten only for archaea and some bacteria. The metals are bound and transported as their oxo-anions, molybdate and tungstate, which are similar in size. The hyperthermophilic archaeon *Pyrococcus furiosus* depends strictly on the presence of tungstate. The transport protein WtpA from *P. furiosus* binds tungstate more strongly than molybdate. WtpA is related in sequence to *Archaeoglobus fulgidus* ModA. The crystal structure of the latter protein, with bound tungstate, features octahedral metal coordination [3], which differs from the tetrahedral geometry observed for non-selective proteins. We have measured XAS for *P. furiosus* WtpA and *A. fulgidus* ModA with molybdate and tungstate at the Mo 1s and W Acknowledgement. The authors thank the European Commission, Research Infrastructure Action under FP6 “Structuring the European Research Area Specific Programme”, Contract # RII3-CT-2004-506008 for supporting access to the EMBL.

[1] F. C. Kupper et al., Proc. Natl. Acad. Sci. USA 105 (2008) 6954-6958.

[2] M. C. Feiters et al., J. Am. Chem. Soc. 127 (2005) 15340-15341.

[3] K. Hollenstein et al., J. Biol. Inorg. Chem. online DOI 10.1007/s00775-009-0479-7.

Location: “Allara e Grosso” Hall
Time: 19:15

Synergic approach to xafs analysis for the identification of unknown metal-sites in proteins

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X-ray Absorption Fine Structure is an ideal tool to selectively probe the local structure of metal ions in proteins. However, the efficiency of XAFS in the investigation of metal sites in proteins is strongly limited by two main difficulties in data analysis: the selection of suitable structural starting models and the presence of multiple solutions. Although much work has been done in the last years in order to tackle these issues [1],[2], we are still far from a direct analysis approach which allows the identification of the amino acids bound to a metal-site in a protein.

We propose here an original method based on a synergic approach which combines multiple scattering EXAFS analysis performed within the rigid body refinement frame, *ab-initio* XANES simulations free from the muffin-tin approximation, structural information of amino acids and metal binding clusters provided by the Protein Data Bank and Debye-Waller factor calculations based on Density Functional Theory. A simplified version of this method has been used to investigate the Zn²⁺ binding sites in charge translocating membrane proteins where it has allowed the identification of the zinc coordinating amino acids with a high level of confidence [3,4,5]. In this study a further effort has been made towards the building of an automatic procedure. The method has been tested using three Zn metalloproteins which exhibit a set of characteristic zinc binding sites, whose structure is known from protein crystallography. The results show that it is possible to uniquely identify metal binding motifs in proteins on the basis on XAFS data.

[1]N. Dimakis, and G. Bunker, Biophys. J. 91, L87 (2006)

[2]G. Wellenreuther G. and W. Meyer-Klaucke, XAFS13 Proceedings 882, 322 (2007)

[3]L. Giachini et al., Biophys.J. 93, 2934 (2007)

[4]F. Francia et al., FEBS Letters 581, 611 (2007)

[5]L. Giachini, et al., FEBS Letters 581, 5645 (2007)

Location: “Allara e Grosso” Hall
Time: 19:30

Zinc binding effect on Cu coordination mode in prion protein octa-repeat subdomain

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Conversion of the prion protein (PrP) from its normal cellular form (PrP^C) to the scrapie form (PrP^{SC}) is responsible for a class of infectious, neurodegenerative diseases referred to as the transmissible spongiform encephalopathies. Among the different functions attributed to PrP^C, Cu(II) interaction is the only one that has been correlated with physiological impairments linked to the disease. In particular, it has been shown that the PrP is able to bind Cu(II) in its N-terminal octarepeat domain. XAS [1] and EPR [2] have been used to characterize the Cu(II) binding modes in the full length PrP and in the N-terminal octarepeat domain. EPR measurements [3] recently showed that the presence of Zn(II) modulates the binding mode of Cu(II) ions to the synthetic tetra-octarepeat peptide of the PrP. Interestingly enough the interaction mode is found to be dependent on the two metal ions concentration ratio.

In the work presented here, we exploited the possibility offered by XAS spectroscopy of looking at the structure around each one of the two metal ions, Cu(II) and Zn(II), while they are simultaneously present in the same sample. We collected XAS data at both the Zn and Cu K-edges on tetra-octarepeat synthetic peptides, which had been previously characterized by EPR measurements [3]. XAS experiments, besides confirming EPR results, have been able to characterize the mode of coordination of Zn along the Cu titration curve.

[1] S. Morante, R. Gonzalez-Iglesias, C. Potrich, C. Meneghini, W. Meyer-Klaucke, G. Menestrina, and M. Gasset, J. Chem. Phys. 279, 11753 (2004).

[2] M. Chattopadhyay, E. D. Walter, D. J. Newell, P. J. Jackson, E. Aronoff-Spencer, J. Peisach, G. J. Gerfen, B. Bennett, W. E. Antholine, and G. L. Millhauser, J. Am. Chem. Soc. 127, 12647 (2005).

[3] E. D. Walter, D. J. Stevens, M. P. Visconte, and G. L. Millhauser, J. Am. Chem. Soc. 129, 15440 (2007).

Location: "Allara e Grosso" Hall
Time: 19:45

Regulatory site structure of Fe-metalled PerR protein: Quantitative XANES analysis

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(5) Deceased.

All forms of life maintain reducing enzymes within their cells that protect cells from oxidative stress. PerR from *B. subtilis* (peroxide regulon repressor) is the prototype for a group of related peroxide sensing repressors found in many bacteria. PerR contains a structural Zn and can be activated to bind DNA by either Fe(II) or Mn(II) as corepressor thereby generating two forms of PerR (PerR-Zn-Fe and PerR-Zn-Mn correspondingly), which differ in their sensitivity to peroxide. In this context, solving the 3D local structure of regulatory site of PerR is of strong interest of further insight its reactivity. However the structure of Fe-metalled PerR has not been reported yet. The local structural information of iron active site in PerR-Zn-Fe metalloregulator was extracted using the quantitative analysis of the Fe K-edge X-ray absorption near edge structure (XANES). The combination of two techniques has been applied: fitting experimental XANES spectra with a multidimensional interpolation approximation (FitIt programme package [1]), and calculating XANES spectra with full potential approach (beyond the muffin-tin approximation) using FDMNES programme [2]. It was shown that the five protein ligands (three histidines and two aspartates) are arranged to bind Fe in a square pyramidal environment located to interact with one peroxide molecule on the axis of the pyramid. Moreover values of the bond distances and angles were obtained.

[1] G. Smolentsev et al., Phys. Rev. B 75, 144106 (2007)

[2] Y. Joly, Phys. Rev. B 63, 125120 (2001)

P4.3: Data analysis I

Location: "Aranjo Ruiz" Hall
Time: 18:00

Improvements in modeling EXAFS with many-pole self-energy and Feff8.5

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While theoretical standards such as those from Feff have many advantages for EXAFS analysis, the quality of fit statistics and estimation of parameter uncertainties has always been somewhat problematic using them. Even though the calculations reproduce EXAFS features sufficiently to give accurate bond distances to 0.01Å or so, fits to high-quality experimental spectra will have fit residuals far larger than the experimental uncertainties. One of the causes for this misfit is from approximations made in the phenomenological calculations of the inelastic losses used, though this has been difficult to test conclusively in the past. Recent improvements[1] in calculations of inelastic losses using a many-pole self-energy (MPSE) using a real-space calculation of the dielectric function have been shown to give significant improvements in XANES calculations. Here, we discuss the use of MPSE calculations for EXAFS analysis, and show that these calculations from Feff8.5 can improve fit quality for EXAFS, reducing χ^2 by a factor of 2 or more compared to Feff6. This approach may also allow the semi-physical fit parameter S_0^2 to be avoided. The implications for improving precision for EXAFS analysis and the nature of the remaining fit residual are discussed.

[1] J. J. Kas, *et al*, Phys Rev B **76** 195116 (2007)

Location: “Aranjo Ruiz” Hall
Time: 18:20

Quantum Mechanics-Classical Molecular Dynamics approach to EXAFS

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EXAFS spectroscopy is a structural tool providing with the information on the local atomic structure around an atom of particular type in a region of about 3 to 10 Å, which depends strongly on a degree of thermal and static disorder present in a compound. While a reliable theory of EXAFS is currently available, there is still a lack of accurate accounting for disorder effects, in particular, beyond the first coordination shell: in this region one needs to account for many-atom distributions leading to the so-called multiple-scattering (MS) effects. This problem strongly limits the conventional routine analysis and interpretation of the EXAFS signals to the first coordination shell.

In this work, we present a recently developed approach [1] to the simulation of configuration-averaged EXAFS spectra using a combination of Quantum Mechanics and Classical Molecular Dynamics (QM-CMD) methods. Proper use of ab initio quantum mechanics allows a number of empirical parameters, used in the molecular dynamics simulation, to be decreased, whereas the molecular dynamics allows accounting for temperature effects. The application of the method to cubic perovskite SrTiO₃ will be presented.

[1] A. Kuzmin and R.A. Evarestov, J. Phys.: Condens. Matter 21 (2009) 055401.

Location: “Aranjo Ruiz” Hall
Time: 18:40

Combined techniques in the structural investigation of ions in solution: the symbiosis XAS-Molecular Dynamics

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Recent developments in the investigation of ionic solutions by means of the X-ray absorption fine structure technique are described. New theoretical advances in the calculation of X-ray absorption cross sections have considerably improved the reliability of theoretical standards allowing the use of both the XANES and EXAFS spectra to unveil the structural and dynamical properties of electrolytic solutions. Relevant cases of ion-solvent coordination determined by combining computational methods, EXAFS and XANES techniques will be illustrated.

Location: “Aranjo Ruiz” Hall
Time: 19:00

Simultaneous RMC fit of the total scattering and EXAFS data

Victor Krayzman¹, and Igor Levin¹

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Local atomic arrangements in complex crystalline materials, such as solid solutions, often deviate from the average structure traditionally determined from Bragg diffraction. EXAFS and x-ray/neutron total scattering both yield versions of instantaneous atomic pair-distribution functions (PDF) and, as such, are sensitive to local atomic order; moreover, these two techniques provide highly complementary information. In the present project, we developed Reverse Monte Carlo (RMC) refinements of local structure using simultaneous fitting of the total scattering and EXAFS data. The algorithm, implemented as an extension to the public-domain RMCProfile software, incorporates treatment of both single and multiple scattering in EXAFS thereby enabling accurate modeling of the EXAFS signal over several coordination shells around the absorber. We applied these RMC refinements to several perovskite-like solid solution systems and demonstrated that a combined use of EXAFS and total scattering (PDF+Bragg) provides sufficient constraints to recover reliably even subtle details of local atomic configurations in complex perovskites. Additionally, this approach provides an opportunity to benchmark EXAFS measurements/modeling against x-ray/neutron PDF. The presentation will describe key aspects of combined refinements and illustrate them using several specific examples, including $\text{Ca}(\text{Zr}, \text{Ti})\text{O}_3$ and $\text{Sr}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ systems.

Location: “Aranjo Ruiz” Hall
Time: 19:20

Determining the number of species from multi-component XAFS data

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The advent of laterally resolved XAFS spectroscopy with micrometer and sub-micrometer resolution has opened up new possibilities for the study of heterogeneous systems in materials, biological, and environmental science. Often, the X-ray resolution is sufficient to pin down the nature of pure species, but in some cases the spectra are still multi-component and data processing is required to determine the number and identity of each species in the mixture. One solution to the problem consists to record a series of spectra at many points-of-interest (POIs) and to calculate the dimension of the system by principal component analysis (PCA) [1-3]. The paradigm is that this dimension equals the number of species. This assumption is correct if their proportions in the dataset vary, which is the case when their distributions in the sample are heterogeneous [4]. The dimension of the system is given by the number of meaningful abstract components in the PCA. Three criteria are generally used: the cascade or variance of the eigenvalues (EVs), the factor indicator function (IND), and the F-test on reduced EVs. However, none of them is fully satisfying because they do not consider the signal/noise ratio in the data nor systematic errors. Thus, determining the system dimension from real data has proven to be difficult. To progress on this problem, ninety nine Cu K-edge micro-XANES spectra were recorded from contaminated soils at POIs selected from micro-SXRF maps to represent the total range of chemical associations, and analyzed statistically by including the experimental error to the data analysis.

[1] Malinowski E. R. (1991)

[2] Wasserman S. R. et al. (1999)

[3] Ressler T. et al. (2000)

[4] Manceau, A et al. (2002)

Location: “Aranjo Ruiz” Hall
Time: 19:40

Conventional error analysis in conventional EXAFS analysis: lessons from Nyquist and Fourier

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Residuals in an EXAFS fit to real data using theoretically calculated backscattering functions such as provided by FEFF are far larger than expected from known sources of experimental error. This unavoidable systematic uncertainty, together with other systematic error sources, not only limit the ultimate accuracy of the technique, but also affect the ability of the covariance matrix to represent the real errors on the fit parameters in a conventional least-squares fitting routine. Consequently, reported errors are not reliable in many EXAFS studies in the literature. This situation has made some EXAFS practitioners leery of conventional, covariance-matrix-based error analysis. However, such error analysis, if properly applied, can teach us more about our data, and even about the power and the limitations of the EXAFS technique. We present a description of how conventional error analysis is properly applied in *r*-space fitting to EXAFS data. Using simulations, we demonstrate the veracity of this analysis by, for instance, showing that the number of independent data points from Nyquist’s theorem is balanced by the degrees of freedom obtained from a conventional χ^2 statistical analysis. We are then able to discuss fundamental model tests, such as the F-test, both with simulated data and real data where random noise dominates. Finally, by comparing such analysis with real data, we can determine the role that systematic errors play, and quantify their effect. In short, this study serves as a reminder to the EXAFS community of the role of fundamental noise distributions in interpreting our final results.

P4.4: Related Phenomena

Location: “Betti” Hall
Time: 18:00

Chemical information in hard X-ray photon-in photon-out spectroscopy

Pieter Glatzel¹

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X-ray absorption spectroscopy (XAS) is widely used as an element-selective technique to study the chemical environment. The instrumentation at synchrotron radiation sources as well as analysis and calculation of XAS has reached such a high level that this technique is now attractive to a very large user community. Standard XAS, however, cannot answer all questions and complementary techniques that address the electronic structure in more detail add to the repertoire of hard X-ray techniques. We discuss in this contribution how energy analysis of the scattered photons in addition to control of the incident photon energy extends the range of applications of XAS and addresses some problems that XAS cannot solve.

A number of spectroscopic techniques become available using such an experimental setup.[1, 2] Some of them are:

- High-Energy Resolution Fluorescence Detected (HERFD) XAS
- Non-Resonant X-Ray Emission Spectroscopy (XES)
- Resonant X-Ray Emission Spectroscopy (RXES) and resonant inelastic X-ray scattering (RIXS)

The first technique complements and improves the current standard XAS experiments while the last two open up possibilities for detailed studies of the electronic structure using a photon-in photon-out technique. The hard X-ray probe makes all techniques suitable for in-situ (operando) studies and experiments under extreme conditions (e.g. high pressure). This contribution will provide an overview of the possibilities for chemical analysis and address the current level of theoretical modeling.

[1] P. Glatzel and U. Bergmann, *Coord. Chem. Rev.*, 249 (2005) 65.

[2] F.M.F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids*, Taylor and Francis, New York, 2008.

Location: “Betti” Hall
Time: 18:20

Resonant x-ray scattering in 3d-transition-metal oxides: anisotropy and charge orderings

G. Subias¹, J. Garcia¹, J. Blasco¹, J. Herrero-Martin², and M. C. Sanchez¹

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The transition metal oxides have fascinated chemists and physicists for many decades with their intriguing structural, magnetic and electronic properties, leading to high- T_c superconductivity, colossal magnetoresistance or multiferroic behaviour. All these effects reflect in atomic charge, spin and orbital degrees of freedom. Accurate investigation of all these electronic degrees can be made by resonant x-ray scattering (RXS).

RXS combines high-Q resolution x-ray diffraction with the properties of the resonance providing information similar to that obtained by atomic spectroscopy (element selectivity and a large enhancement of scattering amplitude for this particular element and sensitivity to the symmetry of the electronic levels through the multipole electric transitions). Since electronic states are coupled to the local symmetry, RXS reveals the occurrence of symmetry breaking effects such as lattice distortions, onset of electronic orbital ordering or ordering of electronic charge distributions. In many cases, all these effects are coupled and a careful analysis of the polarization and azimuthal dependencies of resonant effects is required to unravel the physics that is at the origin of the resonant signal.

In this talk, we shall discuss the strength of RXS by describing various applications in the observation of anisotropy and charge orderings in 3d transition-metal oxides, using both hard and soft x-rays. Examples of these resonant effects are (I) charge ordering transitions in manganites, Fe_3O_4 , ferrites and nickelates and (II) forbidden reflections and orbital order in Mn^{3+} perovskites, spinel ferrites and cobaltates. In all the studied cases, the electronic (charge and/or anisotropy) orderings have been found to be controlled by the structural distortions.

Location: “Betti” Hall
Time: 18:40

Study of double-photon interaction for a single atom x-ray absorption spectroscopy

Masashi Ishii¹, B. Towlson², E. Whittaker², Y. Shiraki³, and B. Hamilton²

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(2) The Photon Science Institute, The University of Manchester, Alan Turing Building, Manchester M13 9PL UK

(3) Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

We have been developing a new scanning probe microscopy with an x-ray source for nano-detection of x-ray interaction with materials. In previous studies, we successfully found evidences of x-ray interaction in electrostatic force (EF), and discovered EF detected by a micro tip depends on x-ray photon energy, resulting in x-ray absorption spectroscopy (XAS) spectra of nano structures [1-2] such as a single carbon nano tube.

For an ultimate goal of XAS, “a single atom” analyses, we are trying to refine probing efficiency of the x-ray interaction. Here, we propose a method enhancing x-ray interaction in EF by double-photon irradiation. Basically, the x-ray interaction in the EF can be explained by the photon induced emission of localized charges in a nano structure. In this study, we introduce another photon for charge refilling that compensates the one-sided charge emission by x rays. The controlled emission and refilling realize a steady electron transition and emphasizes fine x-ray absorption in EF.

The double-photon irradiation experiments were performed at Diamond Light Source in UK. The charge refilling was demonstrated with a visible-infrared (V-IR) light. The sample was SiGe quantum dot (QD) made by self-organization. The local EF measurement under the photons was performed by a custom-made electrostatic force microscopy produced by UNISOKU, Japan.

We irradiated continuous x rays and pulsed V-IR light on the sample, and local EF was detected by a fixed probe on a single QD. It was found that EF increased by x-ray irradiation while it synchronously decreased by V-IR irradiation pulse. This finding proves the charge emission by x rays and refilling by V-IR. Moreover, we confirmed that the EF decay during V-IR irradiation is hastened by Ge L-edge absorption.

[1] M. Ishii, B. Hamilton, et. al., App. Phys. Lett. 90 (2007) 063101.

[2] M. Ishii, B. Hamilton, and N. R. J. Poolton, J. Appl. Phys. 104 (2008) 103535.

Location: “Betti” Hall
Time: 19:00

Collective spin-excitations in a quantum spin ladder probed by high-resolution Resonant Inelastic X-ray Scattering

Justine Schlappa¹, T. Schmitt¹, F. Vernay¹, V. N. Strocov¹, V. Ilakovac², B. Thielemann¹, H. M. Rønnow³, Vanishri S.⁴, A. Piazzalunga⁵, X. Wang³, L. Braicovich⁵, G. Ghiringhelli⁵, C. Marin⁴, J. Mesot^{1,3}, B. Delley¹, and L. Patthey¹

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(3) Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(4) INAC/SPSMS/DRFMC, CEA-Grenoble, 38054 Grenoble Cedex 9, France

(5) CNR/INFN Coherentia/Soft - Dip. Fisica, Politecnico di Milano, 20133 Milano, Italy

Resonant Inelastic X-ray Scattering (RIXS) is a powerful bulk-sensitive probe of the microscopic electronic properties of matter. In the soft x-ray range the excitation energy can be tuned such that the photon scattering cross section with the partially occupied electron states is greatly enhanced. For example in studies with copper-oxides by choosing the photon energy to the Cu L_{2,3} edge (Cu 2p → 3d transition) the charge, orbital and spin degrees of freedom of the Cu 3d states can be investigated [1]. Here we present high-resolution RIXS study of the magnetic and electronic excitations in the low-dimensional spin system Sr₁₄Cu₂₄O₄₁. This compound, which consists of two different copper-oxide layers: the so-called spin-ladders and spin-chains, is known to display a range of intriguing phenomena. Among others the chains develop a charge density wave at low temperatures and the ladders possess a real quantum mechanical ground state with a finite spin gap [2]. With Cu L₃-RIXS we map out the dispersion of two-triplon excitations from the ladders, their elementary magnetic excitations, achieving excellent sensitivity over almost the full Brillouin-zone and directly determining the two-triplon energy gap [3]. Using O K RIXS, oxygen site-sensitive hole-excitation are studied, giving insight into the character of the holes in the ladders and the chains. Our results are supported by calculations within an effective Hubbard model for a finite-size cluster. The experiments were performed at the ADDRESS beamline of the Swiss Light Source using the SAXES spectrometer [4,5].

[1] A.Kotani and S.Shin, Rev.Mod.Phys. 73, 203 (2001)

[2] T.Vuletić et al., Physics Reports 428, 169-258 (2006)

[3] J.Schlappa et al., arXiv:0901.1331v2 [cond-mat.str-el]

[4] V. N. Strocov et al., <http://sls.web.psi.ch/view.php/beamlines/address/index.html>

[5] G. Ghiringhelli et al., Rev. Sci. Instrum. 77, 113108 (2006)

Location: "Betti" Hall
Time: 19:15

RXS to study the charge/orbital ordering in mixed valence transition metal oxides far from half doping

Javier Herrero Martin¹, Gloria Subias², Joaquin Garcia², Javier Blasco², and Maria Conception Sanchez²

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(2) Dpto. Fisica de la Materia Condensada, Instituto de Ciencia de Materiales de Aragón, CSIC- Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza (Spain)

Temperature driven metal to insulator transitions in mixed valence transition metal (M) oxides have been for long understood as the result of electron localization into a M^{m+}/M^{n+} ordered sequence in the crystal cell sites. This charge ordering (CO) has been mostly studied on systems with $M^{m+}/M^{n+}=1$ and $(m+n)/2=$ half-integer. However, in the last years it has been shown that the actual charge segregation is far from being integer but smaller in many cases, even by a factor $\sim 5-10$. Most of these studies have profited from the Resonant X-ray Scattering (RXS) technique, which permits to characterize and quantify CO and related phenomena such as orbital ordering (OO). Moreover, it can help to elucidate subtle changes in the crystal structure when this is not accurately known at low temperatures. Here we present a work very recently performed on several compounds showing a low temperature CO and/or OO phase. On one hand, the series $R_{1/3}Sr_{2/3}FeO_3$ ($R=La, Pr, Nd$), where $M^{m+}/M^{n+}\neq 1$ and formal valence of Fe atoms is $+3.67$. In spite of the classical vision based on an ordered sequence with 335335... Fe formal valences along the [111] cubic crystal direction, our RXS data at the Fe K edge and consequent tensorial analysis indicate that the charge segregation on Fe is rather small, non-integer and it necessarily coupled to changes in the crystal cell symmetry thus arising kind of a charge density wave (CDW). On the other hand, $La_{0.4}Sr_{1.6}MnO_4$, formally containing $Mn^{3.6+}$ but showing a differentiated phenomenology. We here observe incommensurate weak CO reflections at the Mn K edge, in agreement with previous results from other groups. Moreover, the presence of OO-type reflections with π periodicity point to the presence of an anisotropic distribution of charge. The joint analysis of these data seems to be hardly reconcilable to a model just based on a CO of Mn atoms. A weak electron-lattice modulation favouring an incommensurate CDW seems to be a more plausible model.

Location: "Betti" Hall
Time: 19:30

The Metal-Insulator-Transition in VO_2 investigated by Resonant Inelastic X-ray Scattering

Kejin Zhou¹, K. J. Zhou¹, T. Schmitt¹, J. Schlappa¹, F. Vernay¹, V. N. Strocov¹, B. Delley¹, and L. Patthey¹

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Vanadium dioxide VO_2 undergoes a metal-to-insulator transition (MIT) from a paramagnetic metal with tetragonal rutile structure to a nonmagnetic semiconductor with monoclinic structure below 340K, characterized by a sudden conductivity drop of several orders of magnitude [1]. Despite decades of studies the nature of this MIT is still not fully understood in which the band gap opening is dominated by the crystallographic distortion [2] or by the electron correlation effects either [3]. We investigate changes of the electronic structure across the MIT in VO_2 by temperature dependent Resonant Inelastic X-Ray Scattering (RIXS) at the ADDRESS beamline of the Swiss Light Source. RIXS is a unique photon-in / photon-out spectroscopic probe for determining the energy and symmetry of charge neutral excitations (e.g. crystal field or spin excitations) in strongly correlated materials. Our high-resolution RIXS study at the V L_3 -edge reveals clear changes in the crystal field originating from the crystallographic distortion accompanying the MIT, especially a remarkable electronic excitation at -0.45 eV broadens and nearly merges with the elastic peak when going from the insulating to the metallic phase. Further detailed investigation on temperature dependence of the excitation shows flat and saturated hysteresis behavior distinct to the sharp one acquired by x-ray absorption [4]. Differences between experiment and simulation within multiplet theory are discussed in relation to screening and charge fluctuation effects.

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998); D.B. McWhan et al., Phys. Rev. B 10, 490 (1994); A. Zylbersztein and N.F. Mott, Phys. Rev. B 11, 4383 (1975)

[2] M. Gupta et al., Phys. Rev. B 16, 3338 (1977); R.M. Wentzcovitch et al., 72, 3339 (1994)

[3] S. Shin et al., Phys.Rev. B 41, 4993 (1990); S. Biermann et al., Phys. Rev. Lett. 94, 026404 (2005)

[4] T. C. Koethe et al., Phys. Rev. Lett. 97, 116402 (2006)

Location: “Betti” Hall
Time: 19:45

Novel insights to cobalt 1s pre-edges with resonant X-ray emission spectroscopy

Gyorgy Vanko¹, and F. M. F. de Groot²

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(2) *Utrecht University Sorbonnelaan 16 3584 CA, Utrecht Netherlands*

The metal 1s pre-edges in compounds of 3d transition metals are rich in information, as they can reflect valence and spin state, coordination number and local symmetry simultaneously. However, often there are several obstacles to address the fine details of the pre-edge, including its low intensity, the poor separation from the tail of the main edge, and the large overlap and smearing due to the large lifetime broadening of the 1s core hole in the XAS final state. Combination of absorption and emission spectroscopy, the resonant X-ray emission spectroscopy (RXES) can overcome these difficulties and can unveil the details of the underlying transitions. In this presentation we wish to show intriguing examples of RXES applied to cobalt oxides, which demonstrate that resonant techniques are often indispensable to pre-edge studies. These include the case of Co_3O_4 , where the resonances of different sites happen to appear at the same incident energy; LaCoO_3 , whose deceptive spectral shapes in the pre-edge often lead to a faulty assignment; and non-local (or off-site) transitions, that gauge intersite p-d hybridization between neighbouring metal atoms.

In addition, the exceptional resolving power of the presented 1s2p RXES experiments allows us to demonstrate the coherent second-order nature of the underlying scattering process.

A relevant part of the talk is covered in Ref. 1.

[1] G. Vanko, F. M. F. de Groot, S. Huotari, R. J. Cava, T. Lorentz, M. Reuther,
arXiv:0802.2744v1: <http://arxiv.org/abs/0802.2744v1>

Wednesday 29th July

M3: Plenary session M3

Location: “Benedetto XIII” Hall
Time: 8:30

Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces: an XAFS and XMCD study.

Klaus Baberschke¹

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Metalorganic molecules like Fe-porphyrin or haemoglobin have been investigated in great detail in the past. Its importance is obvious and has been measured mostly with molecules in random orientation, in the past. Here we report on experiments of a single monolayer of Fe-porphyrin in UHV aligned flat on ferromagnetic Ni and Co films [1]. NEXAFS with linear and circular polarization is the spectroscopy of choice; it is element specific and measures the electronic structure as well as the magnetism at once. For the flat oriented monolayer of porphyrin molecules we have measured the angular dependence of XAFS at the C and N K-edge and of XMCD at the Fe L-edges. The paramagnetic Fe-spin is aligned with respect to the ferromagnetic substrate. This can be parallel or antiparallel [2,3]. Also nonmagnetic substrates like Cu (100) plus an external magnetic field will align the magnetic Fe-moment. This altogether opens a huge field for switching the 3d-spin from parallel to perpendicular of the molecular plane, which in turn will modify the electronic transport properties and act as a “single molecule switch”. We will discuss the details of the NEXAFS and XMCD spectra.

The present work has been performed in collaboration mainly with H. Wende and with the other co-authors of ref. 1-3. The work was initiated and supported by grant: BMBF 05KS4-KEB (Wende/Baberschke).

[1] H. Wende, M. Bernien, J. Luo, et al. Nat. Mater. 6, 516 (2007)

[2] M. Bernien, J. Miguel, C. Weis, et al. Phys. Rev. Lett. 102, 47202 (2009)

[3] M. Bernien, X. Xu, J. Miguel, et al. Phys. Rev. B 76, 214406 (2007)

Location: “Benedetto XIII” Hall
Time: 9:15

Current and next generation synchrotron light sources - enabling discovery in structural biology

Keith Hodgson¹

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It is now well established that synchrotron radiation produced by electron storage rings is an essential, indeed critical, tool for enabling forefront science in structural molecular biology (and other fields as well). In part this has come from the much higher average brightness provided by the 3rd generation sources, a number of which are in operation or in construction worldwide. Developments in accelerator physics over the past decade or so have provided the underpinning technology to enable a different approach to producing synchrotron radiation based upon linear accelerators rather than storage rings. Linac-based light sources can have properties that differ significantly from that of storage rings, including much shorter pulses, higher average and peak (per pulse) brightness and full coherence (in the case of the x-ray free electron lasers - XFELs). This talk provides a perspective on recent and future advances for XAFS studies enabled by new instrumentation and methodology developments for both the current third generation of x-ray sources and the coming XFELs.

Location: “Benedetto XIII” Hall
Time: 10:00

R. Pettifer MEMORIAL

Borrmann Spectroscopy

S. P. Collins¹, D. Laundry², and M. Tolkiehn³

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(3) *HASYLAB/DESY, Notkestr. 85, 22603, Hamburg, Germany*

We describe observations of a very large enhancement of the quadrupole contribution to XANES spectra in the Borrmann Effect. This new finding[1], made seven decades after the discovery of the Borrmann Effect and predicted by the late Dr R F Pettifer, represents the latest discovery from one of the most remarkable effects in x-ray physics.

The Borrmann Effect[2,3,4], also known as ‘anomalous transmission’, is the transmission of a monochromatic x-ray beam through a high quality crystal of sufficient thickness to stop the beam almost completely, and occurs under conditions of Laue diffraction. As the x-ray beam passes through the crystal a standing wave field is established perpendicular to the diffracting planes, with nodes at the equally-spaced planes of atoms. X-ray absorption then occurs, not under the usual conditions of a plane wave, but with a wave field given by the coherent sum of two plane waves. The result is a radical change to the absorption spectra and selection rules.

In this paper, we outline a phenomenological model of spectroscopy under Borrmann conditions, which predicts a large relative enhancement of electric quadrupole absorption. We show that small thermal atomic displacements are expected to lead to a large increase in dipole absorption by moving the absorbing atoms away from the wave field nodes. In contrast, there is no such increase in the quadrupole absorption, which is driven by the field gradient, maximised at atomic planes. We thus expect that the quadrupole enhancement should be strongly temperature dependent, thus providing a means to separate the two contributions.

We describe experimental data on the temperature dependence of the Borrmann spectra in gadolinium gallium garnet and other crystals. The phenomenological model is shown to work remarkably well in some cases, while others highlight the need for a new theory of the Borrmann Effect that includes a modern treatment of anisotropic x-ray absorption and resonant scattering.

[1] R F Pettifer, S P Collins & D Laundry *Nature* 454 196-199 (2008)

[2] G Borrmann *Phys. Z.* 42, 157-162 (1941).

[3] G Borrmann *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* 106, 109-121 (1954).

[4] B W Batterman, & H Cole *Rev. Mod. Phys.* 36, 681-717 (1964).

S3: Complementarity of XAS and diffraction techniques

Location: “Benedetto XIII” Hall
Time: 11:00

Total scattering and the atomic pair distribution function: an alternative route to the local and intermediate structure

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(2) *Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory Upton New York 11973 USA*

XAFS has proved itself to be a powerful and versatile tool for studying local structure in complex materials. Recently, an alternative diffraction based approach has been gaining popularity, the atomic pair distribution function (PDF) analysis of x-ray or neutron diffraction data. The method has been used for more than 70 years to study the structure of liquids and amorphous materials. With the advent of powerful x-ray synchrotrons and pulsed neutron sources, coupled with fast computing, the method has become invaluable in the study of local structure in complex crystals and nanocrystalline materials. It is highly complementary to XAFS in the sense that it gives local and intermediate range structural order but is not a chemically resolved technique. I will describe recent developments in PDF analysis with scientific examples, and discuss its relationship and complementarity to XAFS.

Location: “Benedetto XIII” Hall
Time: 11:25

Comprehensive three dimensional models of structurally disordered systems - capturing the local and bulk structure in an experimentally consistent manner

Daniel Timothy Bowron¹

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Structurally disordered systems pose many challenges for the analysis of experimental data relating to their atomic structure. In particular there is an inherent requirement for any analytical framework to appropriately capture, within a statistically reasonable model, the key structural motifs that underpin the system's physical or chemical properties. The development of modern computational methods now allows us to address this challenge, and powerfully combine the capabilities of a range of experimental probes of atomic and molecular structure. These new methods can now provide detailed insight into the short and medium range structure of multi-component liquids and glasses. The approach that will be outlined is based upon Empirical Potential Structure Refinement [1]. This technique was originally developed to produce three dimensional atomistic models of disordered materials that are consistent with experimentally measured neutron and X-ray diffraction data. The increases in computing power have now allowed the method to be integrated with the widely used FEFF package for the calculation of EXAFS spectra [2,3,4] and this powerful addition to the analytical framework allows the chemically specific local structure captured in the model, to be tested in detail. The combination of the sensitivity of the spectroscopic probe to chemically dilute local environments with the bulk structural capabilities of the diffraction methods, allows us to generate comprehensive structural models that can better assist us to understand the functional properties of the disordered states of matter. A selection of examples of the method applied to solid and liquid state systems will be presented.

- [1] A.K.Soper, Phys. Rev. B, 72, 104204 (2005)
- [2] D.T.Bowron and S.Diaz-Moreno, J. Phys. Chem. B, 111, 11393-11399 (2007)
- [3] D.T.Bowron, Mat. Sci. Eng. B, 149, 166-170 (2008)
- [4] D.T.Bowron, Pure Appl. Chem., 80(6), 1211-1227 (2008)

Location: "Benedetto XIII" Hall
Time: 11:50

Strain and composition of semiconductor nanostructures by grazing incidence Diffraction Anomalous Fine Structure spectroscopy

Hubert Renevier¹, M.I. Richard², N. Ayape-Katcho³, M.G. Proietti⁴, O. Landré⁵, V. Favre-Nicolin⁵, G. Bauer⁶, and B. Daudin⁵

(1) Institut Polytechnique de Grenoble LMGP, Grenoble INP - MINATEC, 3 parvis L. Néel - BP257 38016 Grenoble France

(2) Université Paul Cézanne, IM2NP, UMR 6242, Faculté des Sciences de St Jérôme 13397 Marseille Cedex 20, France.

(3) IQFR-CSIC, Dep. Quim. Inorganica - Universidad Complutense de Madrid, Spain

(4) Departamento de Física de la Materia Condensada, ICMA, CSIC-Universidad de Zaragoza, calle Pedro Cerbuna 12, 50009 Zaragoza, Spain

(5) SP2M, INAC, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

(6) Johannes Kepler Universität Linz, Institut für Halbleiter-und Festkörperphysik, Austria

The knowledge of strain, chemical composition, atomic inter-mixing and ordering, is of great importance to understand the growth mechanism as well as the electronic and optical properties of as grown or encapsulated nanostructures [1].

The determination at short and long range order of these structural properties is a challenging issue. We would like to show that a combination of Diffraction Anomalous Fine Structure (DAFS) spectroscopy, Multiwavelength Anomalous x-ray Diffraction (MAD) and a quantitative data analysis based on Molecular Dynamics, provides a unique tool to solve the problem [2, 3, 4, 5]. MAD is used to map the scattering amplitude of the resonant atoms, in the reciprocal space. It gives information on the average strain, composition and size of resonant atom containing iso-strain volumes. DAFS gives information on the local environment of resonant atoms (chemical selectivity) located in an iso-strain volume selected by diffraction (spatial selectivity).

We will present a brief insight on the basic principles of MAD and DAFS methods and report on the structural properties of free standing and capped nanostructures. We will focus on recent results obtained on GaN/AlN nanowires [6], AlGaIn nanowires, capped GeSi pyramids, free standing and capped Ge/Si domes [5]. We will also show EXAFS results for some of the samples illustrating the complementarity of XAFS and DAFS.

[1] J. Stangl, V. Holy, and G. Bauer, Rev. Mod. Phys. 76, 725 (2004).

[2] A. Letoublon et al., Phys. Rev. Lett. 92, 186101 (2004).

[3] J. Coraux et al., Phys. Rev. B 75, 235312 (2007).

[4] C. Lamberti, Characterization of Semiconductor Heterostructures and Nanostructures (Elsevier Science, Amsterdam, 2008).

[5] M. I. Richard et al., Eur. Phys. J. Special Topics 167, 3 (2009).

[6] O. Landre et al., Appl. Phys. Lett. 93, 183109 (2008).

Location: "Benedetto XIII" Hall
Time: 12:15

Crystallography with online optical and X-ray absorption spectroscopies demonstrates an ordered mechanism in copper nitrite reductase

Richard William Strange¹

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By performing PX and XAS data collection in situ on a metalloprotein crystal it is possible to identify metals through anomalous diffraction measurements, determine metal redox states and to monitor crystals for radiation damage at the metal sites. By combining the PX and XAS data during analysis, it becomes possible to obtain atomic resolution 3D information from medium or even low resolution crystal structures and to use XAS derived parameters to aid crystallographic refinement. The inclusion of in-situ single crystal optical instrumentation to the experimental station provides another method for examining the 'true' state of metalloprotein active sites during crystallographic data collection. The importance of using spectroscopy and XAS for identifying well defined redox states of metalloproteins during crystallographic data collection is demonstrated using crystals of nitrite reductase from *Alcaligenes xylosoxidans*, which contains both type-1 and type-2 Cu centres [1]. It is found that the type-1 Cu centre photoreduces quickly, resulting in the loss of the 595 nm peak in the optical spectrum, while the type-2 Cu centre remains in the oxidized state over a much longer time period, for which independent confirmation is provided by XAS data as this centre has an optical spectrum which is barely detectable using microspectrophotometry.

[1] I. Hough, M. A., et. al J. Mol. Biol. 378, 353-361 (2008)

Location: “Benedetto XIII” Hall
Time: 12:40

Structural studies (XAS, DFT, XRD) of Amyloid-beta metal binding and oligomer formation in Alzheimer’s Disease

Victor Streltsov¹, Vidana Epa¹, Stewart Nuttall¹, and Jose Varghese¹

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Alzheimer’s disease (AD) is a neurodegenerative disorder characterized by the presence of Amyloid-beta ($A\beta$) peptide plaques. However, current views suggest that soluble $A\beta$ oligomers, and not the plaque burden, may be the major drivers of $A\beta$ -mediated neuronal dysfunction. The $A\beta$ oligomerization can be facilitated by metals and the neurotoxicity of $A\beta$ has been related to its ability to form complexes with Cu. The $A\beta$ -Cu complexes are involved in redox reactions that produce reactive oxygen species (ROS). Details of the Cu binding site in $A\beta$ may be critical to the etiology of AD. Frustratingly, obtaining atomic resolution information for such $A\beta$ metal complexes and oligomers has been a major challenge, due in part to the propensity of $A\beta$ to form fibrils and aggregates [1].

Here we present the structure of $A\beta$ (1-16) (metal-binding region) complexed with Cu(II) in solution determined by combining XAFS and DFT analyses [2]. The Cu binding site includes three histidines, glutamic or/and aspartic acid and axial water. XANES was used to probe the substrate mediated Cu(II)-Cu(I) reduction in $A\beta$ -Cu(II) complexes by ascorbate and the neurotoxin 6-hydroxydopamine, however dopamine and, in particular, cholesterol are incapable of reducing $A\beta$ -Cu(II) complexes [3].

We also present 2.2 Å resolution crystal structure (XRD) of the $A\beta$ (18-41) (fibrillogenic region) constrained within the CDR3 loop of a shark IgNAR single domain antibody [4]. Our results reveal unusual $A\beta$ topologies and inter-peptide interactions, strikingly different from previous fibrillar models. Notwithstanding, we can identify conserved elements within our structure consistent with motifs recognised before as critical in $A\beta$ peptide folding and amyloidogenesis.

- [1] V. Streltsov, Eur. Biophys. 37(3), 257 (2008)
- [2] V. Streltsov et al, Biophysical Journal 95, 3447 (2008)
- [3] V. Streltsov, & J. Varghese, Chem. Comm. 3171 (2008)
- [4] V. Streltsov et al, Proc Natl Acad Sci USA 101, 12444 (2004)

Thursday 30th July

M4: Plenary session M4

Location: “Benedetto XIII” Hall
Time: 8:30

Real time XAFS for structural kinetics/dynamics of 2D and nanoparticle catalyses

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Tremendous catalysis can appear with 2D aspect and unique ensemble on surfaces/pore walls and nanoparticles, which may be hard to produce in homogeneous and conventional 3D bulk systems. New strategy and concept lead to tailor-made catalyst design for a target reaction in green sustainable processes, where in situ characterization of the surfaces and nanoparticles by time-resolved XAFS is inevitably important for understanding the origin and mechanism of the tremendous catalysis and dynamic surface events. Dynamic structures of the catalysts relevant to selective catalyses have successfully been characterized by in-situ time-resolved XAFS techniques at SPring8 and KEK-PF at a time resolution of 2 ms - 1 s, depending on the reaction systems. The talk documents structural kinetics/dynamics of active catalysts for typical selective catalyses including direct phenol production from benzene with molecular oxygen on a Re/ZSM-5 catalyst, surface events at a Pt/C cathode catalyst in a PEM fuel cell system, methane reforming on Ni/CeO₂-ZrO₂ solid solution with oxygen storage capacity, and selective oxidation on V/Al₂O₃ and SiO₂, characterized by means of time-gating, quick and energy-dispersive XAFS techniques [1-4]. The structural kinetics/dynamics of catalysts themselves provide valuable information on catalysis mechanisms and rational design of catalysts, which is entirely different from that from reaction kinetics/dynamics of reactant/product molecules.

[1] M. Tada, R. Bal, T. Sasaki, Y. Uemura, Y. Inada, M. Nomura, and Y. Iwasawa, *J. Phys. Chem. C* 111, 10095 (2007).

[2] M. Tada, S. Murata, T. Asaoka, K. Hiroshima, K. Okumura, H. Tanida, T. Uruga, H. Nakanishi, S. Matsumoto, Y. Inada, M. Nomura, and Y. Iwasawa, *Angew. Chem. Int. Ed.* 46, 4310 (2007).

[3] T. Yamamoto, A. Suzuki, Y. Nagai, T. Tanabe, F. Dong, Y. Inada, M. Nomura, M. Tada, and Y. Iwasawa, *Angew. Chem. Int. Ed.*, 46, 9253-9256 (2007).

[4] M. Tada, Y. Akatsuka, Y. Yang, T. Sasaki, M. Kinoshita, K. Motokura, and Y. Iwasawa, *Angew. Chem. Int. Ed.*, 47, 9252-9255 (2008).

Location: “Benedetto XIII” Hall
Time: 9:15

Studying functioning catalysts with X-rays

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The design and construction of better catalysts requires knowledge of the structure performance relation. However, more often than not, the structure of the catalytically active site is unknown. Because the catalyst structure is dynamic, its structure has to be determined under true reaction conditions. Using X-rays to study catalysts is very attractive, because of the high penetration depth of high energy X-rays. Over the years, we have performed XAS studies on supported metal catalysts and aimed at determining the ensemble of atoms that forms the catalytically active site. We have explored high-energy resolution XAS, X-ray emission spectroscopy, which enables the spin-selective detection of the valence band under in situ conditions. This provides valuable information about the reactivity of transition metal catalysts. The structure of a heterogeneous catalyst may vary over time and even within its position in a catalytic reactor. We have determined the structure of a functioning heterogeneous catalyst over time as function of its position in a catalytic reactor and identified strong variations. It will be shown that catalyst characterization is essential to occur in situ, time and space resolved and that if these requirements are met, structure performance relations can be determined.

Location: “Benedetto XIII” Hall
Time: 10:00

Shining X-rays on catalysts at work

Jan-Dierk Grunwaldt¹

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Structure-performance relationships gained by studying catalysts at work are considered the key to further development of catalysts. This requires the structural identification of catalysts preferentially under process conditions, while measuring the catalytic activity at the same time. Here, recent studies on catalysts at work in gas phase reactions and liquid phase are reported and combination with in situ XRD and Raman spectroscopy are highlighted.

In certain cases a variation of the catalyst structure can occur inside a catalytic reactor as a result of temperature or concentration gradients. In addition, rapid structural changes can occur during activation, ignition and reaction over the heterogeneous catalysts. This requires spatially and time-resolved structural information of the catalysts. A prominent example is the partial oxidation of methane over noble metal based catalyst. In order to obtain spectroscopic information on the oxidation state inside the catalytic reactor XAS spectra were on the one hand recorded with a micro-focussed beam and scanning over the sample. On the other hand a 2D-area detector was used that is advantageous for in situ studies since it results in shorter recording times. In addition, the temperature profile was analysed using an IR-camera and the catalytic performance using mass spectrometric analysis. In a more recent experiment the ignition process of the partial oxidation of methane was followed both by time-resolved QEXAFS studies and detection of the change in X-ray absorption giving information in the structural changes in a 2-dimensional way.

S4: Catalysis and Energy Sciences: From EXAFS to QEXAFS and Beyond

Location: “Benedetto XIII” Hall
Time: 11:00

QEXAFS: Technique, science, future

Ronald Frahm¹

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XAFS experiments for the investigation of time dependent processes can be performed in the so-called Quick-EXAFS (QEXAFS) mode, where the spectrum is collected “on-the-fly” using a stable double-crystal monochromator. This technique is especially well suited for in situ investigations in physics, chemistry and materials science. One major field of applications concerns catalytic processes. An optimized monochromator design used for such experiments employs a channel cut crystal, a cam driven tilt table for rapid angular oscillations and a fast readout system for the Bragg angle. This enables the acquisition of full EXAFS spectra with a scan range of up to about 2.5 keV with a time resolution of down to typically 50 ms/spectrum. Since a fast sequential energy scanning technique is used the detection of fluorescence radiation or surface sensitive techniques can be directly applied, which is important for dilute samples like catalysts. A reference sample can be monitored simultaneously with each measurement to detect even minor edge shifts reliably. Even XANES micro tomography on active catalysts is feasible using refractive X-ray lenses for beam focusing.

The technical developments of the QEXAFS technique, its current state and the most challenging results are reviewed. QEXAFS has become very attractive for the investigation of catalysts, and several dedicated facilities are in operation or planned worldwide. Recent scientific investigations - especially from SOLEIL and the new, dedicated QEXAFS monochromator at the SLS demonstrate the state of the art. In addition, the possibilities at different sources (bending magnets, insertion devices, X-FELs) are evaluated, and a comparison to experiments using the energy dispersive mode (DEXAFS) is made. Finally, possible future directions for time dependent XAFS investigations are outlined.

Location: “Benedetto XIII” Hall
Time: 11:25

Combined in situ analysis of Ni₂P/MCM-41 under hydrodesulfurization conditions: simultaneous observation of QXAFS and FT IR

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Supported Ni₂P catalysts are efficient catalysts for hydrotreatment (HT) of petroleum feedstocks and they are regarded hopeful candidate for next generation HT catalysts. We previously reported in situ XAFS analysis of the catalyst under realistic catalytic reaction conditions, that is, under high pressure high temperature liquid phase HDS conditions. It was found that evolution of Ni phosphosulfide phase was formed, which was expected to be the active phase. For detailed study of reaction mechanisms, it is necessary to perform time resolved analysis of surface structural changes associated with adsorbed species under transient conditions rather than at steady state conditions. For that purpose, we installed a QXAFS system to the beam lines at KEK-IMSS-PF, which enables measurement of a Ni K-edge EXAFS spectrum in 10 sec. In addition to that, we combined FT IR with QXAFS, and carried out simultaneous measurement of XAFS and IR. Comparison of XAFS and IR spectra gave us information about structures both of catalysts and adsorbates, which enables us to understand how the active sites contribute to form intermediate species on the catalysts. After activation, a reaction gas mixture was introduced to the catalyst at various reaction temperature. It was found that at the temperature of 513 K when the catalyst showed high HDS activity, a drastic change assigned to evolution of Ni-S scattering was observed with QXAFS in the initial 30 min of the reaction. However, during that period, adsorbed species were not observed with IR, which indicated that the initial change in XANES was due to formation of an active phosphosulfide phase. Subsequently, adsorbed tetrahydrothiophene was observed in IR. Taking all these data into account, the reaction mechanism and the role of phosphosulfide species will be discussed.

Location: "Benedetto XIII" Hall
Time: 11:50

Combined EXAFS and XRPD in understanding the structure and the reactivity of metal organic frameworks (MOFs) upon solvent removal and molecule coordination

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Metallorganic Frameworks (MOFs), also known as "Coordination Polymers" are crystalline nanoporous materials comprised of metal containing clusters connected 3-dimensionally by poly-functional organic linkers. The linkers act as spacers, creating an open porous 3D-structure, with very high pore volume and surface area. This hybrid architecture opens the possibility to design and synthesize a great variety of new porous materials, able to display novel functionalities that are potentially exploitable for a number of applications in catalysis, ion-exchange, non linear optics, as sensors, in gas separation and/or storage [1].

Due to the fact that the organic linkers are almost transparent to X-rays, MOFs are ideal candidates for high quality transmission EXAFS measurements, where signals with good S/N ratio (up to 20 Å⁻¹) can be obtained. The large cell volumes (typically in the 10⁵ Å³ range) makes structure solution from power XRD a difficult task and in several cases EXAFS has been fundamental in confirming/excluding the model used to perform Rietveld refinement [2-5]. Ad hoc conceived EXAFS cells [6] allow to follow in situ the process of solvent removal and interaction with probe molecules from the gas phase.

The importance of parallel EXAFS study in the structure determination is particularly true for samples measured after solvent removal where a reversible loss of symmetry [3,5] with broadening of XRPD peaks [4] is often observed. Experimental XRPD and EXAFS data are further supported by parallel IR/Raman study and by periodic ab initio calculation.

[1] G. Ferey, Chem. Mater., 13, 3084 (2001).

[2] J. Hafizovic, et al., J. Am. Chem. Soc., 129, 3612 (2007).

[3] J. Hafizovic, et al., J. Am. Chem. Soc., 130, 13850 (2008).

[4] K. C. Szeto, J. Phys. Chem. B, 110, 21509 (2006); Chem. Mater., 19, 211 (2007).

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Location: "Benedetto XIII" Hall
Time: 12:15

Removal of oxygen adsorbates on Pt/C and PtNi(1:1)/C alloy nanoparticle catalysts for the oxygen reduction reaction in PEMFCs

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The dissociation of oxygen molecules has long been considered the most important step in determining the velocity of the oxygen reduction reaction (ORR) and consequently has been heavily studied over the past few decades. Recently, however, the removal of adsorbed oxygen species has received an equal amount of attention in the effort to understand the reactivity of the ORR. Using the Materials Research Collaborative Access Team undulator beamline at the Advanced Photon Source and our specially designed *operando* fuel cell, we have measured the time evolution of the platinum L₃ absorption white line of Pt/C nanoparticles and PtNi(1:1)/C nanoparticles at different potentials to investigate the process of removal of oxygen adsorbates. Our experiments show that: (i) overall, there are more oxygen adsorbates around Pt on Pt/C surface than Pt in PtNi/C; (ii) it takes a longer time to remove oxygen adsorbates from Pt/C than PtNi/C; (iii) the variation of the white line intensities of Pt in PtNi/C is much larger than for Pt/C; (iv) the overpotential of PtNi/C is smaller than that of Pt/C; and (v) the white line intensity of Ni in PtNi/C increases along with the lowering of the Pt white line intensity during operation. All these results support the hypothesis that being alloyed with transition metal will reduce the adsorption of oxygen on platinum through a weakening of the bond between Pt and O, together with some other possible effects (e.g. common-ion effect).

Location: “Benedetto XIII” Hall
Time: 12:40

Nano-structured Pt-based catalysts for fuel cell applications probed by in situ XAFS

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Understanding the structure and dynamics of nanomaterials as well as their physico-chemical properties are currently regarded as a challenging research activity having crucial consequences in the material design for various novel applications. Our interest has focused on the materials composed of small quantities (loading below 1mg/cm²) of Pt nanoparticles (3 nm or less in diameter) embedded in some matrix which are widely used in fuel cell (FC) technology. Detailed studies of their micro/nanoscale properties are still relatively difficult to perform, especially when they are under real operating conditions. X-ray Absorption Spectroscopy (XAS) has been recognized as a suitable probe for in situ studies. XAS provides useful complementary information concerning the subtle structural and electronic changes caused by various factors, like the electrocatalyst preparation method, FC working conditions, ageing. However, a sophisticated experimental set-up is needed to obtain in situ high-quality XAS data which could then be safely used for an advanced analysis without the risk of data misinterpretation.

In this contribution, an original multipurpose XAS FC set-up giving in situ high quality data and a new methodology for multiple-scattering extended X-ray absorption fine structure (MS EXAFS) data-analysis of nanocrystalline Pt are presented. In particular, it is emphasized that suitable data analysis should account for sample homogeneity and reduction of the coordination number and degeneracy of three-body configurations, resulting from the measured size distribution and expected surface atoms contributions. Hence, combination of XAFS data with electron microscopy and X-ray diffraction results is crucial for a reliable structural analysis. Detailed results for a few Pt-based electrocatalysts working under various conditions are presented and discussed to demonstrate the efficiency of XAS FC set-up and correctness of data analysis.

P5.1: Catalysis I

Location: “La Muta” Hall
Time: 15:30

Iron-catalysis through the XAS-eye: structures, mechanisms and beyond

Matthias Bauer¹

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Catalysis with inexpensive and un toxic metals is gaining increasing importance in chemical synthesis. Iron compounds proved to be efficient and highly selective catalysts for numerous chemical transformations [1,2]. Thus, iron catalysis nowadays is referred to as the new palladium catalysis. To improve the catalytic activity of such catalysts, it is necessary to understand their working principle, and knowledge about the chemistry of such catalytic systems is highly desired.

X-ray spectroscopy offers the possibility to view iron catalysts from many directions. K-edge EXAFS spectroscopy provides insights into the local coordination, and allows to identify the active species. Also, additional information, like the role of catalyst poisons can be achieved with EXAFS. Moreover, it is possible to identify different binding modes of ligands by analyses of the cross-correlation term in the Debye-Waller factor in combination with Raman and UV/Vis spectroscopy. K-edge XANES allows complementary information about the coordination geometry and the oxidation state, which can be followed by QEXAFS-Raman studies to gain mechanistic insights.

Since catalysts of the same oxidation state can exhibit distinct reactivities, details of the d-electron structure are required in order to understand different catalytic behaviour. These information can be obtained by X-ray emission and RIXS spectroscopy. Beside the exact analyses of such spectra by means of devoted program codes, they can also be used in a comparative way to identify differences in the d-electron structure of iron catalysts.

The described „chemical“ applications of X-ray spectroscopy will be presented for two examples, a Fe(+III) catalyzed Michael addition and reactions involving the Fe(-II) anion $[\text{Fe}(\text{CO})_3(\text{NO})]^-$.

[1] Iron-catalysis in Organic Synthesis, Wiley-VCH, Weinheim, 2008.

[2] J. Christoffers, Synlett, 2001, 723.

[3] M. Bauer et al., PCCP, 2005, 7, 2664.

Location: "La Muta" Hall
Time: 15:50

Reduction and re-oxidation of Cu/Al₂O₃ catalysts investigated with quick scanning XANES and EXAFS

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Copper catalysts are widely used in catalysis, e.g. methanol synthesis, steam reforming and for gas phase oxychlorination. In the present study the structure of copper catalysts supported on alumina were investigated *in-situ* and time-resolved in the subsecond time-regime during reduction and reoxidation with the quick-scanning EXAFS (QEXAFS) technique. Different impregnation times (2 min. and 90 min.) were chosen for the preparation of the catalysts since they show strikingly different reduction behaviour. The oxidation and reduction processes of the resulting catalysts as well as the intermediate phases during switching gas atmospheres were followed with up to 20 EXAFS spectra per second at the Cu K-edge. An energy range of about 450 eV was covered. The experiments were performed at the SuperXAS beamline at the Swiss Light Source (SLS) where a new QEXAFS monochromator was installed. Using a recently developed fast angular encoder system, which is read out simultaneously with the signal of the ionization chambers, accurate EXAFS analysis of the resulting spectra is possible. Three states of copper – Cu(0), Cu(I), Cu(II) – could be unequivocally resolved both during the reduction as well as the much faster oxidation of the catalyst. The stability of Cu(I) was much higher than in Cu/ZnO catalysts. The exact structure of these components and their amounts as function of time is analysed quantitatively. The results of this work do not only lead to a better understanding of the investigated catalysts, but furthermore also demonstrate the latest advances in the QEXAFS technique concerning high speed data acquisition and processing.

Location: "La Muta" Hall
Time: 16:10

In situ X-ray absorption study of CuO-CeO₂/Al₂O₃ catalysts in the total oxidation of propane.

Anilkumar Mettu¹, K. Alexopoulos¹, M.-F. Reyniers¹, H. Poelman², S. Cristol³, V. Balcaen¹, P. Heynderickx¹, D. Poelman², and G. B. Marin¹

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Introduction: The catalytic total oxidation of volatile organic compounds (VOCs) is generally considered an effective method for reducing the emission of pollutants in the environment. The goal of the present study is to investigate the possible changes in the structure and oxidation state of the catalyst's active phase during total oxidation of propane over CuO-CeO₂/Al₂O₃ by in-situ X-ray absorption spectroscopy (XAS).

Methods and Results: The time resolved in-situ XAS measurements were performed using a XAS cell/plug-flow micro-reactor, which consists of a quartz capillary tube mounted horizontally in the setup. The experiments were carried out in transmission mode at the Cu K edge (8979 eV) with time resolution of 0.1s. In order to quantify the ratio of Cu²⁺/Cu¹⁺/Cu⁰ linear combination fitting (LCF) was applied on the obtained XANES spectra using experimental references. No structural changes were observed in the Cu K XANES spectra of the catalyst during heating under He, pre-oxidation (20%O₂/He), and total oxidation (1%C₃H₈-10%O₂/He) reaction conditions, which indicates that the copper phase remained fully oxidized under the applied conditions (i.e. Cu²⁺). A full reduction of the Cu²⁺ towards metallic Cu⁰ occurred between 673-723 K when only propane was fed to the catalyst. However, careful examination of the XANES spectra showed the presence of an intermediate Cu¹⁺ phase (up to 40%). The LCF analysis of catalytic reduction and re-oxidation cycles under different temperatures revealed that at high temperatures, i.e.: 723 K, these processes occur very fast, having a time constant of 0.5s for re-oxidation.

Conclusions: The dynamic structural behavior of the CuO-CeO₂/Al₂O₃ catalyst has been probed under different working conditions by in-situ XAS. During reduction and re-oxidation cycles three copper phases are present, i.e., CuO, Cu₂O and Cu. A two-step mechanism has been observed.

Location: "La Muta" Hall
Time: 16:30

When SOLEIL sheds light on catalysis: methods and results

Camille La Fontaine¹, Laurent Barthe¹, Françoise Villain¹, Valérie Briois¹, François Baudelet¹, Quingyu Kong¹, Xavier Sécordel², Anthony Yoboué², Elise Berrier², Sylvain Cristol², Pascale Massiani³, Eric Marceau³, and Xavier Carrier³

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(3) Laboratoire de Réactivité de Surface, UPMC, 4 place Jussieu, 75252 Paris Cedex 05, France

SOLEIL offers a complete solution for EXAFS experiments on catalysts under working conditions. The dedicated setup involves a multi-purpose gas dosing system, different experimental cells and a mass spectrometer for on-line gas analysis. The cells are designed for EXAFS studies in both transmission or fluorescence modes coupled with Raman spectroscopy, while performing catalytic reactions from room temperature to 600°C at atmospheric pressure. An additional cell, currently under development, will be dedicated to reactions at elevated pressure (20 bar).

In addition, a Quick-EXAFS monochromator will be implemented in May 2009 on SAMBA beamline allowing time-resolved experiments especially well-suited for catalysis. To improve time resolution, the use of Dispersive EXAFS (DEXAFS) on ODE beamline can also be a fair alternative.

Thanks to these new equipments, the first results at SOLEIL in the field of catalysis were gained very recently. Combined XANES/Raman or DEXAFS/Raman experiments were performed on supported molybdenum and rhenium catalysts for methanol conversion. At low loading (1% MoO₃/TiO₂), the molybdate phase is essentially made of isolated monomeric species in tetrahedral geometry. At higher loading (7.5% MoO₃/TiO₂), the catalyst was found to retain a polymolybdate phase with molybdenum clusters involving different coordinations. The coupled XANES/Raman *operando* results converge towards the non-reducibility of monomeric species, as confirmed by the non-activity of low loading catalysts. Conversely, the polymeric phase is reducible from Mo^{VI} to Mo^V under methanol/helium flow as evidenced by XANES. In this case, the catalytic activity was found to reach high conversion rates and high selectivity in formaldehyde (>90%).

These promising results validate the technical developments made at SOLEIL and confirm the relevancy of the time-resolved, coupled *operando* analysis of catalysts.

Location: "La Muta" Hall
Time: 16:45

Complimentary in situ characterisation techniques at realistic working conditions for the Fischer-Tropsch synthesis

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Catalyst deactivation is a major challenge in Fischer-Tropsch synthesis. At present, there is not sufficient knowledge to explain and to distinguish between the proposed deactivation mechanisms. In the present work, Fischer-Tropsch catalysts have been studied using XAS in combination with XRD at conditions close to industrial operation coupled with online product analysis. The information from the two techniques is highly complimentary and thus provides a unique possibility to decouple the potential deactivation mechanisms: XAS is able to give information about the oxidation states of Co during the reaction whereas XRD gives information about particle size and morphology and hence sintering. In addition, in situ Raman spectroscopy has been carried out at similar conditions in order to monitor the oxide species on the catalysts. Vibrational spectroscopies in combination with TPO are also able to detect carbonaceous deposits on the catalysts.

We have recently installed a reactor feeding system at SNBL at the ESRF which allows for working at pressures up to 20 bars with undiluted syngas in the feed. An online MS is used for monitoring the conversion level. The in situ cell makes it possible to combine XRD, XAS and Raman spectroscopy. A similar setup is constructed in our home laboratory where in situ measurements are being performed in a combined FTIR-Raman instrument.

The results from the various techniques are discussed in connection with long-term deactivation studies in a laboratory-scale reactor. A detailed description of the differences between fresh and used catalysts will be presented. A wide range of characterisation techniques are necessary in order to identify the various deactivation mechanisms in Co Fischer-Tropsch catalysts. Furthermore, the techniques have to be employed at realistic working conditions in terms of partial pressures, temperature and conversion level, since these parameters have a significant influence on the deactivation mechanisms.

Local structure of CPO-27-Ni metallorganic framework upon dehydration and coordination of ligand molecules (NO, CO and N₂): comparison between experiments and ab initio periodic calculations

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CPO-27-Ni MOF is a 3D honeycomb network that maintains crystallinity and porosity after solvent removal. A mild thermal treatment vacuo at 393 K removes not only water physisorbed on the but also water directly coordinated to Ni(II) sites [1], leaving the metal center with a coordination vacancy able to strongly coordinate adsorbed molecules [2,3].

Structural (EXAFS vs. XRD), vibrational (IR and Raman) and electronic (UV, XANES, and luminescence) properties are described for the as prepared sample, the dehydrated one and after interaction with NO, CO and N₂ probes. XAFS has been collected at ESRF BM29. High quality data have been obtained up to 18 Å⁻¹ allowing to fit the FT up to 5 Å. Comparison between data collected at 77 and at 300 K allows to reduce the correlation among S_0^2 and D-W factors. Experimental structural, vibrational and energetic data are supported by parallel periodic ab initio calculation with CRYSTAL code, that has successfully described the properties of MOF-5 [4].

NO and CO are strongly bonded at the Ni(II) sites forming almost linear 1:1 adduct at 1.85 ± 0.02 and 2.11 ± 0.02 Å, respectively. Both adsorption causes large modification of the vibrational and electronic properties of the material with respect to the dehydrated one. The whole framework reacts to the adsorption and the whole FT undergo evident modifications visible up to 5 Å. As an example, the first Ni-Ni distance moves from 2.892 ± 0.005 Å in vacuo to 2.95 ± 0.01 and 2.96 ± 0.01 Å upon NO and CO adsorption, respectively. N₂ interacts more gently and its presence can be appreciated in the XAFS spectra collected at 77 K only: Ni(II)-N₂ distance = 2.27 ± 0.03 Å.

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Location: “La Muta” Hall
Time: 17:15

Towards a deeper mechanistic understanding of the Soai reaction: XAS studies of diisopropylzinc as a function of solution environment

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The Soai reaction has over the last decade received considerable attention because it is the sole known example of an amplifying asymmetric autocatalytic reaction scheme that can, in principle, achieve homochirality in a non-chiral environment. It involves the alkylation of a pyrimidyl aldehyde with diisopropylzinc in the presence of the pyrimidyl alcohol that is at the same time the chiral catalyst and the product of the reaction. Several mechanistic models for the Soai reaction have been proposed in the literature, which differ by the structures of the organometallic Zn complexes that are assumed to be the active state of the catalyst that amplifies chirality in this system. Using Zn K-edge XAFS we have now been able to obtain structural details of the complexes formed in THF and toluene. Most importantly, in toluene *i*-Pr₂Zn is a monomeric species with a Zn-C bond distance of 1.89 Å, while THF molecules interact with *i*-Pr₂Zn to form dimeric species with a Zn-C bond distance of 2.03 Å. Zn-Zn scattering in the EXAFS clearly indicates the presence of not more than a single Zn neighbour at a distance of 3.07 Å. Higher order aggregate complexes (trimers, tetramers, etc) do not appear to form in significant concentrations.

P5.2: Magnetic dichroism (XMCD)

Location: “Allara e Grosso” Hall
Time: 15:30

Correlation of magnetic moments and local structure of FePt nanoparticles

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Over the last decade up to now, FePt nanoparticles have gained a lot of research activities driven both by fundamental interest and technological perspective. In this talk, the focus is on the correlation of magnetic properties like the element-specific magnetic moments at the Fe and Pt sites and the effective anisotropy on the local structure of oxide-free FePt nanoparticles. In the as-prepared state, the wet-chemically synthesised particles are in the chemically disordered state. An in-situ hydrogen plasma cleaning procedure ensures that we measure the x-ray absorption of pure metallic FePt nanoparticles. By analysis of the extended x-ray magnetic fine structure (EXAFS) we found not only a lattice expansion in the particles compared to bulk material but also a clear deviation of the local composition around the probe atoms from the averaged value indicating that Fe is in an Fe-rich environment and Pt is in a Pt-rich environment.

To study the effect of this inhomogeneity on the magnetic properties, the composition dependence of magnetic moments in Fe-Pt alloys was investigated experimentally by analysis of the x-ray magnetic circular dichroism (XMCD) and band-structure calculations. Especially the magnetic moments at the Fe sites are found to be a sensitive monitor for changes in the local composition. In the case of the FePt nanoparticles we found significantly reduced magnetic moments at the Fe sites with respect to the corresponding bulk material whereas the magnetic moments at the Pt sites remain largely unaffected by changes of the local composition.

This work was done in collaboration with A. Trunova, M. Spasova, K. Fauth, F. Wilhelm, A. Rogalev, U. Wiedwald, H.-G. Boyen, M. Farle, and H. Wende. For technical assistance we thank P. Voisin and S. Feite and the BESSYII staff, especially T. Kachel and H. Pfau.

Financially supported by the DFG (SFB445), the ESRF and the BMBF (05 ES3XBA/5).

Location: “Allara e Grosso” Hall
Time: 15:50

The accuracy of the XMCD effective spin sum rule

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In the work presented here, the accuracy of the spin sum rule in describing $\langle S_{eff} \rangle$ is extensively studied for Fe^{2+} ($3d^6$), Co^{2+} ($3d^7$), Ni^{2+} ($3d^8$) and Cu^{2+} ($3d^9$). In the case of a $3d^9$ ground state the effective spin sum rule is exact but an error is introduced for all other cases. This error is proportional to the intra atomic interactions and inverse proportional to the 2p hole spin orbit coupling.

The charge transfer multiplet approach was used to obtain ground state values for $\langle S_{eff} \rangle = \langle S_z \rangle + 7/2 * \langle T_z \rangle$. The error is calculated by comparing the ground state value to the one obtained by applying the sum rule in calculated spectra.

The error in the sum rule was obtained as a function of ligand field splitting, charge transfer energy, 3d spin-orbit coupling and exchange energy. We found that the sum rule underestimates $\langle S_{eff} \rangle$ by 20% to 10%. This error has a strong dependence on the 3d spin-orbit, being largest when the spin orbit parameter is zero. Another interesting result is that it is not the intra-atomic exchange (the G1 Slater integral), but instead the intra-atomic dipole-dipole interaction (F2 Slater integral) that causes 90% of the theoretical error [1]. Applying a 3d spin-orbit coupling reduces the error in the effective spin, but at the same time introduces a finite value of T_z , yielding differences between the effective spin sum rule and the spin moment. On the other hand, the error stays approximately constant with the variation of the crystal field splitting or charge transfer energy. These results (re)confirm that without additional spectral simulation, the application of the effective spin sum rule can yield an effective spin that is 20% too small and a spin moment that is off by 50%.

[1] C. Piamonteze, P. Miedema, F.M.F. de Groot, submitted.

Location: “Allara e Grosso” Hall
Time: 16:10

Influence of the magnetic dipole T_z term on the XMCD spectra of clusters

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Spin and orbital sum rules formed the basis for analyzing XMCD spectra of magnetic systems during the last decade. For a long time it has been known that the magnetic dipole term T_z can influence the values of spin magnetic moments m_{spin} as deduced from these sum rules - especially for surfaces and overlayers. It has been tacitly assumed, nevertheless, that neglecting the T_z term will result in a mere shift of the deduced values of m_{spin} , with no dramatic effect on the trends observed, e.g., as a function of the system size. We demonstrate via ab-initio calculations that the T_z term can in fact completely reverse the way the apparent spin magnetic moment of supported clusters (as deduced from the XMCD sum rules) depends on the cluster size. The role of the clusters and of the substrate material is analyzed by comparing XMCD spectra and magnetic moments of Fe and Co clusters of 1-9 atoms supported on Ni(001) and Au(111) surfaces. Complete Fe and Co monolayers on Ni(001) and Au(111) surfaces are investigated as “end points of the sequence” as well.

Location: “Allara e Grosso” Hall
Time: 16:30

XMCD spectroscopy on valence fluctuating and heavy fermion compounds in very high magnetic fields up to 40 T

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Recently, measurement techniques for high-magnetic-field synchrotron x-ray experiments have been significantly developed. Very high magnetic fields over 30 T can be utilized not only for basic experiments such as Bragg diffraction [1,2] and x-ray absorption measurements [3], but also for more advanced experiments such as resonant magnetic diffraction [4] and x-ray magnetic circular dichroism (XMCD) [5,6].

In this work, we performed XMCD experiments of valence fluctuating compounds, $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$, YbInCu_4 , and a heavy fermion compound CeRh_2Si_2 in high fields up to 40 T. These materials show novel field-induced phase transitions with metamagnetism at low temperatures. In all the samples, we observed clear XMCD at the L-edge of rare-earth elements. In the Eu case, we observed distinct two XMCD peaks corresponding to the different valence states, i.e. Eu^{2+} and Eu^{3+} . By contrast, only one clear XMCD peak attributed to the trivalent state was observed in YbInCu_4 and CeRh_2Si_2 . In addition to the valence selectivity, we will discuss the magnetic field dependence of the XMCD spectra and the branching ratio between L_2 and L_3 edges. Comparison between the experimental results and theoretical predictions [8] will also be presented.

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Self-assembled Co nanorods grown on Cu(110)-(2×3)N studied by XMCD

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Magnetism of low-dimensional materials is one of the most attractive current issues because of technological requirements as well as a fundamental interest. We have investigated magnetic properties of Co/Cu(110)-(2×3)N [1] by means of high magnetic field X-ray magnetic circular dichroism (XMCD) [2]. The XMCD measurement system was equipped with 7T split superconducting magnet and a liq. He cryostat, and was installed at UVSOR-II in Institute for Molecular Science. The angular dependent magnetization curves of 0.8 ML Co nanorods on Cu(110)-(2×3)N at 4.9 K were recorded with the electron yield at the L_3 peak top energy. The magnetizations are found to be almost saturated at 5 T for all the axes. The two magnetic anisotropy constants K_P (planar origin) and K_A (rod origin) were determined as $K_P=1.2\times 10^{-4}$ (eV/atom), and $K_A=2.0\times 10^{-5}$ (eV/atom). The planar magnetic anisotropy that makes the surface normal the hardest axis is found to be much larger than that of the rod axial anisotropy. The angle dependence of the XMCD spectra was analyzed using the XMCD sum rules. The results are $m_{orb}^{[001]}=0.23 \mu_B$, $m_{orb}^{[1-10]}=0.19 \mu_B$, $m_{orb}^{[110]}=0.16 \mu_B$, and $m_{spin}=1.01 \mu_B$. The orbital magnetic moment decreases in the sequence of [001], [1-10] and [110], which is consistent with the above magnetic anisotropy constants. This consequently implies that the magnetic anisotropy originates from the difference in the spin-orbit interaction. It is also noted that the spin magnetic moment obtained is significantly smaller than that of the bulk hcp Co due to the formation of strong covalent Co-N bonds.

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Location: “Allara e Grosso” Hall
Time: 17:10

X-ray magnetic circular dichroism at Os L -edge under multiple extreme conditions in $\text{SmOs}_4\text{Sb}_{12}$

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A filled skutterudite $\text{SmOs}_4\text{Sb}_{12}$ exhibits novel features as a heavy fermion system. This material shows a weak ferromagnetic ordering (FO) below 3 K at ambient pressure (A.P.) [1]. Pressure-Temperature (P - T) phase diagram has been investigated by electric resistivity measurements, suggesting that the FO is stabilized by applied pressure [2]. On the other hand, moderate delocalization of the $5d$ -electrons hybridized with the $4f$ -electrons has been proposed by a recent band calculation in a series of $\text{ROs}_4\text{Sb}_{12}$ compounds [3]. Since no information of Os $5d$ electronic states is reported from a microscopic viewpoint, we have investigated the role of Os $5d$ -electrons in the physical properties of $\text{SmOs}_4\text{Sb}_{12}$ by using X-ray magnetic circular dichroism (XMCD) at Os L -edge under multiple extreme conditions at BL39XU of SPring-8.

The XMCD spectrum with the intensity of 0.1% was observed at 2.2 K, 10 T and A.P. The observation of the XMCD signal indicates the presence of hybridization between Sm $4f$ and Os $5d$ electronic states. The positive sign in the spectrum shows that the induced Os $5d$ magnetic moments are antiferromagnetically coupled with Sm magnetic moments. In addition, the enhancement of XMCD signal is observed at high pressure. This result is consistent with the enhancement of magnetic moment expected from the P - T diagram [2]. The intensity reaches a maximum near 0.6 GPa, and decreases with increasing pressure. This behavior well corresponds to the previous result [4]. Consequently, the behavior of Os $5d$ electronic states strongly connects with novel features observed in $\text{SmOs}_4\text{Sb}_{12}$.

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P5.3: Environmental studies

Location: “Aranjo Ruiz” Hall
Time: 15:30

EXAFS studies of catalytic DNA sensors for mercury contamination of water

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Monitoring of metallic contaminants in domestic and agricultural water systems requires technology that is fast, flexible, sensitive, and selective. Recently, metal sensors based on catalytic DNA have been demonstrated as a practical monitoring solution. Very little is known, however, about the atomic scale interactions between the DNA-based sensors and the metal contaminant to which the sensor is targeted. Here we present the results of an X-ray absorption spectroscopy study of a mercury sensor which illuminates the nature of the Hg – DNA interaction. This analysis was performed using a new package of high-level programming tools called DEMETER which is based upon the FEFF and IFEFFIT programs. This new software will form the basis of the next generation of graphical and web-based data analysis software by the lead author.

Location: "Aranjo Ruiz" Hall
Time: 15:50

Experimental evidence of six-fold oxygen coordination for phosphorus

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Phosphorus, a group V element, has always been found so far in minerals, biological systems and synthetic compounds with an oxygen coordination number of four (i.e., PO₄ groups). For the first time, we demonstrate using phosphorus K-edge XANES spectroscopy that this element can also adopt a six-fold oxygen coordination (i.e., PO₆ groups). This new coordination was achieved in AlPO₄-doped SiO₂ stishovite synthesized at 18 GPa and 1873 K and quenched down to ambient conditions. The well-crystallised P-bearing stishovite grains (up to 100 μm diameter) were embedded in the back-transformation products of high pressure form of AlPO₄ matrix. They were identified by elemental mapping (μ-XRF) on the microfocused LUCIA beamline at that time installed at the Swiss Light Source. μ-XANES spectra were then collected at the Al, Si and P K edges at different points of interest located on the elemental maps. In the Al and P rich region the Al and P XANES spectra are characteristic of Al PO₄. In the Si rich region with a very low concentration of P, the P XANES and Si XANES spectra present striking resemblance, Si itself being characteristic of pure stishovite (energy shift compared to Si 4-fold O coordinated and fine structures). We can therefore infer that phosphorus in the corresponding stishovite crystal is involved in an octahedral coordination made of six oxygen atoms.

This change of phosphorus coordination at high pressure within a dense silicate structure is particularly relevant to phosphorus mineralogy in the deep Earth. With a mantle abundance below 0.25 wt.%, phosphorus has been shown to be mainly hosted by silicates (e.g., olivine) in the Earth's upper-mantle, in the four-fold coordinated silicon sites. In the lower-mantle where all silicon is six-fold coordinated, we show here that phosphorus has the crystal-chemical ability to remain incorporated into silicate structures.

Location: "Aranjo Ruiz" Hall
Time: 16:10

A combined XANES and SR-XRF study of the airborne dust preserved in Antarctic deep ice cores across a climate transition.

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Continental glaciers and polar ice sheet are undisturbed archives of paleo-climatic information, because during snow formation and precipitation elements and particles are collected from the atmosphere and trapped in ice in a chronologically ordered way. In particular sites, as in Antarctica, this unperturbed information is preserved for extremely long periods. We investigated a set of ice core samples from TALDICE, the TALos Dome Ice CorE research project, aimed at retrieving an ice core reaching back to the previous two interglacial periods (down to 250.000 years) in order to understand and finally to reconstruct the climatic variations occurred during the middle to late Pleistocene. Aerosol mineral particles extracted from melted ice sections and filtered under controlled conditions were analyzed in a series of combined XRF and XAS experiments at the wiggler beamlines 10-2 and 6-2 at SSRL, using a dedicated HV experimental chamber set up for normal-incidence and total-reflection XRF and XAS experiments. XRF and TXRF data show the presence of continuous variations in the elemental concentrations when crossing a glacial transition, i.e. between samples belonging to Holocene (a warm climatic period) and samples from the Marine Isotopic Stage 3 (MIS 3), cold climatic period. From the XANES analysis of mineral particles, showing iron in octahedral coordination state in minerals most probably belonging to the phyllosilicate family, results a very clear shift of the Fe absorption edge towards low energies from MIS 3 to Holocene, in agreement with hypothesized changes of the dust source and/or the atmospheric circulation in different climatic periods. By combining XRF and XANES results we attempt to recognize different contributions from potential dust Source Areas (PSAs) of the Southern Hemisphere. Results show that with this experimental protocol we may resolve the iron-containing mineral fraction on insoluble dust in ice in the ppm to ppb range.

Location: “Aranjo Ruiz” Hall
Time: 16:30

Speciation of zinc in ash from combustion of biomass and municipal solid waste

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Zinc is one of the metals of concern when environmental impact and toxicity of combustion residues and other wastes are discussed. In our work we have utilized XAFS spectroscopy in order to determine speciation of Zinc in ashes from combustion of biomass and municipal solid waste. Ash samples from combustion of biomass were collected during normal operation of the boilers and during addition of kaolin and elemental sulphur, respectively. These additives are of interest, as it has been shown that they have effect on the corrosion processes, flue gas chemistry and ash quality. Ash samples collected from combustion of municipal solid waste were obtained with and without injection of limestone into the flue gas. The addition of limestone is used to neutralise and bind acid gases, such as HCl and SO₂. In order to determine the distribution of Zinc species in these ash samples by means of XAFS spectroscopy we have combined multishell fitting with principal component analysis (PCA), target transform (TT), and linear combination fitting (LCF).

Location: “Aranjo Ruiz” Hall
Time: 16:50

Tektites and microtektites Fe oxidation state

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Asteroid or cometary impacts onto the Earth surface are known to have played an important role in modifying the composition of the earth crust. Impact glasses, resulting from the rapid cooling of the molten target rock, are clues of the complex melting and metamorphic processes taking place during an impact. Tektites and micro-tektites are a sub class of impact glasses formed during the very first stages of the cratering process by high temperature melting of the target rock. They usually display rounded shapes and can be found over wide areas called strewn fields.

As Fe oxidation state could be a useful probe to obtain information on the formation conditions of tektites, it has been the focus of many studies. However, the difficulties in analysing samples with small dimensions and high Fe dilution have so far hindered the possibility to systematically study the Fe oxidation state in these glasses. To this aim, XAS is an ideal technique as it allows to determine Fe oxidation state also in small samples even at very high dilution without deteriorating the error in the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio.

Fe K-edge XAS spectra have been collected at ID26 beamline of ESRF. Analysis of the pre-edge peak data allowed to accurately determine Fe oxidation state in the samples studied. Tektite glasses display $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios close to 0.05 (± 0.03). No significant variations have been found according to impact age, target rock composition [1]. Even for very large impacts events, tektites have been homogeneously reduced from a presumably a wide range of Fe oxidation state in the target rock down to almost exclusively divalent [2]. Similar behaviour has been observed in molten rock from the first atomic bomb test (Alamogordo, USA) [3]. Contrary to tektites, microtektites from the large Cheasapeake impact show a wide variation in the Fe oxidation state raising the issue of a possible difference in the formation mechanism with tektites [4].

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Location: “Aranjo Ruiz” Hall
Time: 17:10

The use of x-ray absorption spectroscopy in hydrothermal geochemistry: transport and speciation of dissolved metals.

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The accuracy in geochemical modelling of the transport of metals by surface and hydrothermal fluids highly depends on the availability of thermodynamic and speciation data for all the phases involved (gas, brines, minerals, ...). In the hydrothermal fluids involved in the formation of most ore deposits, or in the sequestration of greenhouse carbon dioxide, chloride Cl⁻ is the predominant ligand. The aqueous chloride complexes formed with dissolved metals ions modify strongly the solubility of the corresponding minerals and thus play a crucial role. Despite this, the nature and thermodynamic properties of most chloride complexes in hypersaline brines at elevated temperatures and pressures are poorly understood, especially in (near-) supercritical conditions.

In the present study[1], we consider the case of ferrous iron chloride complexes. We used synchrotron X-ray absorption measurements to determine the speciation of ferrous iron in hydrothermal saline brines (30-500°C, 500 bar, [Cl⁻] 0-12 m). EXAFS analysis and ab initio XANES calculations (FDMNES code) are used to characterise the structure of the iron chloride complexes that are progressively formed by increasing chloride concentration and/or temperature. In particular, the stability at high temperature and chlorinity conditions of the distorted tetrahedral $FeCl_4$ complex is shown.

The application of XAS to the study of minerals-fluids interactions in hydrothermal conditions will be demonstrated with the example of siderite $FeCO_3$ dissolution[2].

[1] D. Testemale, J. Brugger, W. Liu, B. Etschmann, and J.-L. Hazemann, Chem. Geol., accepted (2009).

[2] D. Testemale, F. Dufaud, I. Martinez, P. Bénéth, J.-L. Hazemann, J. Schott, and F. Guyot, Chem. Geol. 259, 8 (2009).

P5.4: Gas phase systems

Location: “Betti” Hall
Time: 15:30

X-ray spectroscopy in a linear ion trap: size-selected transition metal, doped silicon, and protonated water clusters

Tobias Lau¹, Konstantin Hirsch¹, Philipp Klar¹, Andreas Langenberg¹, Fabian Lofink¹, Jürgen Probst¹, Robert Richter¹, Jochen Rittmann¹, Marlene Vogel¹, Vicente Zamudio-Bayer¹, Thomas Möller¹, and Bernd von Issendorff²

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While rare gas clusters in molecular beams have been investigated intensively by X-ray spectroscopy, similar studies on size-selected metal or semiconductor clusters were out of reach up to now because of the very low target density that could be obtained with conventional cluster beam experiments. To overcome this limitation, a linear ion trap for X-ray spectroscopy on size-selected cluster ions has recently been set up in our laboratory. We will discuss experimental details and present a selection of recent results obtained at BESSY II on the anomalous $L_{2,3}$ branching ratio in transition metal clusters, on 3d valence electron localization in chromium and manganese clusters, on the electronic and geometric structure of doped silicon clusters, on the oxygen 1s absorption spectrum of protonated water clusters, and on adsorbate molecules attached to size-selected clusters. In all these examples, local and element specific X-ray spectroscopy provides the key for understanding the electronic and geometric properties of the investigated species. Furthermore, size-selected clusters also provide insight into the X-ray absorption process itself, showing that the anomalous $L_{2,3}$ branching ratio in 3d transition metals is rather dependent on core-hole screening than on 2p spin-orbit splitting [1].

An outlook will be given on the prospects of direct core level photoionization spectroscopy which gives access to the core level binding energies as will be discussed for size-selected silicon and aluminum clusters.

[1] J. T. Lau, J. Rittmann, V. Zamudio-Bayer, M. Vogel, K. Hirsch, Ph. Klar, F. Lofink, T. Möller, and B. von Issendorff, Phys. Rev. Lett. **101**, 153401 (2008).

Location: “Betti” Hall
Time: 15:50

Structure and hydrogen uptake of free titanium clusters in a supersonic beam probed by combined XAS and multicoincidence technique.

Tommaso Mazza¹, Paolo Piseri¹, Luca Ravagnan¹, Michele Devetta¹, Gero Bongiorno¹, Matteo Amati^{1,2}, Marcello Coreno³, Cristina Lenardi^{1,4}, Monica de Simone⁵, and Paolo Milani¹

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Understanding the role of transition metal clusters in complex nanophase systems is a key issue in the perspective of developing and optimizing functionality of nanostructured materials with technological relevance. XAS, due to its intrinsic local character, is a technique of choice for probing the chemical and geometrical environment of atoms of selected elements in nanostructures; XAS in free clusters, combined with multi-coincidence techniques, can answer relevant questions about the structure of nano-scale objects.

We present a XAS investigation of complex free clusters, reporting the results for titanium-hydrogen system as a case study. Clusters are produced by a Pulsed Microplasma Cluster Source, which yields a very intense and stable supersonic cluster beam from inert gas condensation of vaporized metal; the free clusters can be exposed to H₂ in a pick-up cell. Analysis of the Ti2p XAFS features, prior and after cluster exposure to H₂, yield a quantitative evaluation of hydride formation; contextual measurement of ion-ion coincidence spectra after cluster photo-fragmentation with 1D momentum resolution for the fragment ions enabled us to probe the structural arrangement of the clusters, clearly determining their fractal character and its evolution with cluster growth conditions or under H₂ exposure; for this purpose a model for the fragmentation process of core-level excited complex clusters has been developed establishing a relationship between cluster fractal dimension and time- and space- correlation patterns of fragment ions.

This study aims at moving first steps towards an evolution of core level absorption techniques from application to simple systems such as molecules and small clusters to systems with a higher degree of complexity (nanophase aggregates, cluster-molecule assemblies); the use of a setup providing extensive information contextually acquired within a single experiment is identified as a preferential approach towards these systems.

UV-visible emission as a probe of core excitations applied to small molecules

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Core hole states predominantly decay via the emission of an electron or a soft x-ray photon, hence UV-visible fluorescence spectroscopy does not appear particularly suitable for studies of core electron processes. The final states of the decay are, however, usually excited, and they may directly emit low-energy photons or they may dissociate into excited fragments that fluoresce. Indeed, total (undispersed) fluorescence yields of small molecules reveal the same features below the core ionization potential (IP) as the corresponding photoabsorption spectra. Dispersed measurements of Balmer emission from hydrogen-containing molecules such as water [1] show that fluorescence is particularly sensitive to core-to-Rydberg excitations. Above the core IP, fluorescence can be used to detect double excitations [2]. Using synchrotron radiation as the excitation source, we have carried out dispersed and undispersed fluorescence studies in the core level regions of molecules that do not contain hydrogen atoms such as N₂, CO₂, O₂ and SF₆. The partial UV fluorescence yield of N₂ measured at the N 1s → π^* excitation interestingly shows narrower line shapes than the total ion yield (TIY) measured simultaneously. In CO₂, the total fluorescence yield (TFY) measured above the O 1s IP considerably differs from the TIY; in particular, the shape resonances appear reduced in TFY. These observations can be explained but it requires a detailed understanding of the molecules studied.

[1] E. Melero García et al, Phys. Rev. Lett. 96, 063003 (2006).

[2] A. Kivimäki et al, Phys. Rev. A 75, 014503 (2007).

Location: “Betti” Hall
Time: 16:30

NEXAFS characterization of sp-rich carbon clusters in the gas phase

L. Ravagnan¹ (P. Piseri presenting author), T. Mazza¹, G. Bongiorno¹, M. Devetta¹, C. Lenardi², M. Amati³, P. Rudolf⁴, M. Coreno⁵, and P. Milani¹

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Sp-coordinated linear carbon chains are of enormous interest for nanotechnological applications, however due to their alleged instability, they have not been considered as possible building blocks of carbon nanosystems. We recently demonstrated that large carbon clusters where sp and sp² hybridization coexist can be formed in the gas phase and deposited on a substrate [1,2]. We characterized in situ by Raman and NEXAFS spectroscopy the films obtained by deposition of the carbon clusters demonstrating that sp chains survive upon deposition and influence substantially the structural and functional properties of the cluster-assembled film [1-3]. Here we present the NEXAFS characterization on the sp-sp² carbon cluster in the gas phase, prior to deposition. Total electron yield spectra show the presence of the ethylenic pi* resonance at 284.7 eV typical of sp² carbon and of the acetylenic pi* resonance at 285.9 eV, which is the fingerprint of sp chains [3]. We have followed the evolution of these features prior and after cluster deposition and we have characterized their dependence from cluster formation conditions. We also present our recent results on the study of multi-electron-multi-ion correlation patterns, providing a deeper insight in the complex interaction between free clusters and VUV photons. In particular, the analysis of electron-electron detection signal coincidences provides access to selected relaxation channels (thermal electron emission and fragmentation) which have been studied as a function of incident photon energy and cluster formation conditions. The possibility of using NEXAFS on free clusters and to study their post ionization relaxation processes, opens new possibilities for the understanding of the structure and the mechanism of formation of carbon nanostructures, in particular of sp nanowires.

[1] L. Ravagnan et al., PRL 98, 216103 (2007)

[2] L. Ravagnan et al., PRL 89, 285506 (2002)

[3] L. Ravagnan et al., Carbon 44, 1518 (2006)

Location: “Betti” Hall
Time: 16:50

Interaction mechanism of gas-SWNTs probed by XANES

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X-ray absorption near-edge structure (XANES) spectroscopy has been applied to investigate the interaction of gas molecules (H₂, He, and N₂) with single-walled carbon nanotubes (SWNTs) under ultrahigh vacuum (UHV) and ambient pressures of up to 450 Torr. Upon increasing pressures, the C K-edge XANES spectra of SWNTs show the splitting of feature π^* and a broadened σ^* feature, which indicate a molecular scattering mechanism resulting the wall deformation of SWNTs. XANES experiments performed under UHV and ambient pressure show that the interaction between gas molecules and SWNTs is reversible. First principle calculations of molecular scattering have revealed the collision induced deformation of SWNTs. The charge transfer between gas molecules and SWNTs has minor effect to the XANES spectra. The results suggest that molecular collision is a significant phenomenon when the interaction between gas and SWNTs needs to be considered for different applications such as gas sensors.

Location: "Betti" Hall
Time: 17:10

Atomic absorption background: K edge of iodine and L edges of cesium

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Atomic absorption background (AAB) can be directly determined only on a monatomic sample of an element: noble gases and volatile metals with monatomic vapors (Rb, Zn, Hg, K, Cd) have been studied so far. AAB comprises the intra-atomic effects in photoabsorption in the sharp detail which may be lost in approximate forms extracted from spectra of dense samples by elimination of XAFS signal.

Recently, AAB has been determined for K-edge absorption in iodine [1] (ESRF project HD-156 at BM29) and L-edge absorption in cesium (HASYLAB project II-20042065 EC at station C). In the first case, a mixture of atomic and molecular species was prepared by thermal dissociation of iodine vapor at 1000°C, and AAB was extracted by combining the absorption data at different densities of the vapor. The result shows that the specific shape of the AAB is determined by strong groups of valence and subvalence excitations, identified by deconvolution [2] or a comprehensive modeling of excitation channels.

In the second case, experimentally demanding due to the low photon energy, and the high reactivity of the hot Cs vapor, the question of the basic shape of the AAB in the region between the L edges is clarified. The unusual convex shape used to be explained by a "dipole" interaction of the photoelectron with the ion. We show that the shake-off channels of 2p5p and 2p5s multielectron excitations are enhanced to produce the overall convexity of the absorption profile between the edges.

In analysis of disordered samples with weak structural signal, as well as in lanthanide elements exhibiting an extremely strong 2p4d excitations in the middle of EXAFS region, the use of the routine spline approximation of AAB may not be adequate. The improvement provided by the application of the proper AAB will be presented.

[1] J. Padežnik Gomilšek, I. Arčon, S. de Panfilis, and A. Kodre, Phys. Rev A 79, 032514 (2009)

[2] A. Filipponi J. Phys. B 33, 2835 (2000)

P6.1: Catalysis II

Location: "La Muta" Hall
Time: 18:00

In situ observation of redox reactions of Pd/Sr-Fe-O for exhaust emission catalyst

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Catalytic converters involving a three-way catalyst (TWC) have been widely used to simultaneously reduce pollutant gases in automotive exhaust emissions. TWCs are usually composed of precious metals such as platinum (Pt), rhodium (Rh), and palladium (Pd) loaded on γ -Al₂O₃ as an oxide support [1]. In spite of efforts to preserve resources of precious metals, huge amounts of precious metals produced each year are consumed just for the purification of exhaust emissions (ca. 30% of Pt, 90% of Rh, and 60% of Pd).

Here we show that the amount of precious metals can be cut down by 70% using a new Pt-free catalyst, where Pd is loaded on triple phases of a Sr-Fe-O system with a unique "multi-phase-domain" (MPD) structure where a single grain is composed of nano-sized domains. We investigated reduction and oxidation (RedOx) reactions of Pd using a reaction cell system for *in situ* XAFS measurements including the dispersive XAFS [2,3]. Experiments were carried out at Photon Factory, KEK, Japan. *In situ* XAFS measurements have successfully shown the kinetics that Pd atoms in the MPD-structured oxides change their states reversibly between metal and oxide in response to the gas atmosphere during several RedOx cycles. Measurements with a time-resolution of 0.1 s were utilized to investigate early-stage kinetics when switching RedOx reactions. It was revealed that RedOx reactions of Pd are accompanied by change of oxygen deficiency in the oxide. High performance of the new catalyst can be attributed to that RedOx reactions of Pd are promoted by oxygen diffusion in the MPD-structured oxides.

References

[1] R. M. Heck and R. J. Farrauto, Catalytic Air Pollution Control: Commercial Technology (Van Nostrand Reinhold, New York, 1995).

[2] T. Matsushita and R. P. Phizackerley, Jpn. J. App. Phys. 20, 2223 (1981).

[3] Y. Inada, A. Suzuki, Y. Niwa, and M. Nomura, AIP Conf. Proc. 879, 1230 (2006).

Location: “La Muta” Hall
Time: 18:20

Development of X-ray emission spectroscopy in single site catalysis

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The local electronic configuration of the metal ion is reflected in the pre-edge region of the spectrum, arising from resonant excitations into the lowest unoccupied orbitals. Detailed XANES studies on transition metal complexes have demonstrated the sensitivity of X-ray absorption K edges and their (pre)edge features to the chemical environment, e.g. oxidation state, site symmetry, crystal field splitting. XANES is however still not fully understood and mainly used as a fingerprint for oxidation states or geometries. Here, developments in resonant inelastic X-ray scattering (RIXS) spectroscopy are pursued.

In RIXS spectroscopy, the emitted energy is measured as function of incident energy, thus yielding 2-dimensional (2D) X-ray information. The 2D picture is crucial to identify the correlation between incident and emitted energies, and gives information on the electronic density of states of the system. The advantage of RIXS over L- and M-edge XAS is that both incident and emitted energies are relatively high in energy, thus allowing in situ measurements on working catalysts.

Systematic RIXS studies using structurally known compounds, in combination with theory and complementary techniques, have been performed obtaining fundamental insights in the RIXS data obtained. The technique was explored from the previously studied 3d to the unexplored 4d and 5d transition metals. Full RIXS planes have been acquired as a function of crystal orientation angle to determine the orientation of the molecular orbitals (MOs) and assign the different features. Important insights in charge transfer within the systems have been obtained.

Currently the electronic properties of single site homogeneous catalysts are studied in detail. Information on the orientation of MOs, the charge transfer and their accessibility for reactants is obtained, providing insights in the properties required for (enantio)selective catalysis.

Location: “La Muta” Hall
Time: 18:40

Distinguishing interstitial and surface hydrogen in and on nano-sized palladium catalysts using Pd K and L₃ edges X-ray absorption spectroscopy

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Bulk-dissolved hydrogen (hydrides) are more energetic than surface hydrogen and can thus hydrogenate surface adsorbates upon emerging to the surface [1]. They, therefore, strongly affect the activity and selectivity in the hydrogenation of unsaturated hydrocarbons [2]. Understanding the detailed geometric and electronic structures of palladium hydrides and the effect of palladium particle size onto their formation is critically important. By using in situ Pd K and L₃ edge X-ray absorption spectroscopy, the structure and formation of palladium hydrides and surface hydrogen adsorption was studied as a function of particle size [3]. Hydride formation was observed by lattice expansion in Pd K-edge XANES spectra and by EXAFS analysis. In Pd L₃ edge XANES the hydrides was characterised by extra spectral features caused by the new Pd-H antibonding state. The L₃ edge spectra were reproduced using full multiple scattering analysis and density of state (DOS) calculations. We were able to distinguish hydrogen adsorbed on the surface and absorbed in the bulk, which is vital to understand their roles in catalytic reactions.

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[2] Morkel, M.; Rupprechter, M.; Freund, H.-J. *Surf. Sci.*, 2005, 588, L209-219.

[3] Tew M. W.; Miller, J. A.; van Bokhoven, J. A. to be submitted.

Location: "La Muta" Hall
Time: 19:00

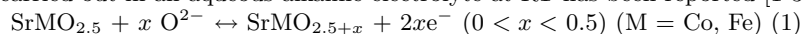
In situ electrochemical oxygen intercalation inside SrFeO_{2.5} investigated by time resolved EXAFS and XANES: a comparison with the SrCoO_{2.5} system

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Oxygen ion conductors at low temperatures are materials of major interest for a series of applications (fuel cells, battery electrodes, sensors, etc.). Solid oxygen ion conductors work, however, only at fairly high temperatures, which makes their application, specially for fuel cells, limited. The reversible intercalation of oxygen into brownmillerite type defect perovskite SrMO_{2.5} (M = Co, Fe), carried out in an aqueous alkaline electrolyte at RT has been reported [1-3]:



We followed reaction (1) by XAFS during in situ electrochemical reaction using an ad hoc conceived cell optimized to minimize the thickness of the solution, which is highly absorbing at the Co (Fe) K-edge. Spectra have been collected in transmission mode at ESRF BM29. A single XAFS scan required 40 min. For the SrCoO_{2.5} system, the electrochemical current was set to perform the complete $\Delta x = 0.5$ oxidation in 2500 min, resulting in 60 successive spectra. The stoichiometry variation per spectrum was of $\Delta x = 0.008$: a sufficiently low value to consider the sample almost unchanged between the first and the last sampled points of a single spectrum. Similar conditions have been adopted for the SrFeO_{2.5} case. A complete evolution of the Co (Fe) local environment and of the oxidation state of the transition element as a function of the charge transfer x has been obtained from this study. Analogies and differences between the two systems are discussed.

[1] A. Nemudry, P. Weiss, I. Gainutdinov, V. Boldyrev, and R. Schöllhorn, Chem. Mater., 10, 2403 (1998).

[2] R. Le Toquin, W. Paulus, A. Cousson, C. Prestipino, and C. Lamberti, J. Am. Chem. Soc., 128, 13161 (2006).

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Location: "La Muta" Hall
Time: 19:15

In situ XAS probes partially oxidized platinum generating high activity for CO oxidation

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In situ x-ray absorption spectroscopy identified the role of partially oxidized platinum in generating high activity during carbon monoxide oxidation over Pt/Al₂O₃, Pt/TiO₂ and Pt/SiO₂. Two activity regimes were identified: low-activity at high CO concentration and low temperature, and high activity at low CO concentration and high temperature. CO covers and poisons metallic platinum in the low activity regime. Ignition corresponded to the abrupt increase in CO conversion, switching from low activity to high activity, and was accompanied by oxidation as observed in the increased intensity of the XANES. EXAFS analysis indicated breaking of Pt-Pt bonds and the appearance of a Pt-O scatterer. An additional Pt-Pt scatterer at high activity had a bond length shorter than the Pt-O-Pt length of an oxide, similar to that of metallic Pt-Pt, indicating that the catalyst particles were composed of a metallic platinum core and a surface oxide. The partially oxidized catalyst had a lower oxygen coordination number and shorter Pt-O bond length than bulk PtO₂, suggesting that a strongly defected platinum oxide was formed with a possibly square planar coordination. The catalyst structure showed a dynamic behavior and the amount of oxide depended on the concentration of reactants in the gas phase. By complementary information from in-situ infrared spectroscopy, ignition was accompanied by the abrupt disappearance of adsorbed linear and bridged CO species, which are less likely to stick to an oxidic surface. All the reverse changes happen with the sudden decrease in CO conversion during extinction: partially oxidized catalyst becomes reduced and covered with CO. Smaller particles of Pt/Al₂O₃ reached high activity at lower temperature than the larger particles. Pt/TiO₂ reached high activity at the lowest temperature and was the least oxidized while Pt/SiO₂ required the highest temperature and was the most oxidized.

Location: “La Muta” Hall
Time: 19:30

Dynamic structural change of Pd/LaFeO₃ nanoparticles under redox atmosphere and CO-NO catalytic reaction studied by dispersive XAFS

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Pd/LaFeO₃ is known to keep the metal particle size small even after the long time redox processes because Pd atoms make complex oxides with LaFeO₃ perovskite-type crystal under the oxidative atmosphere. We observed the local structure of Pd atoms by dispersive XAFS optics from the viewpoint of dynamical structure change of Pd during metal-oxide change and CO-NO catalytic reaction.

Pd *K*-edge XAFS spectra were observed at BL14B1 of SPring-8 by dispersive mode. We attached the dispersive XAFS system to BL14B1 at 2006. Laue configuration with (422) reflection plane was adopted for bend crystal polychromator. The transmitted x rays were observed by CCD camera (640 × 480, 12 bits) with Gd₂O₂S(Tb) phosphor.

The local structural transformation of Pd nanoparticles on LaFeO₃ and Al₂O₃ during metal-oxide change was investigated at 200-500 °C by 20-50 Hz rate. It was recognized that, under the reductive atmosphere, Pd atoms show similar speed of movement from oxide to metal state both on LaFeO₃ and Al₂O₃. However, under the oxidative atmosphere, Pd atoms on LaFeO₃ show faster movement from metal to oxide state with single reaction step than those on Al₂O₃ with two-step oxidation. The faster oxidative reaction speed is the key of preventing sintering of Pd metal nanoparticles on LaFeO₃.

CO-NO reactions on Pd metal nanoparticles were also observed by 0.2-0.5 Hz rate. Slow observation mode made the four EXAFS parameters: coordination number, interatomic distance, Debye-Waller factor and edge shift, determined during catalytic reaction. There are two particular difference between Pd particles on LaFeO₃ and Al₂O₃. Large enhancement of interatomic distance of Pd particle was only observed on Al₂O₃. Saturated surface oxide layer of Pd particle is rapidly created on LaFeO₃.

Location: "La Muta" Hall
Time: 19:45

Combining EXAFS, TEM, and chemisorption in determining the particle size and dispersion of fcc-metal nanoparticles deposited on high surface area supports: a general model

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Supported noble metal catalysts, are among the most widely used catalysts for both fine and bulk chemicals. Their activity and selectivity toward different molecules is strongly related to the particle morphology and dispersion, that is determined experimentally mainly by EXAFS, TEM and chemisorption (CS).

Once the particle morphology is assumed, from the average metal-metal coordination number $\langle N \rangle$, EXAFS provides an estimation of the average particle size. Once the average CO/metal surface stoichiometry is assumed, CS results in the determination of the fraction of surface metal atoms D . Both techniques requires assumptions and result in an output that is a simple average value. TEM is more informative, as it provides both the particle morphology and the particle size distribution. However an incorrect particle size distribution may be obtained, as very small particles may escape detection, and the limited number of sampled particles may be not representative of the overall distribution. The combination of the 3 techniques is thus important to obtain cross checks.

From geometrical models [1], it is possible to define, as a function of the particle diameter d the evolution of both the D and $\langle N \rangle$. Such relationships have been often used in the past to correlate the average particle size $\langle d \rangle$ determined from TEM with EXAFS and CS results.

Using a set of Pd samples supported on high surface area carbons and oxides, it is shown that by considering not just the $\langle d \rangle$ value but the complete particle size distribution obtained from TEM, a much better agreement is obtained with both EXAFS and CS results. A Monte Carlo approach is then proposed to establish the degree of confidence of a TEM investigation, characterized by a n sampled particles resulting in a particle size distribution of mean value $\langle d \rangle$ and variance σ in determining EXAFS and CS results.

[1] J.M. Carrizales, et al., Nanostruct. Mater., 8, 269 (1997).

P6.2: Biology II

Location: "Allara e Grosso" Hall
Time: 18:00

Biomedical applications of X-ray absorption and vibrational spectroscopic microscopies in bioinorganic chemistry

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Hard X-ray microprobe techniques: synchrotron-induced X-ray emission (SRIXE) for elemental mapping at a sub-micron level; micro-XANES (X-ray absorption near-edge structure) for chemical information; and differential phase contrast (for mapping of morphology); are providing unprecedented information on biotransformations of drugs, toxins and carcinogens, as well as normal biological processes and disease conditions at the molecular and cellular levels. These techniques can be complemented by vibrational spectroscopic mapping/imaging and/or fluorescence images of the same cells, which provide information on changes in biochemical distribution, concentrations and secondary and tertiary structure of biomolecules in cells under disease conditions or during the treatment of diseases. When combined, these microprobe techniques can provide information that can lead to improved drug design to maximise efficacy and reduce side-effects, and to provide early warnings of potential hazards of certain treatments.

Biomedical applications of microprobe and bulk X-ray absorption techniques, and vibrational spectroscopy techniques will be discussed with respect to: the biotransformations and biodistributions of anti-diabetic Cr dietary supplements and the potential risks of taking such supplements; [1] and the biotransformations and biodistributions of anti-diabetic V drugs.

Acknowledgements: This research was supported by the Australian Research Council (ARC Discovery grants and ARC Professorial Fellowship), the Australian Synchrotron Research Program, the Australian Synchrotron, and DOE.

[1] A. Levina, P. A. Lay, Chem. Res. Toxicol. 21, 563-571 (2008).

Location: "Allara e Grosso" Hall
Time: 18:20

XAFS study of gold adsorption to *Bacillus subtilis* and *Pseudomonas putida* bacterial cells

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Bioaccumulation of gold by bacteria occurs in a range of natural environments. To understand the mechanism of Au precipitation in geological systems, it is important to investigate adsorption reactions of Au to bacteria. Although a number of laboratory studies have investigated interactions between Au and metabolizing bacteria, no systematic study of the sorption of Au to non-metabolizing bacteria has been undertaken.

Batch adsorption experiments show almost totally irreversible uptake of Au from Au (III)-chloride solution by non-metabolizing Gram-positive *Bacillus subtilis* and Gram-negative *Pseudomonas putida* non-metabolizing bacteria. For both species, the adsorption is greatest at low pH, and decreases at higher pH. In order to determine the binding mechanisms, XAFS experiments were conducted on Au - *B. subtilis* and Au - *P. putida* biomass samples with fixed Au (III) concentrations and varying bacteria concentrations and pH. All samples were quick-frozen with liquid nitrogen and kept frozen during XAFS measurements to minimize radiation damage from the beam.

Both XANES and EXAFS data on both bacterial species indicate that more than 80% of the Au (III) atoms on the bacterial cell wall were reduced to Au (I) atoms. In contrast to what has been observed for Au (III) interaction with metabolizing cells, no Au (0) or Au-Au nearest neighbors were observed in our experimental systems. For both species, the XAFS data suggest that although $[Au(Cl/OH)_4]^-$ complexes dominate the speciation of gold in solution, Au on the bacterial cell wall is characterized predominantly by binding of Au atoms to a mixture of amine/carboxyl and sulfhydryl functional groups, and the relative importance of the sulfhydryl groups increases with increasing pH values. The XAFS data for both species provide a framework for interpreting the bulk adsorption experiments, and enhance our ability to account for the behavior of gold in bacteria-bearing geologic systems.

Location: "Allara e Grosso" Hall
Time: 18:40

Geometric and electronic structures of Ni(I) and methyl-Ni(III) intermediates of methyl-CoM reductase.

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Methyl-coenzyme M reductase (MCR) from methanogenic archaea catalyzes the terminal step in biological methane synthesis and is responsible for all the biologically generated methane.[1] The active-site of MCR includes a non-covalently bound Ni tetrapyrrolic cofactor called coenzyme F₄₃₀, which is in the Ni(I) (MCR_{red1}) state in active MCR.(2) MCR uses the two cofactors CoBSH and Me-SCoM to generate methane and the heterodisulfide CoBS-SCoM. Two catalytic mechanisms have been proposed: mechanism I involving a nucleophilic attack of MCR_{red1} on Me-SCoM to form a Ni(III)-methyl (MCR_{Me}) intermediate(3) and mechanism II involving the attack of MCR_{red1} on the sulfur of Me-SCoM forming a CH₃[•] radical and a Ni(II)-thiolate species.(4) In this study, a combination of Ni K-edge XAS studies and DFT calculations have been performed on an inactive Ni(II) state of MCR (MCR_{red1-silent}) and the two catalytically relevant intermediate states MCR_{red1} and MCR_{Me}. High *k* EXAFS data are used to reveal a 5-coordinate active site in MCR_{red1}. A combination of experimental data and theoretical calculations demonstrate the presence of a long Ni-C bond (~ 2.04 Å) in MCR_{Me}. The data support mechanism I as the relevant catalytic mechanism. The role of the unique F₄₃₀ cofactor in the stability of the different Ni oxidation states is explored.

[1] Thauer, R. K. (1998) *Microbiology* 144, 2377–2406.

[2] Ellefson, W. L., Wolfe, R. S., and Whitman, W. B. (1982) *Prod.Natl. Acad. Sci. U. S. A.* 79, 3707–3710.

[3] Duin, E. C., Cosper, N. J., Mahlert, F., Thauer, R. K., and Scott, R. A. (2003) *J. Biol. Inorg. Chem.* 8, 141–148.

[4] Pelmeshnikov, V. and Siegbahn, P. E. (2003) *J. Biol. Inorg. Chem.* 8, 653–662.

Location: “Allara e Grosso” Hall
Time: 19:00

Local atomic and electronic structure of novel experimental anticancer drugs

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The novel organogold(III) complex $[\text{Au}(\text{bipy})(\text{OH})_2][\text{PF}_6]$ is presently being evaluated as a potential antitumor agent [1]. Based on experimental evidence collected so far it is hypothesized that this compound produces its cytotoxic effects through a molecular mechanism that is profoundly different from that of classical platinum(II) drugs. However, the precise biochemical mode of action of cytotoxic gold compounds is yet unclear. The nature of the reactions of gold(III) compounds with their biomolecular targets strongly depends on the exact local atomic and electronic structure of the gold(III) center. In the present report we have applied an advanced theoretical analysis of XANES which was shown to be a powerful tool for the precise determination of the local atomic structure of molecules [2].

Experimental XANES spectra above the Au L_3 edge were obtained at GILDA beamline at the ESRF synchrotron facility and XANES above the Au $M_{4,5}$ edge for $[\text{Au}(\text{bipy})(\text{OH})_2][\text{PF}_6]$ were measured on the beamline DXR-1 of Dafne Light Synchrotron Facility (LNF, Frascati). Theoretical analysis of Au $M_{4,5}$ and L_3 XANES spectra was made by means of two different ab initio methods: full multiple scattering method within muffin-tin approximation (FEFF8.4 code) and non muffin-tin finite difference method (FDMNES2008 code). It was found that theoretical simulations beyond the muffin-tin approximation have better agreement with the experiments.

A density functional theory (DFT) was used as a complementary to XAFS analysis tool for geometry optimization (starting from model proposed in Ref. [1]) and electronic structure determination of $[\text{Au}(\text{bipy})(\text{OH})_2][\text{PF}_6]$. DFT calculations (ADF2008 code) provided precise information on 3D electronic density distribution, ionization potentials, bonding energy and HOMO - LUMO orbitals shape.

[1] Giordana Marcon et al, J. Med. Chem. 2002, 45, 1672-1677.

[2] Smolentsev, G. et al Phys. Rev. B 75, 144106 (2007).

Location: “Allara e Grosso” Hall
Time: 19:15

X-ray absorption studies of tissue surrounding cobalt-chromium-molybdenum orthopedic implants

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Metal on metal (MOM) hip implants are being increasingly used owing to their long operating life, however in some cases the device has to be removed due to tissue inflammation, a better understanding of the mechanism of this incompatibility may help alleviate these problems in future MOM hips.

The aim of the study was to determine the distribution and types of metallic species present in tissue surrounding Co-Cr-Mo (ratio 60:30:7) MOM hip replacements. Tissue samples were extracted from patients with unexplained inflammation and untreated frozen samples along with samples prepared using routine histological methods (formalin etc.) were examined and compared. XRF mapping revealed mainly Cr which was localized to the cellular regions. Co and Mo were also found but to a lesser extent. micro-EXAFS of the Cr showed it to be mainly chromium orthophosphate. The Co was found to be metallic in the main with the Mo in an oxidized state. The method of tissue preparation did not impact on the results. The concentration of metals found in the tissue does not reflect the concentration of the implant material therefore we conclude that the body metabolizes the Mo and Co more efficiently than the Cr which forms a less soluble phase. The mechanism of formation of the orthophosphate is discussed.

Location: "Allara e Grosso" Hall
Time: 19:45

X-ray imaging and Zn K edge microXANES shows Clioquinol and Disulfiram activity in prostate cancer in vivo

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In industrialized countries, prostate cancer is one of the most frequently diagnose and the second leading cause of death in men. Tumor development depends on certain growth factors, proteases and copper (Cu). Zn is one of the essential elements for the human body. Zn has been shown to play an important role in the structure and function of many enzymes, including oxidoreductase, alcohol dehydrogenase (ADH) and matrix metalloproteinases (MMPs). The human prostate normally accumulates 2-5 times more Zn than any other tissues and 35% of that Zn exists as 'free' or loosely bound. It is well known that Zn content in prostate cancer tissue is at a lower level than in normal tissue, mainly because premalignant and malignant cells are not capable of accumulating high Zn levels. Therefore the Cu/Zn balance is altered in tumors because tumor cells tend to accumulate more Cu and at the same time fail to accumulate Zn. The mechanisms behind these changes are not fully understood. CQ is a quinol that selectively binds with both Cu(II) and Zn(II), forming very stable complexes. Disulfiram is a drug used to support the treatment of chronic alcoholism. Both drugs have shown antitumor activity in cultured cells. To further investigate the in vivo activity of clioquinol (CQ) and disulfiram (DSF) in tumor tissue, we report here measurements of elemental mapping of Cu, Zn and other essential trace elements in normal and tumor prostate tissue. We also investigated the chemical status of Zn in normal and tumor tissue, XANES measurements at the Zn K edge were performed for that purpose. Our results show that CQ and DSF interact selectively with tumor cellular Zn in vivo.

P6.3: Data analysis II

Location: "Aranjo Ruiz" Hall
Time: 18:00

EXAFS measurements with femtometer accuracy: isotopic effect in the first, second, and third coordination shells of germanium

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Recently we have shown that isotopic effect in polycrystalline germanium can be successfully probed by the extended x-ray absorption fine structure (EXAFS) technique with femtometer accuracy (see highlight ESRF 2008)[1]. The analysis of the first coordination shell in two powders ⁷⁰Ge and ⁷⁶Ge has evidenced[1] the effect of isotopic mass difference on the amplitude of relative atomic vibrations, reflected in the temperature dependence of the difference of Debye-Waller factors, and on the difference of nearest-neighbor average interatomic distances.

In this work we extend our analysis of the available Ge K-edge EXAFS data[1] to the second and third coordination shells, where a contribution of multiple-scattering (MS) effects into EXAFS signal is expected. The Debye-Waller (DW) factors have been obtained for two isotopes of ⁷⁰Ge and ⁷⁶Ge using the best fit procedure of the EXAFS signals within the MS approximation in the temperature range from 20 to 300K. The determined temperature dependencies of the DW factors have been used to calculate the characteristic frequencies within the Einstein model. The obtained values of the characteristic frequencies are in good agreement with those[2] expected from the variation of the isotopic mass.

[1] J. Purans, N. D. Afify, G. Dalba, R. Grisenti, S. De Panfilis, A. Kuzmin, V. I. Ozhogin, F. Rocca, A. Sanson, S. I. Tiutiunnikov, P. Fornasini, Phys. Rev. Lett. 100, 055901 (2008).

[2] H.D. Fuchs, C.H. Grein, M. Bauer, M. Cardona, Phys. Rev. B 45, 4065 (1992).

Location: “Aranjo Ruiz” Hall
Time: 18:20

Negative thermal expansion and local dynamics

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The macroscopic thermal expansion of crystals is generally considered the result of a competition between a positive contribution due to bond-stretching and a negative contribution due to tension effects. When the tension effect prevails, negative thermal expansion (NTE) appears. EXAFS can give original information on the local origin of NTE. The quantities of interest are the bond thermal expansion (first cumulant), the perpendicular and parallel MSRDs, and their ratio, which measures the anisotropy of relative atomic vibrations.

A systematic EXAFS study has been performed in the last years on NTE crystals characterized by simple structures: diamond-zincblende [2,3], cuprite [4], delafossite [5]. Some general features emerge from the results. The bond thermal expansion is always positive. Within each family of isostructural compounds, the stronger is the lattice NTE, the larger is the positive bond expansion; besides, a correlation can be established between NTE properties and anisotropy of relative vibrations.

These results open the question whether some quantitative correlation can be established between bond-stretching and tension effects on the one hand, and EXAFS quantities (bond expansion and anisotropy of relative vibrations) on the other.

[1] G.D. Barrera et al., J. Phys.: Condens. Matter 17, R271 (2005)

[2] G. Dalba et al., Phys. Rev. Lett. 82, 4240 (1999)

[3] M. Vaccari et al., Phys. Rev. B 75, 184307 (2007)

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[5] S.I. Ahmed et al., Phys. Rev. B, in press

Location: “Aranjo Ruiz” Hall
Time: 18:40

Accurate measurement and physical insight: latest results of the x-ray extended range technique for high accuracy absolute XAFS

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Over recent experiments [1-7] we have developed methods for measuring XAFS in neutral atoms, simple compounds and organometallics which can reach accuracies of below 0.02%. This is 50 - 500 times more accurate than earlier methods, and 50 - 250 times more accurate than claimed uncertainties in theoretical computations. The data and methodology is useful for a wide range of applications, including synchrotron and laboratory techniques relating to fine structure, near-edge analysis and standard crystallography. We will discuss key features of the method and results, including theoretical issues raised by the new accuracies. In the past year we have developed a new technique to measure nano-roughness from these studies, and the author has been appointed to the International Commission on XAFS. Future opportunities include the theoretical and analytical development of new code for ab initio structural determination.

[1] J. L. Glover, et al., ‘High-accuracy measurements of the X-ray mass-attenuation coefficient and imaginary component of the form factor of copper’, Phys. Rev. A 78 (2008) 052902

[2] M. D. de Jonge, et al., ‘Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of tin over the energy range of 29 keV – 60 keV’, Phys. Rev. A 75 (2007) 032702-1-14.

[3] M. D. de Jonge, et al., ‘Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of molybdenum over the energy range of 13.5 keV-41.5 keV’, Phys. Rev. A 71, 032702 (2005)

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[7] C.T. Chantler, et al., Optical and Quantum Electronics 31 (1999) 495-505

Location: “Aranjo Ruiz” Hall
Time: 19:00

Variable angle XAFS study of multilayer nanoheterostructures: determination of selective concentration profile and depth-dependent partial atomic distributions

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The discovery of oscillations of interlayer exchange coupling (IEC) with the thickness of the spacer layer in metallic magnetic superlattices opens a new field in low dimensional magnetism. Non-commensurability of the lattice constants and de Broglie wave-length for electrons in the multilayers leads to the “aliasing” effect and suppression of short range oscillations of the IEC. It is essential to extract layer and interface information to clarify the mechanism of the IEC. However, it is difficult to directly obtain the depth resolved atomic structure with conventional XAFS, because this technique observes only the average over the whole multilayer film.

We propose a new method for studying multilayer structure using angle resolved XAFS measurements. The integral equation describing a connection between the fluorescence intensity for spectrum of element C, the incident beam energy E, the incident angle ϕ and a selective concentration profile, depth-dependent EXAFS has been derived. It is a Fredholm integral equation of the first kind, it belongs to the class of ill-posed problems and for solution it needs special methods. We use the regularization method [1].

The effectiveness of the method has been tested on the model crystalline three-layer solids with BCC structure: Cr/Fe/Cr. XAFS measurements at the K edges of Fe and Cr are performed using synchrotron facility of Russian Research Centre “Kurchatov Institute”, Moscow.

[1] A.N Tikhonov, V.Ya. Arsenin, *Solution of Ill-Posed Problems*, John Willey and Sons, Inc., New York, 1981

Location: “Aranjo Ruiz” Hall
Time: 19:15

Unified concept on the chemical variation of pre-edge structure

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Representative XANES spectra of 3d- and 4d-transition metal compounds at K-edge and those of 5d elements at L1-edge were selected from scientific publications to give an overview of the pre-edge features with regard to the intensity, assignments and general tendencies related to various factors (the selection rule, coordination number, number of d-electrons, symmetry of the coordination sphere and the natural level width). As is well known, the pre-edge peak intensity for Td symmetry is larger than those for Oh symmetry for all 3d elements. The intensity closely and simply relates to the number of 3d electrons and is almost independent of the kind of element and the oxidation number. The d^0 compounds give the highest peak, and the intensity decreases monotonously with the number of 3d electrons occupied, and reaches zero at d^{10} (Fig. S1). The intense pre-edge peak is not due to 1s-3d transition, but to the p-component in d-p hybridized orbital. The mixing of metal 4p orbitals with the 3d orbitals depends strongly on the coordination symmetry, and the possibility is predictable by group theory. The features of pre-edge peaks in K-edge XANES spectra for 4d elements and the L1-edge for 5d elements are analogous with those for 3d elements although the pre-edge peak is broadened due to the wide natural width of the core level. In a case that a central atom possesses the identical coordination environment and number of the d-electron, approximately the same natural width at the absorption edge, the corresponding XANES would be the identical spectral configuration including the pre-edge peak (Fig. S2).

Location: “Aranjo Ruiz” Hall
Time: 19:30

Structure of reaction intermediates refined by quantitative analysis of time-resolved XANES spectra

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A method for the analysis of time-resolved XANES spectra is proposed. It combines principal component analysis of the series of experimental spectra, multidimensional interpolation of theoretical XANES as a function of structural parameters and ab-initio XANES calculations. It allows to determine the values of structural parameters for intermediates of chemical reactions and the concentrations of different states as a function of time. The application of this method to a reaction with methylrhenium trioxide (MTO) catalyst in solution, for which experimental data were measured using stopped-flow Energy Dispersive X-ray Absorption Spectroscopy (ED-XAS) technique with time resolution 1.8 s was performed. The second example demonstrates refinement of structural parameters for photoexcited states of metal complexes on the basis of laser initiated time resolved (LITR) pump-and-probe XANES data measured with time resolution 100 ps. The work is supported by a joint Civilian Research and Development Foundation grant (US, # RUC1-2870-RO-07) / Russian Foundation of Basic Research (Russia, 07-03-91142) and Southern Federal University development programme.

Location: “Aranjo Ruiz” Hall
Time: 19:45

Mott transition in V₂O₃: a high resolution X-ray absorption spectroscopy study

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V₂O₃ is an archetypal system for correlation-induced Mott-Hubbard metal-insulator transitions (MIT). It presents a rich phase diagram involving antiferromagnetic insulating, paramagnetic metallic and paramagnetic insulating regimes, determined by external parameters like temperature, pressure or doping (with Cr or Ti). The accurate description of the MIT in V₂O₃ remains an unsolved problem in the physics of strongly correlated materials, also because of the lack of detailed experimental data on its electronic structure over the whole phase diagram.

In order to help clarify this important open issue, we have performed high resolution x-ray absorption spectroscopy (XAS) at the V K-edge of (V_{1-x}Cr_x)₂O₃, to probe its electronic structure as a function of temperature, pressure and doping. The XAS spectra were measured at the ID-26 (ESRF), FAME (ESRF), ODE (SOLEIL) and BL12XU (Spring-8) beamlines in the partial fluorescence yield mode with the advantage of improved resolution - below the core-hole lifetime - compared to standard techniques. We primarily focused on the V K pre-edge region (mainly corresponding to quadrupolar 1s → 3d transitions) which shows the greatest sensitivity to the d states. Clearly visible changes are observed in this spectral region when passing from the metallic to insulating regimes, in particular in the paramagnetic phase. The polarization dependence of the XAS spectra provides new information about the orbital occupancy change in d states, which is known to play a central role in the physics of V₂O₃.

Thanks to the combination of high resolution and bulk sensitivity, we show that XAS can contribute to providing an accurate picture of the electronic changes in V₂O₃ through the MIT, serving also as critical test of the validity of recent theoretical models that have been proposed beyond the simple one band Hubbard picture for this prototype system.

P6.4: Actinides and nuclear waste

Location: "Betti" Hall
Time: 18:00

Double-electron excitation in absorption spectra of actinides

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The excitation of a inner-shell photoelectron is usually accompanied by the excitation of outer-shell electrons. Early systematic studies were performed by using noble gases because their absorption signal is not affected by photoelectron backscattering from neighbored atoms. Up to now, most of the elements until Bi were investigated for multielectron excitations even in the presence of photoelectron backscattering effects from extended X-ray absorption fine structure. All elements with Z larger than Bi comprise only radioactive isotopes and their multielectron features are more difficult accessible. Recently we found evidence for multielectron excitations in the L-absorption edges of Th, Pa, U, Np, Pu and Am hydrates [1,2]. The strongest resonances result from [2p4f] double electron excitations, but there is also evidence for [2p5d] excitations. The [2p4f] resonance energies follow systematically the trend observed by Di Cicco and Filippini for Hg, Pb and Bi [3]. The actinide elements show numerous oxidation states in particular for Np and Pu, where they range from III to VII. The electronic configuration involves besides 6d states partly filled 5f shells. This electronic configuration influences the physical and chemical properties and is related to a large variation in the coordination geometry including transdioxo cations, AnO_2^{n+} . There is a clear correlation of the oxidation state, coordination geometry and the spectral feature of the multielectron resonance, resulting from final state density. The resonance intensity of the single electron 2p-6d transition corresponds well with the resonance intensity with the double-electron [2p4f] transition.

[1] C. Hennig, Phys. Rev. B 75, 035120 (2007).

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[3] A. Di Cicco, A. Filippini, Phys. Rev. B 49, 12564 (1994).

Location: "Betti" Hall
Time: 18:20

EXAFS study of Np(V) sorption onto gibbsite (γ -Al(OH)₃)

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Argillaceous rocks have been considered as a potential host rock for radioactive waste repositories. In addition, bentonite is the preferred backfill material for engineered barriers. Clay minerals like montmorillonite and kaolinite contain aluminol and silanol groups as primary binding sites for heavy metals. After a storage time of 1,000 years, Pu and the minor actinides, including ²³⁷Np, will contribute significantly to the radiotoxicity of spent nuclear fuel in the repositories. For obtaining a molecular-level understanding of the interaction between Np(V) and aluminol groups, gibbsite has been selected as a reference mineral.

The sorption of Np(V) onto gibbsite was studied recently in the pH range 6-10 at different ionic strengths in the absence of inorganic carbon and under air-equilibrated conditions [1]. Due to the formation of aqueous Np(V) complexes with carbonate, the presence of inorganic carbon has a strong influence on the sorption behaviour of Np(V) at pH > 8. The independence of the amount of Np(V) sorbed on ionic strength suggests inner-sphere sorption.

For obtaining an adequate surface complexation model to describe the results of the batch experiments, Np L_{III}-edge EXAFS measurements were performed at the ROBL (ESRF). Wet paste samples with Np(V) loadings of ~0.3 μ mol/g were prepared at pH 9.0 in the presence and absence of inorganic carbon. The EXAFS structural parameters will be discussed in detail and compared to those of EXAFS measurements on Np(V) sorption onto kaolinite and montmorillonite. An important difference between these two reference clays and gibbsite is that the formation of Np(V)-carbonate complexes at the mineral surface as in the case of kaolinite [2] and montmorillonite has not been observed for gibbsite.

[1] T. Wu, S. Amayri, and T. Reich, Radiochim. Acta 97, 99 (2009).

[2] T. Reich, T.Ye. Reich, S. Amayri, et al., AIP 882, 179 (2007).

Location: “Betti” Hall
Time: 18:40

Spatially resolved XRF, XAFS, XRD, STXM and IR investigation of U-rich natural analogue clay

Melissa Anne Denecke¹, Pauline Michel¹, Thorsten Schäfer¹, Florian Huber¹, Joerg Rothe¹, Karen Rickers², Kathy Dardenne¹, Boris Brendebach¹, Tonya Vitova¹, and Marcel Elie³

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(2) Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY, Notkestr. 85, D-22603 Hamburg, Germany

(3) UMR G2R 7566, Université Henri Poincaré, F-54506 Vandœuvre-lès-Nancy Cedex, France

We report our most recent results of spatially resolved X-ray fluorescence, X-ray absorption fine structure and X-ray diffraction investigations with a micrometer-scale resolution (μ -XRF, μ -XAFS, μ -XRD) on U-rich clay originating from Autunian shales in the Permian Lodève Basin (France). This argillaceous formation is a natural U deposit associated with organic matter (bitumen). The goal of this study is to elucidate which mechanism of U immobilization led to U enrichment, either adsorption/co-precipitation with iron hydroxides, with clay minerals or their associated organic material, by determining the U oxidation state in the sample and ascertaining if any correlation between the U distribution and that of other elements or mineral phases present in the organic-rich fine-grained pelites exists. Combination of results from hard X-ray μ -XRF, μ -XAFS and μ -XRD studies using an X-ray beam with micrometer dimensions at the INE-Beamline for actinide research at ANKA and/or Beamline-L at HASYLAB with those from scanning transmission soft X-ray microscopy (STXM) and synchrotron-based Fourier transform infrared microspectroscopy (μ -FTIR) recorded with beam spots in the nanometer range, give sufficient information to put forward a hypothesis for U-immobilization [1]. Such investigations support development of reliable assessment of the long term radiological safety for proposed nuclear waste disposal sites.

[1] P. Michel, M.A. Denecke, T. Schäfer, B. Brendebach, K. Dardenne, J. Rothe, T. Vitova, F. Huber, K. Rickers, M. Elie, G. Buckau, Proceedings to the 5th Nuclear Energy Agency (NEA) Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinide-XAS-2008), Soleil, France.

Location: “Betti” Hall
Time: 19:00

A combined XAFS, LIBD and ESI TOF-MS study on the formation of polynuclear An(IV) complexes and colloids

Jörg Rothe¹, Clemens Walther¹, Boris Brendebach¹, Sebastian Büchner¹, Markus Fuss¹, Bernd Schimmelpfennig¹, Melissa A. Denecke¹, and Horst Geckeis¹

(1) Forschungszentrum Karlsruhe - Institut für Nukleare Entsorgung, P.O. Box 3640, D-76021 Karlsruhe, Germany

The long term radiotoxicity of spent nuclear fuel disposed of in deep underground repositories after discharge from nuclear power reactors is determined by actinide elements, mainly plutonium. Water intrusion into the repository might cause container corrosion and leaching of the waste matrices, leading to the release of Pu and other actinides into the geological environment. Performance assessment for a future nuclear waste repository requires detailed knowledge on actinide aqueous chemistry in the aquifer surrounding the disposal site.

Tetravalent actinides (An(IV)) exhibit a strong tendency towards hydrolysis (i.e., complexation with OH⁻ ligands) and subsequent polymerization and oxide/hydroxide colloid formation. These species provide a potential pathway for migration of actinides away from the repository. Therefore, it is of fundamental interest to study their generation and properties in-situ. To this end, X-ray Absorption Fine Structure Spectroscopy (XAFS) at the INE-Beamline for actinide research at ANKA, Electrospray Mass-Spectrometry (ESI TOF-MS) and Laser Induced Breakdown Detection (LIBD) are combined at FZK-INE in a comprehensive attempt to characterize Zr(IV) (An(IV) homologue), Th(IV) and Pu(IV) polymerization and colloid formation over a wide range of pH and metal concentrations.

C. Walther, J. Rothe, M. Fuss, S. Büchner, S. Koltsov, T. Bergmann, Anal. Bioanal. Chem., 388(2) (2007) 409

Location: "Betti" Hall
Time: 19:20

Selenite retention by siderite: *In situ* and *ex situ* XAFS experiments

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(1) CEA, Laboratoire de Réactivité des Surfaces et Interfaces CEN de Saclay, bat. 391 91191 Gif-sur-Yvette CEDEX France

⁷⁹Se is amongst the major contributors to the potential radiotoxicity of High Level nuclear Wastes. It can be released as selenite upon alteration of the waste package. Understanding selenite behavior in rocks and soil components is essential to predicting the bioavailability of this trace radioelement. Siderite (FeCO₃) is naturally present in clay rocks and can form in the corrosion layer of the steel containers of HLW. This Fe(II)-bearing mineral may reduce selenium oxyanions and lead to the formation of sparingly soluble Se(0) or FeSe(1-2), yet both the mechanism of selenite-siderite interaction have not been fully investigated yet. The immobilization mechanism was probed by both *ex situ* and *in situ* XAFS experiments at the Se K α edge on the SAMBA (SOLEIL) and BM29 (ESRF) beamlines. All the experiments are realized using a synthetic siderite suspension (30 g.L⁻¹, I = 0.15 M).

Ex situ experiments were conducted inside glovebox under reducing atmosphere (H₂/CO₂/N₂ 5:10:85) to protect siderite from oxidation. Selenite retention was investigated by batch method, adding small aliquot of selenite for a final concentration of 1 to 20 x 10⁻⁴ M. XAFS samples were taken at given time, filtered, conditioned as wet paste, frozen in liquid nitrogen, and measured inside a cryostat. Those experiments showed total immobilization of selenite ions within 24 h and total reduction of selenite within 10 days, with evidences that the reduction kinetic is different from that of the immobilization.

In situ experiments were conducted in a specially designed electrochemical cell preserving reducing conditions. Time dependent XANES acquisition showed that that even though selenite is reduced with the same time constant, the reduction product appears to be different from the one observed on *ex situ* experiments. One can therefore question the effect of the *ex situ* sample preparation (e.g. freezing) on selenium final stage speciation.

Location: "Betti" Hall
Time: 19:40

Sulfur incorporation in high level nuclear waste glasses: a S K-edge XAFS investigation

Boris Brendebach¹, Melissa A. Denecke¹, Günther Roth¹, and Siegfried Weisenburger¹

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Borosilicate glasses are widely used for the immobilization of high level radioactive liquid waste originating from spent nuclear fuel reprocessing due to their remarkable chemical, especially radio-chemical and thermal properties. The Institut für Nukleare Entsorgung (INE) at the Forschungszentrum Karlsruhe (FzK) has developed a vitrification technology to immobilize high level liquid wastes into glass by a single stage process. As high level liquid waste from the 1960s to 1970s often contains a significant amount of sulfur, which tends to undergo phase separation when incorporated into borosilicate glasses, INE has developed a tailored waste glass composition able to incorporate unusual high amounts of sulfur.

We perform X-ray absorption spectroscopy measurements at the sulfur K-edge to elucidate the electronic and geometric bonding of the sulfur atoms in the borosilicate glass. The sulfur is incorporated as sulfate, most probably as sodium sulfate, which can be deduced from the X-ray absorption near edge structure by fingerprint comparison with reference compounds. This finding is backed up by Raman spectroscopy investigation. In the EXAFS data, no second shell beyond the first oxygen layer is visible. We argue that this is due to the sulfate being present as small clusters located into voids of the borosilicate network. Hence, destructive interference of the variable surrounding prohibits the presence of higher shell signals. The knowledge of the sulfur bonding characteristics is essential for further optimization of the glass composition and to balance the requirements of the process and glass quality parameters, viscosity and electrical resistivity on one side, waste loading and sulfur uptake on the other side.

Friday 31th July

M5: Plenary session M5

Location: “Benedetto XIII” Hall
Time: 8:30

X-ray views of the defect structure and chemistry of environmental nanoparticles

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Major goals of environmental science are to control mobility of toxic elements and to remediate contaminated soils, sediments, and subsurface waters. These goals cannot be met without first having in hand a fundamental understanding of the composition, defect structure, and surface properties of environmental nanoparticles. Key problems are their low dimensionality, short-range order and high density of defects, the multiplicity of reactive surface sites, and the partitioning of elements into coexisting phases. In most cases, the information sought can be obtained by application of synergistic X-ray techniques, including microfluorescence (micro-SRXF), microdiffraction (micro-XRD), high-energy scattering (HEXS), and microspectroscopy (micro-EXAFS), as well as data modelling with meaningful structure models. In this approach, micro-SRXF is used to map trace contaminants in a natural matrix, thus determining their distribution and relative abundance with unrivalled sensitivity. Then, micro-XRD, complemented by powder XRD and HEXS, is employed to identify nanocrystalline minerals and, more importantly, to determine the nature of structural and chemical defects (stacking faults, cationic and anionic vacancies and occupancies, site occupation of impurities, stoichiometry) through modelling of their scattering properties. Finally, micro-EXAFS gives the uptake and complexation mechanism of trace contaminants by individual constituents. Since the distribution of trace elements is heterogeneous on nanometer to micrometer length scales and nanoparticles are generally aggregated in environmental systems, the combination of these three microscopic techniques provides just the tools needed to scrutinize the nature of environmental matter. This new kind of hybridization of experimental and modelling approaches to the characterization of natural nanoparticles will be illustrated with examples that show its potential for expanding our knowledge in environmental science.

Location: "Benedetto XIII" Hall
Time: 9:15

X-ray absorption spectroscopy and environmental mineralogy

Roy Albert Wogelius^{1,2}

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Environmental degradation can come from many sources, from acid mine drainage to actinide contamination. X-ray absorption spectroscopy can be used to provide short-range order information over most of the periodic table, and has therefore become a cornerstone technique in helping to constrain the chemistry of a wide variety of environmental systems. Mineralogy has a long and rich literature involving the use of X-ray techniques to study natural solids, and has in particular embraced and developed the use of XAS, especially in tandem with other analytical methods. As a result, current research has seen many advances which are broad in scope, covering diverse problems ranging from sulfur speciation (and microbial survival) in soils[1] to arsenic coordination chemistry in hydrothermal systems[2].

Given the complicated chemistry (and biology) typically involved in natural systems XAS has become a critical component of the environmental mineralogist's analytical toolbox because it can provide information supplementary to a range of standard laboratory methods. However, perhaps the most exciting advances result from combining EXAFS measurements with other methods such as glancing incidence surface techniques or rapid-scanning X-ray fluorescence. Examples of XAS applications in soil microbiology, geochemistry, radiochemistry, and biomarker analysis[3] will be presented and discussed.

[1] P. Mirleau, R. Wogelius, A. Smith, and M.A. Kertesz, Appl. Env. Microbiol. 71, 6571 (2005).

[2] J.M. Charnock, D.A. Polya, A.G. Gault, and R.A. Wogelius, Am. Min. 92, 1856 (2007).

[3] A.G. Gault, H.A.L. Rowland, J.M. Charnock, R.A. Wogelius, I. Gomez-Morilla, S. Vong, M. Leng, S. Samreth, M.L. Sampson, and D.A. Polya, Sci. Tot. Env. 393, 168 (2008).

Location: "Benedetto XIII" Hall
Time: 10:00

The diversity of actinide polyhedra from aqueous to complex molecular systems

Christophe Den Auwer¹, C. Den Auwer¹, A. Jeanson¹, H. Funke², D. Guillaumont¹, C. Hennig², C. Le Naour³, P. Moisy¹, E. Simoni³, and C. Vidaud⁴

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Actinide molecular chemistry is surprisingly rich compared to lanthanide chemistry because the 5f orbital extent is rather large compared to the lanthanide family. Consequently, actinide 5f and 6d valence electrons are relatively available for hybridization with ligand orbitals. As a result, stable or metastable oxidation states span from III to VII for the early actinides and corresponding coordination spheres are characterized by large polyhedra like pentagonal or hexagonal bipyramids, prisms or capped prisms, dodecahedra, all with coordination numbers between 6 and 14. In acidic water solution, formal oxidation state as well as atomic number are two crucial variables that define the cation coordination polyhedron. Using EXAFS and XANES data at the actinide LIII edge, the variety of geometry of the first water coordination sphere will be exemplified for various transuranium aqueous species. Small aminocarboxylic ligands (like nitrilotriacetic acid) that often play the role of protecting ligands against hydrolysis have also been investigated for the Th to Pu series. EXAFS results that have been correlated to quantum chemical calculations show an homogeneous behavior of the actinide at oxidation state IV. For larger ligands, steric effects may become significant and one can ask how the ligand may accommodate the large cation coordination sphere. Metalloprotein for instance bear primary, secondary and tertiary structures that all play a crucial role in bonding. We have selected in this work transferrin, a diferric metalloprotein that is well known to coordinate a large variety of cations from transition metals of f-elements. For a given actinide oxidation state, IV, but for various atomic numbers (Th, Np, Pu) EXAFS data at the cation LIII edge exhibit significant discrepancies that are related to a change in coordination geometry. In that sense, the metalloprotein may be viewed as a complex selective system.

PS1: Poster Session 1

Location: “Benedetto XIII” Hall
Time: Mon-Tue 11:30-13:30

Theory

Poster no. PS1.1 - Session 1

Al and Si K-edge XANES in some minerals and zeolites via non-MT FDMNES calculations

Leon A. Avakyan¹, Jeroen A. van Bokhoven², Valerii V. Khrapko¹, Yelena A. Kozinkina¹, and Lusegen A. Bugaev¹

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Calculations of Al and Si K-edge XANES in the strongly covalent compounds, performed using the muffin-tin (MT) approximation, often result in significant disagreements with the experiment, which increase with decreasing symmetry [1,2]. To understand the origin of these disagreements, Al K-edge XANES in corundum, diaspore, Na Y-zeolite and Si K-edge XANES in zeolites faujasite, mordenite, beta are calculated beyond the MT-approximation using finite difference method (FDM) by the FDMNES code [3]. The theoretical spectra reproduced all experimental features. This agreement confirms the assumption that the main source of the inaccuracies in XANES description is caused by using the MT-approximation [2]. Using the FDMNES approach, the following effects on Al and Si K-edge XANES are studied: i) the size of the cluster around the absorbing atom; ii) the core-hole effect; iii) the adequacy of the used procedure for convolution of the calculated spectra.

[1] D. Cabaret, P. Sainctavit, P. Ildefonse, and A-M. Flank, J Phys.: Condens. Matter 8, 3691 (1996).

[2] L. Bugaev, J. van Bokhoven, V. Khrapko, L. Avakyan, and J. Latokha, J. Phys. Chem. B (2009).

[3] Y. Joly, Phys. Rev. B 63,125120 (2001).

Poster no. PS1.2 - Session 1

MXAN: new improvements for potential and structural refinement

Maurizio Benfatto¹, and Stefano Della Longa²

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(2) *Dipartimento di Medicina Sperimentale, Università L'Aquila, Via Vetoio, 67100 L'Aquila, Italy.*

Multiple Scattering (MS) theory, via the MXAN package, is able to reproduce the experimental XANES data of aqua ions, small molecules, and metal sites in biomolecules from the edge up to 150-200 eV [1,2]. Recently, owing to its ability to handle differential XANES spectra, it has been successfully applied to analyse time-resolved XAS experiments [3,4]. In this paper, we present the last advanced of the method, including the potential description and optimization, and a new way to account for the inelastic losses of photoelectron in the final state. Improved parameterization also includes new routines to handle the structural determinants via generalized degrees of freedom. Examples will be presented to illustrate the method.

[1] M. Benfatto and S. Della Longa J. Synchrotron Rad. 8: 1087 (2001)

[2] S. Della Longa et al. Phys. Rev. Lett. 87:155501-1/4 (2001)

[3] M. Benfatto et al. J Phys Chem B 110: 14035 (2006)

[4] S. Della Longa et al. Inorg. Chem. In the press

Poster no. PS1.3 - Session 1**The 1s x-ray absorption pre-edge structures in transition metal oxides**Frank M. F. de Groot¹, Gyorgy Vanko², and Pieter Glatzel³*(1) Utrecht University Sorbonnelaan 16 3584 CA Utrecht Netherlands**(2) KFKI Research Institute for Particle and Nuclear Physics, P.O. Box 49, H-1525 Budapest, Hungary**(3) European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble Cedex, France*

A procedure is outlined to analyze the pre-edge structures in 1s X-ray Absorption Near Edge Structure (XANES) of transition metal oxides and complexes. The general understanding is that the 1s core levels can be explained with the single-electron-excitation model, while the 2p XAS spectra need a charge-transfer multiplet analysis, in particular for 3d transition metal systems [1]. The 1s XANES spectra are divided into the main edge due to transitions from the 1s core state to the 4p conduction band and at lower energy small pre-edge structure are observed. These pre-edge structures are assigned as quadrupole transitions from the 1s core state to the empty 3d states. In case the inversion symmetry of the transition metal is broken, the pre-edge gains additional intensity due to the local 3d4p wavefunction mixing, effectively allowing dipole transitions to the 4p character of the 3d-band.

Isolated transition metal complexes can be well described with this model. Bulk transition metal oxides can be described similarly, but for trivalent and tetravalent oxides, additional structures are visible in the pre-edge region. These additional structures are assigned to non-local dipole transitions. The 1s4p dipole transitions have large cross section at the 3d-band region due to the strong metal-metal interactions, which are oxygen mediated. This yields large intensity at the 3d-band region and this intensity is visible at a different energy than the local 1s3d quadrupole transitions due to the smaller core-hole effects due to the delocalisation of the excited electron. These non-local dipole peaks are clearly visible in TiO₂, Fe₂O₃ and LaCoO₃, in particular if measured with HERFD-XANES [2,3].

[1] F. de Groot, A. Kotani, Core Level Spectroscopy of Solids (Taylor and Francis, 2008)

[2] F. de Groot, G. Vanko and P. Glatzel, J. Phys. Cond. Matt. 21, 104207 (2009)

[3] P. Glatzel, et al. Phys. Rev. B 77, 115133 (2008)

Poster no. PS1.4 - Session 1**Single and multiple scattering XAFS Debye-Waller factors for crystalline materials using periodic Density Functional Theory**Nikolaos Dimakis¹, Thomas Mion¹, and Grant Bunker²*(1) University of Texas-Pan American 1201 W. University Dr 78539 Edinburg TX USA**(2) Illinois Institute of Technology Chicago IL 60616 USA*

We present an accurate and efficient technique for calculating thermal X-ray absorption fine structure (XAFS) Debye-Waller factors (DWF) applicable for crystalline materials. Using Density Functional Theory (DFT) on a 3x3x3 supercell pattern of MnO structure under the nonlocal hybrid B3LYP functional paired with Gaussian local basis sets we obtain the structure normal mode eigenfrequencies and eigenvectors; these parameters are in turn used to calculate single and multiple scattering XAFS DWFs. The DWFs obtained via this technique are temperature dependent expressions and can be used to substantially reduce the number of fitting parameters when experimental spectra are fitted with a hypothetical structure. The size of the supercell size limits the R-space range that these parameters could be used; therefore corresponding DWFs for paths outside of this range are calculated using the correlated Debye Model. Our method is compared with prior cluster calculations and with corresponding values obtained from fitting experimental XAFS spectra on manganosite with simulated spectra.

Poster no. PS1.5 - Session 1**Probing the spin and orbital high-field susceptibility of magnetic solids on the basis of the XMCD sum rules**Hubert Ebert¹, and S. Mankovsky¹*(1) University Munich, Dept. of Chemistry Butenandtstr. 5-13 81377 Munich Germany*

It is demonstrated that the magnetic circular dichroism in X-ray absorption (XMCD) can be used to probe the spin and orbital high-field susceptibilities of spontaneously magnetic solids on the basis of the so-called XMCD sum rules. A corresponding theoretical description is presented that is formulated in terms of the fully relativistic multiple scattering Green's function formalism. Examples for the field-induced changes in the XMCD spectra of ferromagnetic 3d-transition metals are presented, that are induced by an external magnetic field. Application of the sum rules to the field-induced changes in the XMCD spectra, clearly demonstrates their relation to the high-field susceptibility. Corresponding results for disordered transition metal alloys will be shown.

Poster no. PS1.6 - Session 1**Parameter free calculations of K-edge XMCD in metals: theory and applications**Christos Gougoussis¹, Matteo Calandra¹, Ari Seitsonen¹, Christian Brouder¹, Abhay Shukla¹, and Francesco Mauri¹*(1) CNRS and Institut de Minéralogie et de Physique des Milieux Condensés, case 115, 4 place Jussieu, 75252 Paris cedex 05, France*

We present a first principles method to calculate K-edge XAS and XMCD in materials. The method relies on plane-wave expansion, pseudopotentials and the continued fraction approach [1]. Core-hole effects are included and correlation is treated in the DFT+U approximation where the value of U is calculated from first principles [2,3]. The code is freely distributed under the gnu licence [4].

We apply the method to XMCD spectra to iron and other compounds. We study the effects of earth-core pressure in iron in order to get a better understanding of the magnetic and structural phase transition at high pressure [5]. We discuss the relative importance of the different contributions to the XMCD spectra.

[1] M. Taillefumier et al, Phys. Rev. B **66**, 195107 (2002)[2] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005)[3] C. Gougoussis, M. Calandra, A. Seitsonen, Ch. Brouder, A. Shukla and F. Mauri, Phys. Rev. B **79**, 045118 (2009)[4] P. Giannozzi et al., <http://www.quantum-espresso.org>[5] O. Mathon et al, Phys. Rev. Lett. **93**, 255503 (2004)**Poster no. PS1.7 - Session 1****Applications of full potential multiple scattering theory to K-edge XANES of 3d metals.**Keisuke Hatada^{1,2}, Kuniko Hayakawa^{1,3}, Calogero R. Natoli¹, and Jesús Chaboy⁴*(1) LNF-INFN via E.Fermi 40 00044 Frascati Roma Italy**(2) Institut de Physique de Rennes UMR UR1-CNRS 6251 35042 Rennes France**(3) Centro Fermi Piazza del Viminale 1 00184 Roma Roma Italy**(4) Departamento de Física de la Materia Condensada Facultad de Ciencias Universidad de Zaragoza Pz. San Francisco s/n, E-50009*

Recently we developed a Full-Potential Multiple Scattering (FPMS) code which provides a straightforward extension of the corresponding Muffin-Tin (MT) scheme and can handle the potential without any geometrical approximation. It lends itself therefore to a detailed study of the optical potential used in absorption spectroscopy. In this paper we present the results for the K-edge XANES of 3d metal foils for several kind of potentials, comparing with the corresponding calculations in the MT approximation.

Poster no. PS1.8 - Session 1**Effects of full potential and inelastic losses on XANES spectra**Joshua J. Kas¹, A. L. Ankudinov¹, and J. J. Rehr¹*(1) University of Washington, Seattle Washington USA*

Currently, the multiple scattering theory of XANES is only semi-quantitative due to the use of muffin-tin potentials and phenomenological models to account for many-body effects. Here we present several improvements in the theory of XANES which address these limitations. First, a many-pole model of the GW self-energy[1] has been developed and applied to calculations of XANES. The method is widely applicable over a broad range of energies, with modest computational cost. Results show improved agreement with experiment. Our many-pole model is implemented within the FEFF XAS code. In addition, a standalone version is available which can be used to correct ground state XANES calculations *a posteriori* by convolving with an energy dependent Lorentzian. We have applied this approach to PARATEC[4] calculations of XANES spectra. Second, we have developed an interface between a wave-function based quantum chemistry code[2] and a full potential version of the FEFF code (FEFF-FP)[3]. Several theoretical and methodological advances are also investigated: (1) an overlapping *fuzzy* Voronoi cell is used to help minimize instabilities caused by sharp cell boundaries; and (2) a re-expansion of the Green's function is applied to calculations of the density of states (DOS) for bound state energies. Calculations of the DOS from FEFF-FP is shown to agree well with that of other codes. Results for the XANES spectra of several molecules are presented. Agreement with experiment is dramatically improved by including full potential effects. Supported in part by NIH NCRR BTP grant RR-01209.

[1] J. J. Kas et al., Physical Review B **76**, 195116 (2007).

[2] F. Neese, J. Chem. Phys. **115**, 11080 (2001).

[3] A. L. Ankudinov and J. J. Rehr, Physica Scripta T**115**, 2427, (2005).

[4] Nicolas Trcera et al., Physics and Chemistry of Minerals, 67 (2008).

Poster no. PS1.9 - Session 1**Transition potential DFT NEXAFS calculations on water**Mikael Leetmaa¹, Mathias Ljungberg¹, Anders Nilsson^{1,2}, and Lars G. M. Pettersson¹*(1) Stockholm University AlbaNova University Center SE-10691, Stockholm, Sweden**(2) Stanford Synchrotron Radiation Laboratory, P.O. Box 20450, Stanford, California 94309, USA*

A combined experimental and computational Near Edge X-ray Absorption Spectroscopy (NEXAFS) study on water [Wernet et al. Science 304 (2004) pp. 995] triggered an intense debate concerning the number of strong hydrogen bonds in liquid water. We provide here a background theoretical description of the transition potential Kohn-Sham DFT core-level spectrum calculations of relevance. We address technical aspects, such as the choice of core occupation, the influence of basis set description and vibrational broadening, as well as the reliability of the spectrum calculations. This is illustrated with examples from an extensive computational study of NEXAFS on water in gas-phase, liquid and ice.

Poster no. PS1.10 - Session 1**O K-edge 2nd derivative x-ray absorption spectroscopy in the pre-edge and continuum spectral regimes: occupied states of transition metal (TM) and rare earth (RE) atoms**Gerald Lucovsky¹, Carolina Adamo², and Darrel Schlom² (Kejin Zhou presenting author)

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Complex oxides, layered stacks of TM oxides separated by normal metal, or TM or RE atom oxides, are differentiated spectroscopically by the occupancy of TM/RE d-, or RE f-states in high spin configurations above the valence band edge. These states are evident in the pre-edge and virtual bound state regimes that bracket O K-edge conduction band features. By counting occupied state spectral features for dn complex oxides with n greater than 1, it is shown TM ions with up to 5 occupied 3d-states, and RE ions with up to 7 occupied 4f states occupy the discrete states. Final state features for 3d to 3d' or 4f to 4f' intra-atom transitions are observed in pre-edge spectra, and 3d to 3d* or 4f to 4f* intra-atom transitions in virtual bound state spectra. Complex oxides with 3d occupancy include LaMnO_3 , and YMnO_3 with an Mn d4 structure. Gd in GdScO_3 is also in a Gd^{3+} charge state, but with a Gd f7 structure. XAS pre-edge and virtual bound state spectra for (Y,Ho) MnO_3 ordered complex oxides indicate discrete and separate 3d and 4f state transitions. Ho^{3+} has a 4f10 configuration, exceeding the half-filled occupancy criterion, with occupied resonance states within the valence band and occupied 4f states above the valence band edge. Y^{3+} is in a d0 configuration with no occupied 4d states, but Mn is in a d4 state with 4 occupied 3d-states above the valence band edge. Mn 3d to 3d, and Ho 4f to 4f transitions are separate and distinct. These are distinguished by different spectral energies, amplitudes, half-widths, and energy spacings. The relationship between the Gd^{3+} 4f features and Ti^{3+} 3d spectral features in $\text{Gd}(\text{Sc}_{0.96}\text{Ti}_{0.04})\text{O}_3$ random alloys is qualitatively different. Ti is in a Ti^{3+} charge state, d1, and the spectral features of Ti 3d and Hf 4f features overlap in the spectra identifying a way to distinguish between ordered and random alloy atom bonding. This overlap is supported by SXSP valence band spectra as well.

Poster no. PS1.11 - Session 1**The effect of atomic vibrations in the calculation of the C K-Edge XANES in diamond**Karim Madjer¹, Delphine Cabaret², Francesco Mauri², and Stéphanie Rossano¹

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The calculation of the carbon K-edge XANES in diamond has been investigated in several studies, using different calculation methods. Although the agreement between the experimental and calculated data is quite satisfactory, calculations fail to properly reproduce the area closest to the edge, up to about 5 eV. The experimental diamond spectrum exhibits two features that are poorly reproduced by simulation; a first peak at 3.5 eV, often described as an excitonic peak, and a second peak around 5 eV, generally overestimated by the calculations. It has been shown that vibrations have an important influence on the electronic properties of diamond. The phonons can interact with electronic wave functions to create hybridization states between the p states and the excitonic states, the nature of which are still controversial. Our study shows that this phenomenon could be at the origin of the excitonic peak previously mentioned. We present an ab initio calculation for the diamond XANES spectra, which takes into account the influence of the phonon population, within a 250 atom supercell including the 1s core-hole. The phonon modes and the dynamical matrix of the system are calculated within the Linear Response Theory. The eigenmodes are then used to generate random atomic displacements which are determined by quantum statistics. This permits the computation of different atomic configurations, which are used as a starting point for the XANES calculations. The average XANES spectrum is calculated over several different configurations. The calculations are run using the Quantum-espresso code, which since recently includes a XANES calculation package (XSpectra). Using this method, the agreement between the calculated and the experimental XANES spectrum is strongly improved, providing the evidence of the significant role of the atomic vibrations and showing how the so-called excitonic peak emerges from electronic-phonon coupling.

Poster no. PS1.12 - Session 1**Problem of construction of empirical potential**Yuri Fedorovich Migal¹, and Olga Mikhailovna Kholodova²*(1) Southern Scientific Centre of Russian Academy of Sciences, 41, Chekhov av., 344006 Rostov-on-Don, Russia**(2) Don State Technical University, Gagarin Sq., 344000, Rostov-on-Don, Russia*

As the inverse problem of the theory of x-ray absorption spectra is to be solved, the set of variable parameters of a model must be adequate to the problem posed, i.e. all independent parameters influencing spectral characteristics must be included into account. Along with geometric parameters, also characteristics of the potential describing the interaction between the photoelectron and a many-atom system should be considered. If only geometric parameters are determined from experiment, while a potential is found theoretically, so additional errors arise inevitably. The point is that any pure theoretical potential as a rule is less exact than empirical one constructed according to the same experiment. It should be noted also that so called ab initio potentials used today in most methods of processing of x-ray absorption spectra are in fact semi-empirical. For example, as the muffin-tin model is used, radii of atomic spheres, the exchange parameter and so on are subject to adjustment. Our investigations show that if one analyzes spectral maxima of the one-electron origin in the XANES as experimental data and selects positions and widths of the maxima as the most reliable characteristics measured, so the problem of the construction of an adequate potential is simple sufficiently. In this case, an intratomic potential, measured in Ryd, can be chosen as $V(r) = -2Z \exp(-ar)/r + b$, where Z is the charge of an atomic nucleus, a and b are fitting parameters. We can see that there is no need to calculate an ab initio potential detailed which is approximately good for a wide energy interval, because the potential proposed is more exact for a given interval of E . Moreover, details of spectra are reproduced well, even if the a parameter is fixed (for atoms of the second period it can be equal to 1.5) and only the b parameter is varied. Within this approach, potentials in molecules NO_2 , CH_3NO_2 and solid compound NaNO_2 have been studied.

Poster no. PS1.13 - Session 1**Theoretical calculations for pre-edge region of Fe K-edge XANES spectrum**Toshihiro Okajima^{1,2}, Yukihiro Nagashima³, and Norimasa Umesaki⁴*(1) Kyushu Synchrotron Light Research Center, 8-7 Yayoigaoka, Tosu, Saga 841-0005, Japan**(2) Faculty of Engineering, Kyushu Univ., 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan**(3) Nippon Sheet Glass Co., Ltd., 2-13-12 Kohnoike, Itami, Hyogo 664-8520, Japan**(4) Japan Synchrotron Radiation Research Institute, 1-1-1 Kohto, Sayo, Hyogo 679-5198, Japan*

X-ray Absorption Near-Edge Structure (XANES) spectroscopy has been widely used for the characterization of the electric structures of condensed materials since it is sensitive to change in their local environment, such as chemical bondings and charges. Recently, many high-resolution XANES spectra of iron in glasses and minerals have been investigated in order to obtain the iron oxidation state from the pre-edge region. The dependence of the position of pre-edge feature on iron oxidation state has been used to determine the iron redox ratio in glasses and minerals. Iron also has long been known to play an important role for color of glasses. Especially, it is important for color and emission of the glasses to understand the state of oxidation of iron. In this study, we calculated theoretical Fe K-edge XANES spectrum by the first-principles one-electron theory using the full-potential augmented plane wave plus local orbital method in order to represent in the pre-edge region of the high-resolution Fe K-edge XANES spectra. We calculated the XANES spectra for four types of local environments of iron. These structures referred to the structure of minerals. That is, ferrous irons were 4 and 6-fold coordinated oxygens and ferric iron were 4 and 6-fold coordinated oxygens. The results showed that the pre-edge region of Fe K-edge XANES region was not represented only by dipolar transitions. In the presentation, we will discuss the XANES spectra taking into account of not only dipolar transitions but also quadrupolar transition.

Poster no. PS1.14 - Session 1**Determining the radial pair distribution function from EXAFS spectra by use of the Landweber iteration method**André Rossberg^{1,2}, and Harald Funke^{1,2}*(1) Institute of Radiochemistry Forschungszentrum Dresden-Rossendorf, P.O. Box 51 01 19, 01314 Dresden, Germany**(2) The Rossendorf Beamline at ESRF, Grenoble, France.*

The Landweber iteration method [1] is used to construct the radial pair distribution function (PDF) from an EXAFS spectrum. The PDF as solution of the fundamental EXAFS integral equation is determined in a stable way without additional supplementary conditions due to the semi-convergent behaviour of the Landweber iteration.

For the correct determination of the PDF it is important to know the energy shift dE0. If dE0 is unknown then usually it is determined by a shell fit of the spectrum before an inversion method is applied. If the shell fit model is incorrect then the determined dE0 is erroneous and an inverse method would give a wrong PDF. This leads in turn to the conclusion that the recent inversion procedures are only applicable if the structural model for the investigated system is already known; hence they are not “stand-alone” methods.

A crucial task is the estimation of the optimum number of iterations, the so called “stopping rule”, or the estimation regularization parameter in the case of the Tichonov method [2]. These parameters can influence the solution strongly.

We developed an algorithm based on the Landweber iteration for deriving the appropriate dE0. The performance was tested by several theoretical and experimental EXAFS spectra of metal hydrates (U(IV), Np(IV), Th(IV), Cm(III)). For the estimation of the optimum number of iterations we adopted the L-curve concept which was recently used for the determination of the optimal regularization parameter in Tichonov’s method [2]. The examples show that the Landweber iteration in combination with the simultaneous determination of dE0 and the L-curve concept for the estimation of the stopping rule is a robust way to calculate the PDF. The approach enables the calculation of the PDF even for strong overlapping shells like for Cm(III) hydrate.

[1] L. Landweber, Am. J. Math. 73, 615 (1951).

[2] M. Kunicke, I.Yu. Kamensky, Yu.A. Babanov, H. Funke, Physica Scripta T115, 237 (2005).

Poster no. PS1.15 - Session 1**Local atomic and electronic structure of germanium impurities in wider-band gap CuGaSe₂ chalcopyrite**Th. Schedel-Niedrig¹, V. Koteski¹, S. Doka-Yamigno², J. Hofstetter², H.-E. Mahnke², E. Arushanov³, and M. Ch. Lux-Steiner²*(1) VINCA, P.O. Box 522, 11001 Belgrade, Serbia**(2) Helmholtz Zentrum Berlin GmbH, Glienicker Str. 100, D-14109 Berlin, Germany**(3) Institute of Applied Physics, Academy of Sciences of the Republic Moldova, Academiei 5, Chisinau 277028, Moldova*

We present here a complementary study on the local atomic and electronic band structure of Germanium atoms as dopants in single and polycrystalline wider-band gap CuGaSe₂ chalcopyrite studied by using extended x-ray absorption fine structure (EXAFS) spectroscopy and ab initio calculations based on the density functional theory. The EXAFS analyses performed at the Ge, Cu and Ga K-edges are consistent with two structural models where the Ge dopants occupy the cationic sites of GeCu or GeGa of the host lattice. The complementary ab initio calculations show good agreement with the EXAFS results and indicate that the incorporated Ge doped atoms preferentially occupy Ga sites when including relaxation around the dopants. Our corresponding theoretical band structure model predicts the existence of additional localized electronic acceptor and donor defect bands in the band gap of CuGaSe₂ originating from a strong covalent interaction between Ge 4s and Se 4p states for Ge atoms tetrahedrally surrounded by Se nearest neighbor atoms (see figure). A theoretically predicted anti-bonding Ge-Se 4sp³ defect band appearing well above the Fermi level for the Ge¹⁺ Ga point defect system can be directly linked to a Ge dopant-related donor-acceptor-pair transition as observed in a recent photoluminescence study.

Poster no. PS1.16 - Session 1**Differences in XANES of isostructural and isoelectronic delafossites**Ondrej Sipr¹, Francesco Rocca², Antonin Simunek¹, and Paolo Fornasini³*(1) Institute of Physics AS CR, Cukrovarnicka 10, CZ-162 53 Prague, Czech Republic**(2) IFN-CNR, Istituto di Fotonica e Nanotecnologie del Consiglio Nazionale delle Ricerche, Sezione "FBK-CeFSA" di Trento, Via alla Cascata 56/C, I-38050 Povo (Trento), Italy**(3) Dipartimento di Fisica, Università di Trento, Via Sommarive 14, I-38050 Povo (Trento), Italy*

Materials with similar structure and with similar chemical properties are expected to yield similar x-ray absorption near-edge structure (XANES) spectra. In our work we analyze Cu K-edge XANES of delafossites CuScO₂ and CuLaO₂. Trigonal (3R) CuScO₂ and CuLaO₂ are isostructural and isoelectronic (Sc and La belong to the same group of the periodic table), hence their Cu K-edge XANES should be very similar. However, significant differences were found in the measured Cu K-edge XANES of 3R CuScO₂ and 3R CuLaO₂. These differences can be understood by considering the calculated polarization dependence of the XANES spectra and the differences between the phaseshifts of Sc and La.

A pre-edge peak appears in the XANES of delafossites around 8980 eV. In the calculated spectra, this pre-peak is present only in the component with the polarization vector lying in the *ab* plane. Our analysis suggests that this pre-peak is connected with scattering of the photoelectron by at least seven Cu atoms in the *ab* plane and fourteen O atoms which linearly coordinate these seven Cu atoms. In this respect the situation is analogous to the case of Cu K-edge XANES of Cu₂O.

Poster no. PS1.17 - Session 1**The role of spin state on the local atomic and electronic structures of some metalloporphyrin complexes**S.A. Suchkova¹, A. Soldatov¹, K. Dziedzic-Kocurek², and M.J. Stillman³*(1) Southern Federal University Zorge str.5 344090 Rostov-on-Don Russia,**(2) Yagellonian University, Krakow, Poland,**(3) University of Western Ontario, London, Ontario, Canada*

The porphyrin molecule is an archetypal metalloorganic complex, which shows up in many biochemical molecules like chlorophyll, haemoglobin and cytochrome. The prospect of switching the spin in the metalloporphyrin ring is a particularly interesting one, as this could be used, for example, for spin-dependent electric transport through biomolecular devices. This molecules can be used in various applications like optical switches, information storage and non linear optics. Here, we study the molecular spin state of chloro-hemin, hemin cyanide and hemin carbonyl molecules by ADF code. Chloro-hemin has been studied by analyzing the Fe K-edge X-Ray Absorption Near Edge Structure (XANES) spectra. At the first stage of investigation we guess for approximate initial geometry, then, we perform the geometry optimization with different molecular spin states and look for configuration with minimal total energy. Method: Density Functional Theory (ADF 2007) Results of geometry optimization of chloro-hemin molecule performed with the GGA OPBE functional, showed that configuration with total spin $S=5/2$ has minimal total energy. This configuration corresponds well with the geometry structure obtained from X-Ray diffraction (Fe-N-N angle is 13.3°) [1]. The similar calculations were carried out for hemin carbonyl and hemin cyanide molecules and showed that for these structures minimal energy is found to be for $S=1/2$. The experimental Fe K-XANES spectra of the investigated compound have been collected. The theoretical analysis of the experimental data has been performed on the basis of two methods: real-space full multiple scattering theory (FEFF8.4 program code); finite difference method (FDMnes2007 program code).

[1] Donald F. Koenig, The Structure of a-chlorohemin, Acta Cryst. (1965). 18, 663

Poster no. PS1.18 - Session 1
Quantum confinement effect in diamond-like Si cluster

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In many works, diamond-like Si clusters are used as models to simulate, and qualitatively describe the local properties of defects and impurities in bulk Si semiconductor. However, in extrapolation from cluster to bulk crystal, one must consider electronic structure varying with clusters' size. In this work, we therefore studied diamond-like Si clusters ranging from Si₁₀H₁₆ to Si₂₆H₃₀ saturated with hydrogen atoms by using the density functional (DF) method. The obtained geometric and electronic properties, such as bond length and angle, binding energy, charge distribution, and HOMO-LUMO gap, both exhibit the cluster-size-dependent feature, which is so-called quantum confinement effect. LUMO in diamond-like Si clusters decreases with cluster size increases, unlike that of diamond-like hydrocarbon in which the LUMO is nearly constant with cluster size variation. We further investigated the dependency of electronic properties of Si₂₂H₂₈ and Si₂₆H₃₂ on their corresponding isomer shapes, and found the strip-like isomer has the lowest energy gap compared with other isomers for both clusters. These results were also confirmed by the time dependent density functional (TDDF) and Slater transition potential (TP) method.

Data analysis

Poster no. PS1.19 - Session 1
The assignment of edge peak in Ag (I) XANES

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A peak appearing at L_{2,3} x-ray absorption edge often provides the amount of empty d states of the x-ray absorbing atoms. Monovalent Ag compounds formally have a d¹⁰ state (no d empty states) but always show a small but distinctive peak at the edge. In this paper we systematically study the edge peak of Ag⁺ compounds in order to understand its origin based on the molecular orbital picture. The edge peak can be formally assigned to the transition from 2p to 5s or the ligand empty state, which is enhanced by the hybridization of Ag d orbitals through three promotion mechanisms: 1: backdonation of d electrons to the empty states of the ligand, 2: simple s-d hybridization of Ag 4d and 5s, 3: s-d hybridization with two-electron excitation for compounds with high symmetry. The origin of the peaks can be mostly assigned to the second mechanism. The peak intensity has a negative correlation with electronegativity and has a positive correlation with the strength of the covalent bond and/or softness of the ligands.

Poster no. PS1.20 - Session 1**Resolution of interatomic distances by Fourier-transform analysis of energy restricted XAFS in amorphous and disordered compounds**Lusegen A. Bugaev¹, Leon A. Avakyan, Vasilii V. Srabionyan, and Aram L. Bugaev*(1) Department of Physics, Southern Federal University, Zorge str. 5, 344090 Rostov-on-Don, Russia*

The application of the criterion for signals frequencies resolution within the problem of close interatomic distances determination by the Fourier-transform analysis of energy restricted X-ray absorption spectra is studied. Combinations of different model signals in wave numbers (k) space, characterized by the distances R , not distinguished a priori according to this criterion $\delta R = (1 - 1/N_{idp}) \cdot \pi / (2\Delta k)$ (δR – distances resolution, N_{idp} – the number of signal's independent parameters, Δk – length of the signal in k -space) are considered. By this analysis it is revealed that if the fitting procedure employs the form of the criterion function, similar to the functional form of the studied signal (as we have in X-ray absorption spectroscopy) then the proposed scheme of the fit of the Fourier-peak of coordinating atoms around the absorbing one [1] permits to identify the model of local structure distortions in amorphous and disordered compounds, with the difference in interatomic distances ($\delta R = 0.03 \text{ \AA}$ for $\Delta k = 3 \text{ \AA}^{-1}$), which is of \sim ten times smaller than its value, estimated by the general criterion of resolution.

[1] L. Bugaev, L. Avakyan, M. Makhova, and I. Alekseenko, *Optika Spektroskopiya* 105, 962 (2008).

Poster no. PS1.21 - Session 1**Systematic Errors in Speciation Studies by XAFS**Grant Bunker¹, and Firouzeh Tannazi²*(1) Illinois Institute of Technology, 3301. S. Dearborn, Chicago, IL 60616**(2) Neuroradiology Division, Johns Hopkins University, Baltimore, MD, USA*

XAFS is widely used for determining chemical speciation in environmental samples in their natural state. In this work we identify and quantify serious systematic errors arising from incorrect models of photon migration in complex granular media. Monte Carlo and analytical results will be presented that indicate special caution must be taken when interpreting results of such *in situ* experiments. Potential solutions to these problems will be proposed.

Poster no. PS1.22 - Session 1**Polydispersity and XAFS simulations**Sebastiano Cammelli^{1,2}, C. Degueldre¹, G. Kuri¹, J. Bertsch¹, D. Lützenkirchen-Hecht², and R. Frahm²*(1) Paul Scherrer Institute Villigen PSI 5232 Villigen Switzerland**(2) Fachbereich C- Abteilung Physik Bergische Universität Wuppertal Gaußstraße 20D - 42097 Wuppertal*

Nanoclusters are important for catalysis and nuclear industries [i], and EXAFS is an important experimental technique for determining their local atomic structures. In practical cases samples do not contain homogeneous clusters of just one size. The determination of average cluster sizes is strongly influenced by the specific distribution of cluster sizes. Combinations of different cluster sizes might provide very similar results; this issue is called polydispersity. It has already been pointed out by Moonen et al. [ii] that fcc clusters of 147 atoms have the same amount of atoms in the first and second shells (8.9 and 4) as combination of clusters composed of 13 (32%) and 1415 (68%) atoms. In this case, according to their study, experimental data analysis cannot do anything to solve this problem. The first detectable difference appears in the 3rd shell where the linear composition shows 13.8 atoms and the 147 atoms cluster reveals only 13.0 atoms. However, this difference is very hard to determine even if high quality data are available. An improvement in the determination of the mean size and shape of small particles by EXAFS was done by A. Jentys [iii], who provided an empirical method to calculate the coordination numbers in the first five shells as a function of the total number of atoms involved in the cluster. This study shows that EXAFS could provide an accurate estimation of the cluster mean size only if it consists out of less than 150 atoms. The goal of this study is to understand if there are any principal limitations related to polydispersity. Here a new approach based on EXAFS simulations followed by linear combination (LC) on EXAFS spectra is presented. The simulations were performed on monoatomic Cu clusters and biatomic Cu - Fe clusters. The main result of this study concerns the possibility to overcome the polydispersity issue for nanoclusters with less than 140 atoms for the monoatomic case.

Poster no. PS1.23 - Session 1**Databases for absorption, XAFS and XANES, and future opportunities for research and investigation**Christopher Thomas Chantler¹*(1) University of Melbourne School of Physics 3010 Parkville Victoria Australia*

Databases for absorption include the IUCr data, particularly of Creagh, Hubbell and Maslen et al.; the XCOM data of Hubbell and Scofield et al.; and the recent XERT database of Chantler. Others exist, whether particularly for isolated atoms, diffraction, or condensed matter. The needs of XAFS and XANES have often been somewhat different, for example needing fine spacing near absorption edges and the ability to take account of hole widths, discrete excitations, shake transitions and chemical environments to name a few. Typically, this relates to a programming environment rather than a database, and two particular examples are provided by FEFF and FDMNES. Key purposes and applications of these packages will be discussed, and a little about how they should or should not be used.

Poster no. PS1.24 - Session 1**Asymmetry of distance distributions from path-integral Monte Carlo simulations**Paolo Fornasini¹, and S. A. Beccara¹*(1) University of Trento - Dept. Physics Via Sommarive 14 I-38100 Trento Italy*

The relation between bond thermal expansion, measured by the first EXAFS cumulant, and asymmetry of the distribution of interatomic distances, measured by the third cumulant, is still a controversial issue [1,2]. Accurate experimental information can be obtained only for the first-shell, the analysis of the outer shells being complicated by multiple scattering effects.

Path-integral Monte Carlo calculations using a semi-empirical many-body potential were able to reproduce the first-shell experimental cumulants of copper as a function of temperature [3]. The calculations have now been extended to include the first four coordination shells of copper [4] and of gold. One finds that the asymmetry parameter $\beta = C_3^*/(C_2^*)^{3/2}$ is much smaller for the outer shells than for the first shell, while the maximum value of the distributions of distances of the outer shells undergoes a non-negligible positive shift when temperature increases.

The bond thermal expansions not only depend on the asymmetry of the distributions of distances, but also on their shift, the dependence being different for different shells. This result indicates that the third cumulant cannot be used to evaluate the thermal expansion, and suggests that the error caused by neglecting the third cumulant in the EXAFS analysis is less important for the outer shells than for the first shell.

[1] M. Vaccari et al. Phys. Rev. B75, 184307(2007)

[2] F. D. Vila et al. Phys. Rev. B76, 014301(2007)

[3] S. a Beccara et al., Phys. Rev. B68, 140301(2003)

[4] S. a Beccara and P. Fornasini, Phys. Rev. B77, 172304 (2008)

Poster no. PS1.25 - Session 1**Predetermining acceptable noise limits in EXAFS spectra in the limit of stochastic noise**Yung-Jin Hu^{1,2}, and Corwin H. Booth²*(1) University of California, Berkeley 419 Latimer Hall 94720-1460 Berkeley CA USA**(2) Lawrence Berkeley National Laboratory One Cyclotron Road 94720-8169 Berkeley CA USA*

The effect of stochastic noise on Extended X-ray Absorption Fine Structure (EXAFS) data measurement, analysis, and fitting are discussed. Stochastic noise reduces the ability to uniquely fit a calculated model system to measured EXAFS data. Such noise can be reduced by common methods that increase the signal-to-noise ratio, such as increasing scan time, beam flux, or the concentration of the element of interest in the sample. However, these methods are not always practical, for instance, when one cannot arbitrarily increase the absorbing species concentration. Therefore, predetermined quantitative knowledge of how much stochastic noise is acceptable when fitting for a particular model system is essential to maximizing the chances of a successful EXAFS experiment and minimizing wasted beamtime. This paper outlines a method to estimate, through simulation, the acceptable level of stochastic noise in an EXAFS spectra to successfully fit a proposed model compound.

Poster no. PS1.26 - Session 1**Arsenic local structure in iron(III)-arsenate co-precipitates**De-Tong Jiang¹, and Ning Chen^{2,3}*(1) Department of Physics, University of Guelph, Guelph, ON N1G 2W1 Canada**(2) Canadian Light Source, Saskatoon, SK S7N 0X4 Canada**(3) Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK S7N 5E2 Canada*

Iron(III)-arsenate co-precipitation is a common method for arsenic immobilization in industrial metallurgical process solutions. Under the condition of termination pH values lower than 8 and room temperature, the co-precipitates possess a poorly-crystalline scorodite structure [1]. Using non-linear least-square curve-fitting in both the k-space and R-space for the arsenic K-edge XAFS data, some generalities of the arsenic local structure in the iron(III)-arsenate co-precipitates are investigated. In particular we discuss the advantages of analyzing the Fourier transform data in R-space to identify the multiple-scattering contribution from the paths within the arsenate tetrahedron. We show that the analysis including the multiple-scattering paths results in consistent structural parameters for the second nearest neighbor As-Fe shell in such systems from either the k-space or the R-space curve-fits and helps to delineate viable local structure models proposed for the iron(III)-arsenate co-precipitates.

[1] N. Chen, D.T. Jiang, J. Cutler, T. Kotzer, Y.F. Jia, G.P. Demopoulos, and J.W. Rowson, *Geochim. Comochim. Acta* (in press).

Poster no. PS1.27 - Session 1**Interpretation of EXAFS in ReO₃ using Molecular Dynamics simulations**Aleksandr Kalinko¹, Robert A. Evarestov², Alexei Kuzmin¹, and Juris Purans¹*(1) Institute of Solid State Physics, University of Latvia, Riga, Latvia**(2) Department of Quantum Chemistry, St. Petersburg University, Russian Federation*

Analysis and interpretation of disorder effects in the presence of multiple-scattering contribution in EXAFS signal is still a challenging task. This problem can be overcome combining the ab-initio EXAFS theory with molecular dynamics (MD) simulation. The key task in such an analysis is developing an appropriate force-field (FF) potential model. The latter is further used in the MD simulation at required temperature to generate a set of atomic configurations. These configurations are finally used to compute the averaged EXAFS signal, which is compared with the experimental one. In this work we apply the combined MD-EXAFS approach to the analysis of the Re L₃-edge EXAFS spectra in cubic perovskite ReO₃. The simple FF potential model, taking into account two-body Re-O and O-O interactions, was chosen. The FF potential parameters were optimized to obtain good agreement with available experimental values of lattice constant and elastic constants, and with the phonon frequencies, calculated by ab-initio quantum chemistry frozen phonon method. The hybrid B3PW exchange-correlation potential calculations are performed for the 2x2x2 supercell reproducing the phonon frequencies at high symmetry points of Brillouin zone. The MD simulations were performed for a supercell 5x5x5, containing 500 atoms, at temperatures 300K, 423K and 573K. The configuration averaged EXAFS signals were calculated and compared with experimental data from [1] in the ranges $k=2-18 \text{ \AA}^{-1}$ and $R=0-6 \text{ \AA}$. Temperature dependence of EXAFS spectra is well reproduced and allows determination of thermal disorder effects (Debye-Waller factors) for any scattering path. Besides, this approach reduces gradually the number of model parameters, which are solely determined by the FF potential model.

[1] J. Purans, G. Dalba, P. Fornasini, A. Kuzmin, S. De Panfilis, F. Rocca, *AIP Conf. Proc.* 882 (2007) 422.

Poster no. PS1.28 - Session 1**Comparison of EXAFS spectra of simple metal foils**

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Many years ago in early EXAFS experiments, constant amplitude reduction factors S_0^2 based on the absorbing atom were tabulated and proposed useful for all EXAFS measurements of the absorbing atom. However this methodology has not been adopted because of differences in beamline parameters and samples were found to affect the value for S_0^2 . Often the current methodology for determining the best value for S_0^2 is to measure standards such as simple metal foils in the same detector geometry and with the same beamline parameters as that of the unknown sample. EXAFS beamlines have evolved since the early experiments such that it could now be feasible to use standard S_0^2 values for all EXAFS measurements of a specific element. To test this concept, we compare the EXAFS spectra of Cu (and other) metals from several different beamlines and synchrotrons to address the dependence of S_0^2 values on beamline specific parameters. The S_0^2 values are determined from the EXAFS spectra of several metal foils to 5 Å with a minimum of EXAFS parameters.

Poster no. PS1.29 - Session 1**Derivative pre-edge and virtual bound state continuum O K-edge XAS spectra of “immobile” and mobile TiO₂ (mono-) vacancies and HfO₂ divacancies**

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Spectroscopic studies of XAS O K-edge spectra discriminate between mono- and di-vacancy bonding, as well as mobile and immobile vacancies. Spectral assignments are based on differentiating O K-edge spectra in the two X-ray energy regimes that bracket conduction band states: (i) the pre-edge regime below the conduction band edge, and (ii) the virtual bound state regime above the conduction band. The underlying quantum mechanics for this approach is that two electrons bound to each empty O-atom bonding site must occupy d-state orbitals on the Ti or Hf atoms digitally, rather than statistically. Therefore, electronic states of vacancies are described by equivalent transition metal (TM) atomic states occupied in high spin configuration dn stacked arrangements. These defect states are qualitatively similar to occupied Mn³⁺ states in LaMnO₃: 4 occupied 3d states in a high spin configuration at the valence band edge. 3-fold coordinated O-mono-vacancies in TiO₂ are represented by an equivalent Ti d2 state. Doublet features are obtained from 2nd derivatives of O K edge spectra in the (i) pre-edge regime below as final state features of intra-spin crystal field split d to d' transitions, and (ii) in the continuum region above the conduction band as final states in anti-bonding d to d* transitions. There are two distinct pairs of d2 states: one with a 0.5 eV energy spread assigned to immobile vacancies within nano-grains, and a second with a smaller spread of 0.24 eV assigned to mobile vacancies at internal grain boundaries and/or nano-grain edges. Qualitatively similar spectra are obtained for immobile and mobile divacancies in HfO₂. The respective spectral width of the four discrete mobile divacancy features is 1.15 eV, and smaller than the 0.82 eV spectral width of immobile divacancy features. The smaller spectral widths of the mobile vacancy features reflect a reductions in Ti neighbors for the Ti mono-vacancies, and from Hf neighbors for Hf divacancies.

Poster no. PS1.30 - Session 1**MAX : multiplatform application for x-ray absorption**Alain Michalowicz^{1,2}, J. Moscovici^{1,2}, D. Bouvet-Muller^{1,2}, and K. Provost^{1,2}*(1) Institut de Chimie et des Matériaux Paris Est (ICMPE) CNRS, 2-8 rue Henri Dunant 94320 Thiais France**(2) Université Paris 12 Val de Marne-Paris Est 61 avenue du Général De Gaulle 94010 Creteil France*

MAX[1] is a new EXAFS and XANES analysis package written in a multiplatform language, Transcript for Runtime Revolution. Available, with exactly the same code for Macintosh OSX, Windows (XP and Vista), LINUX, with automatically system adapted user interfaces. Online helps and tutorials for CHEROKEE and RoundMidnight

1) ABSORBIX : Calculates X-ray absorbance of pure and diluted samples, and optimize samples concentrations and thickness for X-ray absorption experiments.

2) CHEROKEE : complete treatment of EXAFS and XANES data. Reads and treat any XAFS data text file. EXAFS extraction : pre-edge-edge jump determination, atomic background subtraction (polynomials, cubic splines and splines smoothing), energy dependent EXAFS normalization Fourier transform and filtering, signal/noise evaluation. XANES normalization.

3) ROUNDMIDNIGHT : EXAFS fitting, based on CERN MINUIT minimization code. EXAFS modeling of single and multiple scattering paths with the standard EXAFS formula, using the FEFF scattering paths expansion. FEFF files or free format for phases and amplitudes. FEFF or empirical mean free path. Parameters restrains and constrains. Improved statistical treatment, error estimation, and quality of fit analysis. Easy-to-use graphical user interface (RoundMidnightRev) in front of the FORTRAN fitting code (RoundMidnightFit). New : comparison and fit of FEFF multiple scattering models to complete unfiltered EXAFS spectra in k and R-spaces.

4) CRYSTALFFREV : From crystal structures and molecular modeling to FEFF 7 and 8 input files for EXAFS multiple scattering expansion and XANES full multiple scattering. Accepts PDB and CIF input file formats. Cluster orientation. Random distributions of vacancies and substituted species.

Available on our web site : www.icmpe.cnrs.fr -> SAX group-> Software downloading page.

[1] <http://xafs.org/Software>

Poster no. PS1.31 - Session 1**Changes in local structure of Fe(II) ion in water and acetone based electrolytes**Wojciech Olszewski¹, Krzysztof Szymański¹, Piotr Zaleski¹ and Dariusz A. Zajac^{2,3}*(1) Faculty of Physics, University of Białystok, Lipowa 41, 15-424 Białystok, Poland**(2) Deutsches Elektronen-Synchrotron-HASYLAB, Notkestrasse 85, 22607 Hamburg, Germany**(3) H. Niewodniczański Institute of Nuclear Physics of PAN, Radzikowskiego 152, 31-342 Kraków, Poland*

Electrodeposition of metallic layers has a wide range of technical applications. Commonly used aqueous electrolytes are not appropriate in case of chemically reactive metallic layers like Rare Earths, aluminium or alkaline metals.

We have found a method of electroplating shiny 3d metallic layers (Fe, Co, Ni, Cu and Zn) from electrolyte, which consists mainly of acetone. Small concentration of cations (about 0.03 M) and the same current conditions of deposition for each element make this deposition method promising for applications.

At the initial stage of the experiments we have noticed some differences in deposition process for conventional aqueous and acetone electrolytes. Thus we decided to investigate solutions by XAFS to see the possible differences in local structure of the cations. We hope that this may help in understanding the kinetic properties of chemical reactions during deposition processes.

XAFS measurements were performed at Fe K edge at HASYLAB E4 beamstation. The experiment included measurements of solutions with different acetone concentration. For wide range of concentration we observe only slight changes in absorption curves. But from some threshold acetone concentration we note the significant differences, present at extended as well as at near absorption edge region. Our results indicate that there is a change of local structure of 3d cations.

Although acetone based electrolyte contains small amount of water, crucial for electrodeposition process, local structure of Fe(II) ion differ from that of Fe(II) in water solutions. The investigation of local iron ion structure in acetone based solution are in progress.

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Poster no. PS1.32 - Session 1**CARD: the implementation of a new method to analyze RefEXAFS data**

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Nowdays engineering new materials with specific surface properties needs nano-scale chemically selective and surface sensitive characterization techniques. Extended x-ray absorption fine structure collected in reflection mode at glancing incidence angles (RefEXAFS) is a well known technique that satisfy all these requirements. Due to the dependence of the reflectivity on both the real and imaginary part of the refractive index, the oscillations that appear in RefEXAFS spectra are not simply connected to the absorption coefficient and this has limited up to now the use of this potentially useful technique.

In this contribution we present a novel fast and automated method [1] implemented in the program CARD (Code for the Analysis of Reflexafs Data). The procedure calculates the theoretical fine structure signals appearing in the reflectivity spectrum starting from the *ab initio* calculations (ex. FEFF paths). The corrected signals can then be used in complex structural refinement (i.e. also including multiple scattering paths) with usual fitting programs of EXAFS data. The first model implemented within this method is a film on a substrate and is applied on a test case of a gold film, comparing the fit results of measurements taken at several grazing angles with a standard transmission measurement of a Au foil. The code is written in Python using iEffit libraries, presents a graphical user interface and is distributed to the community under open source license.

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Poster no. PS1.33 - Session 1**Local atomic and electronic structure of ZnO:Nd**

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New method of multidimensional interpolation [1] is applied to the analysis of X-ray absorption near edge structure (XANES) spectra at the Nd M5- and O K-edge in ZnO films doped with rare earths (Nd) with different doping concentrations [2]. All these spectra were measured at the Pohang Accelerator Laboratory (PAL), Korea, in the KIST beamline by the total-electron yield mode. Changing in the shape of the O K-edge XANES indicates incorporation of rare earths ions into semiconductor lattice with increasing of doped concentration, while the Nd M5-edge XANES spectra are almost similar for all doping concentration [2]. Full multiple scattering theory (FEFF8.4 code) was used for the theoretical simulations of XANES spectra. Several possible positions of a single rare earth ion in ZnO lattice have been tested. We have found that the Nd M5-XANES spectrum is clearly depends on parameters of the local atomic structure around Nd atom (i.e. interatomic distances to first and second nearest neighbor atomic shells). Both substitution and octahedral intestinal sites are probable starting models for analysis of the Nd and Nd M5-edges. Similar approach is applicable to other trivalent rare earth ions like Gd doped ZnO. The structural parameters were refined using multidimensional approach as implemented in FitIt2.0 code [1]. It is possible to use this method of multidimensional interpolation for the investigation of the materials with not well-known geometry. This work was partially supported by RFBR (Russia) grant # 07-02-91687 and Russian Ministry of Education by grant RNP 2.1.1.5932

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Poster no. PS1.34 - Session 1**Further steps towards automatic treatment of BioXAS data: *KEMP 2* and *ABRA***Gerd Wellenreuther¹, and Wolfram Meyer-Klaucke²

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In the recent years we developed software tools for the automatic treatment of BioXAS data. Data reduction and quality control is covered by *KEMP* [1], which now has been made available as a modularized and beamline-independent version *KEMP 2* [2]. Automatic data refinement and analysis for typical biological metal ligands is performed on the EMBL-Hamburg computer cluster by *ABRA* [3]. In combination, these packages quickly provide the user with a first estimate of the binding motif, requiring only raw XAS data measured in fluorescence mode.

KEMP 2 includes averaging of individual scans, a check for photo reduction, background subtraction and normalization as well as the extraction of EXAFS and XANES. Special emphasis has been on the straightforward use for non-experts and the easy adoption of different data formats.

ABRA attempts to fit any given spectrum with combinations of the generic binding motif $S_x\text{His}_y\text{O}_z$. In order to properly sample the entire coordination space typically different 400 structural models are refined and analysed. The quality of each model is judged not only based on the quality of the individual refinement (e.g. χ^2), but also on expert knowledge like ideal bond distances, bond-valence sum analysis, quality of Debye-Waller factors and Fermi-energy. An additional meta-analysis suggests the most-likely binding motif and provides errors margins for the occupancy of individual ligands.

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Disordered systems**Poster no. PS1.35 - Session 1****Local atomic structure around Ni, Nb, and Zr atoms in Ni-Nb-Zr-H glassy alloys**Shuichi Emura¹, Hiroshi Oji^{2,3}, Katsumi Handa⁴, Junko Ide⁴, Tetsuo Honma², Norimasa Umesaki², Shinichi Yamaura⁵, Mikio Fukuhara⁵, and Akihisa Inoue⁵,

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Recently, the proton-tunneling-induced Coulomb oscillation has been observed in the hydrogenated Ni-Nb-Zr glassy alloys [1], whose metal alignment has not been resolved, and the mechanism of this phenomenon is not clear yet. The structural model can give the basic information for the phenomenon of the proton-tunneling-induced Coulomb oscillation, and to elucidate the hydrogen effect on the atomic configuration in the Ni-Nb-Zr glassy alloys, we measured Ni, Nb, and Zr K-edges X-ray Absorption Fine Structure (XAFS) spectra of the Ni-Nb-Zr glassy alloy films with two different chemical compositions, i.e. Ni₄₂Nb₂₈Zr₃₀ (Zr₃₀-H0) and Ni₃₆Nb₂₄Zr₄₀ (Zr₄₀-H0), and their hydrogen-charged ones, i.e. (Ni₄₂Nb₂₈Zr₃₀)_{0.91}H_{0.09} (Zr₃₀-H9) and (Ni₃₆Nb₂₄Zr₄₀)_{0.89}H_{0.11} (Zr₄₀-H11). The resultant XAFS spectra of these samples deduce that there is the significant difference in the structural response between the Zr₃₀at% and the Zr₄₀at% alloys when hydrogen atoms are charged [2]. The curve-fitting analysis indicates that the hydrogenation does not alter the local alignment around the three metal atoms for the Zr₃₀ alloy, but for the Zr₄₀ alloy, elongate the inter-atomic distances of Zr-Zr, Zr-Nb and Nb-Ni. On the basis of the curve fitting results, we propose the distorted icosahedral Zr₅Ni₅Nb₃ cluster models.

The XANES spectra, which are richer in structural information than XAFS, at each (Ni, Zr and Nb) edge of Zr₄₀-H11 present the distinct shape from the other samples. The edge shoulder vanishes or weakens, suggesting the conversion of the electronic state of the metal ions owing to the hydrogenation. The post-edge energy region shows clear multi-scattering effect by charging hydrogen atoms., and the hydrogen position may be able to be decided. In this conference, we will mainly discuss on the hydrogen effect based on XANES spectra.

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Poster no. PS1.36 - Session 1**NEXAFS study on annealing temperature dependence of hydrogenated amorphous carbon films**Yuichi Haruyama¹, Masahito Tagawa², Kumiko Yokota², and S. Matsui¹*(1) University of Hyogo 3-1-2 Kouto, Kamigori 678-1205, Ako, Japan**(2) Graduate School of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe, Hyogo 657-8501, Japan*

Since amorphous carbon thin films have interesting properties such as high hardness, low friction coefficient, and chemical inertness, the study of amorphous carbon thin films has attracted a great deal of attention for wide applications [1-2]. In order to produce good amorphous carbon films, various vapor phase methods have been extensively attempted so far, and the properties of the hydrogenated amorphous carbon (a-C:H) films formed by vapor phase methods have been studied. In the previous studies using Raman and Auger electron spectroscopy, the a-C:H films were thermally stable up to 533 K [3]. However, it was pointed out that the thermal stability in the a-C:H films was not good at more than 573-673 K due to the hydrogen desorption and the graphitization of a-C:H films [3].

In the presentation, the electronic structure in a-C:H films was investigated as a function of the annealing temperature using near edge X-ray absorption fine structure (NEXAFS) spectra. After annealing at 473 K, no clear change was observed. With increasing annealing temperature at 673 K, a peak appeared at 295.0 eV. With further increasing annealing temperature at more than 873 K, NEXAFS spectra in the a-C:H film were observed to be similar to that in graphite. The NEXAFS results suggest that the graphitization of the a-C:H film proceeds by annealing at more than 673 K. From the evolution of the NEXAFS and photoemission spectra on the annealing temperature, the thermal changes in a-C:H films are discussed.

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Poster no. PS1.37 - Session 1**A neutron diffraction, X-ray diffraction, Molecular Dynamics and EXAFS study of the rare earth ion coordination in rare-earth gallate glasses**Pinit Kidkhunthod¹, and A. C. Barnes*Department of Physics University of Bristol BS8 1TL Bristol United Kingdom*

Recently we have prepared some new pure rare-earth gallate glasses $\text{Re}_2\text{O}_3\text{-Ga}_2\text{O}_3$ using aerodynamic levitation and laser heating. The materials are of interest with regard to their optical properties. The aim of this study was to investigate the rare-earth coordination at both the local and intermediate range using a combined multi-technique approach. EXAFS measurements are sensitive to the local rare-earth coordination whereas neutron and X-ray diffraction give good information about the intermediate range rare-earth to rare-earth correlations. Analysis of the EXAFS results using conventional methods based on local cluster models did not give a good agreement with the data. In this poster we present a comparison of our EXAFS results with calculations based on: a Molecular Dynamics (MD) simulation of the glass using standard Buckingham potentials and a Reverse Monte Carlo (RMC) refinement of this MD configuration to obtain agreement with the X-ray and diffraction data. The results show a better agreement with the EXAFS data with an improvement noticed for the RMC refined data. The ultimate aim is to simultaneously refine the MD configuration with both diffraction and EXAFS data.

Poster no. PS1.38 - Session 1**Local structure of arsenic-doped amorphous selenium**John A McLeod¹, Alex Moewes¹, Safa O. Kasap², Robert Johanson², George Belev², Dan Tonchev², Ning Chen³*(1) Department of Physics and Engineering Physics, University of Saskatchewan, S7N 5E2, Saskatoon, SK, Canada**(2) Electrical Engineering Department, University of Saskatchewan, S7N 5A9, Saskatoon, SK, Canada**(3) Canadian Light Source, University of Saskatchewan, S7N 0X4, Saskatoon, SK, Canada*

Amorphous selenium (a-Se) is used in commercial direct conversion X-ray image detector (DCXID) in medical imaging applications. These devices provide rapid, high-resolution, digital X-rays. Under normal operation conditions, the a-Se in the DCXID spontaneously crystallizes, and crystalline Se is unsuitable for use as a photo-conductor since small crystalline grains in the panel cause information loss in the image. It has been found experimentally that doping with low concentrations of arsenic (around 0.2% As by atomic concentration) will retard the rate of crystallization, but the mechanism is not understood. We have studied the local structure of As-doped a-Se using extended X-ray absorption fine structure (EXAFS) spectroscopy at the As and Se K-edges, and supplementary soft X-ray emission and absorption spectroscopy at the As and Se M_{4,5}-edges. A full data set from a-Se samples with a broad range of As-doping concentrations (0%, 0.2%, 0.5%, 2%, 6%, 10%, 19%, 39%) and poly-crystallinity (achieved by baking samples at various temperatures above the glass transition temperature) has been collected. Based on analysis of the data using EXAFS scattering curve fitting and density functional theory calculations we propose a model for the inclusion of As-dopants into a-Se and the impact this has on long-range crystallization from the perspective of the local structure near the As-dopants.

Poster no. PS1.39 - Session 1**A first step toward understanding nucleation processes: in situ high-temperature X-ray diffraction and absorption investigations**Daniel R. Neuville¹, E. Strukelj¹, B. Cochain¹, L. Hennet², D. Thiaudière³, B. Guillet⁴, M. Roskosz⁵, M. Comte⁶, J.P. Itié³, and P. Richet¹*(1) CNRS-IPGP 4 place Jussieu 75005 Paris France**(2) CEMHTI-CNRS, Orleans**(3) SOLEIL, Orme des cerisiers, St Aubin**(4) Laboratoire de Physique Theorique de la Matiere Condensee, Université Pierre et Marie Curie (Paris 6), UMR CNRS 7600, 4 place Jussieu, 75252 Paris Cedex 05, France**(5) LPTSE, Université de Lille, Villeneuve d'Ascq**(6) Corning SAS CETC 77210 Avon*

Nucleation is the first step of the transition between the amorphous and crystalline states and thus plays a key role in Earth and Materials sciences whenever crystallization takes place. In spite of its considerable importance in igneous petrology and industrial applications (ceramics, glass-ceramics, etc.), nucleation remains known poorly because of the difficulties of investigating the structural rearrangements that take place at a nm scale when an ordered atomic packing begins to develop in a melt. In addition, the structure of amorphous phases is not only difficult to determine, but the wealth of information available for glasses is not necessarily applicable to nucleation because of the existence of temperature-induced structural changes in melts. In view of the basic geological and industrial importance of the SiO₂-Al₂O₃-CaO system, we have investigated a calcium aluminosilicate whose crystallization has already been studied. And because elements such as Ti or Zr can promote rapid nucleation, information can be gained about the structural changes they induce by probing specifically their own environment. In this work we have thus performed a high-temperature study of the very first steps of crystallization in a calcium aluminosilicate with 7 mol % ZrO₂ by X-ray absorption measurements at the Zr K-edge at 1873 K on the homogeneous melt and 1173 K on a nucleating supercooled liquid. To complement these results with information on medium range order (MRO) X-Ray diffraction experiments have also been performed under the same conditions. As a reference, the glass has been investigated by both techniques at room temperature.

Poster no. PS1.40 - Session 1**Measurement of magnetostrictive bond strain in a-TbFe₂**

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In rare earth-transition metal compounds, the huge anisotropy of the 4f electron cloud, the high moment, and the high Curie temperature, lead to large magnetostriction at room temperature [1]. In these systems, when the orientation of the magnetic moment of the 4f shell is rotated with respect to the crystallographic axes by an external magnetic field, it is assumed that the anisotropic 4f charge density is rigidly co-rotated and atomic displacements from the equilibrium positions are expected to occur. Internal distortions in TbFe₂ were predicted 40 years ago [2] but to date have not yet been detected.

With the aim of elucidating the atomic origin of the giant magnetostriction observed in rare earth (RE) Fe₂ compounds, we have initiated an EXAFS study at the Fe K and at the RE L₃ absorption edges on amorphous RE-Fe₂ films such as TbFe₂, DyFe₂ and TbDyFe₂, in the attempt to identify and eventually quantify magnetostrictive atomic displacements in these compounds. This has been made possible thanks to recent developments which have enabled the measurement of femtometer atomic displacements [3].

Here we present first measurements of Fe-Fe and Fe-Tb magnetostrictive bond strain obtained on an amorphous Tb₂₈Fe₇₂ film, using linearly polarized X-rays and the energy dispersive X-ray Absorption Spectroscopy beamline ID24 at the ESRF [4]. This work represents the first application of these new methods to the investigation of amorphous matter.

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Poster no. PS1.41 - Session 1**Amorphous SiO studied by non-resonant x-ray Raman scattering**

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Amorphous silicon monoxide, i.e. a-SiO_x with $x \approx 1$, has been studied intensively over the past years due to its relevance for micro- and opto-electronic applications. It serves as a starting material for the production of Si nanocrystals in oxide matrices. Native a-SiO shows a temperature-induced disproportionation. During annealing regions of Si and SiO₂ grow by coalescence at the cost of the sub-oxides (Si(Si_{4-x}O_x) with $x = 1, 2, 3$) contained in the bulk material. This results in a formation of Si nanocrystals. The disproportionation and nanocrystal formation is investigated in the temperature range between 600 °C to 1200 °C by means of non-resonant inelastic x-ray scattering (NRIXS) at the Si L_{2,3}-edges and x-ray diffraction (XRD), respectively. NRIXS, also often referred to as x-ray Raman scattering (XRS), is sensitive to the change in the sub-oxide content in the annealed samples so that the disproportionation can be characterized. The sub-oxide contribution to the XRS spectra is extracted and compared with state of the art calculations based on molecular dynamics simulation of Si nanocrystals embedded in a SiO₂ matrix. The experimental results imply a structure of the native a-SiO in which regions of Si and SiO₂ are separated by ultra thin sub-oxide interfaces.

Poster no. PS1.42 - Session 1**Phase separation and nanocrystal formation in GeO**

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Bulk amorphous germanium monoxide (α -GeO_x with $x \approx 1$) is studied both in and ex situ regarding the temperature-induced disproportionation, i.e. phase separation of GeO_x into Ge and GeO₂. The formation of Ge nanocrystals was investigated by XANES/EXAFS at the Ge K-edge employing fluorescence yield detection and also by X-ray diffraction (XRD) at the wiggler beamlines BL8 and BL9 of the 1.5 GeV synchrotron radiation source DELTA. The study of group IV semiconductor nanostructures has attracted much attention in recent years. Especially germanium/oxygen systems, analogous to silicon/oxygen systems, are an interesting class of materials due to their potential as precursors for the synthesis of Ge (Si) nanocrystals in an oxide-matrix. Because of their charge-retention properties and their visible photoluminescence, these structures are relevant regarding the search for new opto- and microelectronic devices. Additionally, freestanding group IV semiconductor nanocrystals have been used as diagnostic agents in proof of principle experiments. Here, their non-toxicity is of considerable advantage over current compound semiconductor analogs.

The disproportionation of α -GeO_x was characterized in the temperature range between 160 and 640 °C. The onset and end temperature for the phase separation can be determined to be 250 and 440 °C, respectively. Moreover, the in situ experiments yield information about the time dependence of the phase separation process. XRD proves the occurrence of Ge nanocrystals of several nanometers in diameter embedded in a GeO₂ matrix for temperatures above 500 °C. These findings are consistent with a structural description of α -GeO within a model in which the native amorphous monoxide is proposed to be a frozen non-equilibrium system of a disproportionation in the initial state similar to the case of amorphous SiO.

Poster no. PS1.43 - Session 1**Swift heavy ion irradiation induced porosity of GaSb: correlation between local atomic environment and micro-structural evolution**

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We report on X-ray absorption fine structure (XAFS) measurements of GaSb which was subjected to swift heavy ion (SHI) irradiation. Irradiation was performed on 2 micrometer thin GaSb layers grown on InP by metal organic chemical vapor deposition, using 185 MeV Au ions. At this energy, the energy transfer to the GaSb is virtually entirely due to interactions with the target electrons, i.e. ballistic collisions are negligible. The irradiation renders GaSb porous and, when performed under an angle of 45 degrees with respect to the surface normal, plastic flow of the material is observed in the direction of the projection of the ion beam. The latter has previously only been observed for amorphous materials, however, XAFS measurements reveal residual crystallinity after irradiation albeit with enhanced local disorder. The porous layer thickness and the related porous micro-structure is critically dependent on the angle of irradiation. We will present XAFS measurements of GaSb irradiated at different angles and show how the local atomic structure is correlated to the observed different evolution of the micro-structure.

Poster no. PS1.44 - Session 1**Local atomic and electronic structure in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films with different doping concentrations**Nikolay Smolentsev¹, Alexander V. Soldatov¹, and Shiqiang Wei²*(1) Southern Federal University, Rostov-on-Don 344090, Russia**(2) National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China*

Recently, diluted magnetic semiconductors (DMSs) have attracted much attention because of their possible application in new spintronics based devices. Among those, Mn-doped ZnO material has been studied extensively in the past few years as one promising candidate. $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films (with different doped concentrations $x=0.005$, $x=0.010$, $x=0.025$ $x=0.050$ and $x=0.010$) were deposited on Si(100) substrates by pulsed laser deposition method. The XANES measurements were carried out on beamline U7C at the national synchrotron radiation laboratory of China, Hefei above the Mn K-edge. It was found that Fermi level and intensity of the white line decreases with increasing of doped concentrations. Pre-edge features also decrease in intensity and in energy due to changing of the valence state with growing doping concentrations. The local atomic structure around Mn have been studied in (Mn,Zn)O films using non-muffin-tin calculations (FDMNES2008 code) and multidimensional interpolation of XANES spectra (FitIt2.0 code [1]), which makes it possible refinement of the atomic spatial distribution with high accuracy.

This work was partially supported by RFBR (Russia) – NSFC (China) grant and Russian Ministry of Education by grant RNP 2.1.1.5932.

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Poster no. PS1.45 - Session 1**Icosahedral liquid frustration in transition metals**Angela Trapananti^{1,2}, Andrea Di Cicco², Simone De Panfilis³, and Adriano Filipponi⁴*(1) Sincrotrone Trieste, 34012 Basovizza, Trieste (Italy)**(2) Dipartimento di Fisica, Università di Camerino, 62032 Camerino, Macerata (Italy)**(3) CRS-SOFT INFN-CNR, Dipartimento di Fisica, Università di Roma La Sapienza, 00185 Roma (Italy)**(4) Dipartimento di Fisica, Università dell'Aquila, 67010 Coppito, L'Aquila (Italy)*

Since the Frank's hypothesis over a half-century ago, a growing number of first principles molecular dynamics studies reveal the existence of local icosahedral structures in late transition metals such as Cu, Ni, Fe. Recently, increased icosahedral frustration in liquids of metals with partially filled d-bands has been proposed to explain the melting slopes measured experimentally for Ni and Fe that are considerably lower than measured for Cu, and lower than theoretical predictions employing models in which preferred liquid structures are neglected [1].

In a previous work, we have used x-ray absorption spectroscopy (XAS) and Reverse Monte Carlo modelling to investigate the presence of icosahedral atomic configurations in liquid Cu [2]. Weak local icosahedral order could be observed in the liquid phase.

We present here the results of an x-ray absorption spectroscopy study of liquid and undercooled Ni recently performed by using a similar approach. The experiment itself is very challenging because of the high melting temperature of Ni ($T_m=1728$ K) and particular care had to be taken to optimize the sample preparation in order to avoid sample contamination and to achieve large undercooling below the freezing temperature. To our knowledge, these are the first XAS measurements of liquid and undercooled Ni.

Analysis of the three body correlations and additional geometrical analysis of the structural models obtained by Reverse Monte Carlo modelling of the experimental data using bond orientational order parameters gives the fraction of nearly icosahedral clusters. Results are discussed in connection with our previous findings on liquid Cu to establish the role played by the filling of d-bands in the formation of preferred local ordering in the liquid phase of transition metals.

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EXAFS of Water Systems

Poster no. PS1.46 - Session 1

X-Ray spectroscopy of frozen salt solutions: The liquid nature of ions in frozen salt solutions at temperatures below the eutectic temperature

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Natural ice contains many impurities, for example salts, acids or organic matter. These impurities play a key importance to the Earth's ecosystem. For example, the halogen salts in Sea ice serve as a source for atmospheric bromine compounds, which are a key to the catalytic ozone destruction. One important parameter to assess the role of impurities in ice is the phase state of impurity. It defines the chemical reactivity of the substances and its mobility in the ice.

As the solubility of impurities in ice is very low, most impurities accumulate in confined reservoirs, such as grain boundaries or triple junctions. Typically, these reservoirs are micron-sized. It is unclear whether salts can precipitate in such small inclusions in a frozen solution, or whether the inclusions host a metastable supercooled solution. Moreover, disorder may occur in such small confined reservoirs. Hence, salty inclusions may be in a liquid or liquid-like state at temperatures below the eutectic point, where only a solid phase should exist.

For this study we grew ice from solutions of NaCl and NaBr of different salt concentrations. Using synchrotron based X-Ray absorption and fluorescence spectroscopy at the Cl1S and the Br1S edge XANES and EXAFS were taken. Using this technique, we can show that for both salts all spectra exhibit dominant liquid features, even at temperatures well below the eutectic temperature.

Poster no. PS1.47 - Session 1

Solvation layer influence on the structure and nuclearity of zirconium and titanium complexes in polar solvents

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The structure and number of atoms per complex in zirconium and titanium alkoxides (metoxide, propoxide and butoxide) and inorganic salts in different solutions are investigated using XAFS techniques, optical spectroscopy and laser diffractometry. Solvents for organic solutions were - parent and heavier alcohols, toluene, benzene, hexane. Inorganic salts were dissolved in water, sulfur, nitric and hydrochloric acids. The presence of the stable solvate shell tightly bonded to the main complex is determined. The structural changes of the solvate shell during the variation of pH and composition of the solutions were observed. It is shown that existing distance from metal atom to a molecule of the solvate shell is longer than maximum length of the direct chemical bond.

The existence of the hierarchic structures in zirconium and titanium alkoxide solutions is obtained. The basic element of hierarchic structure is main metal alkoxide complex. These basic elements are arranged in the hierarchic structure of the second level owing to solvation effect and ligand interaction. The third level formations - of a hundreds angstrom in size - are associated together apparently due to the hydrogen bonding.

Poster no. PS1.48 - Session 1**Local electronic structure of water as a solute in pyridine**Kathrin M. Lange¹, Stefanie M. Greil¹, Ulrich Schade¹, and Emad F. Aziz¹*(1) Helmholtz Zentrum für Materialien und Energie Berlin, BESSY, Albert-Einstein-Straße 15, 12489 Berlin Germany*

The hydrogen bonding of water molecules in non-aqueous, oxygen-free solution is investigated by oxygen 1s X-ray absorption (XA) spectroscopy. Pyridine (Py) is used as solvent; the concentration of water is increased from 1 to 12 mass%. Due to the low mass% of water in Py, combined with sonicating the solution in situ, up to 6 % a single water molecule is considered to be accommodated in a distinct solvation pattern characterized by relatively strong hydrogen bonding. The observed O 1s XA spectrum of such confined water seems to be very similar to the analogous spectrum of neat liquid water. Yet, the small but significant spectral differences provide microscopic details on water hydrogen bonding inaccessible from the neat water XA spectra. Upon increasing the H₂O concentration the hydrogen bond strength between a H₂O and Py molecule decreases, inferred most clearly from the spectral changes of the O 1s XA pre and main peak. Upon increasing the water to 1-6 % the first solvation shell Py molecules reorient as to maximize interaction with the solute water molecules. Instead of water acting as hydrogen bond donors to the nitrogen of the pyridine, it acts as a hydrogen bond donor to the π -system of the ring. Increasing the water to a concentration higher than 12 %, the XA spectra show water cluster. In order to confirm our interpretation, infrared measurements are performed for water in Py solvent from mass% of 0.02 up to 40 %. The character of the hydrogen bonding between H₂O and Py depending on the H₂O concentration can be sensitively monitored by the shift of characteristic stretching bands of H₂O between 3100 and 3700 cm⁻¹. The obtained change in the strength of the hydrogen bonding is in accordance with the observation made by the X-ray measurements. Moreover, this observation has not been reproduced for D₂O in Py. Our conclusion is supported by DFT calculations in respect of optimized geometry.

Poster no. PS1.49 - Session 1**Oxygen 1s x-ray absorption spectroscopy of size-selected protonated water clusters**Tobias Lau¹, Jürgen Probst¹, Konstantin Hirsch¹, Andreas Langenberg¹, Robert Richter¹, Jochen Rittmann¹, Marlene Vogel¹, Vicente Zamudio-Bayer¹, Thomas Möller¹, Philippe Wernet², Mikael Leetmaa³, Lars Pettersson³, and Bernd von Issendorff⁴*(1) Institut für Optik und Atomare Physik, Technische Universität Berlin, EW 3-1, Hardenbergstraße 36, D-10632 Berlin, Germany**(2) FYSIKUM, AlbaNova, Stockholm University, S-10691 Stockholm, Sweden**(3) Helmholtz-Zentrum Berlin, Wilhelm-Conrad-Röntgen Campus, Albert-Einstein-Straße 15, D-12489 Berlin, Germany**(4) Fakultät für Physik, Universität Freiburg, Stefan-Meier Straße 19, D-79104 Freiburg, Germany*

Size-selected water clusters can serve as ideal model and reference systems for hydrogen bonding in liquid water and ice. Since target density is the limiting factor in gas-phase X-ray absorption spectroscopy, we combined an intense protonated water cluster source with a linear ion trap to accumulate size-selected clusters and to perform X-ray absorption along the trap axis. Briefly, protonated water clusters were produced and subsequently thermalized to 80–100 K. After size-selection in a quadrupole mass filter, the clusters were stored in a linear quadrupole ion trap with helium buffer gas cooled down to liquid nitrogen temperature, where X-ray absorption was measured in ion yield mode at BESSY II beamline U49/2-PGM-1. Besides an interest in the properties of protonated water clusters itself, we use the spectra to test various theoretical approaches for the calculation of the x-ray absorption spectra of liquid water and ice.

Size-selected protonated water clusters $H^+(H_2O)_n$ ($n=2-21, 28$) were investigated with X-ray absorption spectroscopy at the oxygen 1s edge. The most pronounced changes in the X-ray absorption spectra are observed from the protonated water dimer to the protonated water trimer, followed by a gradual evolution of excitation energy and intensity ratios up to $H^+(H_2O)_{21}$. The X-ray absorption spectrum of $H^+(H_2O)_{28}$ is already close to bulk ice.

We will present an interpretation of the experimental data based on theoretical spectra and discuss implications for the electronic and geometric structure of protonated water clusters.

Poster no. PS1.50 - Session 1**XAFS measurements on Zr in aqueous fluids at high pressures and temperatures using a modified hydrothermal diamond-anvil cell**André Stechern¹, Max Wilke¹, Christian Schmidt¹, Sakura Pascarelli², and Craig E. Manning³*(1) Deutsches GeoForschungsZentrum (GFZ), Telegrafenberg, 14473 Potsdam, Germany**(2) European Synchrotron Radiation Facility, 38043 Grenoble, France**(3) Dept. of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567, USA*

High-field-strength elements such as Zr are important geochemical indicators for processes in the Earth's crust and the upper mantle. Aqueous fluids play a significant role in the transport of heat and matter in these systems. However, the dissolution mechanism and complexation of Zr in these fluids at high pressure and temperature conditions are so far unknown. Here, we present an experimental setup to investigate in-situ the structural environment of elements in low concentrations in aqueous fluids up to 800 °C and 1.5 GPa. Zirconium K-edge X-ray Absorption Spectra (XAS) were collected at the energy dispersive XAS beamline ID24 at the ESRF. This setup employs a bent crystal to disperse and focus a polychromatic X-ray beam onto the sample. Instead of acquiring spectra in the standard transmission mode, the low concentration of Zr in the fluid required fluorescence measurements. The fluorescence signal was collected while scanning a slit downstream the polychromator. This ensured that the energy and position stability of the beam in the course of an energy scan is not affected by motion of X-ray optical components. Experiments were carried out in a modified hydrothermal diamond-anvil cell. The special design of the front anvil, with an 80 µm deep recess and a window in the body of the cell, permits the detection of the fluorescence signal at an angle of 90° with respect to the incoming beam. We have investigated the effect of silicate melt components in aqueous fluids on the Zr complexation. First results show clear differences between the local environments of Zr in a HCl solution and in a H₂O-Na₂Si₂O₅ aqueous fluid.

Poster no. PS1.51 - Session 1**X-ray absorption fine structure of bromide ions attracted by cationic surfactants at the heptane-water interface**Hajime Tanida¹, Hirohisa Nagatani², and Makoto Harada³*(1) Japan Synchrotron Radiation Institute Kouto 1-1-1, Sayo 679-5198 Hyogo Japan**(2) Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo 1-14, Nagasaki 852-8521, Japan**(3) Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro, Tokyo 152-8551, Japan*

The liquid-liquid interface between two immiscible solutions is a two-dimensional reaction field and is used in separation science, synthesis of thin-layer materials, and biomembrane model. The distribution and structural analyses of interfacial species at a molecular level are crucial for understanding mass-transfer, adsorption, and heterogeneous reaction mechanisms at the interface. The concentration profile and coordination structure of the interfacial species, however, has not been studied in detail because of the lack of a suitable technique to overcome the interface between the organic and aqueous phases. We have developed a new total-reflection XAFS technique to study the interfacial species at the liquid-liquid interface [1]. The experiment was performed at BL39XU of SPring-8 in Hyogo, Japan. The experimental cell formed a smooth and flat-top convex meniscus at the liquid-liquid interface. The angle of incidence of the X-ray to the interface was 0.5 mrad. The fluorescence intensity from the interfacial region was detected by a 7-element silicon drift detector. The liquid-liquid system was composed of heptane as an upper phase and water as a lower phase. The water phases are 10 mM NaBr or 0.10 mM stearyltrimethylammonium bromide aqueous solutions. Dimethyldilaurylammonium bromide was dissolved in chloroform and spread to form a monolayer on the 10 mM NaBr aqueous phase. The Br K-edge XAFS spectra from the bromide ion at the heptane-water interface were successfully obtained in the presence of the cationic surfactants, stearyltrimethylammonium or dimethyldilaurylammonium ions. A significant change in the spectra was observed. This demonstrated that the hydrated structure of bromide ions attracted by the cationic surfactants at the heptane-water interface is different from neat interfaces or bulk aqueous phases.

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Poster no. PS1.52 - Session 1**The structure of liquid water: combining information from EXAFS and x-ray and neutron diffraction**

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Determining the radial distribution functions (RDFs) of a liquid is one of the most important ways to characterize its structure, especially since these correlation functions can be probed by experiment. In the case of water, it has proved surprisingly difficult to reach consensus on the details of the RDFs, most notably for the O-O correlation. Here we report on reverse Monte Carlo structure modeling of liquid water, where we combine EXAFS and diffraction data in order to solve the apparent disagreement in the literature on the O-O RDF, determined with these different techniques. Structures from molecular dynamics (MD) simulations are furthermore analyzed in detail and compared with experimental data in reciprocal space. We find that x-ray diffraction requires the first O-O RDF peak to be lower than for most MD models, and that the focusing effect arising from straight hydrogen bonds plays an important role for the EXAFS oscillations.

Poster no. PS1.53 - Session 1**New insights in the local structure of Cu²⁺ in CuBr₂ solutions by EXAFS**

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The configuration of 3d transition metal ions in strong II-I electrolyte solutions, such as NiCl₂, ZnBr₂, CuBr₂, at different concentrations have been investigated for decades [1, 2] and there is a general consensus that complexes of MX₄⁻² ions co-exist with [M_(aq)]²⁺ in highly concentrated solutions [2, 3]. However the ratio of the two above complexes in highly concentrated solutions and whether MX₄⁻² exists in dilute solutions are still debated. In this contribution we present an accurate investigation of CuBr₂ solutions trying to give answer to the above issues. XAFS (X-ray absorption fine structure) analysis of data collected at the Cu-K edge in CuBr₂ solutions at 0.1 M and 0.5 M and in a saturated solution has been performed. We found that when saturated, in the solution there is an obvious contribution of Br ions around Cu²⁺ and the structural parameters are in agreement with previous studies [1, 4, 5]. On the contrary, for the 0.1 M and 0.5 M solutions the EXAFS analysis demonstrated that no Br ions are present in the first shell around Cu ion, not in agreement with other works claiming that CuBr₄⁻² exists in dilute solutions even at high proportion [2, 3].

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Extreme Conditions

Poster no. PS1.54 - Session 1

Kinetics of iron redox reactions in silicate melts: A high temperature XANES study on silicate melts.

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Silicate liquids are materials of prime importance in the glass and metallurgical industry as well as in the earth sciences where these melts have controlled heat and mass transfer at all scales throughout the whole geological history. Because iron is the most common transition metal in either natural or industrial silicate glasses, the difficulties originating in these possibly complex variations must be resolved to arrive at a better understanding of magmatic processes or to optimize vitrification and glass properties. Specifically, iron oxides affect melts properties in a complex way because iron occurs as Fe^{2+} and Fe^{3+} ions, whose abundances markedly depend on chemical composition, temperature and pressure. Moreover, each redox states of iron are associated to different structural role: Fe^{2+} is generally in octahedral coordination and acts as a network modifier while Fe^{3+} is generally found in tetrahedral coordination in a network former role. Because XANES spectroscopy allows to determine redox state and to derive structural information about iron, our goal was to follow the evolution of redox state through XANES experiments. The set of iron bearing sample investigated at the threshold K of iron includes natural melts such as basalt, rhyolithe, phonolite, komatiite and andezite. Redox equilibria were examined as a function of both time and temperature just above T_g and at superliquidus temperature. We observed a shift of the pre-edge position and of the main resonance as a function of time and temperature. We present here some XANES experiments at high temperature up to 2100K at the Fe K-edge, in liquids and glass. From these XANES spectra, redox kinetics can be obtained and discussed as a function of temperature and chemical composition.

Poster no. PS1.55 - Session 1

Pressure induced amorphisation and the amorphous-amorphous transition in nano-TiO₂

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Titanium dioxide can be found in a number of crystallographic phases, some of which are stabilized only under high pressure or recovered by decompression to atmospheric pressure. The increase in surface to bulk ratio when the grain size reaches the nano-scale, generally induces new physical properties, including unusual pressure responses. The novel phenomenon of grain-size dependent pressure induced amorphisation (PIA) in TiO₂ nano-materials has been evidenced by several experiments in recent years.

We have monitored the local environment of Ti well into the regime of PIA (≈ 30 GPa) for the nanometric (6 nm) form of TiO₂ anatase, for comparison with the behavior of the bulk analog, using a technique sensitive to the very local order. The phase transformations of bulk anatase to α -PbO₂ and to baddeleyite occur in the range of 12 GPa and 18 GPa, respectively. For nano-anatase, PIA has been observed above 20 GPa. Within this high density amorphous (HDA) phase the first oxygen shell around the Ti atom corresponds to 3 ± 0.5 O at 1.89 Å and 3 ± 0.5 O at 2.07 Å. The average Ti-O distance is larger than in the case of the octahedral environment of anatase. Prior to amorphisation a transition to an intermediate crystalline phase occurs. The nature of this phase depends on the experimental conditions (in one case we have identified the α -PbO₂ structure). On decompression to ambient pressure a new low density disordered (LDD) phase is observed. EXAFS analysis gives inter-atomic distances of 2 ± 0.5 O at 1.84 Å and 2.5 ± 0.5 O at 2.06 Å, thus the Ti atoms are mainly in a five-fold coordination. This is corroborated in the pre-edge features which are distinct from the HDA phase or α -PbO₂ recovered product of bulk pressurised anatase or rutile. It resembles that of sol-gel derived amorphous TiO₂ samples, where five-fold coordinate Ti features are predominant.

Poster no. PS1.56 - Session 1

Pressure-induced magnetic transition in Fe_3O_4 and CoFe_2O_4 spinels

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The pressure dependence of the x-ray magnetic circular dichroism (XMCD) has been measured in order to investigate the correlation between magnetic behaviour and structural properties in spinel ferrites (Fe_3O_4 and CoFe_2O_4).

Room temperature XMCD spectra has been collected at the Fe K-edge measuring the difference in absorption between two helicity states of the photon. Experiments were carried out in the EXAFS dispersive beamline ID24 at the ESRF. We measured from ambient pressure (AP) up to almost 23 GPa in the case of Fe_3O_4 and to 27 GPa in case of CoFe_2O_4 . The pressure was applied to the powder samples using a non-magnetic cube Diamond-Anvil Cell equipped with a pair of 1.2 mm thick diamond anvils.

The XMCD spectra of Fe_3O_4 decreases monotonically as the pressure increases being the dichroic signal half of that observed at ambient pressure in opposite to the recent reported discontinuity observed at about 12-16 GPa [1]. On the other hand, the dichroic signal completely disappears at 27 GPa in the CoFe_2O_4 ferrite. This result evidences a pressure-induced phase transition from a ferromagnetic state to a non-magnetic state. We note that the two signals, one from the tetrahedral Fe atoms and the other from the octahedral ones, disappear simultaneously indicating the disappearing of the ferromagnetic order of the two sub-lattices. In addition to this phenomenology, a clear variation of the XANES spectra at the same pressure indicates that this transition comes from a structural change. Moreover, when releasing the pressure, the dichroic signal is not recovered, even in new measurements at ambient pressure. Further studies to determine the origin of this phase transition and the possible structural changes induced by pressure are in course nowadays.

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Poster no. PS1.57 - Session 1

Solvation and ion pairing in aqueous gallium bromide, chloride and nitrate solutions up to supercritical conditions

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The effect of ion pairing in aqueous solutions at high temperature and high pressure conditions on physicochemical properties and reactions is a very dense topic. Such a study can provide insights on the metal transport in the hydrothermal fluids and on the metal extraction in decontamination process using supercritical fluids. The formation of pairs of oppositely charged ions completely dissolved at ambient conditions is mainly related with the decrease of the solvent permittivity with the temperature increase. In this context we focussed the study on the speciation of aqueous gallium due to its importance in high technology applications which calls for a comprehensive understanding of its geochemistry. An exhaustive set of speciation and thermodynamical data was already determined for the GaOOH system in a broad range of conditions up to 520 K[1], but its speciation at higher temperatures remains unknown[2]. We studied the speciation of gallium in acidic conditions in presence of nitrate, bromide and chloride ligands, from normal to supercritical conditions. Our X-ray absorption spectroscopy measurements enable to determine both the gallium speciation and its molality as a function of temperature. In supercritical conditions, gallium is mainly tetrahedrally coordinated (GaBr_4^- and GaCl_4^- structures) or octahedrally (aqueous nitrate complex, $[\text{Ga}(\text{NO}_3)_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$) depending on the initial conditions. For the gallium bromide system, precipitation of GaOOH above 373 K is observed in agreement with previous studies[1,3]. The role and relative strength of the different ligands will be discussed. The pertinence of using bromide ligands as analogues for chloride ligands will also be considered.

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Poster no. PS1.58 - Session 1**Theoretical and experimental evidence for a post-Cmcm phase of copper iodide**

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The three copper halides (CuCl, CuBr and CuI) all have the same zincblend crystal structure at ambient conditions. Their ionicities approach the critical threshold at which the zincblend structure becomes unstable with respect to the more closely packed NaCl or CsCl structures. The available experimental evidence shows that all the three copper halides have a large number of high pressure polymorphs and the structural sequence of this family appears more complex than for the more covalent III-V and II-VI semiconductors having also the zincblend crystal lattice at ambient conditions. No diffraction studies have been performed at pressure above 40 GPa and no direct investigation of the pressure evolution of the local structure using x-ray absorption spectroscopy has, to our knowledge, been reported for CuI.

Within this contribution we report the results of x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) experiments in a diamond anvil cell to investigate the structure of CuI at high pressure [1]. We show that copper iodide adopt the Cmca symmetry above 42 GPa and this phase remains stable up to 80 GPa. The application of crystal structure predictions allowed the structure of this new phase to be solved. This finding has important implications for a full understanding of the structural sequence of $A^N B^{8-N}$ compounds: at low pressure, the I-VII copper and silver halides do not always fit into the trends usually expected for III-V and II-VI analogues but their structure has never been investigated either experimentally or theoretically up to such high pressure.

[1] A. Trapananti, G. Aquilanti, S. Pascarelli, A. R. Oganov, W. A. Crichton and M. Mezouar, in preparation (2009)

Poster no. PS1.59 - Session 1**High pressure local structural changes in amorphous and crystalline GeO₂**

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The nature of amorphous-amorphous transformations (AATs) under pressure in the classic network-forming glasses represents a strongly debated issue in modern condensed matter physics. Although amorphous GeO₂ (a-GeO₂) is one of the most studied materials undergoing polyamorphism at high pressure, conflicting results were obtained in previous works and the detailed pressure evolution of germanium local environment is still far from being clarified.

Therefore, a new *in situ* EXAFS investigation of high pressure local changes in a-GeO₂ (and, for comparison purposes, quartz-like crystalline q-GeO₂) has been performed [1] at BM29 beamline of ESRF. Pressure up to 13 GPa was obtained through a large volume Paris-Edinburgh press. The pressure evolution of the Ge-O distance and coordination number, as well as the absorption edge position, allowed us to monitor the details of the phase transition.

The main results [1] can be summarized as follows:

- i) in the low-pressure range (below about 5 GPa) both q- and a-GeO₂ undergo possible deformation and rotation of GeO₄ tetrahedra, while the Ge-O bond does not experience any average compression;
- ii) the tetrahedral to octahedral transformation in q-GeO₂ is quite sharp and located at about 8.5 GPa, although at least the full 6 – 12 GPa pressure range should be considered as the transition region;
- iii) in a-GeO₂ the analogous structural change is instead quite continuous and gradual, and the full octahedral state is not reached at 13 GPa;
- iv) no evidence is provided of the recently claimed intermediate state with a constant average coordination of five in the 6 – 10 GPa pressure range;
- v) a continuous breakdown of intermediate range order in glassy GeO₂ is observed up to about 10 GPa.

This work contributes to a deeper understanding of the mechanisms underlying the AAT in glassy GeO₂.

[1] M. Vaccari et al., J. Phys.: Condens. Matter 21, 145403 (2009)

Poster no. PS1.60 - Session 1

Pressure dependence of magnetic states in Laves Phase RCo₂ (R=Dy, Ho, and Er) compounds probed by XMCD

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Laves Phase RCo₂ compounds (R=Dy, Ho, and Er) have provided a subject of many studies on instability of the Co 3d magnetic states. Magnetic phase transition in this system originates in the Co 3d states and the molecular field due to the R moments. The phase transition is classified as a first-order at ambient pressure and changes to a second-order at a critical pressure P_t . The magnitude of P_t shifts to lower pressure in the order of the R elements. For a better understanding of the phase transition, it is necessary to clarify the following key issues: pressure-induced suppression in the Co magnetic moment (M_{Co}) and contribution of the molecular field. For this purpose, X-ray magnetic circular dichroism (XMCD) is a powerful technique to probe the magnetic states with an element-selectivity.

Here, we present an XMCD study of RCo₂ (R=Dy, Ho, and Er) under multiple conditions (H=5 T, T=5 K, and P up to 4.2 GPa). The XMCD spectra at the Co K-edge and R L_{2,3}-edges were recorded at SPring-8 BL39XU.

The pressure dependence of M_{Co} is determined from the intensity of the negative peak near the R L₂ absorption edge [1]. This peak includes contribution of M_{Co} due to hybridization between R 5d and Co 3d. The intensity gradually increases with increasing pressure and approaches that of RAl₂. This means that M_{Co} is reduced at high pressure. The enhancement of the negative peak for DyCo₂ is remarkably small compared with those for HoCo₂ and ErCo₂, so that M_{Co} of DyCo₂ is more stable under pressure.

In the case of Co K-edge, the amplitude of the XMCD decreases with increasing pressure. Furthermore, the profile changes at the pressures above P_t . The XMCD is strongly influenced by the magnetic state of R [1]. Hence, it is considered that the effect of molecular field acting on Co significantly varies at P_t .

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Poster no. PS1.61 - Session 1

High-pressure XAFS study of nano particle and stabilized cubic ZrO₂

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XAFS spectra measurements near the Zr K-edge for stabilized cubic ZrO₂ (+10% CaO) and pure monoclinic ZrO₂ with particle size of 20-50 nm and 0.1-0.5 μ m were performed under pressure up to 7.8 GPa using a multi-anvil high-pressure device and synchrotron radiation at BL14B1, SPring-8, Hyogo. X-ray absorption near-edge structure (XANES) spectra are quite sensitive to the three-dimensional atomic configuration around X-ray absorbing atoms. They are useful for phase study under high temperature and high pressure. Pure ZrO₂ crystallizes in the baddeleyite type structure (monoclinic) at ambient conditions. On compression, it transforms to an orthorhombic phase with distorted fluorite type structure. ZrO₂ adopts different local structures depending on the particle size. The size effect is also observed on the pressure induced transition between monoclinic and orthorhombic phases. The nano sample shows the transition around 6 GPa, while the transition in bulk sample occurs at 3.5 GPa. The second-nearest Zr-Zr distances in nano sample is 0.02 Å longer than that in bulk sample. It was found that both samples have nearly the same compressibility and transform to high pressure phase at a certain specific Zr-Zr distance. The pressure dependence of effective pair potentials $V(u)=au^2/2$ for Zr-O and Zr-Zr bond have been investigated by EXAFS Debye-Waller factors. The phonon energies of various phases under pressure have been estimated using the potential parameter a by calculating the dynamical matrix.

Material Science

Poster no. PS1.62 - Session 1

EXAFS and negative thermal expansion in CdTe

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CdTe has the zincblende structure and is affected by a negative thermal expansion (NTE) of the lattice parameter below about 70 K. The NTE strength and temperature interval in CdTe are intermediate between those of Ge and CuCl. Temperature dependent EXAFS measurements have been performed on CdTe, to study its local dynamical properties and compare them with those of other diamond-zincblende NTE semiconductors. The cumulant analysis of the first-shell contribution to EXAFS has shown that the bond thermal expansion is positive within the full explored temperature range, 20 to 300 K, like for all other NTE materials studied by EXAFS up to now. The perpendicular MSRD has been obtained from the difference between bond and lattice thermal expansions. The effective force constants obtained by fitting Einstein models to the temperature dependence of the parallel and perpendicular MSRDs are 3.76 and 0.9 eV/Å², respectively. The values of these force constants, as well as the ratio of perpendicular to parallel MSRD, which measures the anisotropy of relative vibrations, are intermediate between the values previously found for Ge [1] and CuCl [2]. A qualitative correlation can be established between local dynamical quantities measured by EXAFS and NTE properties.

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Poster no. PS1.63 - Session 1

Local structure around Er³⁺ in SiO₂-HfO₂ glass and nanocrystalline waveguides with low HfO₂ contents

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Er³⁺-doped SiO₂ glass has been the basic material for fabricating photonics and optoelectronics devices. Introducing oxide glasses into the basic hosting material may enhance the solubility of the rare earth ion in the host glass and alter the crystal-field around these ions. Recently, this procedure has been extended to growing nanocrystalline phases of the co-dopant oxide, where the rare earth ions may substitute the cations. In the past, we reported on Er³⁺-doped SiO₂ planar waveguides having HfO₂ content between 10 and 50 mol %. In the present study we are interested in the changes of the local environment of Er³⁺ samples with low HfO₂ (less than 10 mol %).

Planar waveguides with the compositions 1 mol % Er³⁺-doped (1-x)SiO₂-xHfO₂ (x=0.0, 0.9, 1.8, 5, and 8 mol %) were prepared by sol-gel route and deposited on amorphous SiO₂ substrates using dip-coating technique. All the samples were densified at 900 °C for 72 h. Replicates of the glasses with 5 and 8 % were successively heat treated at 1100 °C for 30 min to grow HfO₂ nanocrystals. The local structure around Er³⁺ ions in all samples was characterized by fluorescence Er L₃-edges EXAFS measurements at BM08 GILDA Beamline of ESRF.

In the glassy waveguides, EXAFS data show the presence of Er³⁺ ions in HfO₂-rich regions for HfO₂ concentrations over 5 mol %. It is found that the local structure around the rare earth ions is dependent on HfO₂ content. This information complements the previous one on high HfO₂ contents, where the local structure around Er³⁺ ions remains unaltered for HfO₂ concentrations between 10 and 50 mol %. In the nanocrystalline samples, even at 5 mol % HfO₂, it was possible to grow HfO₂ nanocrystals. For these samples, EXAFS data suggest the substitution of Hf by Er ions in the present nanocrystals.

Poster no. PS1.64 - Session 1**XAFS studies of nickel nanoparticles synthesized by laser ablation**

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We have synthesized the nickel nanoparticles by pulsed laser ablation. The nickel disc in sodium dodecyl sulfate (SDS) with surfactant concentration of 10mM and 20 mM. was used with the focused output of fundamental harmonic from Nd:YAG laser operating at the first harmonic ($\lambda = 1064$ nm). The laser power was fixed at 35 mJ/pulse with 10 ns pulse width and 10 Hz repetition rate and was used for the ablation for 60 minute. UV-Visible absorption, x-ray diffraction, and Transmission Electron Microscopy techniques were used for the characterization of produced nanoparticles. The powder samples were characterized by XRD measurements using Cu K α radiation at 40 KV with wavelength 1.5405 Å. A vibrating sample magnetometer (VSM) device was used to measure the magnetic property at the room temperature of nanoparticles. The EXAFS studies of pure nickel foil and for the synthesized nanoparticles with concentration 10mM of SDS show similar structures. The position of the main peak is same. The only difference was observed in the reduction of the amplitude, which can be attributed to the coordination number. The nearest neighbor distance was similar as for pure nickel foil. The Debye-Waller factor was also similar on comparison. There was no trace of oxide and hydroxide in the EXAFS data which suggest that the synthesized nanoparticles contains only nickel metal.

Poster no. PS1.65 - Session 1**In-operando x-ray absorption spectroscopy of Li-ion batteries over hard and soft x-ray regimes**

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We present the first ever soft X-ray absorption spectroscopy of active materials in a Li-ion battery during its operation. In-operando O K edge and Co L edge near edge X-ray absorption fine structure (NEXAFS) was used to examine the cathode of an intact solid-state lithium ion battery. The novel technique allowed for the simultaneous acquisition of partial electron yield and fluorescence yield data during the first charge cycle of a LiCoO₂-based battery below and above the intercalation voltage. The NEXAFS work complements hard X-ray absorption spectroscopy of LiCoO₂ and the related Li[LiNiMn]O₂ based batteries at the transition metal K edges. The design of the soft X-ray cell enables a wide variety of in situ spectroscopies, microscopies, and scattering techniques of Li-ion battery materials.

Poster no. PS1.66 - Session 1**X-ray absorption spectroscopy investigation of BSTO thin films and bulk using the Ti and Sr K-edges analysis**Igor Alperovich¹, Alexander Soldatov¹, Vladimir Mukhortov¹, and Yan Zubavichus²*(1) Southern Federal University, Rostov-on-Don, Russian Federation 5 Zorge St. 344058 Rostov-on-Don Russian Federation**(2) Kurchatov Research center, Moscow, Russian Federation*

The analysis was carried out of the experimental Sr and Ti K-edge X-ray absorption near edge structure (XANES) spectra obtained at the Kurchatov Center of Synchrotron Radiation and Nanotechnology (Moscow) of the series of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ (BSTO) different thickness films and bulk, which are of great consequence to microelectronic applications. The films to study were grown on the LaAlO_3 substrate and have thickness between 6 and 1140 nanometers. The Sr K-edge X-ray absorption fine structure (XAFS) revealed the variation in relative intensities of the first three peaks and the Ti K-edge XAFS demonstrated different peak's position according to film thickness.

Theoretical analysis was performed within the framework of self-consistent, real space multiple scattering and finite difference methods with help of FEFF8.4 and FDMNES2007 codes, respectively. The calculations were carried out by means of both muffin-tin and full (beyond muffin-tin approximation) potentials. Also, the spectra were simulated with WIEN2k code on the basis of linearized augmented plane wave (LAPW) method. Shape dependence of the spectra upon film thickness was discussed. A careful account is given to the correlation between the XANES and calculation parameters including such ones as lattice constant value, crystal structure, Ba-Sr relative concentration, type of potential and others.

Poster no. PS1.67 - Session 1**Ru L-edges X-ray absorption near edge structure spectra analysis: probe of various methods**Igor Alperovich¹, Alexander Soldatov¹, and Yulia Pushkar²*(1) Southern Federal University, Rostov-on-Don, Russian Federation**(2) Purdue University, West Lafayette, IN, U.S.A.*

Ru L-edge X-ray absorption near edge structure spectra provide insights on the electronic configuration of the Ru centers in materials and catalysts. This was demonstrated for Ru-containing oxides and perovskites [1-2]. Changes in the Ru oxidation states are central to the catalytic activity of the Ru based compounds in water oxidation [3,4].

We present a comparative analysis of several theoretical approaches for simulation of the $L_{2,3}$ -edges of the Ru coordination complexes. The relatively small multiplet effects for the 2p core levels of the 4d metal implies that single electron codes can be used as a first approximation [5]. We tested FEFF8.4 and FDMNES2009 codes utilizing the framework of self-consistent, real space multiple scattering and finite difference methods. Crystal field multiplet calculations is a powerful method for simulation of the splitting of the L-edges related to changes in Ru oxidation state [1,6]. We used the CTM4XAS code which includes atomic multiplet effects. Charge transfer effects and changes in the local symmetry were taken into account in simulations of the model complexes $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$, $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+/3+}$ and $[\text{Ru}(\text{bpy})_3]^{2+/3+}$.

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Poster no. PS1.68 - Session 1**High-energy-resolution fluorescence detected X-ray absorption at Mn K edge in Cu-III-S₂:Mn (III = Al, Ga, In) chalcopyrites**Rajmund Bacewicz¹, A. Pietnoczka¹, and M. Sikora^{2,3}*(1) Faculty of Physics Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland**(2) Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland**(3) European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France*

Local order is studied in Mn-doped ternary semiconductors with chalcopyrite structure. Room temperature ferromagnetism has been found in some of such systems making them suitable for spintronic applications. Magnetic ordering of Mn ions in chalcopyrite structure depends crucially on the site occupation of Mn in the host lattice. Analysis of the site preference of Mn (Mn_{Cu} vs. Mn_{III}) by the XAFS technique is difficult due to small differences in the local environment of Mn for these two sites and relatively small differences in photoelectron scattering amplitude of Cu and the III-group elements [1]. However, theoretical calculations using both pseudopotential and LMTO methods indicate differences in the Mn 3d density of states distribution for Mn on the III-group atom site and the Cu site. Thus, differences can be expected in the Mn XANES pre-edge structure. To detect such differences, we used the spectral sharpening effect of the 1s-3p (3d) Resonant Inelastic X-ray Scattering (RIXS) technique.

We report the Mn K-edge X-ray absorption spectra detected by the high-energy-resolution fluorescence at the manganese K β emission line at ID26 beamline of ESRF. The spectra are compared with the theoretical XANES calculated for different atomic sites by the finite difference method - the FDMNES program by Yves Joly [2]. A comparison of the pre-edge position of the studied chalcopyrites with MnS indicates that dominant charge state of Mn in all compounds is 2+. On the other hand, 3d state spin derived from the K β emission spectra is between 2 and 2.5 due to the Mn-S bond covalency. No definite Mn site assignment has been reached.

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Poster no. PS1.69 - Session 1**EXAFS studies of nickel superalloys**Norman Binsted¹, and Bryan Edwards²*(1) N. Binsted, 7 Cavendish Close, SO51 7HT, Romsey, England**(2) STFC Daresbury Laboratory, WA4 4AD, England*

Nickel-based alloys designed for high performance, high temperature applications such as aero engine components rely on solid-solution or precipitation strengthening to achieve their design targets. Such alloys may contain up to nine essential components and three or more beneficial phases: typically the FCC (austenite) matrix, an ordered Ni₃X phase (gamma prime or gamma double-prime), and a grain-boundary phase such as a carbide. Understanding the role of each component in terms of its effect on local structure in the alloy would complement more readily measured properties obtained from diffraction and electron microscope studies, such as the crystal structure and the nature and density of dislocations. As a feasibility exercise we have examined 6 Ni-superalloy samples using EXAFS, X-ray powder diffraction and X-ray fluorescence mapping using an electron microprobe. A number of interesting results have been obtained so far, yielding information on the relationship between local structure and long range order in work-hardened and annealed samples, on element distribution between phases, and a quantitative understanding of local lattice distortions using Multiple-Scattering RMC methods. We also demonstrate the importance of adequately correcting for self-absorption in fluorescence EXAFS studies of these materials.

Poster no. PS1.70 - Session 1**Formation of SiF₄ filled cavities in silicon**

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An understanding of the relation between the local structure of dopants and the modification they induce on the physical properties of semiconductors is a prerequisite for insightful materials design. This kind of study acquires great importance as the dimensions of semiconductor devices continuously decrease and atomic correlations have increasing relevance, providing strong motivation for the use of XAFS.

F implantation is commonly used to reduce diffusion of B dopants in Si in ultra-shallow junctions. The common interpretation is that this effect is due to the creation of vacancies (Vs) induced by F, but an experimental investigation is missing. In the framework of our previous study of the B site in Si [1], we have studied the present issue using F K-edge XAFS with fluorescence detection on the ALOISA undulator beamline of ELETTRA.

We have studied different specimens implanted with F or F + B. The EXAFS analysis determined a Si-F distance of 1.55 Å, much lower than the value expected for F-V complexes (1.67 Å). The XANES lineshapes do not vary in presence of B, confirming the absence of a direct B-F interaction. FEFF simulations of the XANES spectra of numerous F-V clusters proposed in the literature do not reproduce the experimental ones, while a good agreement is obtained by both simulation and experimental comparison with spectra of the SiF₄ molecule, in which the Si-F distance is 1.54 Å.

Thus, the conclusion is that F is mainly incorporated in the form of SiF₄ molecules inside nano-cavities; such cavities are observed in complementary transmission electron microscopy investigations. SiF₄ filled cavities are therefore responsible for the reduction of B diffusion in Si.

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Poster no. PS1.71 - Session 1**XANES study of the oxidation state in superconducting TbFeAsO_{0.85}**

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X-ray absorption near-edge structure (XANES) spectra of the TbFeAsO_{0.85} superconductor were recorded at Fe K-, As K- and Tb L₃-edges. The Fe K-edge XANES results show that the electronic configuration of Fe in the TbFeAsO_{0.85} sample is a mixture of the basic *d*⁶ (Fe²⁺) state and *d*⁷ (plus ligand hole) configuration in the ground state. Besides, there appears a pre-edge peak around 7112 eV representing the 1*s*→3*d* transition, which is a dipole forbidden process. Such a pre-edge feature for TbFeAsO_{0.85} is particularly stronger than other standard compounds due to the local tetragonal ligand field allowing dipole transitions into 3*d* related states. The Tb L₃-edge XANES spectrum of TbFeAsO_{0.85} superconductor shows essentially Tb³⁺ in this sample. In contrast, the As K-edge spectrum of TbFeAsO_{0.85} clearly shifts to lower energy relative to the that of As powder, indicating that the oxidation number of As in TbFeAsO_{0.85} is negative. Considering the valence of Fe and Tb, we assume that the oxidation state of As in TbFeAsO_{0.85} is approximately 3-.

Poster no. PS1.72 - Session 1**Fe 3d-electron behavior in ternary-iron-arsenide superconductors probed by X-ray absorption spectroscopy**Jie Cheng^{1,2}, Wangsheng Chu¹, Gang Wu³, Xianhui Chen³, Wensheng Yan², and Ziyu Wu^{1,2,4}(1) *Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P.R. China*(2) *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P.R. China*(3) *Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, China*(4) *Theoretical Physics Center for Science Facilities, Chinese Academy of Sciences, Beijing 100049, P.R. China*

The recent discovery of Fe-based high-T_c superconductors (HTSC) has revived hopes on the HTSC research field. The basic issue is to estimate whether the superconductive mechanism of Fe-based superconductors is similar with that of cuprate HTSCs. Just like the Cu-O layers in cuprate HTSCs, Fe-As layers in Fe-based HTSCs have been regarded as the superconductive layer. The character of Cu 3d-electron is crucial to understand the essential physics of the strongly correlated electronic systems. Generally, Cu 3d-electron of cuprate HTSCs in normal state has been thought of the localized one, bound to atom lattice, while it turns into itinerant one, moving freely in the lattice, in superconductive state. Therefore, it is very urgent to understand the character of Fe 3d-electron in newly discovered iron-based superconductors.

The recent investigations show a strong evidence of the itinerant character of Fe 3d-electron for CeFeAsO_{0.89}F_{0.11} [1] and FeSe_{1-x} [2] iron-based superconductors, which is very different from Cu 3d-electron in cuprates. So how about Fe 3d-electron in the ternary-iron-arsenide superconductors, another important type of iron-based superconductors?

Here we measured Fe L_{2,3}-edge XAS spectra of Ba_{1-x}K_xFe₂As₂, as well as Fe and As K-edge XANES spectra of these compounds. Our data presents a strong evidence of Fe 3d-electron localized character, much different from iron-oxypnictide and FeSe_{1-x} superconductors. Moreover, the holes introducing into FeAs double layers by the potassium doping located on the hybridized orbital of Fe 3d orbitals with As 4p orbitals. The behavior of Fe 3d-electron in ternary-iron-arsenide superconductors is much similar with that of Cu 3d-electron in cuprate HTSCs. This result indicates we should realize the complexity of the superconductive mechanism of the iron-based superconductors.

[1] F. Bondino et al., Phys. Rev. Lett. 101, 267001 (2008)

[2] A. Yamasaki et al., arXiv:0902.3314v1

Poster no. PS1.73 - Session 1**Local structure peculiarities of nanocrystalline compounds RE₂O₃-MeO₂ (RE=Dy, Gd; Me=Hf,Zr)**Roman V. Chernikov¹, A.P. Menushenkov¹, O.V. Kashurnikova¹, V.F. Petrunun¹, V.V. Popov¹, A.V. Fedotov¹, and A.A. Yaroslavlsev¹(1) *Moscow Engineering Physics Institute (State University), Kashirskoe shosse 31, 115409 Moscow, Russia*

Rare-earth systems RE₂O₃-MeO₂: dysprosium hafnate, gadolinium hafnate, gadolinium zirconate have a practical usage in neutron absorption systems, heat insulators, electrolytes. Compounds of this type are described by complicated phase diagrams and mainly crystallize to the pyrochlore and fluorite phases. Fluorite-like structure is usually not ideal in these compounds, that is why structure analysis results are often ambiguous.

Compounds under study belong to the border between the fluorite- and pyrochlore-like on phase diagram. Materials that we have investigated by means of the X-ray diffraction and absorption (XAFS) techniques had different nanocrystallite sizes from 1 to 50 nm. Anomalous diffraction spectra were used for element-sensitive study. We had to apply the RMC and other non-crystalline analysis methods as we found complicated local atomic structure in the fluorite phase. We also used ab initio modelling in terms of density functional theory, because crystalline structural effects are accompanied by changes in electronic structure. We found structure ordering effects in fluorite, that can lead to ideal pyrochlore ordering at high temperatures. These effects prove to be similar for different chemical structures. Obtained data can give the new understanding of the radiation accumulation processes, defects etc. in this class of materials.

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Poster no. PS1.74 - Session 1**Electronic structure of (Zn, Cr)O films studied by x-ray spectroscopy and scanning photoelectron microscopy**

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O K- and Cr L_{3,2}-edge x-ray absorption near-edge structure (XANES), x-ray emission spectroscopy (XES), and scanning photoelectron microscopy (SPEM) were performed to investigate the electronic structure of (Zn, Cr)O thin films deposited on sapphire (0001) at 500 °C by co-sputtering ZnO ceramic and Cr metal targets in an ultra-high vacuum (UHV) system at a pressure of 20 mTorr. The analysis of the Cr L_{3,2}-edge XANES spectra show that the intensities of white-line features decrease monotonically with an increase in co-sputtering power, which indicates that the occupation of Cr 3d states increases with Cr concentration in (Zn, Cr)O films. The O K-edge spectra show that the intensities of XANES features of (Zn, Cr)O films are lower than those of ZnO, which suggests that the occupation of O 2p derived states is enhanced through O 2p-Cr 3d hybridization. However, XES and SPEM spectra show that the line shapes in the valence band of (Zn, Cr)O films are quite different from ZnO since Cr₂O₃ dominates the spinel structure with Cr concentration.

Poster no. PS1.75 - Session 1**The iron isotope effect in ferrous pnictide superconductors probed by EXAFS spectroscopy**

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Discovery of ferrous pnictide superconductors, whose transition temperature recently rose up to 55 K, triggered a search for high-T_c iron-based superconductor, in a similar way to the discovery of copper-based superconductors at the end of 80's. However, the unexpected discovery of a high critical temperature in pnictides is very useful for a better understanding of high-T_c superconductors and, more in general, of the superconductivity mechanisms in non-metallic systems. One of the most important question concerns the superconductive mechanism of iron-based superconductors. Is the same of copper-based systems?

At present, it is well known that the local lattice distortion plays a key role in the superconductivity of cuprate superconductors, together with electrons and spins. Extended x-ray absorption fine structure (EXAFS) is one of the most powerful and special techniques to probe the local lattice distortion at high spatial resolution, and recent EXAFS investigations showed that the temperature-dependent lattice anomalies above T_c are a common feature of all cuprate superconductors. Therefore, it is mandatory provide accurate experimental data about local lattice distortions or vibrations of iron-based superconductors. In this contribution we present experimental EXAFS data at the Fe and As K-edge of ferrous pnictide superconductors with the isotopic substitution of ⁵⁶Fe with ⁵⁴Fe. Data clarify the correlation between Fe-Fe and Fe-As local lattice distortions with both hole doping and iron isotope effect. The results will be useful to understand the role of electron-phonon interaction in these iron-based superconductors.

Poster no. PS1.76 - Session 1**Local structure of nitrogen-hydrogen complexes in dilute nitrides**

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Hydrogenation of dilute nitride semiconductor alloys reverses the counterintuitive band-gap red shift caused by N incorporation, expands dramatically the lattice parameter, and restores the values of the effective mass and gyromagnetic factor. Moreover, all these effects are fully reversible by simple thermal annealing, which permits to tune the emission wavelength after the growth within a range of great interest in telecommunication and photovoltaic technology. The effects of hydrogenation have been accounted for by the hypothesis of formation of specific N-H complexes, and the number and location of H atoms around N has been debated in the literature in the last six years.

We have investigated the structure of nitrogen-hydrogen complexes in GaAsN and InGaAsN dilute nitride alloys by performing x-ray absorption near edge structure spectroscopy (XANES) at the nitrogen K-edge. We simulated the spectra based on first principle calculations of the most recent defective structures proposed in the literature for hydrogenated materials. The comparison between the experimental data and simulations allows us to clarify that the core of the defect is a complex with C2v structure in the neutral charge state, in agreement with the expansion of the lattice parameter measured by X-ray diffraction. Our results are compatible with the presence of H satellites bound to neighboring Ga atoms recently suggested by Nuclear Reaction Analysis but not with complexes involving more than two H atoms bound to the same N. Nevertheless, we were not able to determine uniquely the number of H satellites, which may depend on growth conditions. We also showed that strain related to the epitaxial growth has a very little effect on the XANES spectra.

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Poster no. PS1.77 - Session 1**EXAFS study of the structure of the Zn_{1-x}Be_xSe alloy system**

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Be incorporation in ZnSe results in large increase in its shear modulus and Raman studies show unusual phonon behavior over a range of Be concentration of $0.19 < x < 0.81$ with appearance of additional modes than those expected from MREI model, while outside this range the system behaves like normal alloy showing two mode behavior[1]. This is interpreted as percolation behavior in which this alloy can be described by a composite system made of two pseudo continuous chains with contrasting mechanical properties: a hard-like (HL) Be rich and a soft-like (SL) Zn rich region wherein Be-Se bonds in the HL region undergo a larger tensile stress to match the surrounding lattice parameter than those for low Be dispersed within the SL region. First principle calculation lends support to this concept and suggests different local deformations in SL and HL regions. The two Be-Se features in the Raman spectra refer to vibrations within the hard and soft regions, respectively corresponding to two different Be-Se bond distances. Detection of the possible existence of these two different Be-Se bond lengths in Be doped mixed crystals is the primary motivation of the present work and EXAFS is a very powerful tool to probe such nearest neighbor (NN) bond lengths. EXAFS data have been recorded for these mixed crystals at the Zn and Se K edges and analyzed. The Zn-Se and Be-Se bond lengths as a function of composition have been evaluated from the data after fitting the EXAFS equation. Our analysis however does not seem to indicate two different bond-lengths for Be-Se bond, which may be due to small scattering from the Be atoms and the large EXAFS signal from the Zn atoms. On the other hand the effect is clearly observed in an increase in the value of static disorder factor for Be-Se bonds with higher Be concentration.

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Poster no. PS1.78 - Session 1**X-ray absorption spectroscopy and neutron diffraction study of local distortions in the perovskite-type rare-earth metal cobaltites**

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The discovery of the “colossal” magnetoresistance (CMR) in the manganites with perovskite structure has stimulated the research of the compounds exhibiting large magnetoresistance [1]. Recently cobaltites with perovskite-type structure have attracted a considerable interest because their specific properties make them promising materials for use in solid oxide fuel cell, chemical reactors, gas separation membranes. Moreover, the cobaltites are characterized by a large catalytic reactivity. Therefore they can be used as catalysts for soot combustion in the exhaust in the diesel engine. The aim of this work is to study the close correlations between local atomic and electronic structure and also long-order range of the crystal structure transformations in the $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ (Ln notes La, Pr; A- Sr, Ba, Ca) polycrystalline samples in the temperature range from 5 to 300 K. The sensitivity XANES and EXAFS to chemical composition, local lattice distortion, “chemical pressure” effect and to an overlapping mixture of low (LS: $t_{2g}6e_g0$, $S=0$), intermediate (IS: $t_{2g}5e_g1$, $S=1$) and high (HS: $t_{2g}4e_g2$, $S=2$) spin states of Co^{3+} and Co^{4+} ions in these cobaltites was also considered. Crystal and magnetic structure of these cobaltites were precisely determined by high-resolution X-ray and Neutron diffraction methods. Correlations of the long-range structure parameters with local atomic and electronic structure ones and also with SQUID magnetization measurements, was analyzed. The use of complementary techniques allowed us to access the influence of the rare-earth atoms type and their substitution with strontium atoms on the anisotropy of oxygens thermal vibrations in the directions perpendicular and along the Co-O bonds. The details of local atomic and electronic structure in cobaltites doped by Sr, Ba and Ca are presented and discussed.

Poster no. PS1.79 - Session 1**Broken symmetry of cage surrounding magnetic dopants (Gd or Cr) in GaN**

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Dilute magnetic semiconductors are one group of spintronics materials. Of those GaGdN and GaCrN are the most available candidates for the practice device application. However, the origin of the ferromagnetic behavior is still open in discussion. Here, there is an interesting problem due to the difference in the crystal structures between the dopant ions and the matrix as follows. Dopant ions in matrix having the different crystal structure from the essential structure of the dopant ion are sometimes self-assertive to form the essential structure of the dopant ions. It leads to breakdown of the symmetry at the dopant ion site. This phenomenon is well known as quasi-Jahn-Teller or pseudo-Jahn-Teller effect. To survey the origin of the ferromagnetism in the dilute magnetic semiconductors, GaGdN and GaCrN, we have investigated this phenomenon by XAFS and XANES spectroscopy. These specimens are thin single crystals grown by using molecular beam epitaxial techniques. The dopant magnetic Gd or Cr ions are surrounded by four N ions, of which site symmetry is T_d in Cubic GaN belonging to a space group $F\bar{4}3m$ (Zincblende type) or C_{3v} in hexagonal GaN ($P6_3mc$: Wurtzite type). We found the splitting of the first and the second peaks in the radial distribution function around the Cr ion in the Cr-ion doped cubic-GaN from the Cr K-edge XAFS analysis, and a vacancy in the adjoining N ions to Gd ion in the Gd-ion doped hexagonal-GaN nano-rods from the Gd LIII-edge XANES spectrum. These findings suggest the breakdown of the site symmetry. Moreover, in the pre-edge energy region of the cubic GaCrN and the onset of the LIII-edge of the GaGdN, the polarization effects are found. That is, the spectra show linear dichroism with vertical and horizontal polarization of the incident X-rays to the principal c-axis of the crystal. These facts also support the broken symmetry phenomenon. We try to explain this phenomenon within the electron – lattice interaction scheme.

Poster no. PS1.80 - Session 1**Analysis of local atomic structure of crystal-quasicrystal transition in Al-Cu-Fe**

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Quasicrystals (quasiperiodic crystals) are attracting intense interest due to their unique properties being non typical for their crystalline and amorphous phase analogues. It is assumed that such properties roughly depend on the peculiarities of local atomic structure and interatomic interactions. Recently these materials are found to have interesting tribological properties. Experimental x-ray absorption near edge structure (XANES) spectra of Al-Cu-Fe crystal-quasicrystal have been obtained to study the crystal-quasicrystal transitions in Al-Cu-Fe. The XANES measurements above the Al K edge have been performed at the LNF Synchrotron Center, (Italy). Experimental Cu K- and Fe K-XANES spectra of Al₆₅Cu₂₂Fe₁₃ quasicrystal and its crystal pre-phase have been measured on Laboratory Spectrometer R-XAS Rigaku and Kurchatov synchrotron radiation center (Moscow, Russia).

Investigation of the local atomic structure of Al-Cu-Fe quasicrystal and crystal analogue, has been performed on the basis of the x-ray absorption near edge structure analysis. Analysis of experimental XANES spectra provides a way to determine the 3D local atomic structure of the materials under the study.

Theoretical analysis of the experimental data has been carried out using a self-consistent, real space multiple scattering method (FEFF8.4 code) and a finite difference method (FDMNES2008 code). Different model structures of atomic arrangement have been considered. These models were optimized using of density functional theory (ADF2008 code) and the main parameters of quasicrystalline and crystalline structures (bond distances and bond angles) were determined. Quantitative changes of structural parameters within physically substantiated limits have been studied using multidimensional interpolation approximation method (FitIt2.0 code).

Poster no. PS1.81 - Session 1**Study of $\gamma - Fe_{2-x}Cr_xO_3$ ($0.75 \leq x \leq 1.25$) maghemite-like materials by XAFS and synchrotron-based XRD**

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Ferrimagnetic maghemite-like materials containing Fe^{3+} and Cr^{3+} in comparable amounts have been prepared for the first time by the so-called solution-combustion synthesis[1]. Insight regarding Fe^{3+} and Cr^{3+} interactions is required. One important open question is the distribution of Fe, Cr and vacancies among the octahedral and tetrahedral spinel sites. Concerning vacancies, for the case of maghemite $\gamma - Fe_2O_3$, [2] propose they are located on the 4b octahedral sites of $P4_332$ space group, while [3] suggest they are distributed among tetrahedral and octahedral sites of $Fd - 3m$. Regarding Fe and Cr, it is reasonably expected that Cr^{3+} , as t_{2g}^3 cation, should go to octahedral positions, while Fe^{3+} , a $t_{2g}^3e_g^2$ cation in a high spin configuration, would be in either octahedral or tetrahedral positions.

XAFS spectroscopy, combined with high resolution X-Ray Powder Diffraction (XRD), may contribute to clarify the considered structure. XAFS on both Fe- and Cr- K-absorption edges and synchrotron based XRD measurements on these materials were performed at SSRL. Applying XRD, the vacancy distribution in (Fe-Cr) maghemite structures has been determined. As a general tendency, tetrahedral sites are occupied by Fe and octahedral positions are shared by Fe, Cr and vacancies. XAFS spectra of all considered compositions are alike, showing differences in intensities of transitions. The shape of XANES and EXAFS spectra resembles those of $FeCr_2O_4$. Fitting using IFEFFIT and FEFF of XRD-obtained models confirms the Cr occupancy of octahedral sites, as well as the predominance of Fe-octah and Fe-tetrah closest neighbors backscattering paths, both in SS and MS cases.

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Poster no. PS1.82 - Session 1**Study of microscopic origin of the colossal magnetocaloric effect by EXAFS**Flávio Garcia¹, Gustavo de M. Azevedo, and Gilberto F.L. Fabbri*(1) Brazilian Synchrotron Light Laboratory (LNLS) Rua Giuseppe Máximo Scolfaro, 10000 13083-970 Campinas São Paulo Brazil*

Magnetic refrigeration, based on the magnetocaloric effect (MCE), is an environmental friendly cooling technology. Recently, it was verified that by applying hydrostatic pressure to the MnAs compound a significant increase on the adiabatic variation of magnetic entropy can be obtained[1]. The MCE value is found to be, at least, one order of magnitude greater than the ones observed for the magnetocaloric materials known to date, and it will open the way to the development of room temperature commercial magnetic refrigerators. It was observed that the maximum MCE value reached is far greater than the magnetic limit, assuming magnetic field independence of the lattice and electronic entropy contributions. This effect it was called Colossal MCE. It has been realized that the strong coupling of the spin and lattice could play an important role in the giant MCE. In very recent work, the Colossal Magnetocaloric Effect at room pressure was observed when a small amount of Mn is replaced by Fe or Cu (about 1%) [2]. The first explanation for this surprising behavior is a chemical pressure due to the smaller size of the substitutional elements. In this work, we have investigated the microscopic origin of the colossal MCE, in the MnAs and related compounds (namely 1% Fe or Cu doped MnAs), using EXAFS measurements as a function of the temperature and magnetic field. From our experimental data it was possible to determine the crystallographic sites occupied by the Fe and Cu in this system. Combined to results from others structural and magnetitic characterization techniques these results provided us with key information about the coupling between the magnetic and crystal structures, which are crucial for the theoretical understanding as well as further materials development.

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[2] A De Campos et al., Nature Materials 5 (10): 802 (2006).

Poster no. PS1.83 - Session 1**Understanding electronic structure of (Co, Cu) ferrite by x-ray absorption fine structure**Sanjeev Gautam¹, S Muthurani², M. Balaji², D. Pathinettam Padiyan², K.H. Chae¹, S.S. Kim³, and K. Asokan^{3,4}*(1) Nanomaterial Analysis Center Korea Institute of Science and Technology 136-791 Seoul KOREA**(2) Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, India**(3) School of Materials Science and Engineering, Inha University, Incheon 402-751, Korea**(4) Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110067 India*

Magnetic properties of spinel ferrites strongly depend on their constituent ions. Understanding the effect of substitutional metals on their magnetic and electronic properties will provide methodology to tailor new materials. We investigate the electronic structure of $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0, 0.5$) synthesized by auto combustion method using x-ray absorption fine structure (XAFS). XAFS provides unique opportunity to employ both near edge x-ray absorption fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS) and obtain information both element specific and local structure of absorbing atom. These magnetic materials ($\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0, 0.5$)) were characterized by x-ray diffraction and magnetic measurements [1]. NEXAFS and EXAFS measurements at Co and Fe K-edges on these materials were used to understand their electronic structure. The EXAFS data were analyzed using Athena [2] and successfully fitted to ferrite structure using IFEFFIT [3] from Artemis [2]. Results from this analysis were used to explain the reason for high saturation magnetization in these ferrites and high coercivity of Co-ferrite compared to other materials.

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Poster no. PS1.84 - Session 1**Local environment of Mn in Mn delta-doped Si layers**Robert A. Gordon¹, Qunfeng Xiao,¹ Samer Kahwaji,² Theodore L. Monchesky,² and E. Daryl Crozier¹*(1) Dept. of Physics, Simon Fraser University, 8888 University Dr., Burnaby, BC V5A 1S6 Canada**(2) Dept. of Phys. and Atmos. Sci., Dalhousie University, Halifax, NS B3H 3J5 Canada*

Dilute magnetic semiconductors combine both magnetic ordering and semiconducting behavior, leading to potential spintronic applications. Silicon containing dilute Mn impurities is a potential dilute magnetic semiconductor. We have grown Mn delta-doped films by deposition of 0.7 of a monolayer of Mn on Si(001) by molecular beam epitaxy and capping the film with Si. The magnetic properties are likely sensitive to the distribution of Mn on substitutional or interstitial sites and the formation of metallic precipitates. We have used polarization-dependent XAFS to examine the local structure. We compare to a thicker MnSi film grown on Si(111) and also examine the influence of lead on the manganese environment when used as a surfactant in the growth process.

Poster no. PS1.85 - Session 1**Localization of the Mn impurity in Mn:Ge diluted magnetic semiconductors by X-ray absorption at the Mn K-edge**Roberto Gunnella¹, L. Morresi¹, N. Pinto¹, M. Abbas¹, A. Di Cicco¹, L. Ottaviano², M. Passacantando², and A. Verna²*(1) CINSM-Dipartimento di Fisica, Camerino University, Via Madonna delle Carceri, 62032 Camerino, MC, Italy**(2) Dipartimento di Fisica, l'Aquila University, Via Vetoio, I-67010 Coppito (L'Aquila), Italy*

A unitary picture of the structural properties of $\text{Mn}_x\text{Ge}_{1-x}$ diluted alloys fabricated by either ion implantation or molecular beam epitaxy (MBE) at various growth conditions (from 80K to about 623K and few percents in concentration) is provided by synchrotron radiation x-ray absorption spectroscopy at the Mn K-edge. When the growth temperature exceeds 330K, the MBE samples show a high degree of precipitated ferromagnetic nanoparticles, mainly Mn_5Ge_3 , nucleated from the previous occupation of interstitial tetrahedral sites. Ion implantation at low temperatures (80K) indicates clear signs of substitutional Mn in Ge with a sizeable compressive local strain. The same efficient substitution is observed in the case of MBE samples made by alternate layers of GeMn alloys grown at $T < 433\text{K}$ and undoped Ge thick layers.

Poster no. PS1.86 - Session 1**Two-site behavior of apical atoms of Cu-O-Cl octahedra in checkerboard phased $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$** Sang Wwook Han¹, K. H. Kim², H. G. Lee, and Sung-Ik Lee³*(1) Division of Science Education, Institute of Fusion Science, and Institute of Science Education, Chonbuk National University, Jeonju, 561-756, Korea**(2) Department of Physics, Pohang University of Science and Technology, Pohang, 790-784, Korea**(3) National Creative Research Initiative Center for Superconductivity, Department of Physics, Sogang University, Seoul, 121-742, Korea*

Two-dimensional (2D) charge ordering (checkerboard phase) was observed in superconductor as well as insulator [1]. This raised questions if it is relevant to the pairing mechanism of superconductivity because the 2D charge ordering was observed in the CuO_2 plane of cuprate superconductors [2], in which the quasiparticles were present. Previous experiments from $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ (NaCCOC) crystals provided the evidence of the 2D charge ordering having a $4a \times 4a$ electric lattice [2], suggesting structural distortion and disorder existing in the bonding length of the Cu-neighboring atoms. Extended x-ray absorption fine structure (EXAFS) can detect the disorder because EXAFS describes the local structural properties around a selected species atom. EXAFS measurements of NaCCOC crystals at Cu K edge revealed that the apical Cl atoms of the Cu-O-Cl octahedra had two sites, irrespective of either the Na concentration or the temperature. The long and short bonding lengths differed by approximately 0.25 \AA and their ratio was 1 : 1. The two-site behavior of the apical Cl atoms of the octahedra in the NaCCOC crystals resulted from the removal of degeneracy of the Cu $3d^9$ electron ground state. The EXAFS measurements demonstrated anomalous disorders existing in the bond lengths of Cu-Cu pairs for all specimens below 50 K. The disorders of the Cu-Cu pairs were independent of the T_c value. The two-site behavior of the apical atoms and the anomalous disorders of the Cu-Cu pairs might be related to the checkerboard-phased charges.

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Poster no. PS1.87 - Session 1**XAFS studies of potential ZnO-based spintronics materials**

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ZnO doped with transition metals is a promising candidate for a room temperature diluted magnetic semiconductor (DMS). A robust room temperature DMS material is an important enabler for spintronics applications. While room temperature magnetism has been observed by several groups in doped ZnO, there is still much debate over whether these represent true DMS behavior. Magnetic nano-precipitates or secondary phases are potential complicating factors. Such phases and precipitates can be difficult to detect in thin epitaxial films, the form in which many of these materials are made. As an element specific probe, XAFS measurements have proven invaluable in characterizing doped thin films. In this paper we present as examples XAFS data for Mn and Co doped ZnO thin films. For the Mn doped ZnO, the Mn is found to be Mn(II) and to reside in the tetrahedral Zn sites. There is no evidence for secondary phases or metallic nanoparticles. For Co doped ZnO the situation is more complicated. Many of the samples showed evidence for metallic nanoparticles. The nature of these nanoparticles depends on the preparation conditions. For films prepared with high Co concentrations and an Al co-dopant, the nanoparticles were close packed (hcp or fcc) Co metal. For another set of films which were annealed in Zn vapor to induce magnetism, the metallic particles resembled CoZn. Both Co and CoZn are magnetic and can contribute a spurious magnetic signal unrelated to a true DMS signal.

Poster no. PS1.88 - Session 1**Effect of hydrogenation on the electronic state of metallic La hydrides probed by X-ray absorption spectroscopy at the La *L*-edges**

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The electronic state of La hydride (LaH_x) has attracted interest since the discovery of the metal-insulator (M-I) transition that occurs at $x \sim 2.8$. [1] Changes in the electronic state near the Fermi energy (E_F) due to the hydrogenation are key issues to understand the transition. To study the key issues, X-ray absorption spectroscopy (XAS) is one of the useful methods that provide element- and orbital-specific information of the electronic state.

Here, we present a study of the electronic states for La 5d and 6p in metallic LaH_x ($x=0, 2.0, 2.3, 2.6$) probed by XAS at the La *L*-edges (L_1 , L_2 , and L_3). The hydrogen atoms dominantly occupy tetragonal H_t (octahedral H_o) sites at the hydrogenation below (above) $x=2$, so that the series of the samples allows us to determine the electronic state taking into account the different hydrogen sites.

The XAS measurement was performed at SPring-8 BL39XU. At the L_2 - and L_3 -edges, prominent white-line is observed near the absorption edge. The intensity of white-line gradually increases as the hydrogenation x increases from 0 to 2.6. This enhancement is attributed to that the occupation of both H_o and H_t sites gives rise to an increase in La 5d hole. XAS at the La L_1 - edge of La metal ($x=0$) is characterized by a shoulder structure near the absorption edge, whereas the shoulder largely disappears at $x=2$. This collapse indicates that La 6p density of states near E_F is reduced due to the hydrogenation at H_t site. This study, therefore, successfully demonstrates that the hydrogenation significantly modifies not only La 5d but also La 6p electronic states near E_F . The modification of the electronic states should be associated with onset of the M-I transition.

This work was supported by the Grants of the NEDO project "Advanced Fundamental Research on Hydrogen Storage Materials."

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Poster no. PS1.89 - Session 1**Growth temperature dependence of local structures of $\text{Fe}_{0.05}\text{Si}_{0.95}$ diluted magnetic semiconductors investigated by X-ray absorption near structure**Yong Jiang¹, Tao Yao¹, Jian Ye¹, Qinghua Jiang¹, Hiroyuki Oyanagi², and Shiqiang Wei¹*(1) National Synchrotron Radiation Laboratory, University of Science and Technology of China, 42 HeZuoHua Road, Hefei, Anhui 230029, P.R. China**(2) Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

X-ray absorption near-edge structure (XANES) spectroscopy was used to investigate the local structures of $\text{Fe}_{0.05}\text{Si}_{0.95}$ diluted magnetic semiconductors (DMSs) thin film deposited by radio-frequency (RF) reactive magnetron co-sputtering device at temperatures of room-temperature (RT), 473K and 573K. Using the ab initio self-consistent real-space multiple-scattering approach, the experimental XANES spectra can be well reproduced by the theoretical calculation curves. The results indicate that the majority of Fe atoms are located at Si substitutional sites Fe_{Si} in $\text{Fe}_{0.05}\text{Si}_{0.95}$ at the room temperature. Upon increasing the temperature to 473 and 573 K, the majority of Fe atoms tends to form the FeSi alloy.

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Poster no. PS1.90 - Session 1**The Study of $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ using X-ray Absorption Near-Edge Spectroscopy**Onlamee Kamon - In¹, W. Pattanasiriwisawa¹, A. Yangthaisong¹, and S. Srilomsok¹*(1) Saranaree University of Technology 111 University Avenue 30000 Muang Nakhon Ratchasima Thailand*

The La-doped Barium titanate is an important electronic ceramic material. In this work the $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ compounds prepared by solid state reaction route were investigated. The X-ray Absorption Near-Edge Structure (XANES) at Ti K-edge (4966 eV), Ba L_{III}-edge (5247 eV) and La L_{III}-edge (5483 eV) were analyzed. Result suggests that La^{3+} substitution cause the distortion around Ti-atom while there is almost no change around Ba-atom.

Poster no. PS1.91 - Session 1**N- K- edge nexafs study of the defects induced by indium implantation in GaN.**Maria Katsikini¹, Fani Pinakidou¹, Eleni C. Paloura¹, Elke Wendler², Werner Wesch², and Recardo Mancke³*(1) Aristotle University of Thessaloniki, School of Physics, 54124 Thessaloniki, Greece**(2) Institut für Festkörperphysik, Friedrich-Schiller Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany**(3) Humboldt-Universität zu Berlin, Institut für Physik, Newtonstraße 15, 12489 Berlin, Germany*

Indium implantation is a promising method for the growth of InGaN-GaN heterostructures and nanostructures, such as quantum dots, which find applications in the fabrication of high efficiency light emitting diodes as well as in high-frequency, high - power microelectronic devices. Although ion implantation has the advantage of precise control of the projectile dose and profile, it causes lattice damage which can be recovered via annealing. Here, we apply N - K - edge NEXAFS spectroscopy in order to determine changes in the electronic structure of GaN that are induced after implantation of 700keV In ions at fluencies ranging from 5×10^{13} to 1×10^{16} ions/cm². The NEXAFS measurements were performed in the fluorescence yield mode at the PM3 bending magnet beamline of the BESSY Synchrotron Radiation facility that is equipped with a plane grating monochromator. The NEXAFS results are discussed in combination with Rutherford backscattering characterization that can assess the implantation induced damage. The main effects of ion implantation on the NEXAFS spectra are: (a) broadening of the NEXAFS peaks with increasing implantation fluence, (b) emergence of a pre-edge shoulder (RL1) that is attributed to N interstitials and (c) appearance of a post-edge sharp peak (RL2) that is attributed to molecular nitrogen trapped in the GaN matrix. RL2 corresponds to vibronic transitions since it is also results to a change of the vibrational quantum number of the N₂ molecule. This is evident by the equispaced (by 236meV) peaks that comprise the RL2. Furthermore, the maximum defect concentration deduced from the Rutherford backscattering measurements, the width of the NEXAFS peaks and the area under RL1 and RL2 show a sigmoidal dependence on the logarithm of the ion fluence.

Poster no. PS1.92 - Session 1**XANES and XEOL studies of Eu-doped calcium tungstate in silica synthesized by sol-gel method**Jun Young Peter Ko¹, Yongfeng Hu², Lidia Armelao³, and Tsun-Kong Sham¹*(1) Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7 Canada**(2) Canadian Light Source, University of Saskatchewan, 101 Perimeter Road, Saskatoon, SK S7N 0X4 Canada**(3) Department of Chemistry, University of Padova, via Marzolo 1, 35131 Padova, Italy*

Calcium tungstate (CaWO_4) is well known for its use as a scintillator, and has been studied extensively for its interesting luminescence properties [1]. When scheelite materials, such as CaWO_4 , is doped with a rare earth element (e.g. Eu), it reveals non-radiative pathway for energy transfer to activator, emitting red light. Such materials have great potential for light emitting diode application [1]. Synthesis is typically done via solid-state reaction [2] and Pechini sol-gel method [3].

Here, we present preliminary findings of X-ray Absorption Near-Edge Structure (XANES) at the calcium $L_{3,2}$ -, calcium K- and oxygen K-edges, and X-ray Excited Optical Luminescence (XEOL) of Eu-doped CaWO_4 synthesized by sol-gel method. All Ca $L_{3,2}$ - and O K-edge XANES and XEOL measurements were performed on the High-Resolution Spherical Grating Monochromator beamline 11ID-1, and Ca K-edge XANES measurements were performed on Soft X-ray Microcharacterization Beamline 06B1-1 at the Canadian Light Source.

XANES results demonstrate that the chemical environment around calcium in Eu-doped CaWO_4 is similar to that of standard CaWO_4 . On the other hand, chemical environment around oxygen is very different (silica vs CaWO_4). Moreover, the results suggest that contributions to luminescence are from both silica and CaWO_4 . Using XEOL, luminescence pathways and efficiency associated with the system can be identified.

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Poster no. PS1.93 - Session 1**Electronic structure of some titanium-containing compounds: X-ray absorption near-edge structure investigation**Antonina N. Kravtsova¹, Alexander V. Soldatov¹, Maarten Nachtegaal², Min Wei Tew³, and Jeroen A. van Bokhoven³*(1) Southern Federal University, Sorge str. 5, 344090 Rostov-on-Don, Russia**(2) Paul Scherrer Institut, 5232 Villigen PSI, Switzerland**(3) Institute for Chemical and Bioengineering, ETH Zurich, Switzerland*

Electronic structure of some titanium-containing compounds has been studied by analyzing the Ti K -edge X-ray absorption near-edge (XANES) spectra. Experimental Ti K -XANES spectra of Zn_2TiO_4 and Al_2TiO_5 and reference compounds - TiO_2 (rutile and anatase phases), were measured at the SuperXAS beamline of the Swiss Light Source (SLS) (Villigen, Switzerland). Theoretical Ti K -XANES spectra of TiO_2 (rutile and anatase phases), Zn_2TiO_4 and Al_2TiO_5 were simulated on the basis of full multiple scattering theory and finite difference method using FEFF8.4 and FDMNES2007 codes. The calculations were done within the muffin-tin approximation for potential shape and using a full potential. The influence of muffin-tin effects on the shape of Ti K -XANES spectra of the titanium-containing compounds was determined. A much better agreement between the theoretical and experimental spectra was obtained when using the full potential compared to the muffin-tin approximation.

The electronic structure of the TiO_2 (rutile and anatase phases), Zn_2TiO_4 and Al_2TiO_5 was determined by calculating the partial electronic densities of states (DOS) near the bottom of the conduction band and near the top of the valence band. The DOS simulations were done on the basis of density functional theory using the WIEN2k program code. An interpretation of the pre-edge features of the Ti K -XANES spectra of the investigated compounds could thus be achieved.

Poster no. PS1.94 - Session 1**Electronic structure study of Cu doped ZnO by x-ray absorption spectroscopy**Shalendra Kumar¹, S. Gautam², Ravi Kumar³, K.H. Chae², Y. J. Kim¹, B. H. Koo¹, and C. G. Lee¹*(1) Changwon National University School of Nano and Advanced Materials Engineering 641-773 Changwon, Republic of Korea**(2) Nanomaterial Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea**(3) Inter University Accelerator Centre (IUAC), New Delhi 110067, India.*

In the recent years dilute magnetic semiconductors (DMSs) has attracted the interest of researchers due to their potential application in spintronics devices. Initially, it was assumed that DMSs and their properties can be tailored by the partial replacement of cations in semiconducting host matrix by the transition metal (TM) cations [1, 2]. Even though ferromagnetism has been observed in a number of system, experimental studies on TM doped ZnO have produced inconsistent results and the mechanism of ferromagnetism in TM doped ZnO remains unclear. Such controversy about whether the observed FM is an intrinsic or extrinsic property of the material motivated us to study the FM in Cu doped ZnO. As it is well known that Cu is a potential magnetic ion only in +2 state with +1/2 spin and neither metallic Cu nor its oxide (CuO and Cu₂O) is ferromagnetic [3]. In this work we aimed to understand the electronic structural studies of Cu doped ZnO prepared by co-precipitation technique ($Zn_{1-x}Cu_xO$, $x = 0.01$ and 0.05) by x-ray absorption fine structure (XAFS). The Cu doped ZnO samples exist in wurtzite lattice as substitution atom without forming secondary phases. Magnetic measurements indicate that all the samples are ferromagnetic at room temperature and the magnetic moment decreases with increase in the concentration of Cu ions [4]. The EXAFS data is simulated using Artemis [4, 5] and successfully fitted to wurtzite structure of Cu-ZnO. The results indicate that Cu atom exist in Cu²⁺ and replaces Zn ion in tetrahedral symmetry.

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Poster no. PS1.95 - Session 1**Formation of TiO₂ - particles in solution-sol-gel (SSG) process investigated with QEXAFS and UV/Vis**Dirk Lützenkirchen-Hecht¹, Emiliano Fonda², Francoise Villain³, Valerie Briois², and Ronald Frahm¹*(1) Fachbereich C - Physik, Bergische Universität Wuppertal, Gauss-Strasse 20, 42097 Wuppertal, Germany**(2) Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, 91192 Gif sur Yvette, France**(3) Laboratoire de Chimie Inorganique et Matériaux Moléculaires - UMR 7071, Université Pierre et Marie Curie - Paris 6, 4 place Jussieu, 75252 Paris cedex 05, France*

TiO₂ - particles are important for many applications because of their high refractive index, their capability to absorb ultraviolet light and - last not least - because they are non-toxic. Thus they are used in cosmetics, food, paper, paints, dielectric mirrors and surfaces for glasses to mention only a few examples. Another important application is the use of TiO₂ in catalysis, especially as photocatalyst for water and air purification. For this purpose a high specific surface is necessary, which directly leads to the use of small, i.e. nano-sized particles. Here these particles were formed with the Solution-Sol-Gel (SSG) process which includes the hydrolysis of the titanium alkoxide Ti(OPrⁱ)₄ as precursor and the condensation to TiO₂ via nucleophilic substitution and aggregation. These sub-processes were investigated in-situ and time resolved with QEXAFS at the Ti K-edge and UV/Vis-spectroscopy in parallel. The experiments were performed during the first QEXAFS measurements at the SAMBA beamline at SOLEIL. To reach an adequate time resolution for the fast hydrolysis process was a special challenge in this experiment because of the high parasitic absorption by the solution due to the low X-ray energy at about 5 keV. With quantitative methods for the QEXAFS data like Principal Component Analysis (PCA) and Linear Combination Fits (LCF) the participating species could be identified and more important their amounts as a function of time were determined. Complementary the UV/Vis data was used to correlate the amounts of each appearing component to the particle size. Systematic variations of the water addition rate and the reaction temperature allow a detailed insight into the mechanisms of the SSG process.

Poster no. PS1.96 - Session 1**Oxidation state of sulphur, iron and tin at the surface of float glasses**Pierre A. Lagarde¹, Anne-Marie Flank¹, Jacques Jupille², and Hervé Montigaud³(1) *Synchrotron SOLEIL, l'Orme des Merisiers, BP 48 91192 Gif sur Yvette cedex (France)*(2) *IMPMC, Université P. & M. Curie, Campus de Boucicaut, 140 rue de Lourmel 75015 Paris (France)*(3) *Saint-Gobain Recherche 39, quai Lucien Lefranc, BP 135 93303 Aubervilliers Cedex (France)*

Sulfur is an important element of glasses, not because of its amount, always very low (less than 0.4 % in weight of SO₃), but because of its role since it actively participates to the refinement process and, combined to other elements, it can be responsible for the coloration of the glass. Iron is also of a major importance in most of the glasses. In the case of the float glass, the two faces, because of the fabrication process, are different in terms of composition (presence of Sn for one face) and also in terms of oxidation state of these minority elements (Fe, Sn, S). There should be a subtle interplay between the concentrations and the oxidation states of these different minority elements, and anyway these variations occur over a thickness of the order of few micrometers below the surface.

Using the high intensity and the focusing properties ($2 \times 2 \mu\text{m}^2$) of the x-ray beam from the Lucia beamline, we have therefore studied the speciation of iron and sulfur near the two faces of float glasses of different thicknesses, in relation with the behavior of the presence of tin on one face. This has been obtained by combining elemental x-ray fluorescence cartography and x-ray micro-absorption at the different K-edges.

The first step of this study has been a careful mapping of these elements within an area extending to a few tens of micrometers below the surface. Then the analysis of the near edge structure of the iron, tin and sulfur k-edges has allowed us to follow the variation of the oxidation state of these elements as a function of the depth below the surface.

Poster no. PS1.97 - Session 1**Probing the involvement of non-magnetic Sr ion in the ferromagnetic transition of SrRuO₃, using XAFS**Debdutta Lahiri¹, T. Shibata², S. Chattopadhyay², Surinder M. Sharma¹, and K. B. Maiti³(1) *Bhabha Atomic Research Centre, India High Pressure Physics Division, BARC 400085 Mumbai India*(2) *Illinois Institute of Technology, USA.*(3) *Tata Institute of Fundamental Research, India.*

Recent calculations by Maiti et. al. have shown that non-magnetic ions like Sr/ Ca in Sr/Ca Ruthenates may not be mere spectators in the magnetic transitions but their strong hybridization with O atoms may modify the magnetic ground state by distorting the Ru-O-Ru angle. Our recent XAFS measurements at Sr and Ru K-edges on SrRuO₃ clearly demonstrate that the thermal evolution of Sr-Sr Debye Waller factor (fit result) replicates the ferromagnetic transition curve while the Ru-Ru or the Ru-O Debye-Waller factors merely follow the correlated Debye Model pattern. This implies that while the Ru-O octahedral is rigid, it is the Sr atoms that are moving around. The Debye-Waller factor of Sr-Ru bond is found to be very high and swamps any thermal evolution function. These trends are clearly beyond any fitting artifact as the Fourier transform of the data itself demonstrates these changes. There is no change in bond-length (to the third decimal place) with temperature. Electronic structure calculations are underway, using the structural fit parameters, to understand these remarkable observations

Poster no. PS1.98 - Session 1**XANES K-spectra of sulfur in the complicated semiconductor**Anatolii Aleksandrovich Lavrentyev¹, B.V. Gabrelian¹, I.Ya. Nikiforov¹, P.N. Shkumat¹, and J.J. Rehr²(1) *Don State Technical University Gagarin sq.1 344010 Rostov-on-Don Russia*(2) *University of Washington, Seattle, WA98195, USA*

Both experimentally and theoretically the X-ray absorption spectra of sulfur in the ternary compounds TlAsS₂, TlGaS₂, and TlInS₂ with complicated crystallographic structure were investigated. The experimental absorption spectra were studied by transition way using the X-ray spectrograph with the focusing crystal Si by Johann method. The resolution of apparatus was about 0.2 eV. The theoretical forms of spectra were calculated in the frame of the cluster version of the multiple scattering theory using the FEFF8 code [1]. The difficulties in these calculations were connected with complicated crystallographic structure of the compounds. The number of nonequivalent positions of sulfur in the elementary cell achieved 8. For each of them the cluster of about 200 atoms was built and XANES spectrum was calculated. The averaged calculated K-spectra correspond to the experimental ones satisfactorily.

Poster no. PS1.99 - Session 1**EXAFS Study of Double Perovskite ($\text{Sr}_{2-x}\text{Ca}_x$) FeMoO_6 ($0 \leq x \leq 2$) and Sr_2CrMo_6 ($\text{M} = \text{Mo}, \text{W}$) Systems**Jyh-Fu Lee¹, T. S. Chan¹, and R. S. Liu²

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The local atomic structures of the double perovskite ($\text{Sr}_{2-x}\text{Ca}_x$) FeMoO_6 ($0 \leq x \leq 2$) and Sr_2CrMo_6 ($\text{M} = \text{Mo}, \text{W}$) systems have been probed by extended X-ray absorption fine structure (EXAFS) spectroscopy at the Fe and Cr K-edges. It was found that the Fe-O distance decreases from 1.999 Å ($x = 0$) to 1.991 Å ($x = 1.0$) in ($\text{Sr}_{2-x}\text{Ca}_x$) FeMoO_6 with a tetragonal structure. When the x value is increased further from 1.5 to 2.0, the Fe-O bond distance decreases from 2.034 Å to 2.012 Å (monoclinic structure). On the other hand, Cr-O, Cr-Sr and Cr-W bond distances in Sr_2CrWO_6 are all slightly larger than the corresponding bond distances in $\text{Sr}_2\text{CrMoO}_6$, which is attributable to the larger ionic radius of W^{5+} (0.62 Å) than Mo^{5+} (0.61 Å).

Poster no. PS1.100 - Session 1**Effect of oxygen vacancy on room-temperature ferromagnetism of rutile Co-doped $\text{TiO}_{2-\delta}$ thin films**Qinghua Liu¹, Wensheng Yan¹, Zhihu Sun¹, Zhiyun Pan¹, Tao Yao¹, Ziyu Wu¹, and Shiqiang Wei¹

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The x-ray absorption near-edge structure (XANES) spectroscopy and first-principles calculations were employed to study the local structure and magnetic origin of rutile Co-doped $\text{TiO}_{2-\delta}$ thin film with room-temperature ferromagnetism. The experimental Co K-edge XANES can be reproduced by the calculated spectrum of substitutional Co^{2+} with the presence of neighboring O vacancy (V_O). Furthermore, the first-principles total energy calculations reveal that the formation of O vacancy can be facilitated by the neighboring Co doping, demonstrating the presence of $\text{Co}^{2+}\text{-V}_\text{O}$ complex in TiO_2 matrix. The calculated electronic structures show that the O vacancy induces a shallow spin-split donor state with t_{2g} character within the gap region, and leads to a strong exchange interaction between the localized carriers captured by O vacancy and the substitutional Co^{2+} ions. As a result, the ferromagnetic coupling between the Co^{2+} ions in Co-doped $\text{TiO}_{2-\delta}$ system is significantly enhanced.

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Poster no. PS1.101 - Session 1**XAFS studies of Pt nanoparticles deposition on Si nanowires**Lijia Liu¹, Michael Murphy¹, J.Y. Peter Ko¹, and Tsun-Kong Sham¹

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We have studied the Pt $\text{L}_{3,2}$ -edge X-ray absorption fine structures (XAFS) of Pt nanoparticles (PtNPs) deposited on silicon nanowires (SiNWs). SiNWs were fabricated via electroless chemical etching of a silicon wafer. The as-grown SiNWs were uniform and perpendicular to the substrate, and were used as the template for PtNPs deposition. PtNPs were electrolessly reduced from their ionic solution by HF-treated SiNWs, and were found deposited on the tips of SiNWs. For comparison, we have also examined the Pt $\text{L}_{3,2}$ -edge XANES of Pt-Au bimetallic nanoparticles co-deposition on SiNWs, and Pt on activated carbon (commercial catalysts).

We found that the deposited PtNPs showed similar resonance peaks but a less intense whiteline compared to Pt foil. It is also interesting to note that when Au was deposited together with Pt, the resonance peaks were slightly shifted due to the formation of Pt-Au bimetallic alloys. When carbon, instead of silicon, served as the substrate of Pt, the white line intensity was greatly increased. Since the whiteline intensity is a measure of d charge population of Pt, this unique feature that associates with d charge redistribution upon catalyst formation can further be used to track the performance of PtNPs catalysts deposited on other carbon-related substrate (carbon nanotubes, etc).

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Poster no. PS1.102 - Session 1**Investigations of porous silicon produced by etching of c-Si in water solution of NH_4F** K. M. Lysenkov¹, E.O. Filatova¹, A.A. Sokolov¹, V.M. Kashkarov², and D.E. Marchenko³*(1) St.-Petersburg State University Ulyanovskaya str,1 198504 St.-Petersburg Russia**(2) Voronezh State University Universitetskaya pl,1 394006 Voronezh Russia**(3) BESSY Albert Einstein str,15 D-12489 Berlin Germany*

Porous silicon is extremely interesting due to channeling-like effects into it. It is known that por-Si produced using traditional method oxidize vastly in time; this confines its practical application ability. At present time is noted a search of new methods, which should allow producing por-Si films with less quantity of oxides and with more stable properties.

The aim of this work was investigation of por-Si produced with non-traditional method worked out – by electrochemical etching of c-Si (100) in water solution of NH_4F with addition of isopropyl alcohol. Investigations were carried out by X-ray reflection spectroscopy and NEXAFS spectroscopy.

For the sample obtained by non-traditional method, Si $L_{2,3}$ reflection spectrum contains details of amorphous phase of Si and details corresponding to SiO_2 structure, while reflection spectrum of traditionally produced sample contains only SiOx structure.

NEXAFS spectra of sample obtained by non-traditional were measured in energy range 97-115 eV for incidence angles from 5^0 to 55^0 . It was established that Si $L_{2,3}$ absorption spectra of por-Si contains both Si and SiO_2 structures. Shape and intensity of SiO_2 structure is invariable for all the incidence angles concerned, while sufficient change of the shape of Si $L_{2,3}$ structure of Si is marked in the angular region from 5^0 to 45^0 . One can predict this effect is due to change of a pores' square illuminating by initial X-rays. Results of NEXAFS measurements are in a good agree with results of measurements by X-ray reflectivity techniques.

Significant difference in composition of por-Si sample produced using non-traditional method was established in comparison with traditionally produced one.

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Poster no. PS1.103 - Session 1**X-ray absorption spectroscopy studies of the local structures of diluted magnetic semiconductor thin films**Qing Ma¹, C. Sudakar², G. Lawes², R. Naik², V. M. Naik², J. P. Prater³, J. Narayan⁴, D. B. Buchholz⁵, and R. P. H. Chang⁵*(1) DND-CAT, Northwestern Synchrotron Research Center at the Advanced Photon Source, 9700 South Cass Avenue 60439 Argonne IL USA**(2) Department of Physics and Astronomy, Wayne State University, Detroit, MI 48201, U.S.A.**(3) Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, U.S.A.*

Reports from several groups of observation of ferromagnetism in copper doped ZnO thin films prepared under various conditions prompt this study of the local structures of these films using x-ray absorption spectroscopy technique. In this report we present some of the findings on the local structures and discuss their implications to magnetic properties.

Poster no. PS1.104 - Session 1**XAFS study of the Ru 4d orbital occupation in Ruddlesden-Popper strontium ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ($n = 1, 2, 3$): the influence of the lattice distortions on the electronic structure.**

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We report the polarization-dependent XANES study results of the electronic and local atomic structures of the Ruddlesden-Popper (RP) layered strontium ruthenate series, $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$. Ruthenium oxides are a particularly interesting class of materials exhibiting fascinating physical properties like unconventional superconductivity, ferromagnetism and metamagnetism, orbital ordering resulting from the intimate interplay between charge, spin, orbital, and lattice degrees of freedom. In particular, the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ layered system have become a prototype for exploring intriguing physical phenomena due to a subtle interplay between structural anisotropy and distortions, multi-band effects and magnetic fluctuations. Despite the fact that the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ compounds are all based on Ru^{4+} ions, octahedrally coordinated by oxygen atoms, with electronically inactive Sr-site counter-ions, they show a rich variety of magnetic and electronic states with experimental signatures of strong coupling to the lattice distortions driven by the number n of perovskite RuO_6 layers in the unit cell.

Oxygen K-edge XAS spectroscopy has a proven ability to shed light on the site symmetry and the occupation of empty states hybridized with O $2p$ orbitals, and have been successfully employed in $3d$ correlated transition metal oxides such as cuprates, manganites and cobaltates.

By comparing the polarization-dependent O K-edge XANES data with the complementary structural information provided by the x-ray diffraction study, we show how the unoccupied DOS resulting from the hybridization of O $2p$ -Ru $3d$ and O $2p$ -Sr $3d$ are affected by the rotations and tilting of the RuO_6 octahedra. We also present results on the O K edge XANES spectra and partial density of states simulated by means of Full Multiple Scattering theory and directly compared with the experimental data.

Poster no. PS1.105 - Session 1**XAS versus XRD studies of $\text{Ba}_{0.90}\text{Ca}_{0.10}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ Ferroelectrics Materials**

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Ferroelectric materials have been used in a large field of applications because of their excellent dielectric, piezoelectric and ferroelectric properties. Lead-free compositions are of great interest for environmentally-friendly applications and several studies have been performed in a large set of compositions derived from the well known BaTiO_3 ferroelectric ceramic compound. Barium zirconate titanate ($\text{BaZr}_{1-x}\text{Ti}_x\text{O}_3$ or BZT) solid solution has recently received extensive attention due its high strain level and high piezoelectric properties. It has been observed that the substitution of Ba by Ca ions and Ti by Zr ions lead to complex effect on the ferroelectric of the BZT based compound. Although the dielectric properties of these materials have been extensively studied, few systematic works have been done in order to verify the effect of sample composition on the local structure of these samples. Thus, in this work, we present a systematic study of the crystalline and short-range order around barium and titanium atoms by X-ray absorption spectroscopy and synchrotron powder diffraction. The analysis of the XANES spectra collected on the EXAFS line of LNLS at the titanium K edge shows that the substitution of Ti by Zr atoms does not modify significantly the local order around Ti atoms. On the other hand, the measurements of the EXAFS spectra at the Ba K-edge, recorded on the SAMBA line of SOLEIL, shows that the local order around barium atoms were more sensitive to the modification of the sample composition. The analysis of the Ba K edge EXAFS spectra collected at different temperatures below and above the maximum of the dielectric permittivity will be also be discussed. The experimental and theoretical XAFS results will be compared to the X-ray powder diffraction Rietveld refinements.

Poster no. PS1.106 - Session 1**Quantitative elemental analysis using x-ray absorption edge jump**Nobuyuki Matsubayashi¹, Motoyasu Imamura¹, Jiangwei Fan¹, and Isao Kojima¹*(1) National Institute of Advanced Industrial and Science Technology Tsukuba Central 5, 1-1-1, Higashi 3058565 Tsukuba Ibaraki Japan*

A quantity of x-ray absorption by an absorption edge follows Lambert-Beer law so it can be a method for quantitative analysis of an element in various materials without destruction if the coefficient is exactly determined. The determination of the edge jump without affection of state of absorbing atom is one of the technical problems. We have developed the method to determine the edge jump automatically by modifying a method for XAFS analysis. XAFS spectra of K and L3-edge for various element in standard solutions (1 g/dm³ standards for Atomic Absorption Spectrometry by Wako Pure Chemical Industries, Ltd.) in transmission mode were measured using synchrotron radiation at Photon Factory using precise quartz cells with 1 - 4 cm thickness which are certified by Japan Quality Assurance Organization using the three-dimensional measurement system (Carl Zeiss UMM550) traceable to national standard of Iodine-stabilized He-Ne laser (NMIJ). An absorption edge jump of excitation cross section of a specific core electron of an isolation atom is in proportion to the number of atom on optical path. The absorption edge jump per an unit of optical density of element (1 g/cm²) is defined as absorption edge jump coefficient, $C\Delta\mu$ (cm²/g), relation of $\Delta\mu = C\Delta\mu D$, where $\Delta\mu$ is a quantity of the absorption edge jump of the element, D is the optical density of the element (g/cm²). The values of $C\Delta\mu$ for K-edge and L-edge absorption of a series of elements were determined experimentally. The values of $C\Delta\mu$ well agreed with the calculated values from mass absorption coefficient using Victreen formula [1] and semi empirical calculation data by Henke et al.[2].

[1] "The International Tables for X-ray Crystallography" 2, 157 (1972) .

[2] B. L. Henke, E. M. Gullikson, and J. C. Davis, Atomic Data and Nuclear Data Tables, 54 , 181 (1993) .

Poster no. PS1.107 - Session 1**Au subnanometer structures and the Er site trigger the Er photoluminescence efficiency at 1.5 μ m in Er and Au co-doped silica.**Chiara Maurizio¹, Giovanni Mattei², Enrico Trave³, Francesco D'Acapito¹, Giovanni Perotto², Giovanni Pellegrini², and Paolo Mazzoldi²*(1) CNR-INFM c/o ESRF 6 rue J. Horowitz 38000 Grenoble France**(2) Università di Padova, via Marzolo 8 35131 Padova (Italy)**(3) Università Ca' Foscari di Venezia, S. Marta, 30123 Venezia (Italy)*

In these last years it has been shown that specific sensitizers can dramatically enhance the 1.54 μ m Er luminescence efficiency, so that Er-doped materials can be employed in the field of optical communications; among the species that act as sensitizers, there are other rare earths, semiconductor nanostructures, organic complexes and more recently metals like Ag. In this work, we have doped by Au implantation a series of Er-implanted silica samples; the x-ray absorption spectroscopy, performed at the Au L_{III}-edge shows that the interplay between the different preparation parameters allow to form Au nanostructures ranging from isolated and oxidized Au atoms to Au subnano- and nano-clusters. This structural analysis, combined with the x-ray absorption spectroscopy at the Er L_{III}edge is used to understand the photoluminescence properties of these systems. In particular, it is found that sub-nanometric Au particles act as efficient sensitizers for Er luminescence emission at 1.54 μ m.

Poster no. PS1.108 - Session 1**Local crystalline structure of Sm-Co alloys: results of XAFS-analysis**

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Local crystalline structure of hypo- and hyperstoichiometric SmCo_x alloys with $x=5.1, 4.5, 4, 3.5$ after various heat treatments was investigated by means of the x-ray absorption spectroscopy. XANES analysis demonstrates the decrease of L_3 -Sm absorption peak amplitude with Sm concentration growth. Such behavior indicates that doping by samarium increases the 5d-band infill. Fourier and Wavelet analysis of EXAFS spectra reveal the appearance of lattice defects in hypostoichiometric alloys with $x=4$ and 3.5 . Co ions replacement by Sm give rise to the forming of the new phase enriched by Sm. This fact confirms the hypothesis of high-coercivity state induced by phase transformations changing the state of master phase grain surface.

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Poster no. PS1.109 - Session 1**XAS studies of $\text{Pb}_{1-x}\text{R}_x\text{Zr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ ($\text{R} = \text{La}, \text{Ba}$) ferroelectrics materials**

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Solid solutions of lead zirconate and lead titanate ($\text{PbZr}_{1-y}\text{Ti}_y\text{O}_3$ or PZT) represent an important technological family of ferroelectrics and antiferroelectrics whose properties and phase transitions have been extensively studied. These materials have been used as capacitors, actuators, transducers and electro-optic devices. It is well known that the substitution of Pb^{2+} by La^{3+} or Ba^{2+} atoms lead to a significant variation on electrical and structural properties of the $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ ceramic system. For samples containing a large amount of La^{3+} or Ba^{2+} , a transition from a normal to a relaxor ferroelectric behavior has been observed. From the structural point of view, a transition from a low to a high symmetric phase has been observed. In order to better understand the effect of substitution of Pb^{2+} by La^{3+} or Ba^{2+} atoms at the short-range order structure around Ti and Pb atoms in the $\text{Pb}_{1-x}\text{La}_x\text{Zr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ (PLZT) and $(\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.40}\text{Ti}_{0.60}\text{O}_3)$ PBZT ceramic systems, the X-ray absorption spectra at the Ti K-edge and Pb L_{III} -edge were measured. PLZT compositions with x varying from 0.0 to 0.21 and PBZT compositions with x varying from 0.10 to 0.50 were prepared by using a solid state reaction route. Titanium K-edge and lead L_{III} -edge X-Ray absorption spectra were collected at the LNLS (National Synchrotron Light Laboratory) facility using the D04B-XAS2 beam line. The LNLS storage ring was operated at 1.36 GeV and 100-160 mA. The analysis of the XANES spectra collected at the Ti K-edge shows that the increase of La or Ba amount causes a decreasing in local disorder of the TiO_6 octahedron in perovskite structure. The analysis of the EXAFS spectra collected at the Pb L_{III} -edge indicates that the local structure around Pb atoms is also affected by the introduction of La or Ba atoms in the structure. A possible relationship between the structural results and the dielectric properties will be discussed.

Poster no. PS1.110 - Session 1**XAFS characterization of zircon and scheelite $R\text{CrO}_4$ (R= Er and Y) polymorphs**Maria Elena Montero Cabrera¹, R. Sáez-Puche², E. Climent-Pascual², E. Morán², M. E. Fuentes³, and L. Fuentes-Cobas¹*(1) Centro de Investigación en Materiales Avanzados Miguel de Cervantes 120, Complejo Ind. Chihuahua 31109 Chihuahua Chihuahua Mexico**(2) Departamento Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense Madrid, Ciudad Universitaria, Madrid 28040, Spain**(3) Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus, Chihuahua, Chih. Mexico*

$R\text{CrO}_4$ ($R^{3+} = \text{Er}$ and Y) crystallizes into a tetragonal zircon-type structure at ambient conditions. It is built from edges sharing RO_8 dodecahedra chains which are connected each other by CrO_4 tetrahedra. Scheelite polymorphs (S.G. $I4_1/a$) [1,2] of $R\text{CrO}_4$ were prepared under high pressure conditions (50 kbar) from the corresponding zircon forms of $R\text{CrO}_4$ (S.G. $I4_1/amd$). Cr in this materials develops the relative rare Cr^{+5} oxidation state. Bulk magnetic and specific heat measurements indicate the presence of antiferromagnetism with estimated Néel temperatures of 23 and 21 K respectively. However, the $R\text{CrO}_4$ -zircon type polymorphs show ferromagnetic behavior with Curie temperatures of 15 and 9 K. The differences in the magnetic behavior of both forms have been attributed to the changes found in the Cr-O-R superexchange pathway through which the magnetic interactions take place.

For contributing to clarify this behavior, XAFS measurements on Cr K-absorption edge were performed at SSRL, at beamline 2-3. The pre-edge feature in the XANES zone is well observed and Fourier transforms of the experimental EXAFS spectra show the first peak in practically the same position, in agreement with the tetrahedral environment of the Cr cation. The shift in the energy position between the pre-edge peak and the “shoulder” of the XANES region is about 5.5-6 eV, in agreement with reported data for Cr^{+5} oxidation state [3]. The application of IFEFFIT and FEFF8 codes has allowed a comparative structural characterization of these materials.

[1] E. Climent, J. M. Gallardo, J. R. de Paz, N. Taira, and R. S. Puche, Journal of Alloys and Compounds In Press, doi:10.1016/j.jallcom.2008.10.060

[2] E. Climent-Pascual, J. Romero de Paz, J. M. Gallardo-Amores, and R. Sáez-Puche, Solid State Sciences 9 (2007) 574.

[3] A. Pantelouris, H. Modrow, M. Pantelouris, J. Hormes, and D. Reinen, Chemical Physics 300 (2004) 13.

Poster no. PS1.111 - Session 1**Local order in electrochromic WO_3 thin films**Jacques Moscovici¹, Aline Rougier², and Alain Michalowicz¹*(1) Institut de Chimie et des Matériaux Paris Est, UMR 7182 CNRS et Université Paris 12, 2-8 rue Henri Dunant, 94320 Thiais, France**(2) Laboratoire de Réactivité et Chimie des Solides, UMR CNRS 6007 Université de Picardie Jules Verne, 33 Rue Saint Leu, 80039 Amiens Cedex, France*

WO_3 thin films, grown by the Pulsed Laser Deposition technique, show nice electrochromic (EC) behavior, as they switch from a transparent to a colored (i.e. blue) state when cycled in H_3PO_4 electrolyte. Such EC property is strongly linked to the deposition conditions and in particular to the substrate temperature ($T_s \leq 400^\circ\text{C}$) and oxygen pressure ($10^{-2} \leq \text{PO}_2 \leq 10^{-1}$ mbar). Each set of parameters leads to WO_3 thin films exhibiting specific structural and textural properties on which the EC property largely depends. In respect of the amorphous or poorly crystallized nature of the thin films, X-ray diffraction tool give very limited information and remain insufficient for a clear understanding. The structural evolution of the as-deposited films with the deposition conditions as well as on cycling was investigated by X-ray absorption spectroscopy.

The data were recorded at the L_{III} W edge at room temperature and detected in Total Electron Yield mode. Beneficial comparisons with our earlier work on powders both crystallized (monoclinic, hexagonal, pyrochlore hydrated WO_3) and amorphous (ball-milled samples) enable us to propose a careful characterization of the WO_{3-y} thin films. It reveals that a model of the first coordination shell around W (an average distorted WO_6 octahedron) with two W-O distances do not properly describe the first coordination shell.

The best agreement between experimental and simulated spectra require the assumption of a wider W-O distance distribution, which can be simulated by three to four different W-O distances depending on the substrate temperatures and the oxygen pressure. This presentation will illustrate the advantage of EXAFS and XANES for a better determination of the structure leading to a stronger understanding of the film properties.

[1] J. Moscovici, A. Rougier, S. Laruelle and A. Michalowicz, J. Chem. Phys. 125, 124505 (2006).

Poster no. PS1.112 - Session 1**EXAFS study and characterization of N-doped TiO₂**

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TiO₂ represents one of the most important oxides and has been widely studied for the purpose of solar energy conversion and environmental cleanup. The TiO₂ materials has a wide band gap, 3.2 eV for anatase, which allows the material to absorb ultraviolet light but to be transparent for most of the solar irradiation. For this reason, great efforts have been spent until now to improve the oxide performances by shifting the edge of light absorption toward to the visible region. Recently, it has been reported that the TiO₂ materials, when doped with nonmetal such as N, C and S, etc., exhibits red-shift absorption edge. Among of them, N-doped TiO₂ is the most studied material, but in spite of this fact, the visible light absorption mechanism is still controversial. In this study, we estimated the correlation between band gaps and local structure parameters obtained by Extended X-ray Absorption Fine Structure (EXAFS) study on N-doped TiO₂. Interatomic distances of Ti-O in N-doped TiO₂ were larger than those in non-doped TiO₂. Ti-N distances (1.65 Å ~ 1.70 Å) were much larger than Ti-O distances (1.97 Å) in N-doped TiO₂. The reason for these results is the substitution of N³⁻ for O²⁻. The large repulsion force between N and O induced the smaller Ti-N distances than the Ti-O distances. Moreover, it was proved that the smaller Ti-O distances are, the smaller the band gaps of TiO₂ are.

Poster no. PS1.113 - Session 1**XAFS investigation of double complex salts as precursor for preparing bimetallic nanoparticles**

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Composite materials based on bimetallic nanoparticles present a whole class of catalysts with improved catalytic properties such as selectivity and stability than monometallic ones. Among the many factors known to influence on composition and structure of nanoparticles and therefore properties of the material a precursor is of importance. Double complex salts (DCS) are promising precursors for preparing the bimetallic nanoparticles.

Thermolysis of the DCS, [Pd(NH₃)₄][AuCl₄]₂, is studied through Pd K- and Au L₃-XAFS spectra of the initial complex, final material and products of three stages observed in TG pattern. The thermolysis was carried out in helium flow. The first stage of the DCS decomposition at 190°C concerns with partial exchange of ligands between cation and anion. On the next stage at 300°C the chloride ligands fully substitute the amine ones coordinated by Pd. Au cluster begins to form and exist together with some aurum chloride residues. Similar the local atomic structure is observed around Pd only in the product obtained at 330°C. While only gold atoms in the local environment of Au are detected in Au XAFS spectrum. The Au and Pd XAFS spectra of the final product are similar to those of Au and Pd foils, respectively. It means that two separate Au and Pd particles are formed at 350°C.

Thus XAFS investigation of the DCS thermolysis shows two-stage process of the Au and Pd nucleation and formation of the monoatomic nanoparticles as the final material.

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Poster no. PS1.114 - Session 1**Structure of spinel at high temperature: an in-situ XANES study at the Al and Mg K-edge**

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Only a few studies on the properties and structure of spinel (MgAl_2O_4) have been carried out at high temperature because of technical difficulties associated with their very high liquidus temperatures (i.e., > 2000 K for MgAl_2O_4). However structural determinations are complicated due to cationic disorder arising from the spinel inversion. It is well known that a spinel inversion can be observed at high temperature. The general spinel $[4](\text{Al}_x, \text{Mg}_{1-x})[6](\text{Al}_{2-x}, \text{Mg}_x)\text{O}_4$, has two sites (4-fold and a 6-fold) for each cation. At low temperature $x=0$ and the 4-fold coordinated site is fully occupied by Mg. As the temperature rises, x increases, Al moves into the 4-fold coordinated site and Mg into the 6-fold coordinated site. The parameter x is referred to as the degree of inversion. It has been predicted that the Al and Mg distribution on both sites is not fully random. We present structural information obtained on spinel at high temperature (298-2400 K) using in situ XANES at the Mg and Al K-edge. Using these XANES experiment we have observed change in the different features in spectra at the Mg and Al K-edge, and we interpret them by a substitution of Mg and Al which corresponds to an inversion of the Mg and Al sites. These conclusions are in good agreement with previous X-ray diffraction experiments. Furthermore, both XANES experiments at the Al and Mg K-edge are in good agreement with calculation made using FDMNES code.

Poster no. PS1.115 - Session 1**EXAFS study of filled skutterudites $\text{RT}_4\text{Sb}_{12}(\text{R:La,Ce,Pr,Nd,Sm}, \text{T:Fe,Os})$**

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The filled skutterudites RT_4X_{12} (R: rare earth, T: transition metal, X: pnictogen) show a variety of physical properties (e.g., high thermoelectric power) by changing the combination of R, T, and X. In such combinations, some compounds show characteristic feature called "rattling" that is considered as anharmonic oscillation of rare earth ions accommodated in the Sb icosahedron cage and the feature is strongly related with variational physical properties of this system. We have been applied extended X-ray absorption fine structure (EXAFS) on this system to clarify the microscopic mechanism of "rattling" motion[1]. Temperature dependence of EXAFS thermal (Debye-Waller) factors of R-Sb and T-Sb atomic pairs were analyzed by Einstein model. Thermal oscillation and static distortion are analyzed independently. A good correlation between static distortion of rare earth ions and space inside the Sb icosahedron cage was obtained.

[1] K. Nitta, Y. Omori, D. Kikuchi, T. Miyanaga, K. Takegahara, H. Sugawara, H. Sato, J. Phys. Soc. Jpn., **77**, (2008) 063601.

Poster no. PS1.116 - Session 1**Model compound vulcanization studies by S K-edge XANES spectroscopy**Rattapong Nu-Mard¹, Wirach Taweepreda¹, Prayoon Songsiriritthigul^{2,3}, and Wanwisa Pattanasiriwisawa³*(1) Polymer Science Program, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112 Thailand**(2) School of Physics, Suranaree University of Technology Muang, Nakhon Ratchasima 3000 THAILAND**(3) Synchrotron Light Research Institute, Muang, Nakhon Ratchasima 3000 THAILAND*

In this work, a standard of sulfur cross-linking unsaturated rubber molecule was investigated by x-ray absorption near edge structure spectroscopy (XANES). The low molecular weight olefin, squalene which is structurally related to the natural rubber, allowing a straighter analysis of sulfur cross-link structure and elucidation of the mechanism. The monosulfide linkage of squalenes, compounded with 2,2'-di-thio-bis-benzothiazole, was found the absorption peak at 2473 eV. The absorption peak was shifted to lower energy for the polysulfide linkages when squalenes compounded with sulfur (S8). Moreover, the absorption peaks at high energy revealed the by-products after vulcanization.

Poster no. PS1.117 - Session 1**Fluorescence XAFS analysis of local structures in I-doped (Zn,Cr)Te**Hironori Ofuchi¹, Koichiro Ishikawa², Ke Zhang², Shinji Kuroda², Masanori Mitome³, and Yoshio Bando³*(1) Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan**(2) Institute of Materials Science, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8573, Japan**(3) Advanced Materials and Nanomaterials Laboratories, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

Geometric structures for II-VI diluted magnetic semiconductor I-doped (Zn,Cr)Te films ([Cr] = 5%) with high-temperature ferromagnetism were investigated by using fluorescence XAFS measurement in order to elucidate the relationship between the geometric structures and the magnetic properties. The XAFS analysis has revealed that the local structures around Cr atoms depend on the growth temperature. For the samples grown at 360 and 390 °C, the majority of Cr atoms are tetrahedrally coordinated to Te atoms, indicating formation of substitutional Cr on Zn-site in ZnTe lattice and/or zincblende CrTe. On the contrary, for the samples grown at 300 and 330 °C the additional formation of secondary phases such as Cr-Te compounds was observed. Therefore, it is deduced that the formation of secondary phase such as Cr-Te compounds are related to the increase of Curie temperature. The XAFS analysis has also revealed that the local structures around Cr atoms do not depend on the I concentration. For the samples with the different I concentration, the Cr atoms form substitutional Cr on Zn-site in ZnTe lattice and/or zincblende CrTe, corresponding the result of TEM measurement[1].

[1] S. Kuroda et al., Nat. Mater. 6, 440 (2007).

Poster no. PS1.118 - Session 1**Fluorescence XAFS study of local structures in high-k gate dielectrics
HfSiON/SiON/Si annealed at various nitrogen gas partial pressure**Hironori Ofuchi¹, Hironori Ofuchi¹, Satoshi Toyoda^{2,3,4}, Kazuto Ikeda⁵, Guo Lin Liu⁵, Zhiyuan Liu⁵, and Masaharu Oshima^{2,3,4}*(1) Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan**(2) Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan**(3) Core Research for Evolutional Science and Technology of Japan Science and Technology Agency, Chiyoda-ku, Tokyo 102-0075, Japan**(4) Synchrotron Radiation Research Organization, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan**(5) Semiconductor Technology Academic Research Center, Kohoku-ku, Kanagawa 222-0033, Japan*

Geometric structures for HfSiON/SiON/Si films annealed at various N₂ gas partial pressure were investigated using fluorescence XAFS measurement at Hf L_{III}- and L_I-edge. The XAFS analysis has revealed that the local structures around the Hf atoms strongly depend on the N₂ gas partial pressure. For the sample annealed at the N₂ gas partial pressure of 10 Torr the HfSiON and Hf silicides coexist, and for the samples annealed at the N₂ gas partial pressure above 100 Torr the Hf atoms form HfSiON only. These results indicate that the Hf silicidation between HfSiON/SiON interface can be suppressed by annealing at proper partial pressure of N₂ gas.

Poster no. PS1.119 - Session 1**Local structure of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ with a defect spinel structure**Hiroki Okudera¹, Kei-ichiro Murai², Akira Yoshiasa³, Maki Okube⁴, Takeshi Takeda⁵, and Shinichi Kikkawa⁵

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The structures of Fe oxides, FeO (wustite), Fe_3O_4 (magnetite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) are closely related with each other, having different number of cations in a c.c.p. assembly of oxide ions. FeO has a NaCl structure. Fe_3O_4 has an inverse spinel structure with tetrahedral and octahedral cation sites. From ionic-crystal point-of-view, a half of Fe^{3+} occupy tetrahedral sites and equal numbers of Fe^{2+} and Fe^{3+} share octahedral sites. It is confirmed that careful oxidation of Fe_3O_4 yields $\gamma\text{-Fe}_2\text{O}_3$ and *vice versa*. In $\gamma\text{-Fe}_2\text{O}_3$, selective formation of cation vacancies at octahedral cation sites and their ordering cause symmetry lowering down from $Fd\bar{3}m$ to $P4_132$. The $\alpha\text{-Fe}_2\text{O}_3$ (hematite) has a corundum structure with h.c.p. assembly of oxide ions.

Since XANES spectra are quite sensitive to three-dimensional atomic configuration around X-ray absorbing atoms and oxidation state of the atom, they are useful for phase study. In this study, local structures around Fe and EXAFS Debye-Waller factor with effective pair potentials $V(u) = au^2/2$ for Fe-O, Fe-N and Fe-Fe pairs have been investigated by the XAFS technique at Fe K-edge for Fe metal, Fe nitrides (FeN , Fe_2N , Fe_4N), and synthetic and natural Fe oxides (FeO , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4). The chemical shift of threshold energy in XANES spectra was not apparent between Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ at room temperature, while these phases can be distinguished from the detailed comparison of XANES spectra. The XANES spectra of γ - and $\alpha\text{-Fe}_2\text{O}_3$ are clearly different. The chemical shift of threshold energy, radial distribution around Fe, and the relationship between interatomic distances and Debye-Waller factors are discussed.

Poster no. PS1.120 - Session 1**Low-temperature lattice anomaly in $\text{LaFeAsO}_{0.93}\text{F}_{0.07}$ probed by x-ray absorption spectroscopy: Evidence for strong electron-lattice interaction.**Hiroyuki Oyanagi¹, C. J. Zhang¹, H. Oyanagi¹, Z. H. Sun¹, Y. Kamihara², and H. Hosono²

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The local structure of newly discovered FeAs superconductors (LaFeAsO) has been studied by x-ray absorption spectroscopy (XAS) in order to understand the nature of pairing mechanism in the novel superconductors. We performed the Fe and As *K* edge EXAFS measurements over a wide temperature range using a state-of-the-art pixel-array fluorescence detector [1]. The results indicate that local Fe-As lattice fluctuation occurs well above T_c . The carrier (electron)-induced local lattice anomaly, strongly correlating with the disappearance of magnetic instability indicates that the lattice effects are involved in the superconducting coherence as in the case of cuprates [2]. Remarkable drop of the Fe-As distance and Fe-Fe mean-square relative displacement (MSRD) upon carrier doping indicates the increased pd hybridization by carrier doping.

The temperature dependence of the MSRD for the nearest neighbor Fe-As shell, derived from the Fe *K* and As *K* edge EXAFS data for the $\text{LaFeAsO}_{1-x}\text{F}_x$ ($x=0.07$), showed a clear upturn behavior at much higher temperature than T_c ($T < 70$ K). A sharp drop of MSRD occurs at the onset of superconducting transition ($T_c^{\text{onset}} \approx 29$ K) reflecting superconducting coherence. We find close similarity in the lattice distortion with that of cuprates where in-plane oxygen atoms are displaced in a breathing or Q_2 -like mode. From detailed comparison of MSRD as a function of normalized temperature (T_c/T_c^{onset}) for $\text{LaFeAsO}_{0.93}\text{F}_{0.07}$ and cuprates ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$), we suggest that strong electron-lattice interaction is an important ingredient of the pairing mechanism in the doped FeAs systems as well as cuprates.

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Poster no. PS1.121 - Session 1**In-situ EXAFS study of nucleation process of CdSe nanoparticles**Hiroyuki Oyanagi¹, Z. H. Sun¹, H. Oyanagi¹, M. Uehara², K. Yamashita², A. Fukano¹, and H. Maeda^{2,3}*(1) National Institute of Advanced Industrial Science and Technology, 1-1-1, Umezono, Tsukuba, Ibaraki, 305-8568, Japan**(2) Microspace Chemistry Laboratory, National Institute of Advanced Industrial Science and Technology Kyushu, Shuku, Tosu, Saga, 841-0052, Japan**(3) Department of Applied Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

Nowadays it is still challenging to probe the nucleation process of nanocrystals due to the short nucleation time [1]. We developed an in-situ EXAFS method for studying the nucleation as well as growth progresses by using a microreactor which can convert the time-dependence to the position-dependence. As an example, we measured the Se *K*-edge EXAFS spectra for CdSe nanoparticles along a microreactor channel and indicated the strong time-dependence of the nucleation growth at the beginning of the reaction. We observed a rapid increase of the reaction yield of CdSe nanoparticles within several seconds starting from TOP-Se solution at 240 °C. It is found that after injection of starting materials, the nucleation occurs abruptly and the CdSe nuclei concentration reaches a maximum and then declines rapidly [2]. The results show the promising capability of in-situ EXAFS combined with a microreactor for investigations of nucleation and growth processes of various nanoparticles synthesized in solution.

References[1] J. Park *et al.*: *Angew. Chem. Int. Ed.* 46, 4630- 4660 (2007).[2] M. Uehara, Z.H. Sun, H. Oyanagi, K. Yamashita, H. Nakamura and H. Maeda *Appl. Phys. Lett.* 94, 063104-063107 (2009).**Poster no. PS1.122 - Session 1****EXAFS study of synthesis of sol-gel prepared Bi₁₂SiO₂₀ thin films**Jana Padeznik Gomilsek¹, Asja Veber², Alojz Kodre^{3,2}, and Danilo Suvorov²*(1) Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia**(2) J. Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia**(3) Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

Miniaturization and optimization of electronic modules creates demands for new components which have to be compact, reliable and of low cost. Microwave dielectric ceramics represents such a group of components. Satellite antennas, radars, mobile phones, pagers, microwave ovens etc. are some everyday devices which include microwave ceramic parts. The quality of such device depends primarily upon the dielectric properties of the material. These properties include a suitable permittivity (ϵ'), a high unloaded Q (Q = 4500) and controllable temperature coefficient of resonant frequency (± 1.5 ppm/K). Our investigations showed that Bi₁₂SiO₂₀ exhibits such dielectric properties.

In this work, Bi₁₂SiO₂₀ thin films were synthesized using a sol-gel method. The sol was prepared from Bi(NO₃)₃·5H₂O and Si(OC₂H₅)₄ as the precursors, 2-ethoxyethanol, ethanol or acetic acid as the solvent and formamid as the drying additive. Thin films from the three synthesis procedures using different solvents were compared at two stages of heat treatment: as prepared xerogels and pyrolysed at 220 °C for 2 min.

Bismuth L₃ EXAFS spectra of the thin films were recorded at the station C of synchrotron laboratory HASYLAB at DESY, Hamburg. Films with thickness of ~700 nm were prepared on Al foil to reduce absorption in the support material. A stack of 12 films gave the absorption edge jump of ~0.6 and a good signal/noise ratio. In Fourier transform only two peaks were resolved due to a low degree of structural order. The first (oxygen) peak in the spectra varied only in Debye-Waller factor while the second (bismuth) peak showed more pronounced differences: in general the number of Bi neighbors decreased after heat treatment indicating the decomposition of the starting structure prior to the growth of the high temperature phase. The strength of the effect depended on the type of the solvent.

Poster no. PS1.123 - Session 1**Estimation of size of nanoparticles by various techniques: A comparative study**Avinash C. Pandey¹*(1) Physics Department University of Allahabad 211001 Allahabad Uttar Pradesh INDIA*

The unique size dependent functional properties of materials at nanometric scale is of tremendous applications due to quantum confinement effect. These size dependent properties have led to the development of various techniques for the exact determination of shape, size and distribution of the material under study. The present study deals with a precise measurement of particle size, shape and distribution of II-VI oxide semiconductor nanoparticles with the well established techniques, such as X-ray diffraction (XRD), small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), transmission electron microscopy (TEM). Furthermore, in the stalk of more precise elaborated techniques for the analysis of particles sizes these results are compared with the EXAFS measurements. The materials under this study were synthesized by chemical precipitation route and found to have size distribution from 2 to 10 nm for spherical particles. Sizes determined from various techniques are in good agreement with each other however small angle scattering technique is more reliable than XRD to determine the sizes of the nanoparticles. The obtained results shows that EXAFS seems to be one of new reliable tool for determination of size of nanomaterials.

Poster no. PS1.124 - Session 1**EXAFS estimation of Size and Shape of Core/Shell and Capped ZnO Nanoparticles**Avinash C. Pandey¹, and Prashant K Sharma²*(1) Physics Department University of Allahabad 211001 Allahabad Uttar Pradesh INDIA**(2) Nanophosphor Application Centre University of Allahabad 211002 Allahabad UP INDIA*

Extended X-ray absorption fine structures (EXAFS) is emerging as one of the new tools for the exact determination of crystallite size and shape of nanocrystalline materials. The present study is focused on the synthesis of ZnO nanoparticles in presence of different capping agents. The particle size and shape of synthesized nanoparticles were estimated by the well established techniques, such as X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, in pursuance of more precise analysis of particle size and shape, these results are compared with the EXAFS measurements. Besides this EXAFS also gives information about local structure, coordination numbers and nearest-neighbor distances, Zn^{2+} occupancy sites in the ZnO lattice in different core/shell/capping states.

Poster no. PS1.125 - Session 1**Polarization dependent studies of InGaN layers by means of XANES**

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InGaN/GaN semiconductor nanostructures are attractive due to their applications as blue laser diodes, UV-light emitters, white light generation and electronic devices. The chemical compositions and ordering of atoms in crystal lattices of such nanostructures are important parameters influencing substantially their electrical and optical performance. The x-ray absorption near edge structure (XANES) method, being sensitive to the electron density of states, is suitable for the study of chemical bonds of a chosen element. InGaN is stable in the wurtzite structure where two kinds of first-neighbor anion-cation bond exist: a single bond along c-axis and three bonds slightly inclined with respect to c-plane. The InN three longer bond lengths are about 0.216 nm and the shorter one along c-axis - about 0.215 nm whereas for GaN three shorter bond lengths are about 0.195 nm and the longer one - about 0.197 nm. Therefore polarization dependent XANES was applied. The coordination geometry around an absorbing atom in different directions (in-plane and out-of-plane of growth) under various directions of the exciting radiation polarization regarding to the sample surface was examined.

The In L3-edge and N K-edge measurements for the thick InGaN layers grown by MBE with different chemical compositions have been performed in total electron yield (TEY) detection mode on beamlines 9.3.1 and 8.0, respectively, at the Advanced Light Source. With decreasing In composition bond lengths are changed. A comparison of experimental TEY measurements for the investigated layers with the theoretically calculated XANES spectra created by the FDMNES code by solving the Schrödinger equation using the finite difference method and FEFF8 code based on full multiple scattering theory within "muffin-tin" potential approximation will be presented.

Poster no. PS1.126 - Session 1**Electronic structures of Me-doped (Me= Co, Ni and Cu) YMnO₃ studied by x-ray absorption spectroscopy**

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X-ray absorption spectroscopy measurements have been performed to elucidate local electronic and atomic structures of 3d-transition metal doped yttrium manganites (YMnO₃) with chemical formulae YMn_{2/3}Me_{1/3}O₃ (Me= Co, Ni and Cu). The Mn L₃- and K-edge XANES results indicate the direct substitution of Me²⁺ for Mn³⁺, so that the positive effective charge of Mn ions are increased. Me-doping is also found to induce substantial broadening of the Mn L₃-edge feature, which suggests enhancement of the delocalization of Mn 3d eg subbands and conductivity. Local spin density approximation (LSDA)+U (Hubbard U parameter) calculation shows that the leading features in the Mn L₃-edge XANES spectra of Me-YMnO₃ are due to majority-spin Mn eg subband not the Mn t_{2g} subband commonly assigned. The comparison between O K-edge XANES spectrum of Ni-YMnO₃ and the LSDA+U calculation shows significant contribution of O 2p and minority-spin Ni 3d eg hybridized states to the second feature of the O K-edge XANES spectra.

Poster no. PS1.127 - Session 1**Influence of Nb substitution on superconductivity in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$: An EXAFS Study**Kaustubh Priolkar¹, Preeti Bhobe¹, and P. R. Sarode¹*Goa University Department of Physics 403 521 Taleigao Plateau Goa India*

The magnetic superconductor $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212) is an extremely interesting material, with a maximum $T_c = 37$ K and $T_M = 136$ K, where T_c is the superconducting temperature and T_M is the Curie temperature. The superconductivity occurs in the CuO_2 layers and the ferromagnetism arises in the RuO_2 layers. Superconductivity is induced in Ru-1212 by hole doping of copper oxide planes. This arises from the overlap of minority spin $\text{Ru}:t_{2g}$ and the $\text{Cu}:3d_{x^2-y^2}$ bands. The substitution of Ru by the non-magnetic, mixed valent cations Nb^{5+} and Sn^{4+} has helped in the understanding of the charge distribution and magnetism of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.

The solid solutions $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($0 \leq x \leq 0.4$) have been synthesized and characterized by X-ray diffraction, resistivity. EXAFS at Ru and Cu K-edge were recorded at room temperature in transmission mode using XAFS beamline at Elettra. Ru EXAFS could be recorded only up to 500 eV beyond the edge due to the limitation of the beamline. Perhaps due to this limitation no significant changes are observed in the Ru-O bond lengths across the series. The local structure around Cu however is affected and has been correlated to observed superconducting properties. Cu EXAFS was fitted in the range 1.3 to 4\AA using all single scattering and linear multiple scattering paths. The Cu-O-Cu bond angle has been calculated using Cu-O and Cu-Cu direct and multiple scattering paths and correlated with the observed decrease in T_c .

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Poster no. PS1.128 - Session 1**Rapid ion-implantation-induced amorphisation of ternary semiconductor alloys due to bond-angle and bond-length distortions**Mark Ridgway¹, Z.S. Hussain¹, E. Wendler², W. Wesch², C.S. Schnohr¹, D.J. Llewellyn¹, and G.J. Foran³*(1) Australian National University, Electronic Materials Engineering, Canberra, Australia**(2) Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Jena, Germany**(3) Australian Nuclear Science and Technology Organisation, Menai, Australia*

We have examined the implantation-induced amorphisation of the ternary $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys over the entire stoichiometry range and relative to their binary end members (InAs and GaAs for $\text{In}_x\text{Ga}_{1-x}\text{As}$, InP and GaP for $\text{In}_x\text{Ga}_{1-x}\text{P}$). Unlike $\text{Al}_x\text{Ga}_{1-x}\text{As}$, these two ternaries did not exhibit amorphisation kinetics between the two binary alloy extremes. Instead, ternaries with intermediate stoichiometries were rendered amorphous at fluences less than that required for both the binary end members. Implantation-induced disorder was quantified with ion backscattering spectroscopy in the channelling configuration and fit to the Hecking model to yield the probabilities of direct-impact and stimulated amorphisation. The phase transformation was dominated by stimulated amorphisation, which was a maximum at the stoichiometry most easily amorphised, while the probability of direct-impact amorphisation was effectively stoichiometry independent. From EXAFS measurements of the unimplanted ternaries, bimodal and stoichiometry-dependent bond-length distributions were measured (with that for $\text{In}_x\text{Ga}_{1-x}\text{As}$ consistent with the pioneering work of Mikkelsen and Boyce). Distortion in both the bond-length and bond-angle distributions was apparent though structural perturbation was primarily accommodated in the latter as consistent with measured deviations from the tetrahedral bond-angle. We attribute the relative ease with which the ternaries were amorphised to the presence of localised regions of strain due to structural distortion. Equivalently, atomistic configurations comprised of strained bond-lengths and bond-angles represent pre-existing and preferential sites for stimulated amorphisation.

Poster no. PS1.129 - Session 1**Occupation preferences in multinary alloys by EXAFS and far-IR spectroscopy - precautions and limits**Benjamin V. Robouch¹, A. Marcelli¹, and A. Kisiel²*(1) INFN - Laboratori Nazionali di Frascati, Via E. Fermi 40, I-00044 Frascati, Italy**(2) Instytut Fizyki, Uniwersytet Jagiellonski, Reymonta 4, 30-059 Krakow, Poland*

EXAFS is a powerful diagnostic technique to investigate crystal local structures. Investigations performed on crystalline systems return averages of observed coordination numbers and of bond distances. In the past we performed accurate analyses of far-IR spectra [1] and of EXAFS observations of prototype groups as zincblende (B3), wurtzite (B4), intermetallide (L1₂) (all three reassumed in [1]), and of cubic Laves (C15) structures [2]. Elemental values for each component co-ordination were obtained. Here we present an extension of the model to a generic ternary (C_{1-x}C'_x)_mI_{m'} alloy derived from the binary compound C_mI_{m'}, limiting the analysis to nearest neighbor (NN) observations of both EXAFS or far-IR spectra. This model is not applicable to covalent compounds of Group IV-IV, or to complex structures like D53 or presently to those of type B81 and similar. We show that the limitation to NN observations reduces the experimental freedom. But now a wide variety of systems can be interpreted and offers the possibility to quantify in a real system the departure due to site occupation preferences of the distribution of each component configuration of a ternary crystal from a random distribution. This quantification substantially improves the understanding of many a crystal response and behavior [3]. The occupation preferences of each component can be obtained independently both from EXAFS and from far-IR spectra. The comparison provides an independent validation of the departure from a non random preference distribution.

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Poster no. PS1.130 - Session 1**The local and electronic structure of FeTiO₃: X-ray absorption**I. S. Rodina¹, A.V. Soldatov¹, and A.J. Berry²*(1) Southern Federal University, 344090 Rostov-on-Don, Russia**(2) Imperial College London, SW7 2AZ London, UK*

The local structure of FeTiO₃ was studied by modelling the Ti *K*- edge X- ray absorption near edge structure (XANES). Experimental Ti *K*- edge spectra of natural ilmenite were recorded at the Photon Factory, KEK (Japan). The local environment of Ti was defined by comparing the experimental spectra with the theoretical spectra calculated using different models. The theoretical XANES spectra were calculated using structural models determined by X- ray diffraction and EXAFS spectroscopy. The simulation was carried out by two methods: 1) the full potential finite difference method (the FDMNES.2008 program code), and 2) the multiple scattering in a real space method (the FEFF_8.4 program code). Several exchange-correlation potentials were used. The influence of the core hole and quadrupole transitions on the Ti *K*- edge XANES spectra was investigated. It was found that the finite difference method beyond the muffin- tin approximation gave better agreement with the experimental data.

Poster no. PS1.131 - Session 1**A fluorescence XAFS study of NaAlH₄ doped with Ti and Ce based precursors**Jörg Rothe¹, Aline Léon², Krzysztof Chlopek², Oleg Zabara², and Maximilian Fichtner²*(1) Forschungszentrum Karlsruhe - Institut für Nukleare Entsorgung, P.O. Box 3640, D-76021 Karlsruhe, Germany**(2) Forschungszentrum Karlsruhe - Institut für Nanotechnologie, P.O. Box 3640, D-76021 Karlsruhe, Germany*

After several years of research on solid hydrogen storage materials, transition metal doped sodium alanates (NaAlH₄) turned out to be the most promising systems with respect to thermodynamics, kinetics and hydrogen storage capacity. However, open questions still remain concerning the alanate activation process upon addition of a catalyst precursor by ball-milling and initial hydrogen cycling, and the alanate long term performance following many hydrogenation/dehydrogenation turns. As there is obviously a strong correlation between the local structure of the dopant and the hydrogen storage capacity and exchange kinetic, X-ray Absorption Fine Structure (XAFS) spectroscopy was applied in a comprehensive effort to characterize the evolution of the valence state and local structure of the catalyst.

NaAlH₄ doped with TiCl₃ and CeCl₃ was prepared by ball milling and cycled under hydrogen in a modified Sieverts apparatus. As-prepared samples and cycled material quenched after a number of hydrogenation/dehydrogenation steps were investigated at the Ti K-edge and the Ce L₃-edge, respectively. It turns out that the evolution of the local Ti environment observed for TiCl₃ as precursor is responsible for the rapid decrease of the reversible hydrogen storage capacity, whereas the stability of the short-range order observed for CeCl₃ as precursor accounts for the stability of the kinetics and hydrogen storage capacity over many cycles. Our comparative study with different precursor materials indicates that the stability of the short-range order upon hydrogen cycling has a decisive influence on the stability of the kinetics and hydrogen storage capacity.

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Poster no. PS1.132 - Session 1**Local structure and synthesis conditions correlations in semiconducting thin films and silicon dopants**Mehmet Alper Sahiner¹, Samuel Emery¹, Michelle Jamer¹, and Joseph C. Woicik²*(1) Seton Hall University Physics Department, 400 S. Orange Avenue, South Orange, New Jersey 07079, USA**(2) National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

Quantitative applications of x-ray absorption fine-structure spectroscopy (XAFS) will be presented applied to major problems of semiconductor industry. First application is on the hafnium based high-k dielectric thin films for the replacement of silicon based oxide gate dielectrics in CMOS devices. The other application is on the problem of the clustering and deactivation of the high dose silicon dopants. Solutions to both of these problems rely on the careful correlations of the detailed local structural information and synthesis or post-synthesis conditions. Sensitive responses of the local structure to synthesis and post-synthesis conditions in pulsed laser deposited (PLD) high-k dielectric thin films and silicon dopants will be revealed by XAFS probing. Our results in high-k dielectric thin films indicate by adjusting the substrate deposition temperature specific metastable phases can be stabilized. Specifically, our XAFS results show that a tetragonal phase of in HfO₂/Si(100) thin films can be stabilized by setting the substrate temperature between 300°C and 400°C during the deposition as opposed to monoclinic equilibrium phase. In arsenic and antimony implanted silicon wafers our XAFS results are shown to be sensitive to subtle changes in structure of the clusters and precipitates formed under various post-synthesis treatments. For both of these applications we use quantitative analysis with calculated XAFS functions for the possible local structures and then apply non-linear least squares fitting to the experimental data in order to reveal the exact local configurations. Detailed XAFS modeling of the data acquired at the National Synchrotron Light Source of Brookhaven National Laboratory will be presented and the local structure and synthesis relations will be discussed.

Poster no. PS1.133 - Session 1**Local structure of gallate proton conductors**Luisa Sciortino¹, Francesco Giannici¹, Alessandro Longo², Diego Messina¹, and Antonino Martorana^{1,2}*(1)Dipartimento di Chimica Inorganica e Analitica, Università di Palermo (2)ISMN-CNR, Palermo*

The use of self-doped LaBaGaO₄ for solid-state proton conduction has been proposed recently. [1] Proton insertion in such materials is achieved through substitution of Ba²⁺ for La³⁺, with formation of oxygen vacancies and subsequent dissociative absorption of water and formation of protonic defects.

Contrary to perovskite, brownmillerite or fluorite ion conductors, in these compounds the tetrahedral GaO₄ moieties are not interconnected, and the structure presents a very low degree of packing, resembling K₂SO₄ structures. The ion conduction mechanisms have been the subject of a single molecular dynamics and neutron diffraction experiment only, which claimed the formation of Ga₂O₇ clusters during the oxide-ion diffusion. [2] On the other hand, the proton conduction mechanism, and more general structure-property relationships in proton conductors with tetrahedral moieties, remain substantially unknown. We present EXAFS data on gallium K-edge, which support the substantial rigidity of the GaO₄ tetrahedra and the importance of Ga-O-Ga bridges, in samples with nominal composition La_(1-x)Ba_(1+x)GaO₄, with 0 < x < 0.2. The structural results, both local and long-range, are then correlated with IR, TGA, and conductivity data, to achieve a complete view of proton and lattice dynamics, and structure-property relations, in lanthanum barium gallates.

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Poster no. PS1.134 - Session 1**XAFS studies of a modified Al-Si eutectic alloy**Carlo U. Segre¹, Srirangam VS Prakash², Soma Chattopadhyay^{1,3}, Tomohiro Shibata^{1,3}, James A. Kaduk⁴, and Sumanth Shankar²*(1) BCPS Dept. & CSRRI, Illinois Institute of Technology 3101 S. Dearborn St. 60616 Chicago IL USA**(2) Light Metal Casting Research Centre (LMCRC), McMaster University, Hamilton, Ontario, Canada-L8S 4L7**(3) Materials Research Collaborative Access Team, Sector 10, Advanced Photon Source, Argonne, IL 60439, USA**(4) Innovene USA LLC, Analytical Development Group, P.O. Box 3011, MC F-9, 150 W. Warrenville Road, Naperville, IL 60566, USA*

Aluminum-Silicon alloys are widely used in automobile and aerospace applications. These alloys need a modification treatment – i.e. addition of trace levels (200-400ppm) of strontium can improve the mechanical properties of the alloy. Microscopic techniques such as TEM and SEM revealed that the addition of trace levels of Sr results in changing the morphology of eutectic Silicon from “plate” like structure to “fibrous” structure. X-ray and Neutron diffraction experiments on these alloy melts revealed that Sr could play a key role in changing the cluster sizes, coordination numbers and bond energies between the Al and Si species in the melt.

To understand the role of Sr in these melts, we have conducted for the first time, Sr- K edge XAFS measurements on Al-10%Sr, the master alloy and Al-12.5%Si-0.04%Sr (AlSiSr) alloy synthesized by addition of Sr using Al-10%Sr master alloy. We observe that Sr is mainly coordinated with Al in Al-10%Sr master alloy forming coordination structure similar to that of the system Al₄Sr. On the other hand, in AlSiSr, Sr is mainly coordinated with Si and Sr-Sr correlations have been observed suggesting the tendencies of Sr clustering. Detailed analysis of these systems will be presented. All the XAFS measurements were carried out at the MRCAT Undulator beamline, Advanced Photon Source, Argonne National Laboratory, Argonne, IL-USA.

Poster no. PS1.135 - Session 1**Local and electronic structure of tribological materials: XANES analysis**Alexander Soldatov¹, A. A. Guda¹, M. A. Soldatov¹, N. A. Myasnikova², and V. I. Kolesnikov²*(1) Southern Federal University Sorge str. 5 Faculty of Physics 344090 Rostov-on-Don Russia**(2) Rostov State University of Railway Communications, Rostov-on-Don Russia*

Tribological materials from the wheel and the wheel chock of a railway train were studied. The samples were taken from new and used wheels and wheel chock. X-ray absorption near edge spectra (XANES) at the Fe L_{2,3} edge of tribological materials were measured at the storage ring facility BESSY-II. Experimental XANES spectra show the variations in the shape of the Fe L_{2,3} edge fine structure – thus, supporting the sensitivity of XANES to the changes in tribological materials during the process of dry friction. Density functional theory (DFT), as implemented in the ADF2008 code, was applied for the optimization of the geometry of the tribological materials under the study within LDA and GGA approaches. Several models of exchange-correlation potentials including hybrid ones were tested. The electronic structure and real space electron density maps for the best structural models of the tribological materials under the study were derived using DFT methodology.

Poster no. PS1.136 - Session 1**Analisis of the nitrogen K-edge x-ray absorption spectra of Zn-porphyrin/C₇₀-fullerene complex for solar cells**S.A. Suchkova¹, C. Castellarin Cudia², and A. Soldatov¹*(1) Southern Federal University Zorge str.5 344090 Rostov-on-Don Russia**(2) Sincrotrone Trieste S.C.p.A, s.s. 14 km 163.5 in Area Science Park, 34012 Trieste, Italy*

Up-to-date organic photovoltaic cells are composed of organic thin films and their application require a clear understanding of the peculiar physics driving the electronic behavior. In artificial photosynthetic models such as Gratzel cell porphyrins in combination with fullerenes are among the most frequently employed building blocks as electron donors and sensitizers as well as of their electron affinity nature (p-type for porphyrins and n-type for fullerenes). Particularly interesting is the D/A dye formed by free-base (metallo)porphyrins directly attached to fullerenes. The geometric structure of the adsorbed molecules and their arrangement are responsible for the physical and chemical properties of the organic film. Zn-porphyrin/C₇₀ double layer was obtained by sublimation and deposition on the clean Si(111) substrate in UHV at room temperature using a resistively heated Ta evaporator. XAS measurements of the N K-edge were performed in the UHV experimental chambers-base pressure 10⁻¹⁰ mbar-of the SuperESCA and ALOISA beamlines at the Elettra Synchrotron facility [1]. The near-edge spectral region (XANES) finds widespread application in many different fields (as "finger-printing" approach) is sensitive to the three-dimensional atomic geometry. By making a comparison between experimental spectra and theoretical simulations, it becomes possible to determine the three-dimensional structure of the Zn-porphyrin/C₇₀ complex responsible for the charge transfer in Gratzel cells. The theoretical analysis of the experimental data has been performed on the basis of finite difference method (FDMnes 2008 program code). To refine a geometry of the complex a number of diverse models were made. Then theoretical N K-XANES spectra were calculated.

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Poster no. PS1.137 - Session 1**Multiple scattering approach to I K-edge XANES for iodine-doped PVA films**

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Iodine K-edge XANES spectra of iodine-doped polyvinyl alcohol (PVA) have been discussed by using multiple-scattering theory. The iodine-doped PVA films are most common type of polarizers in use. The optical properties strongly depend on the ratio of iodide species. In order to study the optical properties, we have to know the intrinsic properties of iodine species and the local structures around iodine anions in the PVA film. The analyses of iodine K-edge EXAFS spectra of I-PVA film showed I_3^- and I_5^- are oriented along the PVA chain[1].

We also measure I K-edge polarization-dependent XANES of I_3^- -rich and I_5^- -rich PVA film. The observed XANES spectra of I_3^- -rich PVA show weaker polarization-dependence than the case of I_5^- -rich PVA film. To analyze the differences due to the different intrinsic properties or the different local structure, we have considered some model structures.

Molecular orbital calculations explain the observed polarization dependence associated with the I $2p \rightarrow \pi^*$ transition. We also apply multiple scattering calculations to obtain structural information on I-I distance and polyanion-PVA chain distance. [1] T.Yokoyama et.al, Bull. Chem. Soc. Jpn., 68, 469-475(1995).

Poster no. PS1.138 - Session 1**Monitoring Degradation of Sulfur Linkages in Dense Natural Rubber Latex Film by XANES Spectroscopy**

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In this work, we present the results of sulfur-crosslinks and oxidation states of sulfur during degradation processes studied by X-ray absorption spectroscopy. X-ray absorption near-edge structure (XANES) spectra have been collected and analyzed to provide the local geometry and electronic environment of sulfur crosslinks of the rubber networks during degradation processes by thermal and ozone aging. We found that the reversion takes place before the onset of oxidative processes at the sulfur bridges. Parallel to the oxidative processes, the production of cyclic sulfanes takes places. This relationship depends on the rubber compositions. Blending of natural rubber latex with nitrile latex improves the ozone aging resistance of the sulfur bonds.

Poster no. PS1.139 - Session 1**X-ray absorption spectroscopy study of Mg-bearing minerals**Nicolas Trcera^{1,2}, Delphine Cabaret³, Stéphanie Rossano², François Farges⁴, Anne-Marie Flank¹ and Pierre Lagarde¹(1) *Synchrotron Soleil - Saint-Aubin - BP 48 91192 GIF-SUR-YVETTE Cedex, France*(2) *Université Paris-Est, Laboratoire Géomatériaux et Géologie de l'Ingénieur (G2I),
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Magnesium is a major component in numerous natural minerals and glasses as well as in technological glasses and glass-ceramics. The study of the structural environment of Mg by direct methods is technically difficult. Among the two most used methods (solid-state NMR and XANES spectroscopy), XANES at the Mg K-edge is the less difficult to conduct experimentally when finding beamline reaching such a low energy edge. However, as it is not straightforward to extract relevant structural information of XANES spectra, *ab initio* calculations are necessary. In this work, we present a XAS study of crystalline compounds containing magnesium in a single 4-, 5-, 6- and 8-fold coordinated site (spinel Mg_2AlO_4 , grandidierite $(\text{Mg,Fe})\text{Al}_3\text{SiBO}_9$, diopside $\text{CaMgSi}_2\text{O}_6$ and pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), in 6-fold coordinated environments with two different sites (olivine Mg_2SiO_4 and enstatite $\text{Mg}_2\text{Si}_2\text{O}_6$) and in a synthetic phosphate model compound containing 5- and 6-fold coordinated magnesium (farringtonite $\text{Mg}_3(\text{PO}_4)_2$). XANES spectra have been collected on the Lucia beamline at the SLS synchrotron using a double crystal beryls (10-10) monochromator and fluorescence detection mode. We performed *ab initio* calculation based on the reciprocal-space non muffin-tin plane-wave method developed in the PARATEC code using pseudopotentials. The absorbing magnesium pseudopotential was obtained by considering only one 1s electron in his electronic configuration. To take into account the core-hole electron interaction, the supercell approach has been used to isolate the absorbing atom. Experimental XANES spectra are modelled with a good agreement, whatever the neighbour types, the magnesium coordination and the number of Mg-sites. The results have allowed us to link the XANES spectrum modifications with the changes in magnesium environment (coordination/site distortions).

Poster no. PS1.140 - Session 1**Study of the local environment of implanted Mn ions in GaSb**Anna Wolska¹, Krystyna Lawniczak-Jablonska¹, Marcin T. Klepka¹, Adam Barcz¹, Anders Hallen², and Dimitri Arvanitis³(1) *Institute of Physics PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland*(2) *Royal Inst. of Technology, Dept. of Microelectronics and Applied Physics, P.O. Box Electrum 226, SE 164 40 Kista, Sweden*(3) *Department of Physics and Materials Science, Uppsala University, Box 530, 75121 Uppsala, Sweden*

GaMnAs is considered as a promising material for novel spintronic applications. The uniform ternary alloys as well as related material containing precipitations of ferromagnetic MnAs have been intensively investigated. It is found, in particular, that nanosized MnAs ferromagnets buried in GaAs can be obtained not only by the MBE method but also by Mn ion implantation into GaAs wafers. Other types of inclusions, like MnSb, also show promising magnetic properties. It is possible to obtain such inclusions during the MBE growth. On the other hand, the implantation method is also well established, but cheaper and easier to carry out within the industrial production process. Therefore, it would be important to find an optimal way of producing the MnSb inclusions with the desirable properties by Mn ions implantation as it has been done in the MnAs case. Here we focus on Mn K-edge measurements for several sets of samples. The GaSb crystals were implanted with Mn ions. The ion energy was kept at 10 keV for one set of samples and 150 keV for the other one. Four different doses and two types of post implantation annealing were used. The first sample set was annealed in a vacuum furnace for 10 min. at 920 K, the second one in an Argon atmosphere for 5 min. at 620 K. The local structure of the Mn ions is discussed by means of the EXAFS measurements. We can establish clear differences in the Mn atom local environment depending on the implantation energy and annealing process. We conclude on the optimal ion energy and annealing process to fine-tune these materials for specific applications.

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Poster no. PS1.141 - Session 1**X-ray absorption study of Ti-Al clusters in Ti doped Na-alanates**Galina Yalovega¹, Alexander Soldatov¹, Antonela Balerna², Aline Léon³, and Maximilian Fichtne³*(1) Department of Physics, Southern Federal University Sorge str. 5 344090 Rostov-on-Don Russia**(2) LNF, INFN, Italy**(3) Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH, Karlsruhe, Germany*

One of the lead candidates for a low cost and high hydrogen density, hydrogen storage material is doped sodium alanate, NaAlH₄. Alanates – complex metal hydrides based on anionic AlH₄ or AlH₆ units. The present work is focused on the theoretical calculation Al K-edge X-ray absorption spectra of NaAlH₄ in order to evaluate the properties of the Ti-Al cluster formed upon cycling under hydrogen.

The hydrogen storage material of Ti-doped Na alanate has been studied using both experimental and theoretical Al K-edge X-ray absorption near edge structure (XANES) analysis.

In order to study the nature of the alanate matrix X-ray absorption spectroscopy was performed at the Al K-edge (1561.1 eV) of the samples. The measurements are carried out at the DXR-1 beamline of Dafne-light synchrotron radiation facility (LNF, Italy) The sample holder is a specially designed cell which allows the samples to be prepared, transferred, and measured without exposing them to air.

The Al K-edge XANES in metallic Al, and Ti-doped alanates has been analyzed theoretically by means of a advanced approach beyond muffin-tin approximation finite difference method (FDMNES 2008) and self-consistent full multiple scattering method using the FEFF8.4 code.

Poster no. PS1.142 - Session 1**Fluorescence EXAFS study of residual Ga in b-FeSi₂ grown from Ga solvent**Hiroomi Yamada¹, Masao Tabuchi², Yoshikazu Takeda¹, and Haruhiko Udon³*(1) Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan**(2) Nagoya University Venture Business Laboratory, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan**(3) Ibaraki University, 4-12-1 Naka-narusawa-cho, Hitachi, Ibaraki 316-8511 Japan*

Semiconducting iron disilicide, b-FeSi₂, has received considerable attention in recent years from ecological and environmental points of view because of its potential for high performance thermoelectric conversion devices working at high temperatures. For the device application, bulk growth technology of b-FeSi₂ is important. However, ordinal growth methods from melt cannot be used for the growth of the b-FeSi₂ single crystals because b-FeSi₂ is a stable phase at lower temperatures of iron silicides. Solution growth is a suitable growth technique to obtain a large-sized and good crystalline quality b-FeSi₂ single crystal. However, in this method the solvent atoms are automatically doped into crystals and may affect electrical properties of them.

In this work, we investigated Ga atoms in b-FeSi₂ grown from Ga solvent by EXAFS and discussed the effect of Ga atoms on electrical properties of b-FeSi₂.

The samples were prepared by a temperature gradient solution growth (TGSG) method. The Fe-Si solute (Fe:Si=1:2) was obtained from 5N-Fe and 5Np-Si and the solvent was 6N-Ga. The growth region temperature, the source temperature and the temperature gradient were 880, 920°C and 40°C/cm, respectively. The fluorescence-EXAFS measurement was conducted at beam line BL-12C at PF in High Energy Accelerator Research Organization. The Ga K α fluorescence X-ray was detected using a 19-element SSD. Analysis of the EXAFS spectra showed that about 60

In order to discuss the electron density of state for the b-FeSi₂, ab-initio calculation was carried out. The cell for the calculation was consisted of 16 Fe and 32 Si, and one of the Fe or Si atoms was substituted by Ga in b-FeSi₂. The results of the calculation indicated that Ga at Si sites works as an acceptor generating holes, and Ga at Si sites compensates holes in b-FeSi₂. As a total it exhibits p-type conductivity.

Poster no. PS1.143 - Session 1**Local structure and magnetic properties of Fe₆₀Co₄₀ mechanical alloy**Dong-Seok Yang¹, Jiyeon Park¹, Young-Goo Yoo¹, and Seong-Cho Yu¹

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Fe-Co system has been interested in the field of memory device application. We fabricated Fe₆₀Co₄₀ mechanical alloys from the Fe-Co mixed powder with high energy ball mill. The local structure and magnetic properties was examined for the samples processed for 1, 2, 4, 6, 12 and 24 hours, respectively. The long range order in the atomic structure was analyzed by the x-ray diffraction (XRD). The Co XRD peaks of Fe₆₀Co₄₀ mixed powder disappeared but Fe peak decreased gradually after 6 hour milling. Local structure around Co atoms and the short range order of the alloys were examined by the extended x-ray absorption fine structure (EXAFS). EXAFS analysis showed that significant structural changes appeared during 4-6 hour milling. Magnetizations of the alloys were measured by the vibrating sample magnetometry (VSM) at the room temperature. The magnetization increased slowly from 4 hour milling. The coercivity increased gradually as the milling time increased and almost saturated at 24 hour milling. The magnetic properties will be discussed in connection with the local structural variations

Poster no. PS1.144 - Session 1**Mn_xGe_{1-x} dilute magnetic semiconductor studied by XAFS**Jian Ye¹, Yu Sun¹, Yong Jiang¹, Zhiyun Pan¹, and Shiqiang Wei¹

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Fluorescence X-ray absorption fine structure (XAFS) technique was used to investigate the local structures of the doped Mn in the Mn_xGe_{1-x} dilute magnetic semiconductors (DMSs) with different Mn content ($x=0.07, 0.25, 0.36$) prepared by magnetron cosputtering method. The results indicate that for the sample with low Mn content ($x=0.07$), the Mn atoms are mainly incorporated in to the lattice of Ge, and locate at the substitutional sites of Ge atoms with the ratio of 75%. With the Mn content increasing to 0.25 or higher, only part of Mn atoms enter the lattice of Ge and the others exist in the form of the Ge₃Mn₅ phase whose content increases with the doped Mn concentration. It is found that, in the Mn_{0.07}Ge_{0.93} the bond length of the first (Mn-Ge) shell is $R_{Mn-Ge}=2.50$ Å, which is bigger than the first (Ge-Ge) shell distance in Ge by about 0.05 Å. These results imply that local structure expansion is induced by dilute Mn substituting into Ge sites.

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Poster no. PS1.145 - Session 1**Local structures of Mn atoms in Mn_xSi_{1-x} thin films probed by fluorescence XAFS**Jian Ye¹, Yong Jiang¹, Tao Yao¹, Zhiyun Pan¹, Zhihu Sun¹, Wensheng Yan¹, Hiroyuki Oyanagi², and Shiqiang Wei¹

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The local structure of the doped Mn in the Mn_xSi_{1-x} dilute magnetic semiconductors (DMSs) prepared by magnetron cosputtering method were studied by fluorescence X-ray absorption fine structure (XAFS) at both Mn *K*-edge and Mn *L*-edge. It was found that the occupation of Mn atoms in the Mn_xSi_{1-x} DMS strongly depends on the Mn content. The Mn *K*-edge XAFS results indicate that for the sample with low Mn content ($x=0.03-0.08$), the Mn atoms are incorporated into the lattice of Si, and substitute part of the Si sites. As the Mn content reaches 0.15, Mn atoms mainly form the phase of Si₁Mn₁ compound. Furthermore, the Mn 2*p* XAS shows that the Mn atoms substituting Si site in the Mn_xSi_{1-x} DMSs are in the zero-valence state but no metallic Mn clusters are formed. The Mn atoms in the Mn_xSi_{1-x} DMSs with high Mn content are in the divalent high-spin Mn²⁺ states.

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Poster no. PS1.146 - Session 1**XAFS investigations of Cu-W cyano-bridged coordination networks.**Dariusz A. Zajac^{1,2}, R. Podgajny³, B. Sieklucka³, Cz. Kapusta⁴, and D. Pinkowicz³*(1) Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany*

A current motivation for the synthesis of heterometallic inorganic-organic hybrid materials incorporating paramagnetic $[M(CN)_8]^{n-}$ ($M = Nb^{IV}$, Mo^V , W^V) ions is the merging of multi-functionality into these systems. Engineering of these materials by selecting appropriate paramagnetic octacyanometalate building block, 3d-metal ion, and organic ligands is key to understanding of possible synergies between magnetic coupling, magnetic ordering Tc and physicochemical properties. Studies of coordination networks very often include the powder or amorphous samples. The challenge for the use of the synchrotron radiation is the strong photo-sensitivity of cyano-bridged coordination networks.

We present XANES/EXAFS characterization of the selected octacyanometalate-3d metal ions-based cyano-bridged coordination networks. Experiments have been done at the beamline C in Hasylab. As an example, 3 samples are here presented: $(dienH_3)[CuW^V(CN)_8]_3$ (sample 1, [1]), $Cu_{2.97}[Cu_4W^V(CN)_8]_{2.06}[W^{IV}(CN)_8]_{1.94}$ (s. 2, [1]), and $K_4W^{IV}(CN)_8$ (s. 3).

XANES spectra at W L_3 edge show the increased area under white line. Thus, the valence state of W for samples 3, 1 and 2 can be assigned to 4+, 5+ and 4.5+, respectively.

EXAFS spectra show that first two peaks (C and N nearest neighbours) are identical for all samples. The third EXAFS peak at 5.1(2) Å corresponds to the Cu nearest neighbours shell. The higher amplitude of this peak for sample 2 than for 1 can be explained by the formation of additional W-Cu cyano bridges and changing from 2D to 3D coordination networks.

First XAFS experiments at 3d ion cyano-bridged coordination networks shows that this technique is very useful. The photo-sensitivity of these samples can be strongly reduced by the decreasing of temperature and the exposure time.

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Poster no. PS1.147 - Session 1**X-ray absorption spectroscopy for partially deuterated ammonium hexachloropalladate.**Dariusz A. Zajac^{1,2}, Z. Lalowicz², A. Birczynski², and A. Szymocha²*(1) Hasylab, DESY Notkestrasse 85 22607 Hamburg Germany**(2) Institute of Nuclear Physics PAN ul. Radzikowskiego 152 31-342 Krakow Poland*

Ammonium hexachloropalladate belongs to the family of ammonium hexachloro-metallates (NH_4)

We present EXAFS data, together with NMR T_1 relaxation time data, for ammonium hexachloropalladate samples deuterated at 30

EXAFS experiments at Pd:K edge reveal clearly that the first shell Cl peak is observed at 2.2(1) Å. The change of position and the change of the FWHM for the first shell Cl peak do not depend on temperature. Peaks of next-neighbour shells are also visible: N at 4.3(2) Å and Cl at 5.4(3) Å and will be later analysed.

The maximum of the D spin-lattice relaxation rate can be explained by rotation of the ammonium tetrahedrons about threefold symmetry axes. The unchanged position of the first Cl peak together with unchanged FWHM indicates that the ammonium ion rotation has a local character and does not affect the Pd and Cl crystallographic sublattice. Only between about 25K and 50K there are small shifts in both values which may be related to a correlation frequency of ammonium ions of the order of 108 s^{-1} in this range.

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Surface

Poster no. PS1.148 - Session 1

Photoemission study of electro-sprayed Poly(3-Hexylthiophene) on hydrogenated Si(111)

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With the properties of easy processing and patterning, organic semiconductors are promising integral part of the Si based devices. Poly(3-Hexylthiophene) (P3HT) can be easily solved in the many solutions and possesses very high carrier mobility, finding its applications in many organic devices such as field effect transistors [1, 2] and organic photovoltaic cells [3, 4]. Polymer film growth on contaminant free surface is extremely challenging but is essential in determining the device properties. Using electro-spray method, we have realized depositing solvent free polymer film (P3HT) on the surface (H terminated Si (111)) which was kept under relatively high vacuum. Core and valence level photoemission spectroscopy was used to investigate the interface structure and adsorption behavior of the polymer on the substrate. Photoemission results showed that P3HT on H terminated Si (111) exhibited neither decomposed nor strongly interacted behavior, rather a weakly bound one, maintaining its inherent structure and property.

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Poster no. PS1.149 - Session 1

High resolution S L_{3,2}-edge XANES studies of self assembled benzoic acid sulphur-derivatives on gold surface

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Understanding and controlling the physical and chemical properties of self-assembled monolayers (SAMs) on extended metal surfaces is an active area of current research[1]. Exploiting SAMs for applied purposes requires a proper control of the properties of the surface-linker groups employed, which for gold surfaces are usually sulphur-based compounds. Typically thiols are used, and monolayer formation on gold substrates is reported to be driven by the chemical bonding between thiolate groups and gold atoms[2] and by interactions between neighboring adsorbate molecules. For sulphide derivatives softer interaction is expected[2]. Understanding deeply the nature of the sulphur-gold bond is thus a key aspect since it allows us to control the properties and stability of monolayers and to engineer the surface properties. To this aim, we report here the study of two benzoic acid sulphur derivatives, 4-mercaptopbenzoic acid and 4-methylsulfanyl-benzoic acid, in the bulk phase and as SAMs on gold substrates, through high resolution XANES measurements at the S L_{3,2}-edge. Similar compounds are often employed in the functionalization of single molecule magnets (SMMs) that can be directly assembled on various substrates. We present this first step investigation to elucidate the expected chemical interaction between the atomic components in sulphur-anchored SMMs and gold surfaces[3]. From S L_{3,2}-edge XANES it is evident that the chemical environment around sulphur atoms results more negatively charged in SAMs than in the precursor molecules, also depending on the chemical nature of the thio-derivative.

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Poster no. PS1.150 - Session 1**Dispersive-NEXAFS as a tool to study surface chemical reactions**Hiroshi Kondoh¹, Hitoshi Abe¹, Kenta Amemiya², Ikuyo Nakai³, and Toshiaki Ohta⁴*(1) Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-Ku, Yokohama 223-8522, Japan**(2) Institute of Materials Structure Science, High-Energy Acceleration Organization, 1-1 Oho, Tsukuba 305-0801, Japan**(3) Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan**(4) SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

We have developed a dispersive-NEXAFS technique to study surface dynamic processes like surface reactions. We conducted real-time monitoring of surface species under the progress of reaction and analyze the reaction kinetics to understand the mechanism. Quantitative analyses for coverage changes of adsorbates provide information on reaction kinetics such as reaction order, rate constant and activation energy. In some cases, reaction intermediates can be also detected during the reaction. We report an example of mechanistic studies on surface chemical reactions with the dispersive-NEXAFS technique; NO reduction on N-covered Rh(111). We continuously measured N K-edge dispersive-NEXAFS spectra of partially N-covered Rh(111) surfaces with exposing to gaseous NO and monitored desorbed species simultaneously with a mass spectrometer. It was revealed from the real-time monitoring that the reaction rate of NO reduction becomes slower as increasing temperature. We found formation of a NO dimer species, which plays a role of an extrinsic precursor. We will also report further development of the dispersive-NEXAFS technique using a new undulator beamline at the Photon Factory.

Poster no. PS1.151 - Session 1**NEXAFS for the characterization of organic contamination during semiconductor manufacturing processing**Matthias Müller¹, B. Beckhoff¹, G. Bedana², G. Borionetti², A. Corradi², L. Frey³, Guerinoni², A. Leibold³, M. Otto³, and A. Nutsch³*(1) Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin, Germany**(2) MEMC Electronic Materials SpA, Viale Gherzi, 31 28100 Novara, Italy**(3) Fraunhofer IISB, Schottkystrasse 10, 91058 Erlangen, Germany*

Organic contamination on wafer surfaces with relevance for nanotechnologies and advanced microelectronics gets crucial as the continuously shrinking feature sizes get comparable to the dimensions of clusters and molecules. Especially, manufacturing of highly integrated circuits requires clean surfaces as processes might cause defects involving light elements (e.g. C, N, O, F). Yield issues are observed e.g. due to change of gated oxide integrity by defects, thickness and degradation. Different sources for organic contamination were identified and are subject of a joint research activity within the European Integrated Activity of Excellence and Networking for Nano and Micro-Electronics Analysis (ANNA) [1]. The environment used for fabrication of microelectronics shows various sources for volatile organic compounds. The sources for VOC are packaging materials and carriers or out gassing and residues of resist layers from lithography. Especially in lithography, non volatile residues remaining on the wafer surface became crucial for subsequent process steps. Silicon wafers from different steps during wafer manufacturing were studied using NEXAFS in Total reflection X-Ray Fluorescence (TXRF) mode and Thermo Desorption Gas Chromatography Mass Spectrometry (TD GCMS). The TXRF employing Synchrotron Radiation in the soft-X-Ray range provides very low detection limits, which allows for a reliable detection of ultra-trace contaminations of light elements on wafer surfaces. Final clean and packaging were identified as areas where detectable organic contamination could be transferred to the wafer surface. The application of TXRF-NEXAFS profits from multi-criteria evaluation of the spectra and the study of reference samples matched with TD GCMS.

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Poster no. PS1.152 - Session 1**Local order depth profiles in thin layers: the contribution of grazing incidence x-ray absorption spectroscopy**Aline Y. Ramos¹, Narcizo M. Souza-Neto^{2,3,4}, Hélio C. N. Tolentino¹, Alessandro Martins⁵, and Antonio D. Santos³

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Magnetic thin films have great appeal in recording media with high data density. The magnetic properties of these films, depending on the material atomic structure, may be modified or induced by the surface and interfaces. For the understanding and improving of these properties, it becomes compulsory to use experimental techniques able to provide in depth selective information. In this work, we put together the X-ray absorption spectroscopy (XAS) to a grazing incidence setup, and then use the variation of X-ray penetration inside the material around the critical angle to get depth resolved information about the structural and magnetic local order [1]. We developed a methodology, analogous to the recursive Parrat's reflectivity method [2], to quantitatively analyse this information. The refracted and reflected amplitudes within a film formed by layers, each one with different contributions are calculated at every depth. A self-consistent routine permits the modelization of experimental XANES data starting from a set of known structures. The methodology was applied in FePt and CoPt films produced by the magnetron sputtering technique [3]. In FePt films, a complete quantitative analysis allowed to characterize an oxidation gradient up to 5 monolayers [4]. In CoPt films, the XANES features associated to the in plane L_{10} chemically ordered structure, are partially lost in high depths away from the surface for films thicker than 50 nm. This layered structure explains in depth dependence of the magnetic perpendicular anisotropy of the films.

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Poster no. PS1.153 - Session 1**Structural characterization of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.0 - 0.20$) thin films using extended X-ray absorption fine structure spectroscopy**Balaram Sahoo¹, S. R. Das², M. Janousch³, V. Kuncser⁴, W. A. Adeagbo⁵, W. Keune⁶, R. Röhlberger¹ and D. K. Pradhan⁷

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When doped with La, BiFeO_3 (BFO) films exhibits an improved spontaneous and saturated ferroelectric (FE) polarization [1-2]. We had grown pulsed-laser deposited $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ films (BLFO, with $x = 0.00, 0.05, 0.10, 0.15$ and 0.20) of 400 nm thickness on Pt coated Si substrates held at 400 °C. The as-grown films were amorphous and were subsequently annealed using rapid thermal annealing at 650 °C in air for 2 min in order to obtain the polycrystalline films. Our BLFO films showed an enhanced spontaneous and saturation polarization by increasing La content [3]. It was argued that the improved FE properties of BLFO films were due to the improved structural parameters in the films.

Although the BFO films are antiferromagnetic, they show weak ferromagnetism. This could be due to strain, defects and disorder, which provide an uncompensation of Fe spins, contributing to the net magnetization. Our BLFO films exhibited higher saturation magnetization than pure BFO film. In order to understand the origin of the ferromagnetism and to correlate the magnetic and FE properties in our BLFO films, knowledge about the position of Fe and La in the crystal structure of the samples is quite essential. For this purpose, we have performed Fe K-edge EXAFS spectroscopy at the LUCIA beamline, SLS, Switzerland. Our results confirmed that Fe remains at the Fe site, and La replaces Bi in the tetragonal (distorted perovskite) structure of BFO. However, an indication of the introduction of small strain into the films because of different atomic sizes of La and Bi has been inferred from the EXAFS and the XANES results. A theoretical band structure calculation has been performed with the *abinitio* method which supports our observations.

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Instrumentation

Poster no. PS1.154 - Session 1

A new XAFS beamline at LNLS

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In this contribution, we present details of the design of a new XAFS beamline, recently commissioned at LNLS-Brazil. The beamline is mounted on a bending magnet port and its optics consists of two Rh-coated mirrors: a pre-monochromator collimating mirror and focusing toroidal mirror after the monochromator, which enable operation in the 4-18 keV energy range and yield a flux of 5E9 photons/sec at 10 keV. We will describe its optics, some operational parameters and the instrumentation available for users. Some commissioning results and examples of recent scientific results will demonstrate the beam line capabilities.

Poster no. PS1.155 - Session 1

X-ray Fluorescence Imaging and MicroXAFS at the BioCAT undulator beamline 18ID at the Advanced Photon Source

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The Biophysics Collaborative Access Team (BioCAT) undulator beam line, 18ID, at the Advanced Photon Source, Argonne, IL is a high performance instrument designed for and dedicated to the study of partially ordered and disordered biological materials. One of the BioCAT's core projects is the development of capabilities for scanning x-ray emission microscopy and micro X-ray absorption spectroscopy of tissue samples. A sagittal bending, double-crystal (Si(111) monochromator provide monochromatic x-ray beams in the range of 4 – 35 keV and 1.3×10^{13} ph/s at 12 keV. The microprobe optics comprises a recently commissioned pair of Rh coated silicon KB mirrors (University of Chicago design) 200 mm long each. The mirrors deliver a microbeam of ca. 3 micron FWHM and 1.0×10^{12} Ph/s. The intensity of the microbeam can be increased 4-fold by prefocusing the incident beam with the beamline main optics, while relaxing the microbeam minimum focal spot size. Typical biological samples show very low metal concentration, making fluorescence the preferred mode of XAFS measurements, a set of fluorescent detectors: including a Ketek Si drift detector, Vortex 4 element detector (from APS detector pool), and Fe, Cu and Zn Bent Laue crystal analyzers are available for that purpose. A motorized Linkam cryostage complete the setup. X-ray mapping is performed in either standard step scan mode with 1 sec dwell time per point typical and continuous scan mode showing 0.1 dwell time typical with full spectrum recorded per point. Current setup allows measuring the multielemental composition map on large tissue sections and XAFS measurement at selected sample spots with minimum adjustments. This paper reports the commissioning results of the new KB mirrors system and the recent results of x-ray fluorescence mapping and microXAFS at the BioCAT 18ID undulator beamline.

Poster no. PS1.156 - Session 1**Catalyst center at the Advanced Photon Source beamline 9-BM**Trudy Bolin¹, Steve Heald¹, Randall Winans¹, Peter Stair^{1,2}, and Jeffrey Miller¹*(1) Advanced Photon Source, 9700 South Cass Avenue, Argonne, IL 60439 U.S.A.**(2) Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208 U.S.A.*

Catalysis is an essential technology for economic prosperity, energy security and environmental preservation in the 21st Century. The importance of catalysis research to meet both the energy needs of the nation and the central role of DOE facilities in advancing catalysis science has been specifically identified in the Energy Policy Act of 2005. One of the recent DOE reports on research needs is entitled: "Basic Research Needs: Catalysis for Energy" from a BES workshop held August 6-8, 2007. In addition, catalysis can be expected to play a major role in a number of other research needs identified in this series of reports. These include Solar Energy Utilization, Clean and Efficient Combustion of 21st Century Fuels, and Research Needs for the Hydrogen Economy. As part of the reports on specific research needs, the DOE also identified five Grand Challenges for Science and the Imagination. Mastery of catalysis and catalytic systems will require advancement in all five of these challenges.

A workshop titled "Catalysis Research at the APS" was held on September 12-13, 2005 in order to assess the requirements and opportunities for supporting catalysis research that makes use of the Advanced Photon Source. In response to the major recommendations of this report, a Laboratory Directed Research and Development (LDRD) proposal was submitted. It received funding in 2008. Plans for providing a beamline and support equipment for in-situ studies of operating catalysts over a wide energy range (2.1 to 24 keV) is discussed. The addition of the capability for concurrent in-situ XAFS and diffraction characterization to 9-BM, and plans for a catalyst preparation and characterization in nearby laboratories is discussed. How this project is viewed as the first step in establishing a center to facilitate catalyst studies at all APS beamlines is also discussed.

Poster no. PS1.157 - Session 1**Evaluation of bending magnet XAFS beamlines at the APS and NSLS**Julie O. Cross¹, Matthew Newville², Bruce Ravel³, Mali Balasubramanian¹, Trudy Bolin¹, Steve Heald¹, Jenia Karapetrova¹, Nadia Leyarovska¹, Qing Ma⁴, and Bruce Bunker⁵*(1) Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA**(2) University of Chicago, GSECARS, 9700 South Cass Avenue 435A, Argonne, IL 60439, USA**(3) NIST, Building 535A, Brookhaven National Laboratory Upton NY 11973, USA**(4) Northwestern University, DND-CAT, 9700 S. Cass Ave. 432A, Argonne, IL 60439, USA**(5) University of Notre Dame, Dept. of Physics, Notre Dame, IN 46556, USA*

We developed a simple procedure for evaluating the readiness of synchrotron User Facility beamlines for XAFS experiments, which can be adopted at any bending magnet beamline. Technical performance of the beamline was quantified in terms of: monochromator calibration over long energy range, harmonic suppression, detector linearity, and noise introduced by beam instability. Access issues for General Users (GU) were also recorded, including: ease of use for "novice" scientists, flexibility of experimental setup for "expert" scientists, beamline support (staffing level, areas of expertise), and availability of beam time via the GU proposal system. We applied the procedure to six independently built beamlines at the Advanced Photon Source during the summer of 2006 and, after some minor refinements, to one beamline at NSLS in 2008. Results from both studies, as well as our subjective observations on optimizing the General User experience, are reported here. Data from the APS[1] and NSLS[2] experiments, along with a template for the procedure, are available on the XAFS.org wiki site.

[1] Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

[2] Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Poster no. PS1.158 - Session 1**Apparatus for X-ray absorption measurements in grazing incidence geometry**Francesco d'Acapito¹, C. Maurizio¹, M. Rovezzi¹, H.G. Pais¹, and F. Bardelli²*(1) CNR-INFM-OGG ESRF 6 rue jules horowitz f-38043 grenoble france**(2) NIS - c/o Dipartimento di Chimica IFM Via P. Giuria 7 I-10125 Torino ITALY*

X-ray Absorption Spectroscopy (XAS) is a powerful technique for the determination of the local structural parameters around a given chemical species as well as to obtain details on the electronic structure. A large part of the samples encountered in material science consist in thin films deposited on surfaces or buried at a moderate depth (a few tens of nm). In this case it is convenient to confine as much as possible the probe beam near to the surface in order to i) maximize the beam intensity in the thin film, ii) limit the beam penetration in the substrate to minimize the spurious signal originated from scattering and fluorescence from other components. The ideal case should be to operate in total reflection condition but frequently, sample parameters like size, surface flatness or surface roughness do not match the stringent conditions posed by this technique. We present an apparatus for the realization of x-ray absorption spectroscopy experiments in grazing incidence mode. The sample holder, cooled at 100 K, allocates up to three samples. The samples are tilted around the polarization vector of the incoming x-ray beam: for samples formed of a thin layer on a substrate, this geometry maximizes the ratio between the fluorescence and the scattering signals. An automatic sample alignment procedure is also described.

Poster no. PS1.159 - Session 1**New developments at the INE-Beamline for actinide research at ANKA**Kathy Dardenne¹, Boris Brendebach¹, Melissa A. Denecke¹, Jörg Rothe¹, Tonya Vitova¹, and Xiaolan Liu¹*(1) Forschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgung (INE) P.O. box 3640 76021 Karlsruhe Germany*

The INE-Beamline for actinide research at the synchrotron source ANKA is operated by the Institut für Nukleare Entsorgung (INE) at the Forschungszentrum Karlsruhe (FZK). Experiments on radioactive samples with activities up to 1^6 times the limit of exemption inside a safe and flexible double containment concept are possible. One great advantage of the beamline is its close proximity to INE's active laboratories with its equipment for manipulation of actinide materials and state-of-the-art spectroscopic, analytical, and microscopic instrumentation. This constellation is unique in Europe.

The INE-Beamline is built to serve in-house research associated with safe disposal of high level nuclear waste such as environmental actinide speciation or coordination-, redox-, and geo-chemistry of actinides. A wide energy range from around 2.1 keV to 25 keV covering the K-edges from P to Pd and the L_3 , L_2 , and L_1 edges for actinides from Th to Cm can be used. The INE-Beamline is optimized for X-ray absorption spectroscopy techniques (XANES/EXAFS), but x-ray fluorescence (XRF) analysis and powder diffraction (XRD) are also possible as well as surface sensitive measurements in grazing incidence geometry (GI-XAFS). INE-Beamline design was driven by user needs. This continues to be the force behind continual upgrades of instrumentation and extension of experimental capabilities.

Some of the new upgrades will be exposed in this presentation. The most recent improvement is the installation of a microfocus option for spatially resolved studies (μ -XRF, μ -XANES, μ -XRD) and investigations of small volumes (e.g., heterogeneous natural samples and diamond anvil high pressure cells). A second improvement is the availability of an electrochemical cell for investigation of redox sensitive systems.

The design, construction and testing of high resolution x-ray emission spectrometer is presented in a separate XAFS14 contribution (Tonya Vitova et al.).

Poster no. PS1.160 - Session 1**I20; the versatile X-ray absorption spectroscopy beamline at Diamond light source**

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The Versatile Spectroscopy beamline at Diamond Light Source, I20, is currently under construction and aims to begin operation in late 2009 and early 2010. The beamline will cover applications across the broadest spectrum of scientific disciplines, from physics, chemistry and biology through material, environmental and geological science. Three very distinctive modes of operation will be offered at the beamline: scanning X-ray Absorption spectroscopy (XAS), XAS in dispersive mode, and X-ray emission spectroscopy (XES). To achieve this, the beamline has been designed around two independent experimental end-stations operating from a pair of canted wigglers located in a 5m diamond straight section. One branch of the beamline will deliver monochromatic x-ray radiation of high spectral purity to one of the experimental hutches, whilst the other branch will constitute an energy dispersive spectrometer. The novel design of the beamline allows both branches to operate simultaneously.

Here, we present an overview of the beamline design, highlighting the unique capabilities of I20. For the monochromatic end station special attention has been paid to the design of the optic components to deliver a very stable x-ray beam at the sample position to allow high spectral quality data to be collected in the energy range of 4 to 34 keV. This branch of I20 is based on a scanning spectrometer operating from a four bounce monochromator. This device guarantees that the x-ray beam delivered to the sample has an energy resolution solely determined by the Darwin width of the installed monochromator crystal cuts, Si(111) or Si(311). For the dispersive branch of the beamline, the aim is to deliver a broad energy bandpass (>10%) from 6keV to 26keV. This broad bandpass will allow the collection of extended XAFS spectra in a single shot and should make the beamline particularly suitable to follow processes that occur on sub-second timescales down to milliseconds and microseconds.

Poster no. PS1.161 - Session 1**XAS at the materials science X-ray beamline BL8 at the DELTA storage ring**

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The possibilities for X-ray absorption spectroscopy (XAS) at beamline BL8 at the superconducting asymmetric wiggler at the 1.5 GeV Dortmund Electron Accelerator DELTA is described. The beamline is designed for X-ray studies in the spectral range from approximately 1 keV to 25 keV photon energy using a triple monochromator setup equipped with YB₆₆, Si(111) and Si(311) crystals. Besides transmission measurements, fluorescence detection for dilute sample systems has been applied, and surface sensitive reflection-mode experiments have been performed. The endstation includes a six-axis diffractometer that is capable of carrying heavy loads like ultrahigh-vacuum systems, high pressure cells or liquid-helium cryostats for reflectivity or DAFS measurements. The results also show that high-quality EXAFS data can be obtained in the quick-scanning EXAFS mode within a few seconds of acquisition time, enabling time-resolved in situ experiments using standard beamline equipment that is permanently available. The performance of the new beamline for XAS, especially in terms of the photon flux and energy resolution, is competitive with other insertion-device beamlines worldwide, and thus several sophisticated experiments including surface-sensitive EXAFS experiments are feasible. Several examples illustrate the excellent performance of the beamline.

Poster no. PS1.162 - Session 1**High pressure facilities at the D06A-DXAS beam-line**Flávio Garcia¹, E. J. Carvalho¹, and G. Azevedo¹*(1) Brazilian Synchrotron Light Laboratory (LNLS) Rua Giuseppe Máximo Scolfaro, 10000 13083-970 Campinas São Paulo Brazil*

High pressure conditions associated with the X-Ray techniques such XAFS and diffraction, can be used to study many physical or chemical systems. The kinetic of chemical reactions, electro-magnetic and structural properties of materials are examples of parameters that can be affected under high pressure conditions characterizing it as an interesting tool in the material science, namely for *in situ* studies. The use of synchrotron light brings great benefits to the study of materials under extreme *in situ* conditions. Due to the small size of the samples and to the complex apparatus necessary to produce such conditions, x-ray sources of high brilliance are essential. Many types of experiments can be performed, including, such as: x-ray absorption spectroscopy (XAS) and X-Ray Magnetic Circular Dichroism (XMCD). In the last year, an intense work has been done at Brazilian Synchrotron Light Source in order to do possible these experiments at LNLS beam lines. The instrumentation available at LNLS counts with some diamond anvil cell specially designed to *in situ* high pressure experiments. The diamonds are mounted in two pistons aligned with the symmetry axes of the cell. The diamond allows that the X-rays pass through the diamonds. The sample is putted on a small hole (around 200micros) performed onto a gasket placed between the diamonds. With this kind of cell, pressures up to 20GPa can be easily reached. Beside the sample, it is placed inside the cell a small ruby chip, which the luminescence lines are used as a manometer. In this work, we will present an overview about the high pressure facilities available for In situ x-rays absorption spectroscopy studies at LNLS, as well as some interesting examples.

Poster no. PS1.163 - Session 1**The X-ray absorption spectroscopy beamline at the Australian Synchrotron**Chris Glover¹, David Sprouster², Lisa Giachini¹, Bernt Johannesssen¹, Garry Foran¹, and Riccardo Signorato³*(1) Australian Synchrotron 800 Blackburn Rd 3168 Clayton Australia**(2) Department of Electronic Materials Engineering, Australian National University, Canberra Australia**(3) Accel Instruments Friedrich-Ebert-Straße 1 D-51429 Bergisch Gladbach Germany*

The X-ray Absorption Spectroscopy beamline at the Australian Synchrotron has been commissioned and began accepting users in early 2009. The beamline has a 1.9 T wiggler as its source, and optically comprises a collimating mirror (Si, Rh and Pt stripes), Si(111) and Si(311) liquid nitrogen cooled fixed offset DCM and a dual toroid (Rh and Pt stripe) focussing mirror. It offers high performance over a wide energy range: 4 - 37 keV focussed. The optical components were delivered as a system from Accel Instruments in 2007.

During commissioning, significant effort was devoted to mediate the sensitivity of the DCM to external vibrations. Flux stability is now routinely better than 0.1% peak - peak / 10 msec. Further commissioning results will be presented: flux stability (stationary and whilst scanning), power handling ability to 700 W on DCM, focus size and stability and energy resolution and repeatability.

Initial experimental EXAFS data (covering Ti - Sb) will be presented to highlight data quality obtained.

Poster no. PS1.164 - Session 1**The commissioning performance and the preliminary experiments of XAFS beamline at SSRF**

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A new high performance XAFS beamline (BL14W1) at the third generation light source facility, Shanghai Synchrotron Radiation Facility (SSRF), is recently in commissioning. The BL14W1 is a general purpose XAFS beamline. The source of BL14W1 is a 38-pole wiggler device with maximum magnetic field of 1.2T and magnet period 80mm. The main optical components include a collimation mirror, a liquid nitrogen cooled double crystal monochromator (DCM) with two sets of Si crystals (Si (111) and Si (311)), a focusing mirror and a harmonic rejection mirror. The focusing mode with energy range from 3.5 keV to 22.5 keV and the unfocused mode with energy range from 3.5 keV to 50 keV are designed. Equipped with a 32-element high pure Ge solid detector, SSRF XAFS beamline can carry out ultra low concentration analytical experiments. This beamline installation was completed in last October and the commissioning is now carried out. In this presentation the detail design of the beamline and its practical performance will be introduced. The preliminary experimental results will be also mentioned.

Poster no. PS1.165 - Session 1**Optimizing for signal-to-noise ratio in QXAFS system of BL14W1 XAFS beamline**

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QXAFS system has been completed in BL14W1 XAFS beamline of Shanghai Synchrotron Radiation Facility (SSRF). For acquiring spectra with good Signal-to-Noise ratio, typical absorption Spectra in different conditions have been measured to optimize parameters for QXAFS experiments. Signal-to-Noise ratios of these spectra have been calculated to estimate their qualities. The conditions for optimizing include different sampling speed, different motor mode and T mechanics compensation. ADC with a 500 kHz sampling speed is enough for QXAFS experiments. The motor mode of Bragg motor should be set to 1/20 step mode to acquire good Signal-to-Noise ratio. T mechanics compensation is also necessary to improve spectra quality in QXAFS experiment.

Poster no. PS1.166 - Session 1**Laboratory EXAFS using photographic method**

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Laboratory EXAFS facilities have been used since long. However, to our knowledge, EXAFS data analysis has not been reported as yet for the spectra recorded photographically. Though from our laboratory, we have been reporting various studies employing X-ray spectrographs using the photographic method of registration of EXAFS spectra, but the data has never been analyzed using the method of Fourier transformation and fitting with standards. This paper reports the study of copper metal EXAFS spectra at the K edge recorded photographically employing a 400 mm curved mica crystal Cauchois type spectrograph with 1.5 kW tungsten target X-ray tube. The data obtained in digital form with the help of a microphotometer has been processed using EXAFS data analysis programs ATHENA and ARTEMIS. The experimental data have been fitted with the theoretical standards. The results have been compared with those obtained from another laboratory EXAFS set up employing 12 kW Rigaku rotating anode, Johansson-type spectrometer with Si (311) monochromator crystal and scintillation counter. The results have also been compared with those obtained from SSRL. The parameters obtained for the first two shells from the photographic method are comparable with those obtained from the other two methods. The present work shows that the photographic method of registering EXAFS spectra in laboratory set up using fixed target X-ray tubes can also be used for getting structural information at least for the first two coordination shells.

Poster no. PS1.167 - Session 1**Q-EXAFS instrumentation at beamline X18B, National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.**

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NSLS operates at 2.8 GeV and 300 mA top filling current. The beamline X18B is a bending magnet beamline with no optics except a channel cut Si (111) monochromator at a distance of 18.0 m from the source. The flux at 10 KeV is of the order of 10^{10} photons / s. There is enough intensity to get a reasonable full range spectrum of 1100 eV in a short time of 120 ms. The monochromator gap is only 3.0 mm, so the beam walk during a typical EXAFS scan is few tens of a micron. The monochromator is coupled with a Heidenhein optical encoder and a 30 cm tangential arm, to change the angle of the monochromator. At the end of the arm a DC motor drives a cam with 9 holes, using a combined pulley and a rubber band system to damp the vibrations and control the speed. The position of the hole is selected by deciding the angular range of the scan, and the tangential arm can be positioned to the absorption energy of the element of interest. A fast LINUX based computer, with 16 bit A / D converter and IK220 energy readout, can collect 2000 data points / s. This instrument is used in time resolved work of oxidation reduction reactions, environment science, electrochemistry and laser excited reactions. Ni foil data taken in 120 ms, using this technique was compared with the same foil data taken conventionally at this beamline in one hour and ten minutes. The QEXAFS instrumentation will be discussed, along with the future plans of another beamline X18A with the capabilities of combined X-ray diffraction and Q-EXAFS.

Poster no. PS1.168 - Session 1**A new XAFS beamline at ALBA synchrotron: soon in operation**

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The ALBA-XAS beamline will provide a $\sim 100\text{-}\mu\text{m}$ -focused monochromatic beam in a wide energy range 2.4–35 keV. Higher energies up to ~ 70 keV are reachable in unfocused mode.

A direct drive double crystal monochromator allows fast rotation of up to $4^\circ/\text{sec}$. It thus enables a sub-Hertz repetition frequency for complete 1-keV-long EXAFS scans or 100 mHz frequency for XANES measurements.

A high resolution fluorescence analyzer will be permanently installed in the experimental station. This spectrometer will also serve as a normal fluorescence detector that is exempt from saturation problems typical for usual solid state detectors. It collects fluorescence in back-scattering geometry and therefore does not require an *ad hoc* side window in in-situ cells or sample vacuum volume. A position sensitive detector allows for energy dispersive images in static mode without doing θ - 2θ scans, which significantly alleviates mechanical requirements.

The sample infrastructure will include cryostats and vacuum chambers for low-temperature/low-energy measurements, gas lines, exhausts, poison gas sensors and ample space for in-situ chemical/catalysis research. A large chemistry lab in close proximity to the beamline with glove box, pellet press, fume cupboards, analytical balance etc. is being planned.

The ALBA-XAS beamline is dedicating a great deal of its efforts to the prominent topic of catalysis. The beamline will provide the Spanish as well as the international user community with a set-up that allows investigating in-situ, and with the aid of complementary spectroscopic techniques, a wide range of solid-gas catalytic reactions at time resolution as low as a hundred of milliseconds; thus, benefiting from the high speed of the direct drive monochromator.

The user operation is planned to begin in 2011. Visit www.cells.es/Beamlines/XAS.

Poster no. PS1.169 - Session 1**Performance of the software-triggered Q-XAFS at the ANKA XAS Beamline**Stefan Mangold¹

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The Quick(Q)-XAFS mode, a continuous data acquisition during the change of the energy, is extremely useful to track fast reactions, e.g. in catalytic processes, in electrochemistry and in fuel cells. Q-XAFS offers the opportunity to produce XAFS-maps of large sample areas in a reasonable time as well as the opportunity to examine in a very short time the quality of samples without a standard step by step EXAFS scan.

At the ANKA XAS beamline (a bending magnet beamline at the ANKA storage ring at the research center Karlsruhe) a Q-XAFS mode on a double crystal fixed exit monochromator (DCM-fe) has been implemented. Due to the combined movement of the bragg axis and the two linear drives the stability of the beam height on the sample position is maintained within 40 micrometers. To ensure a stable detuning of the second crystal of the DCM we use a D-MOSTAB (Struck, Hamburg) to keep the flux in the first ionisation chamber (beam intensity monitor) constant. The data acquisition is done by pure software-triggering of the beamline control software spec. This allows for the read-out of all detector types, including detectors offering only a software read-out (e.g. the digital detector electronics of XIA). Compared to hard-wired solutions this limits the minimum time per EXAFS scan to 1-2 minutes with the fluorescence detector and 30-60 seconds in the transmission set-up, but offers a larger expandability. The accuracy of the DCM and the high precision of the angular encoder allow to use both directions of the energy movement, reducing by this the delay between the scans.

The technical details and the performance of the Q-XAFS at different energies will be presented together we data of two application fields. A comparison between a step-by-step energy scan and several Q-XAFS scans performed in the same integrated scan time will show the better quality of the Q-XAFS data in the edge region.

Poster no. PS1.170 - Session 1**Recent status of 2D photoelectron spectroscopy experimental station at SPring-8**Fumihiko Matsui¹, Tomohiro Matsushita², Yukako Kato², Kentaro Goto¹, and Hiroshi Daimon¹

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Direct three-dimensional atomic structure analysis by stereo atomscope, valence-band angular momentum analysis by circularly polarized photoelectron diffraction, and atomic-layer-resolved magnetic structure analysis by diffraction spectroscopy have been developed at BL25SU, SPring-8 by using a display-type electron analyzer. The circular dichroism of photoelectron forward focusing peak rotation around the incident-light axis reflects the orbital angular momentum of excited core level and is inversely proportional to the distance between the emitter and scatterer atoms. This is the basis for the stereophotograph of the atomic arrangements [1]. Furthermore, these rotations are also found in the case of the valence band photoelectrons. The rotation corresponds to the orbital angular momentum quantum number of valence band. We succeeded in measuring the orbital angular momenta of each valence band of graphite [2]. Lastly, local electronic and magnetic structure information has been obtained by diffraction spectroscopy. X-ray absorption and magnetic circular dichroism spectra from different atomic layers of the Ni thin film were disentangled by use of Auger electron diffraction. Surface and interior core-level shifts and magnetic momenta are determined for each atomic layer individually [3]. Here we report the recent status and progresses of the 2D-photoelectron spectroscopy experimental station at BL25SU.

[1] H. Daimon, Phys. Rev. Lett. 86, 2034 (2001).

[2] F. Matsui et al., J. Phys. Soc. Jpn. 76, 013705 (2007).

[3] F. Matsui et al., Phys. Rev. Lett. 100, 207201 (2008).

Poster no. PS1.171 - Session 1**I18: The first spectroscopy beamline at the Diamond Light Source**

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The first spectroscopy beamline to operate at the Diamond Light Source is beamline I18. This is a microfocus spectroscopy beamline, with an energy range from 2.0 to 20.7 keV. The layout of the beamline will be described with details of the performance of the beamline relative to the design specification.

The beamline exploits the high brightness of the source using bimorph Kirkpatrick-Baez mirrors to produce a spot size as small as 2 microns. The principal detector is a 9 element monolithic germanium detector with an XSPRESS2 backplane developed by STFC for Diamond. There is also a 4-element Silicon drifts detector for lower energy work and a CCD for diffraction. We have designed an electron yield cell for use at elevated temperature. The bespoke sample holder and stage will be detailed.

Some of the initial results from the beamline and the use of the Generic Data Acquisition programme to control the beamline will also be outlined.

Poster no. PS1.172 - Session 1**The new NEXAFS endstation at BESSY II**

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The Near Edge Adsorption Fine Structure (NEXAFS) spectroscopy is widely used in the surface science as well as for the study of polymers and magnetic materials. However, with recent advances in the nanotechnology the requirements for the NEXAFS equipment have also greatly increased. For this reason the new NEXAFS set-up with a number of improved features was recently developed and constructed. The set-up works under ultrahigh vacuum conditions and consists of main chamber, distribution chamber and two preparation chambers. The transfer system allows easily transport the samples between all the chambers. The location of the preparation chamber with respect to the distribution chamber and the main chamber provides the possibility to perform the measurement and the preparation of samples independently. In the park station attached to the distribution chamber there is a place for the samples to be stored for a long time without being exposed to the atmosphere. The fully motorized and computer controlled manipulator makes possible to measure the spectra at different polar and azimuthal angles. For the NEXAFS spectra measurement there is a choice between electron detector for surface and fluorescence detector for bulk samples. The sample can be cooled down to 50 K and heated up to 1000 K. In the preparation chamber it is possible to clean the sample surface by ion sputtering and up to three evaporators can be installed for the deposition of the molecules on the crystal surface. In situ experiments can be also performed due to the availability of evaporators in the main chamber. The special transportation box allows to transport the samples in the high vacuum conditions from NEXAFS endstation to other UHV experimental setups. The complimentary techniques (XPS, LEED and TDS) are also available to support the NEXAFS results.

Poster no. PS1.173 - Session 1**In situ Pt L-edge QEXAFS at the superXAS beam line**

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The superXAS beam line is installed on a superbend port (2.9 Tesla) of the Swiss Light Source (SLS) and delivers a high brilliance beam ranging from 4.5 to 40 keV. This allows for the application of quick-EXAFS (QEXAFS) spectroscopy by means of a dedicated and permanently installed QEXAFS monochromator, which is easily interchanged with a conventional double crystal monochromator. A recent upgrade of this monochromator with an angular encoder on the crystal table allows for a synchronous readout of the energy axis, ion chamber signals and/or diode signals, which could be used for measurements in the fluorescence geometry.

Measurements on a Pt foil and a supported Pt catalyst showed the current time resolution limit (40 ms), but also the available range (0.9 degrees covering all three Pt L-edges), energy resolution (close to that of the Si(111) crystal) and ability to measure in fluorescence mode. The advantage of the QEXAFS system for the study of the dynamics of functional materials under reaction conditions and the ability to pick up short lived reaction intermediates will be shown by two examples: fast variation in catalytic performance and catalyst structure that occur in oxidation of CO and partial oxidation of methane.

Poster no. PS1.174 - Session 1**A combined SAXS/WAXS/QEXAFS setup for time-resolved in situ experiments**

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In order to follow chemical processes and crystallisation from a very early stage (i.e. from amorphous or early nucleation states when diffraction and scattering techniques do not yet provide any structural information) to a later stage when crystalline morphologies have formed, we have developed a combined technique approach. The combined X-ray-based techniques are the small- and wide-angle X-ray scattering (SAXS/WAXS) and quick-scanning EXAFS (QEXAFS).

The combined SAXS/WAXS/QEXAFS set-up has been constructed on BM26A at the ESRF [1]. The set-up is able to probe a fixed volume of the sample during synthesis so that it is possible to follow the evolution in chemical processes through the molecular nanometer and micrometer scales quasi-simultaneously. The advantage of this approach was demonstrated in the study of zeotype crystallization which revealed important new insights into the interplay of the various stages during ZnAPO-34 formation [2]. Though this subject has been studied previously more than once it was difficult to understand and accurately correlate the changes observed by separated measurements. One of the reasons for this is that, in practice, it is difficult to reproduce identical experimental conditions in separated experiments using different equipment. The achieved time resolution was about 5 minutes per combined cycle though the 10-20 s resolution should be possible even with bending magnet sources.

[1] Sergey Nikitenko, Andrew M. Beale, Ad M. J. van der Eerden, Simon D. M. Jacques, Olivier Leynaud, Matthew G. O'Brien, Dirk Detollenaere, Reinier Kaptein, Bert M. Weckhuysen, and Wim Bras, *J. Synchrotron Rad.* (2008), 15, 632–640
 [2] A.M. Beale, A.M.J. van der Eerden, S.D.M. Jacques, O. Leynaud, M.G. O'Brien, F. Meneau, S. Nikitenko, W. Bras, B.M. Weckhuysen, *J. Am. Chem. Soc.* (2006), 128, 12386

Poster no. PS1.175 - Session 1**Novel XAFS capabilities at ELETTRA synchrotron facility**

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The optical layout of the XAFS beamline at ELETTRA is presented along with its powerful capabilities for collecting XAFS spectra in a wide energy range 2.4-27 keV. The ensemble of available instruments allows a variety of different collection modes using various sample environments. In particular, simultaneous x-ray absorption and diffraction patterns can be collected even at high temperature using a special version of the L'Aquila-Camerino furnace and a MAR image-plate detector. Measurements can be performed in transmission or in fluorescence mode. An automated beamline control software allows us to perform successive measurements in different conditions without attending the beamline. Several examples of XAFS and diffraction measurements, as well as single-energy temperature scans will be presented showing the performances of the beamline for nanocrystalline systems and liquid metals.

Poster no. PS1.176 - Session 1**XANES measurements with compact ultra-fast kHz laser-plasma x-ray source**

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A high average power broadband x-ray source is developed in the multi-keV range, based on the thermal emission of plasmas produced with a 1 kHz fs laser focused on high Z element target [1]. This compact ultra-fast x-ray source is optimized in the spectral range of interest for Al K-edge study (1.5 – 1.75 keV). A specific x-ray spectrometer has been realized to get absolute Al K-edge XANES spectra. First results through solid aluminum samples have been registered with spectral fluctuations lower than 1 percent rms compared to the absorption edge, when accumulating laser shots over a few 10 s [2]. That demonstrates its suitability to study atomic and electronic structure of matter during laser-driven ultra-fast phase transitions between solid, liquid or higher energy density states.

[1] M. Harmand et al., subm. to Phys. Plasmas (2008).

[2] F. Dorchies et al., Appl. Phys. Lett. 93, 121113 (2008).

Poster no. PS1.177 - Session 1
New implementation of QEXAFS on BM29

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Time-resolved X-ray absorption spectroscopy is an invaluable tool for the investigation of the dynamical behavior of many physical, chemical and biological processes and has widely been used to study, for example, phase transformations, crystallization, nucleation and growth phenomena, decomposition and combustion reactions or solid-state transformations. Obviously the time resolution achievable with beamline became one of the discriminating factor between the process that it can be studied or not. One of the methods to improve the time resolution on classical beamline consist in the quick-scanning EXAFS (QEXAFS) technique.¹

BM29 is the general purpose X-ray absorption spectroscopy beamline at the ESRF. It is equipped with double crystals fixed exit double-cam Kohzu monochromator. Q-EXAFS acquisition on BM29 it was already available from 1998². The signal were recorded by direct readout of the ionization chambers by means of current amplifiers and a high speed analog to digital converter (ADC) all integrated in the Novelec medium sensitivity amplifiers working in the unchopped mode.

The new configuration is based on two improvements. The former, the use of a lock-in feedback to keep the two crystals in the monochromator in full parallelism therefore at the top of rocking curve. The latter is a new acquisition setup that over skip the integral voltage to frequency converter and perform a direct fast reading of the amplified current by a rapid analog to digital converter. A good signal statistic is obtained by the use of a frequency filter that results in a integration over a step of time. Core of the new configuration it is the MUSST modules developed at ESRF, a fully programmable trigger card with histogramming memory, counters, encoders and I/O channels.

Poster no. PS1.178 - Session 1
B18 - a core XAS spectroscopy beamline for Diamond

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During the past twenty years, XAS has progressed from being a technique only suitable for specialists in X-ray techniques to become a widely applicable tool for people whose principal interests lie elsewhere. This situation has resulted from the steady development of reliable spectrometers and new generations of software for data analysis.

B18 will be a general purpose XAS beamline on Diamond, built on a bending magnet and part of an integrated project including micro-focus and Wiggler beamlines devoted to XAS at this facility. It will cover a wide energy range, from 2 to 35 keV. The design is based on three main optical elements: a collimating mirror, a fixed-exit double crystal monochromator and a double cylinder focusing mirror. In addition, a pair of harmonic rejection mirrors will be used for low energy operations. The monochromator is designed to scan energy both in steps and continuously, hence allowing for both conventional and QEXAFS measurements. The main design novelty is that the appropriate mirror coating will be selected by changing the position of the slits, instead of by moving the optical elements. This will allow us to develop a very high level of automation in the operation of the instrument.

Detection systems will include transmission, fluorescence and electron yield. Experience shows that considerable value is added by combining techniques. Therefore provision has been made for wide angle X-ray diffraction studies to be incorporated into the beamline architecture in order to correlate changes in the short and long-range structures during a single experiment. The instrument will offer a variety of sample environments and the flexibility to integrate set-ups designed by the users. Hence, B18 will be able to contribute to research programs across a wide range of scientific disciplines, e.g. solid state physics and materials, catalysis, chemistry, soft matter, surfaces and biomaterials. The instrument will open to first users in April 2010.

¹Frahm, R. 1989. Rev. Sci. Instrum. 60:2515-2518.

²Filipponi, A et al. 2000. Rev. Sci. Instrum. 71:2422-2432.

Poster no. PS1.179 - Session 1
Soft X-ray spetromicroscopy beamlines at SSRF

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Soft x-ray spectroscopy beamline is the only beamline with photon energies falling within the soft x-ray regions among seven beamlines in phase I construction program executed from the year of 2004 to 2009. The insertion device is an elliptically polarized undulator with a period of 100mm and a minimum gap of 30 mm, corresponding to a minimum 70 eV for its fundamental harmonic radiation. The beamline was designed to transmits those photons from 200 eV to 2000 eV. A plane grating monochromator (PGM) scheme was adopted in the beamline with two gratings (800l/mm and 1200l/mm) covering lower energy regions (200-800 eV) and higher energy region (700-2000 eV) respectively. The designed value of the resolving power was about 6000 at 250 eV. A scanning transmission x-ray microscope was used as the end-station of this beamline. The commissioning of this beamline was started on December 26 of last year. So far, a resolving power has been measured to be over 8000 at 200 eV at small beam current (20 mA), and a spatial resolution of 30 nm has been achieved at end station. Fine commissioning of this beamline is being conducted and some preliminary experiments will come soon.

Poster no. PS1.180 - Session 1
Set-up of a low energy XAFS beamline at DORIS III

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Hitherto the lower limit of the working range at HASYLAB's X-ray Absorption Fine Structure (XAFS) spectroscopy beamlines was 2.8 keV. This excluded for instance the S K-edge from being measured at a HASYLAB XAFS beamline. Since sulphur is a very important element for applications coming from catalysis research, environmental sciences etc. we decided to rebuild XAFS beamline A1 completely to cover the respective energy range.

The new beamline uses the radiation from a standard DORIS III bending magnet (critical energy 16.04 keV). Under these circumstances, the use of mirrors is mandatory for effective higher harmonics suppression. At the new A1 beamline two mirrors are used, the first mirror is a Ni-coated toroidal mirror, placed in a 2:1 focusing position. The second mirror is a plane mirror with one Ni coated stripe and one uncoated (SiO₂) stripe. The in house developed UHV-compatible fixed-exit Double Crystal Monochromator (DCM) is equipped with two Si(111) crystal pairs. The second crystal of one of the two crystal pairs is tilted by 90° around the surface normal to shift the position of glitches. It allows Bragg angles between 5° and 55.5°. Together with the Ni coated mirrors, the resulting working range is 2.4 - 8 keV. This type of DCM which also allows continuous Quick-EXAFS scans is successfully used at beamline C for 3 years.

The set-up of the beamline was completed in March 2009 and user operation will start in April 2009 after an initial commissioning phase. Together with the presentation of the beamline set-up with special emphasis on the monochromator design, we will present results from the characterisation of the beamline during the commissioning phase and from first user experiments.

Poster no. PS1.181 - Session 1**MARS, a new beamline at SOLEIL, for radioactive matter studies**Pier Lorenzo Solari¹, Sandrine Schlutig¹, Hervé Hermange¹, and Bruno Sitaud¹*(1) Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, F-91192 Gif-sur-Yvette Cedex, Saint-Aubin, France*

MARS (Multi Analyses on Radioactive Samples) beamline is the hard X-ray bending magnet beamline dedicated to the study of radioactive matter of the new French synchrotron SOLEIL. The beamline, which has been built thanks to a close partnership and support by the CEA, has been designed to provide X-rays in the energy range of 3.5 keV to 35 keV. This allows to encompass M and L absorption edges of actinides, as well as K edges of transition metals (that are present in alloys and fuel claddings) up to heavy halogens, rare gases and alkalis (fission products in nuclear fuels).

The MARS project aims to extend the possibilities of synchrotron based X-ray characterizations towards a wider variety of radioactive elements (α , β , γ and n emitters) than what is currently available at other facilities. Thus, its specific and innovative infrastructure has been optimized in order to carry out analyses on materials with activities up to 18.5 GBq per sample. So, today, more than 70 different elements and more than 350 different isotopes have been proposed for studies on the beamline by the involved user community.

The arrangement of the different elements in the optics hutch is based on an original scheme which permits to have two alternative optical configurations (monochromatic or dispersive) depending on the nature of experiments to be performed.

At least three main techniques are progressively being proposed on the three complementary end-stations located in the experimental hutch: transmission and high resolution powder diffraction (TXRD and HRXRD), standard and dispersive X-ray absorption spectroscopy (XAS and EDXAS) and X-ray fluorescence (XRF). In addition, by using the KB optics, a micro-focused beam will be available on the second station of the monochromatic branch.

The beamline is currently under commissioning. The first two experimental stations, using the monochromatic branch, are scheduled to be operational at the end of the year.

Poster no. PS1.182 - Session 1**DiffAbs at SOLEIL: a beamline for structural study of materials by combination of XRD, XRF and XAS**Dominique Thiaudiere¹, S. Réguer¹, C. Mocuta¹, G. Geandier¹, F. Kergourlay¹, and F. Alves¹ (E. Fonda presenting author)*(1) Synchrotron SOLEIL l'orme des merisiers, Saint Aubin 91192 Gif sur Yvette France*

DiffAbs bending magnet beamline at SOLEIL Synchrotron is open to users' community since one year. The beamline is mainly dedicated for the structural studies of a great variety of materials, combining X-ray diffraction (XRD), X-ray fluorescence (XRF) and X-ray absorption (XAS) spectroscopies, with the possibility of using either macro- or micro-beams as probe: - the standard "macro-beam" mode covers the 3-23 keV energy range with $200 \times 200 \mu\text{m}^2$ beam-size at the sample position. - The "micro-beam" mode (3-18 keV energy range) will provide $\sim 10 \times 10 \mu\text{m}^2$ beams (end 2009). The broad energy range ensures the XAS study of the K absorption-edges of elements between K and Ru and the L-edges from Ru to U. The almost simultaneous combination of XAS, wide angle scattering (WAXS) and XRD offers the possibility of complementing the local structure information by data on the long range order, which can be of utmost importance for a full characterization of material transformations. Resonant diffraction spectroscopy (e.g. DAFS), will be applied to obtain site- and chemistry specific information. More generally, the study of anomalous diffraction/scattering (variation of the scattering cross section close to an absorption edge of the probed element) will be available as well. We will show the characteristics of the beamline (macro- and micro-beam modes). The experimental setup (6/8 circles kappa diffractometer) and the various sample environments will be addressed. First experiments are also shown, combining XRD and XAS, applied in the main scientific fields of the beamline: behaviour of materials at high and very high temperatures (up to 3000 °C), mechanical properties of nanostructured samples and study of materials from the cultural heritage field.

Poster no. PS1.183 - Session 1**Improvement of XAFS beamline BL01B1 at SPring-8**Tomoya Uruga¹, Hajime Tanida¹, Kazuo Kato¹, Yukito Furukawa¹, Togo Kudo¹, and Noriyoshi Azumi¹*(1) JASRI/SPring-8, 1-1-1 Koto, Sayo-cho, Hyogo 679-5198, Japan*

Beamline BL01B1 was constructed for conventional XAFS measurements using a bending magnet light source at SPring-8 in 1997 [1]. BL01B1 covers a wide energy range from 3.8 to 113 keV using an adjustable inclined double-crystal monochromator and a double mirror system. So far, BL01B1 has been improved to achieve users' demands, such as in-situ quick-scanning XAFS (QXAFS) and high-quality XAFS for thin films and dilute samples. A time-efficient QXAFS method was developed to measure high quality spectra up to high-k regions in the shortest possible time. The method involves sweeping the monochromator continuously at a variable angular speed depending on the k-region using a VME stepping motor controller. During scanning, a pair of crystals of the monochromator rotates without translation motion like a channel-cut crystal. The fluctuation of the beam height at the sample position is kept below 10 microns during a QXAFS measurement in the energy region from 3.8 to 50 keV due to the downstream vertical focusing mirror, which is crucial for measuring the thin films in a glancing angle geometry. This QXAFS method was applied to the fluorescence mode using a 19-element Ge detector combined with a digital X-ray processor system, XMAP.

The conversion electron yield (CEY) mode's XAFS is useful for studies of thin film samples. Single crystalline thin films and/or substrates make a significant amount of noise in the XAFS spectra due to diffractions. We developed a new type of CEY detector having a rotational sample stage that is 50 mm in diameter. Angular oscillations of 4 degrees in the sample rotation stage around the axis normal to the sample surface successfully remove the diffraction noise in the spectra. This report presents the current status of the BL01B1 with its newly developed apparatus.

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Poster no. PS1.184 - Session 1**Opportunities at the "Hard X-Ray Micro/Nano-Probe"-beamline at PETRA III**Gerd Wellenreuther¹, and Gerald Falkenberg¹*(1) HASYLAB @ DESY, Notkestraße 85, 22607 Hamburg, Germany*

In this summer the PETRA-storage ring at DESY (Hamburg, Germany) will produce first x-rays as a dedicated synchrotron radiation source. PETRA III will then be the most brilliant x-ray source worldwide, which especially benefits achieving smallest foci.

The "Hard X-Ray Micro/Nano-Probe"-beamline P06 is devoted to provide focused x-rays with focal-spot sizes in the micro-to nanometer range for energies between 2.4 to 100 keV. In order to truly supply users with "advanced visualization" a variety of contrasts will be used, including x-ray fluorescence, x-ray absorption spectroscopy, x-ray diffraction, phase contrast etc.. Imaging can be done either 2- or 3-dimensional (mapping or tomography). Further, coherent x-ray diffraction imaging will be available.

P06's spectroscopy-undulator will be installed in a low-beta section ($K=2.7$, $E_1=2.4\text{keV}$, $\lambda_U=31.4\text{ mm}$). The source sizes (σ) and divergences are $35 \times 6.9\text{ }\mu\text{m}^2$ and $29 \times 3.9\text{ }\mu\text{rad}^2$, respectively. Scanning as well as tapering the undulator gap will enable energy scans for spectroscopy under stable conditions. Using Si(111) / Si(311) crystals an energy range of 2.4 to 80 keV can be covered. A multilayer monochromator will be available for flux-hungry applications. A double mirror for higher-order suppression can be moved into the beam path (coatings: Si, Cr, Pt). Focusing devices include (pre-)focusing compound-refractive Be-/Al-lenses (CRLs) (energy range 6-100 keV, focus size $\geq 1\text{ }\mu\text{m}$), focusing Kirkpatrick-Baez-mirrors (2.4-30 keV, $\geq 300\text{ nm}$) as well as nanofocusing Si-lenses (10-50 keV, $\geq 50\text{ nm}$).

The experimental area is divided into a microprobe-hutch hosting the CRLs and the KB-mirrors, and a nanoprobe-hutch for the nanofocusing lenses. Both areas are decoupled from the control area by a thermal lock. Sample preparation environments are both available directly at the beamline and in nearby laboratories.

Poster no. PS1.185 - Session 1**Performance of a 4-element Si drift detector: Resolution, maximum count rate, dead-time correction, and incorporation into Athena**

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Due to its low noise and high count-rate capabilities, the Si drift detector is gaining popularity for energy dispersive, fluorescence-yield x-ray absorption fine-structure spectroscopy. Here we report on the performance of a newly commissioned 4-element Si drift detector operating at the NIST beamline X23A2 at the NSLS. It is demonstrated that with analog electronics the detector is capable of acquiring x-ray absorption fine-structure spectra with a total count rate > 400,000 counts per second per detector element. The resolution at this count rate is approximately 200 eV FWHM, which is sufficient to resolve the Mn K α and K β lines. "Fast-channel" dead-time correction utilizing an efficient algorithm to correct the incoming count rate for dead time is described and has been implemented into the Athena data analysis package. For concentrated samples, dead-time correction is necessary above 100,000 counts per second per detector element; however, no dead-time correction is necessary for dilute samples to count rates higher than 250,000 counts per second per detector element. We will also discuss the advantages of digital versus analog electronics and their effect on count rate.

Poster no. PS1.186 - Session 1**SSRF hard x-ray microfocusing beamline**

Yu Xiaohan¹, Li Aiguo¹, Yang Ke¹, Wang Hua¹, and Yan Fen¹

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SSRF microfocusing beamline (BL15U1) is dedicated to hard X-ray microanalysis allowing the combination of fluorescence, spectroscopy, diffraction and imaging techniques. An in vacuum undulator is used provide high brightness radiation covering the required photon energy range of 3.5 to 22.5 keV. A K-B microfocusing mirror is used to produce microfocused beam. A 7-axis sample stage with 100nm resolution and capable of 3 dimensional rotation is used for sample positioning and scanning. A 7-element Si(Li) detector and silicon drift detector is used for micro XRF analysis and micro XAFS experiment. Various applications requiring low detection limits for localization/speciation of trace elements together with structural analysis will be developed at the beamline on the micrometer scale. This beamline has been commissioned recently and 1 μ m x 2 μ m focal spot size at sample position has been obtained. In this poster, a brief introduction and present status of the beamline, together with some preliminary results of micro-XAFS experiment will be presented.

Poster no. PS1.187 - Session 1**QXAFS system of BL14W1 XAFS beamline at Shanghai Synchrotron Radiation Facility**

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BL14W1 XAFS beamline in Shanghai Synchrotron Radiation Facility (SSRF) includes a stable monochromator and a high speed data acquisition system for Quick scanning XAFS (QXAFS) spectroscopy. The devices for data acquisition include two ion chambers, two amplifiers and a high speed ADC. QXAFS scanning program is written with labview8.6. Datalogging and Supervisory Control (DSC) module of Labview8.6 is used for communication between labview8.6 and EPICS. A QXAFS spectrum of Cu foil at K edge was achieved less than 2 seconds. This QXAFS spectrum is in accord with standard conventional XAFS spectrum very well. Energy resolution of the whole system is also good enough to describe fine structure at near edge.

PS2: Poster Session 2

Location: "Benedetto XIII" Hall
Time: Wed-Thu 11:30-13:30

Chemistry

Poster no. PS2.1 - Session 2

Multiple-scattering approach to Hg L₃-edge x-ray absorption near-edge structure (XANES) analyses for Hg_nX₂ (n=1,2 and X=Cl, Br, I)

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The multiple-scattering calculations have been done to analyze the Hg L₃-edge x-ray absorption near-edge structure (XANES) of Hg_nX₂ compounds (n=1,2 and X=Cl, Br, I). This study was done to explain very high chemical shift observed in the case of Hg₂Cl₂ [1]. The spectra were recorded using Technos EXAC 820 EXAFS Spectrometer equipped with rotating anode as x-ray source. The monochromator was Johansson type Ge(400) crystal. The profiles of absorption edges were obtained by averaging the results of a large number of spectra recorded in turn from each sample. The inflection point in the L₃ edge of mercury metal was taken as reference point. The chemical shift reported earlier in the literature was not seen. This difference may be ascribed to different experimental conditions. In the case of Hg₂X₂ the observed Hg L₃-edge XANES spectra show similar structures for all the cases. The chemical shifts of these samples are quite small. Some broadened peak positions on higher-energy region about 20eV from absorption-edge are slightly shifted in these cases. In the case of HgX₂ the observed Hg L₃-edge XANES spectra show different shoulder like structure around the absorption edge. The absorption edges of these samples depend on the intensities of the shoulder-like structures, whereas the XANES spectra on higher-energy region about 20eV from absorption-edge show similar structure in all the cases. The shoulder-like structures around the absorption-edge reflect the electronic structure on the absorbing Hg site.

The XANES theory used in these calculations is based on the short-range order full multiple-scattering theory [2]. The multiple-scattering calculations well explain the observed spectral changes for different ligands referring to the structure obtained by the crystallographic data.

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[2] T. Fujikawa, J. Phys. Soc. Jpn. 62, 2155 (1993).

Poster no. PS2.2 - Session 2**DXAS electronic and structural characterization of nitroprussides**Marcelo Ceolín¹, D. B. Soria², and M. A. Taylor³*(1) Instituto de Investigaciones Físico-Químicas Teóricas y Aplicadas (INIFTA), CONICET and Universidad Nacional del Noroeste de Buenos Aires, Argentina.**(2) Centro de Química Inorgánica (CEQUINOR), CONICET and Departamento de Química, Universidad Nacional de La Plata, Argentina.**(3) Instituto de Física La Plata (IFLP), CONICET and Departamento de Física, Universidad Nacional de La Plata, Argentina.*

Transition metal nitroprussides form an interesting class of solids with appealing properties [1]. The model for the chemical bonding between the metal atom and the ligands is the Dewar-Chat-Duncanson model with σ - donation from the ligands and π - back donation from the d-orbitals of the metal [2,3]. The responsible for the back donation is an empty anti-bonding orbital localized on the nitrogen atom of the NO group with potential interest in optoelectronics because of the possibility of optical pumping of electrons to this orbital [4-6]. Moreover, metal nitroprussides display a rather open structure with nanosized pores available for the storage of small molecules like hydrogen [7,8]. In this work we report an x-ray absorption study of $\text{Co}[\text{Fe}(\text{CN})_5\text{NO}] \cdot n\text{H}_2\text{O}$ and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. We present the thermal evolution of the Fe and Co K-edge XANES between room temperature and 600 °C. Clear indications of charge transfer or coupled structural changes between absorbers and ligands were observed and correlated with simultaneous changes in local symmetry around Fe and Co. The decomposition of the anhydrous salts was followed in detail and the end products were compared with XAS spectra from reference oxides. Acknowledgments: the authors are members of Carrera del Investigador Científico (CONICET, Argentine). The authors are indebt to Laboratorio Nacional de Luz Sincrotron, Brazil for partial financial support.

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Poster no. PS2.3 - Session 2**Copper K-edge EXAFS of Cu(I) and Cu(II) oxide mixtures**Abhijeet Gaur¹, Basant D. Shrivastava¹, and Santosh K. Joshi²*(1) School of Studies in Physics, Vikram University, Ujjain 456010, India**(2) Government College, Badnawar (Dhar) 454660, India*

EXAFS at the copper K-edge has been recorded for cuprous oxide and cupric oxide separately and also for a mixture of the two in a specific ratio at the EXAFS beam line at SSRL. The normalized $\mu(E)$ data obtained for the two oxides, i.e., Cu(I) and Cu(II) oxides separately was linearly combined to fit the normalized $\mu(E)$ data of the mixture using the Linear Combination Fitting (LCF) method in EXAFS software ATHENA. The values obtained for the statistical goodness-of-fit parameters, R-factor and chi-square, show that the fit is reasonably good. This procedure of LCF was also applied to the $\chi(k)$ data where nearly similar results were obtained. The Fourier transform of the $\chi(k)$ data obtained after LCF has also been found to compare reasonably well with the Fourier transform of the $\chi(k)$ data of the mixture. This procedure yielded the percentage of the oxides in the mixture which was found to be nearly the same as the actual percentage which was used to prepare the mixture. Thus, this method can be applied to determine the percentage of two or more species in a sample having two or more oxidation states or in a sample which originally contains a metal only in one oxidation state and gradually gets converted into another oxidation state. The method will also be useful for analyzing a complex containing a metal in two oxidation states at two different sites. Thanks are due to Prof. E. A. Stern for recording the data.

Poster no. PS2.4 - Session 2**XAFS studies of chemically synthesized Fe doped ZnO**Sanjeev Gautam¹, Shalendra Kumar², K. H. Chae¹, Ravi Kumar³, B.H. Koo², and C. G. Lee²(1) *Nanomaterial Analysis Center Korea Institute of Science and Technology 136-791 Seoul KOREA*(2) *School of Nano and Advanced Materials Engineering, Changwon National University, Changwon 641-773, Korea*(3) *Inter University Accelerator Centre (IUAC), New Delhi 110 067, India*

During the last years dilute magnetic semiconductors (DMSs) have attracted the attention of the scientific community due to their potential applications in the spintronics devices. DMSs are formed by the partial replacement of cations in semiconductor transition metal (TM) cations. DMSs are the potential candidate for various technological applications such as: storage, processing, transmission of digital information and optical, magnetic sensors etc [1]. In earlier results, XRD reveals that the sample (nanorods of Fe-ZnO) crystallizes in a single phase wurtzite structure and magnetic studies show the weak ferromagnetism at room temperature [2]. In this work, we report the extended x-ray absorption fine structure study of Fe doped ZnO synthesized by a co-precipitation technique. Preliminary analysis and linear combination fitting shows that Fe replaces Zn in the bulk sample. The EXAFS simulations using Artemis [2, 3] show that the bonding length of Zn-O and Zn-Zn remains almost same after incorporation of Fe atoms in ZnO matrix. Similar results are also reported by others [4] for different materials.

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Poster no. PS2.5 - Session 2**Formation and reactivity of Cr^{II} carbonyls hosted in polar and non polar supports**Diego Gianolio¹, Elena Groppo¹, Jane Estephane^{1,2}, Carmelo Prestipino³, Sergej Nikitenko³, Adriano Zecchina¹, Silvia Bordiga¹, Mostafa Taoufik², Elsje A. Quadrelli², Jean Marie Basset², and Carlo Lamberti¹(1) *Department of Inorganic, Materials and Physical Chemistry, NIS Centre of Excellence and INSTM unit, University of Turin, Via P. Giuria 7, I-10125 Turin, Italy.*(2) *Laboratoire de Chimie Organometallique de Surface, UMR5265 "LC2P2" - CNRS UCBL1 CPE, 43, Boulevard du 11 Novembre 1918; BP 2077 F-69616 Villeurbanne Cedex, France*(3) *ESRF, 6 rue Jules Horowitz, BP220, F-38043, Grenoble CEDEX, France.*

Organometallic complexes hosted inside frameworks are particularly interesting because of possible application in heterogeneous catalysis or electronic devices and optical materials [1]. We present here a detailed spectroscopic investigation on structure and reactivity towards simple reagents (such as CO) of Chromocene molecules (Cp₂Cr where Cp = Cyclopentadiene). The experimental difficulty is essentially determined by their high air sensitivity of Cp₂Cr and of products and by their tendency to form cluster. For this reason we performed a fluorescence EXAFS experiment (ESRF, BM26A: beam vertically focused to 0.3 mm) working with sealed capillaries. Cp₂Cr molecules were encapsulated into the nanovoids of two different matrices: a non polar polystyrene (PS) and a polar NaY zeolite, both of them able to molecularly disperse the Cp₂Cr. In PS stable Cp₂Cr(CO) complexes are observed [2]. In NaY, the presence of high internal electric fields, generated by Na⁺ cations [3], confers to the Cp₂Cr molecules a much higher reactivity towards CO resulting in a red-ox reaction followed by a Cp ring abstraction that can be summarized as [4]: 2Cp₂Cr + Na⁺ Y⁻ $\xrightarrow{\text{CO}}$ [Cp₂Cr(CO)]⁺Y⁻ + [CpCr(CO)₃]⁻Na⁺ + Cp

Concluding, the EXAFS data collected in situ allowed the structural determination of the reaction products and, combined with other spectroscopic techniques (FTIR and UV-Vis) and ab initio theoretical calculations, afforded the full comprehension of the complex reactivity of Cp₂Cr molecules inside the cavities of PS and NaY hosts.

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Poster no. PS2.6 - Session 2**XAFS studies on copper(I) complexes containing scorpionate – based ligands**Marco Giorgetti¹, Maura Pellei², Giancarlo Gioia Lobbia², and Carlo Santini²(1) *Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4 40136 Bologna Italy*(2) *Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino (MC), Italy*

The well known biochemistry of copper underlines the crucial role played by this metal in different enzymes that catalyze oxidation/reduction phenomena correlated with the antioxidant systems of living organisms. It has been established that the properties of copper-coordinated compounds are largely determined by the nature of ligands and donor atoms bound to the metal ion [1]. Phosphine complexes of group 11 metals, especially those including the gold(I) and copper(I) ions, have been proposed as alternative anticancer drugs to the cisplatin reference drug. For instance, [Cu(thp)₄][PF₆] complex has been shown to be about 1 order of magnitude more cytotoxic than cisplatin and some less hydrophobic mixed scorpionates-phosphine copper(I) complexes, [H₂B(tz^{NO2})₂]Cu[(PR₃)₂], were proved to retain high cytotoxic activity against a panel of human tumor cell lines.

Because these materials are frequently polycrystalline and no crystal structure are likely to be obtained using XRD, the XAFS probe is a good alternative for the structural studies, as demonstrated several times in the structural characterization of amorphous and inorganic materials[2].

X-ray Absorption Spectroscopy (XAS) has been used to probe the local structure of copper(I) complexes containing the dihydridobis(3-nitro-1,2,4-triazol-1-yl)borate and the bis(1,2,4-triazol-1-yl)acetate ligands. The EXAFS analysis, performed by using the GNXAS package, has permitted the identification of the local environment of the copper site. Copper is found to be 4-fold coordinated with two sets of Cu-N and Cu-P interactions describing a quasi planar figure. An additional coordination is revealed for the copper(I) complex of bis(1,2,4-triazol-1-yl)acetate due to the interaction of the copper with the acetate of the scorpionate ligand.

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Poster no. PS2.7 - Session 2**Mn K-edge XAS Study of a cubane [Mn₄O₄]⁷⁺ complex which is capable of the light-driven electro-oxidation of water at 1.2V**Rosalie K. Hocking¹, Robin Bribblecombe¹, Annette Koo¹, and Leone Spiccia¹(1) *Monash University Clayton 3168, Australia*

A recent publication [1] reported that when sorbed onto Nafion films, Mn-cubane [MnO₄L₆], where L= diaryl phosphinate compounds are capable of photo catalysing the oxidation of water. This observation has implications for to the mechanism of action of photosystem II. The model cubane compounds are known to produce O₂ from the oxo bridges following UV-photolysis in the gas phase. The mechanism postulated for this (based on mass spectroscopy) is that the reaction proceeds via the photo-dissociation of a phosphinate ligand. In this study, Mn K-edge XAS was measured directly on cubane [Mn₄O₄]⁷⁺ sorbed Nafion films deposited on an electrode surface. Samples were exposed to different potentials and light exposure combinations. The results have been used to assist in the identification of key species important in photocatalysis.

[1] Angew Chem Int. Ed., 2008, 47, 7335-7338

Poster no. PS2.8 - Session 2**Fe and S K-edge XAS study of the redox chemistry of monosulfidic black ooze and related materials**Rosalie K. Hocking¹, Kate Morgan¹, Edward D. Burton², and Perran Cook¹

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(2) Centre for Acid Sulfate Soil Research, Southern Cross Geoscience, Southern Cross University Lismore NSW 2480, Australia

Acid sulfate soils (ASS) are soil and soft sediments in which sulfuric acid may be produced from iron sulfides or has been produced leaving iron oxyhydroxy sulfates in amounts that have a long lasting effect on soil characteristics. If soil material is exposed to rotting vegetation or other reducing material, the Fe-oxyhydroxysulfates can be bacterially reduced to sulfides including pyrite, mackinawite and Monosulfidic Black Ooze (MBO) [1,2], a poorly characterised material known to be a mixture of iron sulfides and organic matter. We have examined a range of natural environments and chemical models of those environments by a combination of Fe and S K-edge XAS. We have found that the effects of particle size on self absorption in natural sediments plays an important role in the spectroscopic identification of the relative proportions of different species present in natural samples. XAS results are coupled to DFT calculations and vibrational spectroscopy to examine some of the mechanisms for oxidation of mono-sulfidic black ooze.

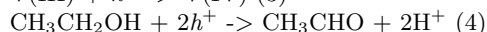
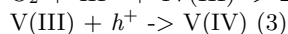
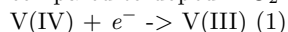
Poster no. PS2.9 - Session 2**State-selective V K $\beta_{5,2}$ -selecting XAFS spectroscopy to elucidate the fate of electrons and holes during photocatalysis under visible light**Yasuo Izumi¹, Yoshiyuki Shibata¹, Kazushi Konishi¹, and Hideaki Yoshitake²

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Photocatalysis under visible light (VL) can solve global environmental/energy problems. We developed V-doped TiO₂ of specific surface area 800 m²/g with uniform mesopores 3 nm. The photocatalytic superiority was investigated by state-selective V K $\beta_{5,2}$ XAFS. High energy-resolution (1.1 eV) fluorescence spectrometer equipped with Johann-type Ge(422) crystal ($R = 225$ mm) was set in KEK-PF 7C/9C [1]. In-situ measurements in ethanol/O₂ under Xe arc lamp filtered (>420 nm) were enabled. Chemical shifts of V K $\beta_{5,2}$ were relatively great, *e.g.* 3.2 eV between V(III) and V(IV).

The doped V valence state before catalysis was IV. The reduction rate from V(IV) to V(III) in ethanol under VL was 14 $\mu\text{mol/h/g}_{\text{cat}}$ (eq.1) based on V K $\beta_{5,2}$ emission [2]. Acetaldehyde formation rate in the condition was 2.4 $\mu\text{mol/h/g}_{\text{cat}}$ (eq.4). Thus, charge recombination probability (0.66) was given (eq.3). In the dynamic equilibrium of V(III) and V(IV) states, XAFS derived from V(III) and V(IV) were obtained by tuning to 5456.3 - 5458.0 eV and 5460.9 - 5462.4 eV, respectively, demonstrating VO(SO₄)-like V(IV) and V₂O₃-like V(III) state structures [1,2]. In O₂ under VL, the V emission peak shifted back to the energy for V(IV) (eq.2). Promoted reduction step (212 $\mu\text{mol/h/g}_{\text{cat}}$) over V₂O₃-like V(III) sites substituting on the Ti sites of TiO₂ with uniform mesopores was found to be the origin of fastest oxidative dehydrogenation of ethanol compared to doped TiO₂ reported so far.

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Poster no. PS2.10 - Session 2**XAFS analysis of halide ion-cyclodextrin inclusion complexes in aqueous solution**Takuma Kaneko¹, Masaki Ueda¹, Shin-ichi Nagamatsu¹, Takehisa Konishi¹, Takashi Fujikawa¹, and Masaichiro Mizumaki²

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Cyclodextrin (CD) forms inclusion complexes with various chemical species. Inclusion of mono-halide ion, which is relatively small among guest anions, has been studied only in terms of thermodynamics and equilibrium constants and few researches about the detailed structure have been reported. We analyzed the structure of inclusion complexes of α -, β -, γ -CD with mono-halide ion in aqueous solution by means of XAFS spectroscopy.

XAFS spectra of these systems are superpositions of contributions from the ions that are included in CD cavities and from the ions that are not included. We analyzed observed spectra using molar fractions of included halide ions calculated from the association constants that were reported in Ref[1]. In case of iodide complex, we assumed that two kinds of iodide ions exist in iodide-CD aqueous solution i.e. hydrated mono-iodide ions and 1:1 mono-iodide-CD inclusion complexes.

Fourier transforms of I K-edge EXAFS spectra of iodide-CD aqueous solution show that the height of the peak caused by the oxygen atoms of water molecules in the first hydration shell decreases as the fraction of included iodide ions increase. This result suggests that dehydration process accompanies the formation of the inclusion complex.

We further report detailed structural study based on multiple-scattering theory[2] of Iodine L-edge XANES spectra and a molecular orbital calculation/molecular dynamics simulations.

[1] J.P.Diard, et al., J. Electroanal. Chem., 189, 113 (1985).

[2] T. Fujikawa, et al., J. Elect. Spect., 129, 55 (2003).

Poster no. PS2.11 - Session 2**In situ S K-edge XAFS measurements of the hydrogen trapping by amorphous CoS(OH)**Nobuyuki Matsubayashi¹, Pavel Afanasiev², Laurent Piccolo², Christophe Geantet², and Yuji Yoshimura¹

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Release of radiolytic hydrogen is a source of serious safety problems in the management of nuclear waste. Hydrogen traps can be used to decrease explosion or swelling risks. We have demonstrated that amorphous CoS(OH) has an ability to absorb H₂ gas up to 0.5 molar ratio of H₂/Co [1]. The understanding of this reaction mechanism was studied by XRD, IR, TEM, XPS, neutron scattering, Co K-edge EXAFS. In the present work, the in situ S K edge fluorescent XAFS measurements have been carried out upon interaction of amorphous Co hydroxy sulfide with hydrogen at 325 K. The measurements were carried out on the BL-9A at the Photon Factory in Tsukuba(Japan). In situ cell was specially designed for these measurements, which included sample holder, heater and gas flow assembly. The in situ cell was installed in the measurement box flushed by helium in order to decrease soft X-rays absorption. Spectra were collected in the fluorescence mode. The measurements were carried out for the CoS(OH) solid before and after hydrogen as well as reference compounds including relevant sulfides of Cobalt, other transition metals sulfides and sulfur. In situ measurements demonstrated that S K-edge XAFS spectra of CoS(OH) were modified after interaction with hydrogen during several hours. At the end of experiment we observed the shape change of XANES that is consistent with the formation of small crystallites of CoS. Comparison with the spectra of other cobalt sulfides allows ruling out their presence. The XANES shape suggested that SO₄²⁻ species were also formed during the reaction.

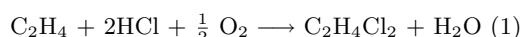
[1]C. Loussot, et al, Chem. Mater. 18, 5659 (2006).

Poster no. PS2.12 - Session 2**Local structure characterization of Ag n-Hexan dithiolate**Carlo Meneghini^{1,2}, T. Comaschi¹, S. Mobilio^{1,2,3}, A. Balerna³, L. Suber⁴, and P. Canton⁵(1) *Dip. di Fisica, Univ. Roma Tre Via della Vasca Navale 84 00146 Rome Italy*(2) *Ogg-GILDA c/o ESRF Grenoble France*(3) *NFN-Laboratori Nazionali di Frascati, via E. Fermi 40, 00044 Frascati (Italia).*(4) *CNR-Istituto Struttura della Materia, P.O. Box 10, 00016 Monterotondo St., Italy.*(5) *Dipartimento di Chimica Fisica Via Torino 155/b I-30170 Venezia-Mestre*

The recent discovery of permanent magnetism in thiol-capped nanoparticles of non magnetic metals like Au and Ag, stimulated an ample interest. The questions regarding the physical origin of magnetic moment in a normally diamagnetic atom and the huge anisotropy constant associated with the permanence of such magnetism at high temperature triggered an ample research work. There is now a general agreement on the role of the charge transfer between the metal atoms at the cluster surface and the S capping ones. Thiol-capped silver nanoparticles were prepared and characterized by TEM and high resolution TEM microscopy showing small ($D \approx 2$ nm) particle sizes. Magnetic measurements revealed a ferromagnetic behaviour, with finite coercivity, up to room temperature. In order to achieve an accurate characterization of local atomic structure of these particles, XAFS measurements have been performed at the Ag and S K-edges, respectively at ESRF (GILDA beamline) and DAFNE (DRX-1 beamline) on the corresponding Ag n-hexan dithiolate complex. XAFS data analysis allow the accurate description of the local atomic structure around either Ag and S ions. The Ag-Ag distance is slightly compressed, as expected in small clusters. The very low Ag-Ag coordination number suggests a large amount of Ag dimers.

Poster no. PS2.13 - Session 2**Interaction of $MCl_xCuCl_2/\gamma-Al_2O_3$ ($M = Li, K, Cs, Mg, La$) with C_2H_4 , O_2 and HCl : an in situ EXAFS investigation of the ethylene oxychlorination reaction**Naresh Babu Muddada¹, Unni Olsbye¹, Terje Fuglerud², Elena Groppo³, Giovanni Agostini³, Diego Gianolio³, Andrea Piovano³, Silvia Bordiga³, and Carlo Lamberti³(1) *inGap Centre for Research-Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway.*(2) *INEOS ChlorVinyls, 3907 Porsgrunn, Norway.*(3) *Department of Inorganic, Materials and Physical Chemistry, NIS Centre of Excellence and INSTM unit, University of Turin, Via P. Giuria 7, I-10125 Turin, Italy.*

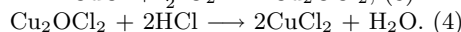
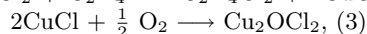
Nowadays, almost all the world production of PVC is obtained by the polymerization of vinyl chloride (VCM). Ethylene oxychlorination:



reaction is a key step in PVC production.

Oxychlorination reaction (1) is performed at 490-530 K and 5-6 atm in fluid or fixed bed reactors. Commercial catalysts are produced by impregnation of γ -alumina with $CuCl_2$ (4-8 wt

In the past some of us have deeply investigated the bare catalyst (without additives) [1-4], showing that the overall ethylene oxychlorination reaction (1) is catalyzed by the $CuCl_2$ phase following a three steps red-ox mechanism: (i) chlorination of ethylene by reduction of $CuCl_2$ to $CuCl$, (ii) oxidation of $CuCl$ to an oxychloride and (iii) re-chlorination with HCl (closure of the catalytic cycle) according to equations (2-4):



Now we have extended the previous study on performing transmission EXAFS experiments on $CuCl_2/\gamma Al_2O_3$ doped with $LiCl$, KCl , $CsCl$, $MgCl_2$, and $LaCl_3$.

[1] G. Leofanti, et al., J. Catal., 189, 91 (2000).

[2] G. Leofanti, et al., J. Catal., 189, 105 (2000).

[3] G. Leofanti, et al., J. Catal., 202, 279 (2001).

[4] G. Leofanti, et al., J. Catal., 205, 375 (2002).

Poster no. PS2.14 - Session 2**High resolution x-ray absorption and x-ray emission spectroscopy in the K and L-edge region of binary titanium compounds**

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For the chemical speciation of binary compounds of tri- and tetravalent titanium, high-resolution x-ray absorption and emission spectra were recorded in the energy regimes of the titanium K- and L-edges in order to evaluate and to qualify both near-edge x-ray absorption fine structure spectroscopy and wavelength-dispersive x-ray emission spectroscopy as spectroscopic methods for this analytical task [1]. A high resolving power in the excitation channel was ensured by use of monochromatic synchrotron radiation provided by BESSY II, where the soft x-ray emission spectra were recorded as well employing a wavelength-dispersive spectrometer [2]. In the hard x-ray range, emission measurements were performed at SPring-8 [3]. A comparison of the information obtained from absorption techniques and those gained from emission spectroscopy will be presented. The compounds were sorted according to the oxidation state of the bonded titanium, to allow for the distinction between inner atomic effects due to different oxidation states and external effects related to the ligand and the crystal structure. It becomes evident, that certain compounds, while hardly distinguishable in their Ti-K XANES spectra, still show significant differences in their emission characteristics. On the other hand, some compounds with little difference in their emission spectra are easily distinguished by their NEXAFS structures. Only the combined use of the complementary methods both in the soft and the hard x-ray range allows for a reliable speciation of tri- and tetravalent titanium compounds.

[1] F. Reinhardt et al., *Anal. Chem.* 81, 1770–1776 (2009)

[2] M. Müller et al., *Phys. Rev. A* 79, 032503 (2009)

[3] K. Sakurai et al., *RSI* 78, 066108 (2007)

Poster no. PS2.15 - Session 2**Molecular mechanisms during amplification of chirality in organometallic systems: in situ studies using XAS**

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Structural determination of organometallic systems capable of amplifying chirality is established by x-ray absorption spectroscopy and calculated bond distances are comparable to other studies. The transition state structure of the Soai autocatalytic reaction using x-ray absorption spectroscopy is reported. The study suggests a zinc alkoxide dimer complex with the core zinc atoms 3.09 Å apart. In toluene, i-Pr₂Zn is linearly bonded with two carbon atoms and a Zn-C bond distance of 1.89 Å. The same bond distance increases to 2.03 Å with the introduction of the Lewis base solvent which additionally causes a Zn-Zn interaction spaced out 3.07 Å in a dimer. Diethylzinc and chiral aminoalcohol form a complex dimer possibly responsible for chiral amplification. This occurs in toluene but not in THF which causes a change in the zinc environment. The dimer complex in toluene has a Zn-Zn distance of 3.24 Å.

Poster no. PS2.16 - Session 2**Conversion of MoO₃ into MoS₂ on high surface area SiO₂ support: an in situ Mo K-edge EXAFS and S K- and Mo-L edges XANES investigation**

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MoS₂ (eventually doped) represents, by far, the most diffused system used as catalyst for hydrotreating of oils feedstock and particularly for the hydrodesulfurization (HDS) reaction. The necessity of improving catalyst efficiency in deep HDS is extremely urgent, caused by stringent environment regulations regarding S content in fuels. Despite the importance of knowledge on the morphology of the catalyst to improve its performances, detailed structural information of this material and crystallite size determination of MoS₂ particles are still a controversial problem [1,2].

We report a combined S k-edge and Mo L₃ edges (taken at the SLS, LUCIA beamline) and Mo k-edge XAS (taken at the ESRF, BM26A) study on MoS₂ nanoparticles highly dispersed on SiO₂ surface obtained by progressive in situ sulfidation of MoO₃/SiO₂. The progressive evolution from MoO₃/SiO₂ to MoS₂/SiO₂ that could be outlined as $3\text{MoO}_3 + 7\text{CS}_2 \rightarrow 3\text{MoS}_2 + \text{SO}_2 + 7\text{COS}$ or as $6\text{MoO}_3 + 7\text{CS}_2 \rightarrow 6\text{MoS}_2 + 2\text{SO}_2 + 7\text{CO}_2$, was recorded and characterized. From Mo edges XANES we were able to follow reduction of Mo atoms from (+6) to (+4) valence state, and from S edge XANES we saw that sulfur, once present, maintains always (-2) valence state. EXAFS spectra at Mo k-edge showed a progressive Mo-O first shell contribution disappearance accompanied by a Mo-S one rise. Compared with reference bulk compounds, the coordination number decrease on successive shells gave information on particle dimension of dispersed samples.

In order to have more exhaustive understanding of the investigated materials, XAS results have been supported by conventional techniques like Raman and IR spectroscopies, TEM microscopy and XRPD.

[1] T. Shido and R. Prins, J. Phys. Chem. B 102, 8426 (1998).

[2] C. Calais, N. Matsubayashi, C. Geantet, Y. Yoshimura, H. Shimada, A. Nishijima, M. Lacroix and M. Breysse, J. Catal. 174, 130 (1998).

Poster no. PS2.17 - Session 2**Structure of $[\text{Ru}(\text{bpy})_n4\text{AP}_{(6-2n)}]^{2+}$ homogeneous complexes: ab initio calculation vs. EXAFS**

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Since the discovery of the antitumoural properties of cisplatin in 1965[1], transition-metal-based compounds have been widely used in clinic as chemotherapeutic agents. Recently, it has been demonstrated that light can be used to activate anticancer metal complexes. Photochemical activation of an appropriate precursor provides a procedure for controlling the site, timing, and dosage of the metal complex, reducing undesired effects in other tissues or organs. Light-irradiation of metal complexes can induce, for example, the formation of very reactive species, as well as promoting selective interaction between metal complexes and target macromolecules (DNA, proteins)[2].

Two Ru-derivatives of potential interest for chemotherapy and their photodissociated products were studied with EXAFS. The experiment was performed at ESRF beamline BM29, acquiring data both in transmission and in fluorescence mode. In particular solutions of $[\text{Ru}(\text{bpy})_2(4\text{AP})_2]^{2+}$ and $[\text{Ru}(\text{bpy})(4\text{AP})_4]^{2+}$ in water before and after light exposure were investigated (bpy=2,2'-bipyridyne, 4AP=4-aminopyridyne). Although the transmitted spectra were characterized by an edge jump of only 0.03, the quality of the $\chi(k)$ function is impressive and in perfect agreement with corresponding function extracted from fluorescence data. The results are complementary with those obtained by 1D and 2D NMR and are compared with the structural data obtained by ab initio calculations.[3] In conclusion EXAFS data show that the first complex photodissociates one 4AP ligand forming a monoaqua derivative in water upon excitation at 473 nm, while the latter gives the cis- $[\text{Ru}(\text{bpy})(4\text{AP})_2(\text{H}_2\text{O})_2]^{2+}$ derivative releasing two ligand upon excitation at 510-530 nm.

[1] B. Rosenberg, L. VanCamp and T. Krigas Nature 205, 698-699 (1965).

[2] W.H. Ang, P.J. Dyson, Eur. J. Inorg. Chem. 4003 (2006).

[3] L. Salassa et al., Inorg. Chem., 48, 1469 (2009).

Poster no. PS2.18 - Session 2**Excited state ligand loss detection in mononuclear Ru complex with pump-and-probe x-ray liquidography**

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Photoactivable metal complexes offer unique features for new applications in medicinal chemistry. When irradiated with visible light, metal complexes can undergo chemical transformation and produce reactive species which are able to target DNA and proteins causing selective cell death [1]. Although these systems have been widely studied using a variety of spectroscopic and computational techniques, it is still very difficult to obtain direct structural information on transient species created in the light-induced processes of these complexes. Laser-pump x-ray-probe techniques are able to directly measure the structural dynamics of molecules in the excited state and, currently, can also be employed for suitable liquid samples (where most of the biological and chemical processes take place).

We present here the results of a Transient X-ray Liquidography [2] experiment performed at ESRF on the ID09B beamline, that successfully probed dissociation of a py ligand from the complex $[\text{Ru}(\text{bpy})_2(\text{py})_2]\text{Cl}_2$ (where bpy = 2,2'-bipyridine and py = pyridine) in aqueous solution. The adopted experimental technique is based on evaluating the difference between the x-ray scattering signal from the sample after and before laser irradiation. Starting from diffraction images acquired at different time delays between pump and probe in the range 300-5000ns, we were able to demonstrate that py ring loss is completed before 300 ns. Our hypothesis is supported by simulation of the experimental curve based on the DFT optimized geometries of $([\text{Ru}(\text{bpy})_2\text{py}]^{2+} + \text{py})$ and $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$. The resulting signal is very well structured and allows to identify the disappearance of the first shell atom (N atom of the py ring), as well as the second and third shell atoms (two couples of C atoms).

[1] P. J. Sadler et al., Proc. Natl. Acad. Sci. USA, 104, 20743 (2007).

[2] H. Ihee et al., Science, 309, 1223 (2005).

Poster no. PS2.19 - Session 2
The restoration of the Mary Rose

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Henry VIII's flagship, the Mary Rose, sank off the coast of Portsmouth in 1545. The lower structure, which was preserved under a layer of anaerobic silt, was raised from the seafloor in 1982 and is currently the focus of one of the world's largest conservation projects.

To prevent shrinkage and cracking, the timber has been sprayed with polyethylene glycol (PEG) following the treatment adopted for a similar historical ship, the Vasa [1]. Unfortunately a problem associated with the presence of sulfur in the wood first discovered for the Vasa [2] is a potential problem for the Mary Rose [3]. The accumulation of reduced sulfur species is a result of sulfate reducing bacteria reacting with sulfate ions in the seawater under anaerobic conditions. When the archaeological wood is removed from anaerobic conditions, the reduced sulfur present can oxidize to sulfuric acid which attacks the cellulose in the wood and leads to structural breakdown. This problem is further exacerbated by the presence of Fe ions, produced via the corrosion of the many bolts, which act as a catalyst for the oxidation process.

A number of conservation techniques are being explored within this collaboration; (1) the removal of Fe by suitable chelating agents (2) the deacidification of the wood by the application of nanoparticles [4] and (3) the determination of the stability of the remaining reduced sulfur compounds under proposed housing conditions. EXAFS and XANES have been used to monitor these processes as a function of the speciation and location of Fe and S throughout the timbers. Complimentary techniques include electron microscopy, thermogravimetric analysis and calorimetry.

[1] Hafors, B., Vasa Studies, 2001. 18.

[2] Sandstrom, M., et al., Nature, 2002. 415 p. 893

[3] Wetherall, K.M., et al., Journal of Archaeological Science, 2008. 35 p. 1317

[4] Giorgi, R., D. Chelazzi, and P. Baglioni, Langmuir, 2005. 21 (23) p. 10743

Poster no. PS2.20 - Session 2

Structural analysis of group V, VI, VII metal compounds by XAFS and DFT calculation

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The characteristics of K, L₁ and L₃-edges XANES spectra of group V, VI, VII metal compounds, which have different coordination number, number of d-electrons and the symmetry of coordination sphere, have been classified. X-ray absorption spectra were recorded at the BL01B1 beam line at the SPring-8, JASRI, Japan and BL1A at UVSOR, IMS, Japan. The L₃-edge x-ray absorption white line reflects electronic states of vacant d orbitals of the absorbing atom since the L₃-edge x-ray absorption white lines of transition metals are attributed to electronic transition from 2p_{3/2} orbital to vacant s and d orbitals of the metal and the contribution of p-d transition in L₃-edge absorption white line is ca. 50 times stronger than that of p-s transition. Two p → d transitions were observed in the second derivative spectra of L₃-edge XANES spectra of all group V, VI, VII metal compounds. These two transitions can be assigned to split d orbitals. The splitting and area of the two white lines depend on the symmetry of coordination sphere because the splitting corresponds to ligand field splitting of d orbitals. The splitting of d orbitals has a linear relation with the pre-edge peak area of K or L₁-edge XANES spectra, which are attributed to the dipole forbidden transition of s → d occurred by mixing of p orbitals with d orbitals. This linear relationship is supported by DFT calculations of several group IV, V, VI structural models (four-, five- and six-coordinated) by B3LYP/LanL2DZ with Gaussian03 program package. The clarification of the relation between the splitting of the white line and the structure of group V, VI, VII metal is important to provide structural information in unknown group V, VI, VII metal site.

Poster no. PS2.21 - Session 2**Determination of trace element imbalances in hair of dementia patients using FL-XAS**Jaruwan Siritapetawee¹, Wanwisa Pattanasiriwisawa², and Unchalee Sirithethawee³*(1) College of Medicine and Public Health College of Medicine and Public Health, Ubon Rajathane University, Warinchamrap, Ubon Ratchathani, 34190, Thailand 34190 Ubon Ratchathani Thailand**(2) Synchrotron Light Research Institute (Public Organization), Muang, Nakhon Ratchasima, 30000, Thailand**(3) Medical Department, Nakhon Ratchasima Rajanagarindra psychiatric hospital, Muang, Nakhon Ratchasima, 30000, Thailand*

The trace elements of hair samples from over 60-year-old of 15 dementia patients and 15 normal controls were examined by x-ray absorption spectroscopy in fluorescent modes (FL-XAS) and wavelength dispersive x-ray fluorescence spectrometer (WDXRFS). Comparisons of trace element levels of properly matched dementia and control groups revealed significantly higher in the amount of calcium and chloride among dementia patients than in the controls. The results of x-ray absorption near edge structure (XANES) spectra showed the advantage of FL-XAS on WDXRFS by it could indicate that the compounds of calcium and chloride containing in the hair of both groups were calcium chloride. This preliminary study presents the possible roles of calcium and chloride in the etiology of dementia in old people.

[1] Forte, G., Alimonti, A., Violante, N., Gregorio, M. D., Senofonte, O., Petrucci, F., Sancesario, G., and Bocca, B. (2005). J. Trace Elem. Med. Biol. 19, 195-201.

[2] Gunter, K. K., Miller, L. M., Aschner, M., Eliseev, R., Depuis, D., Gavin, C. E., and Gunter, T. E. (2002). Neurotoxicology 23, 127-146.

[3] Hershey, C. O., Hershey, L. A., Varnes, A., Vibhaker, S. D., Lavin, P., and Strain, W. H. (1983). Neurology 33, 1350.

Poster no. PS2.22 - Session 2**XAS studies of the effectiveness of iron chelating treatments of Mary Rose timbers**Andrew Smith¹, A. Berko², A.M. Jones³, E.J. Schofield², J.F.W. Mosselmans⁴, and A.V. Chadwick²*(1) STFC Daresbury Laboratory, Daresbury Science and Innovation Campus, Warrington, Cheshire, WA4 4AD, United Kingdom**(2) School of Physical Sciences, University of Kent, CT2 7NR, United Kingdom**(3) The Mary Rose Trust, HM Naval Base, Portsmouth, PO1 3LX, United Kingdom**(4) Diamond Light Source, Didcot, OX11 0DE, United Kingdom*

The oxidation of sulfur in marine archaeological timbers under museum storage conditions is a recently identified problem, particularly for major artefacts such as historic ships excavated from the seabed. Recent work on the Vasa has stressed the role of iron in catalysing the oxidative degradation of the wood cellulose and the polyethylene glycols used to restore mechanical integrity to the timbers.

The use of the calcium phytate as a chelating agent is now established for the preservation of cellulose-based manuscripts written with iron gall ink, where oxidation of the iron can otherwise lead to acid attack of the paper. In our development of new treatment protocols for the long term preservation of Henry VIII of England's flagship, the Mary Rose, we are investigating the potential of chelating agents to neutralise and remove the iron products from the ships timbers. As well as calcium phytate we are exploring the use of aqueous solutions of other chelating agents, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), ammonium citrate (AC), citric acid (CA) and phytic acid (PA) to extract the iron compounds. All of these solutions exhibit some level of iron removal; however the key is to find the most effective concentration and pH of the reagent solution, to minimise the treatment time and to find the most cost-effective treatment for the whole of the Mary Rose hull.

Fe K-edge EXAFS data from samples of the Mary Rose timbers, before and after treatment by a number of the chelating agents mentioned has been collected. These data are providing valuable insights into the effectiveness of the treatment solutions and we will show how this information is enhanced by S and Fe K-edge microprobe XAS to explore the interaction of iron and sulfur speciation within the wood cell structure.

Poster no. PS2.23 - Session 2**Local and electronic structure of Co complexes: XANES and DFT analysis**

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The Co K edge x-ray absorption near edge spectra (XANES) of the complexes were measured at Kurchatov Synchrotron radiation center (Moscow). The theoretical Co K edge XANES spectra were calculated by both full multiple scattering approach (FEFF8.4 code) and finite difference method (FDMNES2008 code) within and beyond a muffin-tin approximation. It is shown that inclusion of the non-muffin-tin effects is important for modeling the Co K XANES spectrum for the complexes under the study and better agreement with experiment was achieved beyond muffin-tin approximation.

Density functional theory (DFT), as implemented in ADF2008 code, was applied for the optimization of the geometry of the Co complexes within LDA and GGA approaches and several models of exchange-correlation potentials including hybrid ones were tested. The results of DFT optimization were analyzed by comparison of the theoretical XANES spectra calculated for the sets of obtained structural parameters with experimental data. Electronic structure and real space electron density maps for the best structural models of the Co complexes under the study we obtained using DFT methodology.

Poster no. PS2.24 - Session 2**Europium oxidation state and coordination in magnetoplumbite type aluminate phosphor**

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In magnetoplumbite structure, functional element can be contained in hexagonal block, and useful magnetic and optical properties are attained. Rare earth doped magnetoplumbite shows a photoluminescence. In phosphor, the oxidation state and coordination environment of luminescent center are reflected in photoluminescence property. In this paper, EuAl₁₂O₁₉ with magnetoplumbite structure was analyzed by Eu LIII XAFS measurement. Eu LIII-edge XANES spectra showed the divalent europium with a little amount of trivalent europium. Fourier transforms of the Eu LIII edge EXAFS was well analyzed by using magnetoplumbite crystal structure model.

Poster no. PS2.25 - Session 2**Influence of aluminium and phosphate on Fe-hydroxyde precipitates**

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To explore the structural evolution of precipitated hydrous iron oxides in natural aqueous environment, Fe-oxyhydroxyde precipitates were formed by forced hydrolysis of acid solutions containing varying ratios of Fe, Al and phosphate. Investigation of the dried solid products showed a complex structural organisation that varied with their content in Al and PO₄. Variations of the XAS spectra collected at the Fe, P and Al K-edges showed that, with increasing Al, a slightly more ordered structure formed out of the initial ferrihydrite. Octahedra organisation around Fe atoms evolved to the one of akaganeite and atoms organisation at longer distance was modified. This result was confirmed by Raman spectra that showed that the ferrihydrite formed in the absence of Al evolved to a disordered akaganeite when Al increased in the synthesis system. In the same time, the amount of Al octahedra linked by edges increased, which we could relate to incorporation of Al in the Fe-oxyhydroxide. Introduction of phosphate in the Fe/Al oxyhydroxy system, induced also structural modification of the precipitates. Features of Al and P edges XANES spectra indicated that PO₄ was included in the structure. Phosphate modified the coordination of aluminium from fully octahedral in PO₄ free systems to partially tetrahedral when adding PO₄. Furthermore, smaller oligomers were formed as shown by the decrease of second neighbours numbers around iron atoms. This work highlights the influence of the physicochemical conditions of formation of Fe-oxyhydroxyde precipitates structure and thus on their stability and reactivity.

Poster no. PS2.26 - Session 2**XAFS study of metal chelates with azomethine ligands**

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The Cu, Ni, Co, Cd metal chelates including the bidentate (N,N -bis(2-tosylaminobenzylidene)-4,4-azobenzene) ligands were prepared and studied by x-ray absorption spectroscopy as a part of investigation of magnetoactive transition metal complexes with controlled spin-spin exchange (the molecular magnets). The EXAFS spectra of CoK-, NiK-, Cu K- and CdK-edges for the complexes were obtained at the Station K1.3b "Structural Materials Science" of the Kurchatov Center for Synchrotron Radiation and Nanotechnology (KCSRNT, Moscow, Russia). The coordination environment of nickel, cobalt, cadmium and copper ions in the complexes has been studied using the IFEFFIT data analysis package. EXAFS investigations have shown that all studied complexes have the distorted tetrahedral environment with typical distances M-N. Besides, the additional coordination of two oxygen atoms of tosylamino fragment was revealed and the distance M-O(Ts) was found to vary depending on the type of the metal. From analysis of XANES at CoK-, NiK- Cu K- and CdK-edges the geometry of coordination centers of complexes is determined in detail. This work was supported by the RFBR (grants N. 08-03-00154, 07-03-00710) and Grant of the President of RF (project No RNP.2.2.1.1-2348).

Poster no. PS2.27 - Session 2**Local structural changes in excited $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ studied by time-resolved XANES**

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Electronic excitation of impurity ions in crystals is often accompanied by transient changes in the local structure of the host. Quantitative information about the transient short- and medium-range organization of atoms can be provided by time-resolved x-ray absorption spectroscopy. We demonstrate a measurement and analysis of the transient changes in the structurally relevant XANES from an optically excited $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ single crystal. To quantify the distortion of the local structure when the Ti^{3+} ion is in the excited ^2E state, we performed time-resolved laser pump/x-ray probe measurements. We have observed transient changes in the titanium K-edge XANES spectrum associated with the alteration of the bond lengths of the ligands caused by the strong Jahn-Teller interaction. The quantitative analysis of the XAS data was performed using MXAN fitting procedure, which is able to fit the experimental X-ray absorption data from the edge to about 200 eV and to recover information about the symmetry and atomic distances of the nearest neighbors of the absorber. To fit the experimental transient spectrum we constructed a model considering coupling of the excited ^2E state of the Ti^{3+} ion to the A_{1g} and E_g local vibrational modes. An account of the A_{1g} distortion in respect to the ground state is necessary to achieve satisfactory quality of the fit. From our analysis we determine the magnitude of the A_{1g} mode, which is not possible by analyzing only optical and magnetic resonance spectroscopic data, and give an estimate of the E_g -symmetry Jahn-Teller distortion, although we are not able to distinguish between compression and elongation of the oxygen octahedron. To improve the quality of the information obtained from the XAS data we must likely require measurements over a much wider energy range with a signal to noise ratio sufficient for transient EXAFS analysis.

Poster no. PS2.28 - Session 2**XAS study of LiFePO₄ synthesized by solid state reactions and hydrothermal method**Ting Zhao¹, D. G. Xia², and Z. Y. Wu^{1,3}*(1) Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, P.O. Box 918, 100049 Beijing, China**(2) College of Environmental and Energy Engineering, Beijing University of Technology, 100022, Beijing, China**(3) National Synchrotron Radiation Laboratory, University of Science and Technology of China, 230029, Hefei Anhui, China*

Following the first report by Padhi et al. [1] on LiFePO₄ as a possible cathode-active material for lithium batteries, the phospho-olivine LiFePO₄ stimulated many researches [2] because of its high energy density, low cost, non-toxicity, environmental benignancy and safety. LiFePO₄ occurs in nature as the triphylite mineral with an orthorhombic unit cell (space group Pnma). It consists of polyoxybiotic framework where LiO₆, FeO₆ octahedra and PO₄ tetrahedra are present. The strong P–O covalency stabilizes the anti-bonding Fe³⁺/Fe²⁺ ratio through the Fe–O–P inductive effect to generate a high operating potential (3.4–3.5V versus Li/Li⁺).

LiFePO₄ is generally synthesized via solid-state reactions. It involves multiple, time-consuming steps at high temperatures. Hydrothermal synthesis of LiFePO₄ is a relative quick, simple and energy efficient way with many advantages. In this study, we find the electrochemical performances of LiFePO₄ prepared by the two methods are dramatically different although a XRD characterization does not show appreciable differences between them.

X-ray absorption spectroscopy (XAS) is a powerful and unique spectroscopic tool that provides element-specific information regarding both the geometric and electronic structure of materials [3]. In this work, we apply both XANES and EXAFS at the Fe K-edge to resolve structural differences existing between the two LiFePO₄ samples. Preliminary data show that the structural disorder, which may affect the Li ions diffusing channels, is severer in LiFePO₄ prepared by hydrothermal method, and this may account for the poor electrochemical performance of the hydrothermal LiFePO₄ sample.

[1] Padhi, A. K. et al. *Electrochem. Soc.* 144, 1188 (1997)[2] Byoungwoo Kang, Gerbrand Ceder, *Nature* 458, 190 (2009)[3] Z. Y. Wu et al. *Physical Review Letters* 77, 2101 (1996)**Biological systems****Poster no. PS2.29 - Session 2****Characterization of metallodrug/protein interactions by x-ray absorption spectroscopy**Isabella Ascone^{1,2}, Anne Vessi eres², Luigi Messori³, Angela Casini³, Chiara Gabbiani³, Antonella Balerna⁴, and Agostina Congiu Castellano⁵*(1) Synchrotron SOLEIL L'Orme des Merisiers Saint-Aubin BP 48 9119 GIF-sur-YVETTE France**(2) ENSCP, Laboratoire Charles Friedel, UMR CNRS 7223, 11, rue P. et M. Curie, 75231 Paris, France**(3) Dip. di Chimica, Universit  di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.**(4) INFN-LNF, Via E. Fermi, 00044 Frascati, Italy**(5) Dip. di Fisica, Universit  La Sapienza, Piazz.le A. Moro, 00185 Roma, Italy*

We have investigated the adducts formed between the antimetastatic complex trans-[tetrachloro(DMSO (imidazole)ruthenate(III)] complex (NAMI-A) and two proteins: bovine serum albumin (BSA) and transferrin (TF) by X-ray absorption spectroscopy. Spectra were recorded at Soleil (France) and at Daphne (Italy) Facilities at the sulfur and chlorine K-edges and at the ruthenium K- and L₃-edges. Data are exploited to elucidate specific features of metallodrug/protein interactions [1].

Monitoring the same system from three chemically independent points of view afforded valuable and new information. Notably, we have shown that the ruthenium(III) center of NAMI-A keeps its oxidation state after binding to BSA. In addition, collected data indicate chloride dissociation from the ruthenium center. The validity of a XAS-based approach to characterize metallodrug/protein systems is discussed. The analysis of EXAFS and XANES spectra recorded at the ruthenium K-edge indicates that ruthenium has a similar coordination environment in NAMI-A/TF and NAMI-A/BSA adducts.

[1] Ascone, I., Messori, L., Casini, A., Gabbiani, C., Balerna, A., Dell'Unto, F. & Castellano, A. C. *Inorg. Chem.* 47, 8629 (2008).

Poster no. PS2.30 - Session 2**EXAFS characterization of the binuclear zinc active site in proteins of the alkaline phosphatase superfamily**Elena Bobyr¹, Helen Wiersma², Daniel Herschlag², Keith O. Hodgson^{1,3}, and Britt Hedman³

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Phosphoryl-group transfer reactions play a fundamental role in a wide variety of biological processes such as cell metabolism, signal transduction, and gene expression. Furthermore, enzymes catalyzing phosphoryl transfer exhibit some of the largest enzymatic rate enhancements identified so far. A significant goal in understanding the biological phosphoryl transfer is unraveling how enzyme active sites achieve high chemical selectivity in catalysis. Particularly, alkaline phosphatase from *E. coli* (AP) and nucleotide pyrophosphatase/phosphodiesterase from *X. axonopodis* (NPP) both catalyze hydrolysis reactions of phosphate monoesters and diesters at structurally similar binuclear zinc active sites ligated by histidine and aspartate protein residues. However, AP preferentially catalyzes monoester hydrolysis with rate accelerations of $>10^{20}$, whereas NPP preferentially catalyzes diester hydrolysis with rate accelerations of $>10^{16}$. To understand how structural features may contribute to the differential chemical selectivity of these binuclear metal sites, we report here studies on AP and NPP by Zn K-edge XAS and, more specifically, by EXAFS analysis that focus on providing comparative high-resolution structural description of the zinc site for wild-type enzymes, as well as for the variety of protein forms modeling the steps of the catalytic cycle.

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Poster no. PS2.31 - Session 2**A combined XANES and Molecular Dynamics procedure for structural characterization of protein systems**Paola D'Angelo¹, Stefano Della Longa², Alessandro Arcovito³, Alfredo Di Nola¹, Massimiliano Anselmi¹, and Giovanni Chillemi⁴

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A general procedure to compute XANES spectra of protein systems starting from molecular dynamics (MD) simulations has been developed and applied to the study of neuroglobin (Ngb), a hemeprotein expressed in the brain of vertebrates. This method allows one to perform a quantitative analysis of the XANES spectra of proteins using a proper description of the thermal and structural fluctuations occurring at the nanosecond time scale. The Fe K-edge XANES spectra of Fe-heme both in the bis-histidine and the CO-bound states of Ngb have been calculated using the structural information obtained from the MD simulations without carrying out any minimization in the structural parameter space. A very good reproduction of the experimental data has been obtained with an agreement between theory and experimental data slightly better than the one previously reported by using static calculations and structural refinement [1]. This improvement in accuracy is due to the damping, at very low energy, of the sharp multiple scattering peaks reflecting photoelectron pathways delocalized along the entire heme cluster, which are more sensitive to structural disorder. The overall results suggest that classical MD methods are suitable to account for protein dynamics even at atomic resolution and that a reliable description of the protein dynamics is important for a correct calculation of the XANES spectra of proteins.

[1] A. Arcovito, T. Moschetti, P. D'Angelo, G. Mancini, B. Vallone, M. Brunori, S. Della Longa, Arch. Biochem. Biophys 475, 7 (2008)

Poster no. PS2.32 - Session 2**X-ray emission and absorption spectroscopy of Ni sites in Ni-Fe hydrogenase proteins and synthetic model compounds**

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Hydrogenase proteins are blueprints for efficient H₂ production using abundant transition metals and thus of high interest for new (bio)technologies. A serious problem is the O₂-inactivation of most enzymes. Luckily, there are also Ni-Fe hydrogenases which naturally are active also in the presence of O₂. For understanding the restraints at the molecular and electronic levels that govern O₂-tolerant H₂-catalysis, we employ x-ray absorption and emission spectroscopy on the metal sites [1-3].

X-ray emission spectroscopy at the K-alpha line of nickel using a horizontal-plane Rowland-circle spectrometer was done at beamline ID26 of the ESRF (Grenoble, France). Complete 1s²p³ RIXS (resonant inelastic X-ray scattering) planes were recorded for resonant excitation in the 1s-3d region of absorption spectra and using K-alpha1 detection. O₂-tolerant enzymes (from *R. eutropha*) and an O₂-inhibited Ni-Fe hydrogenase (from *D. gigas*) were compared. Ni coordination compounds of known structure served as spectroscopic standards.

The results allow to assign structural and electronic features of the Ni site in hydrogenases in various states of the catalytic cycle. Spectral features due to crucial H-binding at Ni become apparent. Possible reasons for the O₂-tolerance of the *R. eutropha* enzymes are discussed [4].

[1] S. Löscher, L. Schwartz, M. Stein, S. Ott, M. Haumann, *Inorg. Chem.* 46, 11094 (2007).

[2] S. Löscher, T. Burgdorf, I. Zebger, P. Hildebrandt, H. Dau, B. Friedrich, and M. Haumann, *Biochemistry* 45, 11658 (2006).

[3] T. Burgdorf, S. Löscher, P. Liebisch, E. van der Linden, M. Galander, F. Lenzian, S. P. Albracht, W. Meyer-Klaucke, B. Friedrich, H. Dau, and M. Haumann, *J. Am. Chem. Soc.* 127, 576 (2005).

[4] O. Sanganas, S. Löscher, M. Ludwig, M. Stein, A. De Lacey, H. Dau, B. Friedrich, O. Lenz, and M. Haumann, manuscript in preparation.

Poster no. PS2.33 - Session 2**X-rays induced lysis of the Fe-CO bond in carbonmonoxy-myoglobin**

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Fe K-edge X-ray-absorption-near-edge-structure (XANES) spectra have been collected on the CO-bound state of sperm whale myoglobin (MbCO). At T=10 K, under X-ray exposure, a slow two-state transition process occurs towards a five coordinate Fe-heme. The pentacoordinate state of the Fe-heme is nearly identical to the myoglobin photoproduct (Mb*) [1] obtained by extended light illumination at 15 K, indicating that the Fe-CO bond in MbCO was broken. CO rebinds by increasing temperature; the starting spectrum is recovered at T=100 K, demonstrating that the X-rays induced process is reversible, i.e. no relevant damage occurred at the heme site in the time course of the experiment at this temperature.

Thus, the overall process is very similar to the well known light-induced low-temperature Fe-CO photolysis of carbonmonoxy-hemeproteins. We already observed X-ray induced lysis of the Fe-CO bond in CO-neuroglobin [2], a globin expressed in the brain of vertebrates. This finding paves the way to novel X-ray experiments (XAS, XRD) aimed at a dynamical characterization of pentacoordinate ferrous states in hemoglobins, the only species competent in binding external ligands such as O₂, CO or NO.

[1] A. Arcovito et al., *Biophys. J.* 88, 2954 (2005).

[2] A. Arcovito et al., *Arch. Biochem. Biophys.* 475, 7 (2008).

Poster no. PS2.34 - Session 2**XAS study of the active site of a bacterial heme-sensor**

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Denitrifying bacteria keep the steady-state concentration of nitrite and nitric oxide (NO) below cytotoxic levels by controlling the expression of denitrification gene clusters via REDOX signalling of specific transcriptional regulators [1]. The NO dependence of the transcriptional activity of promoters regulated by these protein factors, has indicated that they may act as NO sensors in vivo. A protein belonging to the subclass DNR (dissimilative nitrate respiration regulator) from *Pseudomonas aeruginosa* has been recently suggested to be a heme containing protein [2]. There is a great clinical interest in the regulation of denitrification, as in *P. aeruginosa* it is strictly related to virulence [3]. Very recently the three dimensional structure of the apo-form of DNR (in the absence of heme) has been determined by X-Ray crystallography [4], whereas the holo-form (in the presence of heme) has not yet been crystallized. We have investigated the heme local structure in solution of the ferric and ferrous derivatives of holo-DNR by XAS. The Fe K-edge XANES spectrum of the ferric adduct displays typical features of a low-spin hexacoordinate Fe-heme complex, having two histidines ligated. After chemical reduction, relevant changes of the XANES fingerprints suggest a repositioning of the heme inside the hydrophobic core of the protein in agreement with previously reported structural and spectroscopic evidence [4]. Partial release of the axial ligands leaves the Fe(II)heme available, and very reactive, to bind exogenous ligands like NO, thus supporting its role as the cofactor involved in NO sensing activity.

[1] H. Korner et al., FEMS Microbiol. Rev. 27, 559 (2003).

[2] S. Rinaldo et al., Biochem. Soc. Trans. 34, 185 (2006).

[3] M. Hakki et al., Bone Marrow Transplant. 39, 687 (2007).

[4] G. Giardina et al., J. Mol. Biol. 378, 1002 (2008).

Poster no. PS2.35 - Session 2**XAFS Debye-Waller factors for deformed hemes and metal substituted hemes.**

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We present an efficient and accurate method for calculating DWFs for deformed active sites of hemoproteins and metal substituted hemes. Based on the Normal coordinate structural decomposition (NCSD) scheme, the deformation of the porphyrin macrocycle is expressed as a linear combination of the normal modes of the planar species. In our approach we identify the modes that contribute most to the deformation. For these modes we generate a library of metal-porphyrin structures to express the DWF as a function of the characteristic deformation and the sample temperature by using Density Functional Theory (DFT) to obtain the normal mode spectrum of the corresponding metal-porphyrin structure. Our method is tested on Ni-tetraadamantyl porphyrin and cytochrome c structures with more than 500 available scattering paths.

Poster no. PS2.36 - Session 2**pH dependence of the electronic structure of metal-aminoacid (Cu, Zn) complexes in aqueous solution**Pilar Ferrer^{1,2}, Félix Jiménez-Villacorta^{1,2}, Manuela E. Medina^{1,2}, and German R. Castro^{1,2}(1) *SpLine BM25, ESRF (European Synchrotron Radiation Facility), 6 rue Jules Horowitz 38000 Grenoble, France*(2) *ICMM-CSIC (Instituto de Ciencia de Materiales de Madrid), Cantoblanco 28049 Madrid, Spain*

One of the most interesting procedures to investigate the structures and functions of complex macromolecules is to examine simpler molecules presenting similar characteristics. The information obtained about the local structure can be extrapolated to such macromolecules. Many proteins present metal atoms in their structures that act as active sites. Research focused to determine the coordination and binding nature of the metal-aminoacid complexes can throw light on the behaviour of the active site of metalloproteins and metal-enzymes. The role of the metal ions in proteins is usually structural or catalytical, such as Zn atoms in zinc-fingers or Cu atom in superoxide dismutase, respectively. In general, the type of coordination is determined by several factors, being the most important the ligand-metal ratio, which determines the stoichiometry of the complex, and the pH of the solution in which the metal-aminoacid compound is embedded.

X-ray absorption spectroscopy measurements at the metal K-edge have been performed to Cu-alanine, Cu-isoleucine and Zn-histidine in aqueous solution. Measurements have been performed in fluorescence yield mode. Being the metal-ligand ratio of the sample sets 1:2, the pH of the solution has been changed in all the range. By EXAFS and XANES analysis, the metal coordination at one or more ligands is determined. Also, it can be observed that the modification in the pH leads to a change in the aminoacid bonding, due to zwitterion character.

Poster no. PS2.37 - Session 2**Utilization of 'elemental' sulfur by different phototrophic sulfur bacteria (*Chromatiaceae*, *Ectothiorhodospiraceae*): a sulfur K-edge XANES spectroscopy study**Bettina Franz^{1,2}, Henning Lichtenberg³, Josef Hormes^{3,4,5}, Christiane Dahl², and Alexander Prange^{1,3}(1) *Niederrhein University of Applied Sciences, Microbiology and Food Hygiene Rheydter Strasse 277 41065 Moenchengladbach Germany*(2) *University of Bonn, Institute for Microbiology & Biotechnology Meckenheimer Allee 168 53115 Bonn Germany*(3) *Louisiana State University, Center for Advanced Microstructures & Devices (CAMD), 6980 Jefferson Hwy, Baton Rouge, LA 76806, USA*(4) *University of Bonn, Institute of Physics, Nussallee 12, 53115 Bonn, Germany*(5) *University of Saskatchewan, Canadian Light Source Inc. (CLS), 101 Perimeter Road, Saskatoon, SK, Canada S7N 0X4*

Phototrophic sulfur bacteria are generally able to use elemental sulfur as an electron donor for anoxygenic photosynthesis [1]. Elemental sulfur is mainly a mixture of *cyclo*-octasulfur and polymeric sulfur. The purple sulfur bacterium, *Allochromatium vinosum*, strongly prefers the polymeric sulfur fraction showing that sulfur speciation has a strong influence on availability of elemental sulfur [1]. In this study, we investigated by using X-ray absorption near edge structure (XANES) spectroscopy, whether polymeric sulfur is also the preferred sulfur species in other phototrophic sulfur bacteria like *Thiocapsa roseopersicina* (*Chromatiaceae*) which deposits sulfur globules inside the cell and two members of the family *Ectothiorhodospiraceae* forming sulfur globules outside the cell. Furthermore, the role of different dissimilatory sulfur metabolism proteins of *A. vinosum* on uptake of elemental sulfur was investigated. The cultures were fed with 50 mM of elemental sulfur consisting of 68 % polymeric sulfur and 30 % *cyclo*-octasulfur. In all cultures, elemental sulfur was taken up, transformed into intra- or extracellular sulfur globules, respectively, and further oxidized to sulfate. Sulfate concentrations were determined by HPLC and turbidometric assays, respectively. However, the added elemental sulfur was only partly used by the bacteria, one part of the 'elemental sulfur' remained in the cultures and was not taken up. XANES spectroscopy revealed that only the polymeric sulfur fraction was taken up by all cultures investigated. This strongly indicates that polymeric 'chain-like' sulfur is the form preferably used by phototrophic sulfur bacteria of the families *Chromatiaceae* and *Ectothiorhodospiraceae*.

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Poster no. PS2.38 - Session 2**The sulfur-chromium interaction in plants used for phytoremediation: an investigation by chromium and sulfur K-edge XANES spectroscopy**Josef Hormes^{1,2}, Jana Puschna³, Alexander Prange^{2,4}, Amitava Roy², and Gregory Merchan²*(1) Canadian Light Source 101 Perimeter Road S7N 0X4 Saskatoon Saskatchewan Canada**(2) CAMD 6980 Jefferson Hwy. LA 70803 Baton Rouge Louisiana USA**(3) University of Bonn, Institute of Physics, Nussallee 12, 53115 Bonn, Germany**(4) Niederrhein University of Applied Sciences, Microbiology and Food Hygiene, Rheydter Str. 277, 41065 Moenchengladbach, Germany*

To optimize the phytoremediation process for practical applications, it is necessary to better understand the processes that take place and the parameters that influence these processes. We have carried out lab experiments with two different plants (wheat and buckwheat) and with chromium Cr(VI) as contaminant. Plants were grown in a liquid culture medium with two concentrations of Cr(VI) and with two different pH values. The various parts of the plants (i.e. again roots, stems and leaves) were investigated by XANES spectroscopy at the S-K and the Cr – K –edge at the DCM beamline of CAMD. Spatially resolved Sulfur K-XANES and EXAFS spectra were also taken at the CAMD-XMP beamline.

Cr(VI) could not be detected in any of the spectra showing clearly (and as expected) that both plants are changing the valency of the chromium (which is Cr(VI) in the nutrient solution) from +VI to +III. Using the usual fitting process for the spectra using a set of biological reference spectra, the differences between the spectra of roots and leaves can be explained by different concentration of acetate and phosphate in the samples, though the fitting process clearly shows that the right reference is still not included into our basis set. The S-K-XANES spectra of wheat and buckwheat leaves grown in a Cr(VI) solution and in a pure nutrient medium (to our knowledge the first S-K-XANES spectra recorded for the investigation of phytoremediation processes) show significant differences between the contaminated leaves and the natural leaves. These differences are caused by chromium but additional EXAFS experiments could prove that there is no direct Cr-S bound so that the changes are caused by an unknown indirect interaction.

Poster no. PS2.39 - Session 2**Spatially resolved sulfur K-edge XANES spectroscopy of wheat leaves infected by *Puccinia triticina***Josef Hormes^{1,2}, Henning Lichtenberg¹, Alexander Prange^{2,3}, Ulrike Steiner⁴, and Erich-Christian Oerke⁴*(1) Canadian Light Source 101 Perimeter Road S7N 0X4 Saskatoon Saskatchewan Canada**(2) CAMD 6980 Jefferson Hwy. LA 70803 Baton Rouge Louisiana USA**(3) Niederrhein University of Applied Sciences, Microbiology and Food Hygiene, Rheydter Str. 277, 41065 Moenchengladbach, Germany**(4) University of Bonn, INRES-Phytopathologie, Nussallee 9, 53115 Bonn, Germany*

In this study, wheat leaves infected with brown rust, a plant disease of serious economic concern caused by the fungus *Puccinia triticina*, were investigated using spatially resolved XANES (X-ray absorption near edge structure) spectroscopy at the sulfur K-absorption edge. Plants were grown and inoculated with *Puccinia triticina* under controlled greenhouse conditions. Spectra were recorded in fluorescence mode at the XMP (X-ray microprobe) beamline at CAMD using a Germanium detector. The XMP beamline is equipped with a Kirkpatrick-Baez focusing system and a motorized sample stage, housed in a stainless steel/aluminum vacuum chamber. This set-up allows X-ray absorption experiments with a spatial resolution of approx. 60 x 70 micrometers in the low energy X ray range (2.5 keV).

Spectra revealed significant differences between the sulfur speciation of the rust pustules on the leaves and green plant tissue. In the spectra of the green leaf areas the 'white line' at approx. 2472 eV, probably resulting from a superposition of C-S-, S-H- and disulfide bonds, is more intense than the sulfate structure at higher energies (approx. 2481eV), whereas in the spectra of the rust pustules the reverse is the case. In previously measured spectra of isolated *Puccinia triticina* spores sulfate structures played only a minor part. Therefore, the here observed accumulation of sulfate at the sites of the rust pustules does not simply result from a superposition of the spectra of green leaf areas and isolated spores and can be attributed to the host-plant interaction. Spectra were analyzed also quantitatively by fitting them to a linear combination of suitable reference spectra. A second series of XANES spectra recorded at various distances from a rust pustule indicates that modifications of the sulfur speciation in the leaves induced by the fungus significantly extend into visibly uninfected plant tissue

Poster no. PS2.40 - Session 2**Measurement and comparison of absolute values of soft X-ray natural circular dichroism of serine and alanine**

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Natural circular dichroism (NCD, $\Delta\sigma$) is a difference between absorption cross section for left circularly polarized light and for right circularly polarized light. NCD in UV region is well known to reflect the chiral structure. In view of this point, NCD in soft X-ray region (SXNCD) is expected to provide more detailed information on chiral structure at the vicinity of constituent atom [1]. We have reported the SXNCD spectra of serine (Ser) and alanine (Ala) films at around the oxygen K-edge with relative value of circular dichroic constants [2]. In this work, we report the absolute value of $\Delta\sigma$ for Ser and Ala in an attempt to discuss each chiral characteristics in detail.

Measurement of XANES and SXNCD of Ser and Ala films was carried out at SPring-8 BL25SU, Japan. Helicity of circularly polarized light was switched with 1 Hz using the twin helical undulators and kicker magnets. We measured transmitted light intensity through the sample and obtained XANES and SXNCD spectra.

In the case of SXNCD of L-Ser, a positive peak ($\Delta\sigma = +1.2 \times 10^{-21} \text{ cm}^2$) and a negative peak ($\Delta\sigma = -1.7 \times 10^{-21} \text{ cm}^2$) were observed at around 531.5 eV and 532.5 eV, respectively. In contrast, a large negative peak ($\Delta\sigma = -1.4 \times 10^{-20} \text{ cm}^2$) was only observed at 532.9 eV in the case of L-Ala. Every peak was assigned to $1s \rightarrow \pi^*$ transitions. Observed SXNCD peaks were partly described by theoretical calculations [3]. Because of increase of theoretical calculations [3-5], assignment of individual peaks is expected to be carried out in detail.

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Poster no. PS2.41 - Session 2**Confirmation of valency of copper in some complexes of biological significance using xanes**

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Existence of copper (I) complexes in some freshly prepared samples has been proposed by chemical studies, but their stability has not been established. In the present studies, we have recorded the X-ray absorption spectra at the K-edge of copper in the near edge region for the five samples, viz., $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{ClO}_4$, $[\text{Cu}^{\text{II}}(\text{dmp})_2](\text{ClO}_4)_2$, $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}_2$, $[\text{Cu}^{\text{I}}(\text{dmp})_2]1/2\text{SO}_4$ and $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{SO}_4$, where dmp stands for 2,9-dimethyl-1,10-phenanthroline. Out of these five samples, $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{ClO}_4$ and $[\text{Cu}^{\text{I}}(\text{dmp})_2]1/2\text{SO}_4$ were expected to behave as Cu(I) samples. The experimentally estimated X-ray absorption parameters, e.g., edge energy and chemical shift, i.e, shift of K-edge of copper in complex with respect to K-edge of copper metal, show that these two samples also have copper in valency +2 and not +1 as proposed by chemical studies. The reason for this may be that either the complexes are unstable or that the X-ray exposure converted them into copper (II) complexes. The X-ray absorption parameters for the remaining three complexes support them as copper (II) complexes, as expected. Hence, the XANES studies can be useful in confirming the valency states in such type of samples. Further, it has been observed that in all the complexes the K-edge splits in two components K1 and K2 and this suggests tetrahedral and square planar geometry for the complexes, as also proposed from chemical studies.

Poster no. PS2.42 - Session 2**X-ray absorption studies of copper(II) mixed ligand complexes with benzimidazole as one of the ligands**Santosh Keshav Joshi¹, Vijay K Hinge², Basant D. Shrivastava³, Jagdish Prasad⁴, and Krishna Srivastava⁴*(1) Government College, Badnawar(Dhar) 454660, India (2) Physics Department, Ujjain Engineering College, Ujjain 456010, India**(3) School of Studies in Physics, Vikram University, Ujjain 456010, India**(4) Chemistry Department, University of Allahabad, Allahabad 211002, India*

X-ray absorption near edge structure (XANES) measurements have been made on the K-edges of copper in copper benzimidazole [Cu(BzImH)] and five other mixed ligand complexes of copper (II) using benzimidazole as one of the ligands, the other ligands being Cl₂, Br₂, (NO₃)₂, (ClO₄)₂ and SO₄. All these complexes are biologically important molecules. The imidazole ring, as a histidine moiety, and benzimidazole ring as its derivative, function as ligands towards transition metal ions in a variety of biologically important molecules. The effectiveness of the imidazole group to act as metal binding site has been attributed to its availability at physiological pH (pKa ca.7.0) and its capacity to form both sigma- and pi- bonds with metal ions. Various X-ray absorption parameters in the near edge region, e.g., chemical shift, i.e., shift of K-edge of copper in complex with respect to K-edge of copper metal, energy position of the principal absorption maximum and edge-width have been estimated. The shape of the K-edge shows splitting of the K-edge into two components, i.e., K1 and K2 in all of these samples. This feature confirms elongated octahedral and square planar geometries for the complexes which has also been suggested from the chemical studies. Further, the values of the chemical shifts establish the relative ionic character of the complexes that decreases in the following order: Cu (BzIm)₄ Br₂ < Cu (BzIm)₄ Cl₂ < Cu (BzIm)₄ SO₄ < Cu (BzIm)₄ (ClO₄)₂ < Cu (BzIm)₄ (NO₃)₂. The edge-widths of the K-edge also support this relative ionic character.

Poster no. PS2.43 - Session 2**Zn - K - edge EXAFS study of human nails**Maria Katsikini¹, Ekaterini Mavromati¹, Fani Pinakidou¹, Eleni C. Paloura¹, and Dimitrios Gioulekas²*(1) Aristotle University of Thessaloniki, School of Physics, 54124 Thessaloniki, Greece**(2) Aristotle University of Thessaloniki, Medical School, 54124 Thessaloniki, Greece*

The human nail is a modified type of epidermis that is mainly consisted of keratin, a protein that is rich in cysteine. The nails contain in small amounts essential metallic elements e.g. Zn, Fe and they are used in order to monitor the inorganic element concentration in the human body. Here we apply EXAFS spectroscopy at the Zn - K - edge in order to study the bonding geometry of Zn in human nails. The studied nail clippings belong to healthy donors and donors who suffer from pulmonary diseases. The EXAFS measurements were performed at the KMC-II beamline of the BESSY Synchrotron Radiation Facility. The spectra were recorded using a fluorescence detector (XFlash-Rontec) that permits the electronic discrimination of the Zn-K α fluorescence photons and suppresses the background due to preceding absorption edges. Fitting of the first nearest neighboring shell of Zn reveals that it is bonded with N and S, at distances equal to 2.02 and 2.25 Å, respectively. The total number of atoms bonded to Zn varies from 4 to 4.8 while the ratio of the sulphur / nitrogen (S/N) ranges from 0.52 to 1. The sample that belongs to the donor who suffers from lung fibrosis, a condition that is related to keratinization of the lung tissue, is characterized by the highest number of S/N. Simulation of the Zn-K-edge EXAFS spectra with a model of Zn tetrahedrally coordinated with 1 cysteine and 3 histidines using the FEFF8 code is satisfactory.

Poster no. PS2.44 - Session 2**Location of Fe in biopolymers formed by different technological processes**Marcin T Klepka¹, Krystyna Lawniczak-Jablonska¹, and Anna Wolska¹*(1) Institute of Physics PAS al. Lotnikow 32/46 PL-02668 Warsaw Poland*

Recently a lot of attention is paid to transition metal-organic structures based on natural polymers. One of them is chitosan. Chitosan is chitin derivative, which in turn is the basic component of crab and lobster shells. Chitosan and its derivatives have very interesting, and useful properties like bioactivity, biocompatibility, easy biodegradation but the most important is ability to chelate metal ions including heavy and toxic one. These properties decide about variety of current and potential applications e.g. in biomedical products, cosmetics, food processing and removal of metallic impurities from wastewaters. One of the perspective types of materials for biomedical application are transition metal-chitosan complexes. Chitosan after metal binding exhibit magnetic properties what opens possibility to use it as a biotransporter for drugs. Recently, the iron containing biopolymers have been examined as possible drug carriers and controlled release beads for various models of drugs. To achieve this goal a lot of attempts were undertaken to increase the sorbent functionality of the chitosan. The prospective method for this seems to be the crosslinking of polymer chains after complexation with metal ions or the insertion of carboxylic functional group into chitosan. Despite of a lot of information about chitosan including pure crystal structure, it is still not clear how metal ions are bonded with this polymer. Most techniques used to identify metal position are unable to identify surrounding atoms (e.g. Mossbauer spectroscopy). We present the models of Fe bounding in several chemically modified Fe-chitosan complexes. These models were constructed on the base of X-ray Absorption Spectroscopy (XAS) studies. Acknowledgments: This work was supported by national grant of Ministry of Science and High Education N202-052-32/1189 as well as by DESY/HASYLAB and the European Community under Contract RII3-CT-2004-506008 (IA-SFS).

Poster no. PS2.45 - Session 2**Ground state and excited state of a bis(μ -oxo)-dicopper(III) species characterized by XAS and resonance Raman**Wolfram Meyer-Klaucke¹, Stephan Binder², Sonja Herres-Pawlis³, Andreas Eich², Roxana Haase³, Benjamin Schulz², Gerd Wellenreuther¹, Gerald Henkel³, and Michael Rübhausen²*(1) EMBL Hamburg, Notkestr. 85, 22603 Hamburg, Germany**(2) Institut für Angewandte Physik, Universität Hamburg, Jungiusstr. 11, 20355 Hamburg and Center for Free Electron Laser Science, Notkestr. 85, D-22603 Hamburg, Germany**(3) Department Chemie, Anorganische Chemie, Universität Paderborn, 33098 Paderborn, Germany*

Central for the catalytic activity of tyrosinases is the presence of the dinuclear copper center. Two copper(I) ions can jointly activate molecular oxygen by the formation of two isoelectronic motifs forming either a peroxo or μ -oxo form with a P- or O-core. Here, each copper ion is stabilised by three histidine groups. In model complexes, the biomimetic nitrogen donor ligand possesses a key function: it dictates whether a bis(μ -oxo)- or a peroxo-core complex is formed upon reaction with dioxygen.

Here we present an innovative combination of EXAFS spectroscopy and resonant Raman scattering at multiple wavelengths characterizing ground state and structural dynamics of a thermally stabile binuclear bis(μ -oxo) dicopper(III) species. This unique combination of EXAFS and resonance Raman spectroscopy tracking the absorption profile allows to study efficiently charge-transfer complexes in their ground and excited state. We obtain two-fold information on the structural and electronic properties of both states that determines the change in the oxidation state of the copper-ions in Cu_2O_2 -core. In the ground state two Cu(III)-ions coordinated by two nitrogen donors from ligand L are bridged by two μ -oxo groups. For $[\text{Cu}_2\text{L}_2(\mu\text{-O})_2]$ we find in the excited state only small changes in the oxygen-oxygen and copper-oxygen distances. Hence, we observe a change of the oxidation state of the copper-ion of only $0.1 e^-$. The resonance Raman profile taken with eleven different incident photon energies exhibits a double resonance within the charge-transfer-band at 363 nm corresponding to transitions in the LUMO and LUMO+1 state with an energy difference of about $1,300 \text{ cm}^{-1}$ agreeing well with theoretical calculations.

Poster no. PS2.46 - Session 2**XAS and macroscopic sorption study of lanthanide ion adsorption to bacterial cells.**J Fred Mosselmans¹, Bryne T. Ngwenya², Marisa Magennis², Kirk D. Atkinson¹, Janette Tourney², and Robert M. Ellam³*(1) Diamond Light Source, Diamond House, Chilton, Didcot OX11 0DE, England**(2) Environmental and Microbial Geochemistry Laboratory, School of Geosciences, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, Scotland**(3) Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride G75 0QF, Scotland*

This study combines X-ray Absorption Spectroscopic (XAS) measurements with surface complexation modelling of macroscopic adsorption data to identify lanthanide sorption sites on the bacterial surface. The adsorption of selected representatives for light, middle and heavy lanthanides on gram-negative *Pantoea agglomerans* was measured as a function of pH, while biomass samples exposed to 4 mg/L lanthanide at pH 3.5 and 6 were analysed using XAS. Surface complexation modelling was consistent with the light lanthanides adsorbing to phosphate sites, while the adsorption of middle and heavy lanthanides could be modelled equally well by carboxyl and phosphate sites. The existence of such mixed mode coordination was confirmed by Extended X-ray Absorption Fine Structure (EXAFS) analysis, which was consistent with adsorption to phosphate sites at low pH, with secondary involvement of carboxyl sites at high adsorption density (high pH). Spectroscopic analysis suggests that coordination to phosphate sites is mono-dentate at the metal/biomass ratios used. The modelling of the adsorption data suggests that the phosphate sites are located on N-acetylglucosamine phosphate, the most likely polymer on gram-negative cells with potential phosphate sites that deprotonate around neutral pH.

Poster no. PS2.47 - Session 2**Structural Characterization of Brazilian Tourmalines by XAFS**Rogério Junqueira Prado¹, Luiz Antônio de França¹, and Rúbia Ribeiro Viana²*(1) IF/UFMT - Av. Fernando Correa da Costa, s/n - Coxipó - 78060-900 Cuiabá Mato Grosso Brazil**(2) DRM/ICET/UFMT - Av. Fernando Correa da Costa, s/n - Coxipó - 78060-900 Cuiabá Mato Grosso Brazil*

In this work three samples of Brazilian tourmalines (dravite, schorl and liddicoatite) were analyzed by X-ray Absorption Fine Structure (XAFS), aiming the identification of the crystallographic sites occupied by Fe, Mn and Ti atoms in the different samples. It was verified that Fe and Mn atoms are always at the Y site of the tourmalines, as mentioned in literature. On the other hand, the Ti atoms showed a more complex structural data. At room temperature it was verified that dravite and schorl samples also presented Ti atoms at the Y site, an expected result not experimentally confirmed before this work. However, Ti atoms of the liddicoatite sample presented a different local structure similar to that of TiO₂-rutile. In addition, the schorl sample showed an evolution of the local structure around Ti atoms during thermal annealing, starting from the traditional Y site structure at room temperature to that having local order similar to TiO₂-rutile after annealing at 800°C.

Poster no. PS2.48 - Session 2**Cu K-edge XAS study of a new stable Cu³⁺/cyclopeptide complex**Alessandro Pratesi¹, Gabriele Giuli², Maria Rita Cicconi², Tsu-Chien Weng³, Giovanni Pratesi⁴, and Mauro Ginanneschi¹*(1) Laboratory of Peptide & Protein Chemistry & Biology, Department of Organic Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 13 50019 Sesto Fiorentino (FI), Italy**(2) Dipartimento di Scienze della Terra, University of Camerino, Via Gentile III da Varano, 62032 Camerino, Italy**(3) ESRF, F-38043 Grenoble, France**(4) Dipartimento di Scienze della Terra, University of Florence, Via G. La Pira, 4 50121 Florence, Italy*

We recently described the synthesis of some cyclic tetrapeptides containing two His residues in the sequence and we analyzed their copper(II) binding properties in aqueous solution [1]. The Cu²⁺ species obtained are of interest in relation to copper-proteins active-site biomimetics. The study of a 13-membered ring cyclic tetrapeptide c(Lys-DHis-Ala-His) (DK13), synthesized by solid-phase peptide synthesis [2], strongly supports the presence, at alkaline pH, of a stable peptide/copper(III) complex formed in solution by atmospheric dioxygen oxidation. In order to confirm the presence of Cu³⁺ species and to clarify the role of the peptide structure in the mechanism of the copper oxidation, Cu Kedge XANES and EXAFS spectra have been collected for three different cyclo-peptides c(Lys-His-Ala-His) (LK13), c(Lys-DHis-Ala-His) (DK13), and c(Gly-Ala-Gly-Lys) (GK13). Comparison of pre-edge peak features with those of Cu model compounds allowed to determine the Cu oxidation state in the three peptides: Cu is purely divalent in GK13, purely trivalent in DK13, and present as both Cu²⁺ and Cu³⁺ in LK13. Also edge energies and EXAFS derived Cu-N distances (1.79 Å and 1.90 Å for DK13 and GK13 respectively) are consistent with the XANES determined Cu oxidation states. Preliminary theoretical XANES spectra calculated by means of the MXAN code suggest that the CuN₄ unit is not planar but form a pyramidal structure. Despite no satisfactory explanation can be provided yet, available data strongly suggest that the imidazole side chains have an important role in the formation of Cu³⁺ complexes in LK13 and DK13 peptides.

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Poster no. PS2.49 - Session 2**Degradation of platinum-based anticancer drugs by methionin: an EXAFS study**Karine Provost¹, Diane Bouvet-Muller¹, Sylvie Crauste-Manciet^{2,3}, Luca Olivi⁴, Gilberto Vlaic⁴, and Alain Michalowicz¹*(1) ICMPE, équipe SAX, UMR7182 CNRS Université Paris12, PRES Paris Est, 2-8 rue Henri Dunant 94320 Thiais, France**(2) Laboratoire de Pharmacie Galénique, Université Paris Descartes, 75006 Paris, France**(3) Service de Pharmacie, CHI Poissy Saint Germain en Laye, 78105 Saint Germaine en Laye, France**(4) EXAFS Beamline, ELETTRA, Sincrotrone Trieste S.C.p.A. di interesse nazionale, AREA Science Park, 34012 Basovizza, Trieste, Italy*

Three platinum complexes are currently used in chemotherapy in France: cisplatin, carboplatin and oxaliplatin. Cisplatin is the most common, and its reactivity has been widely studied. On the contrary, derivatives of carboplatin and oxaliplatin deserve to be structurally characterized in order to understand their mode of action and their stability in solution.

These drugs react rapidly with nucleophilic species in solution. Their degradation has two consequences: in vitro, it can compromise the stability of the drug in solution before administration; in vivo, the structural modification of these molecules can induce notable changes in their modes of action. Sulfur nucleophilic ligands are particularly interesting: they play a major role in the detoxification of the drugs. Particularly, methionin is involved in the elimination of platinum from the organism. This study deals with the reaction of carboplatin and oxaliplatin with methionin. For both drugs, the reaction product remains in solution. Thus we used X-ray absorption spectroscopy in order to characterize its structure. Spectra have been recorded for different reaction times, up to one month. We present the evolution of the spectra and the structure of the final products, modeled and refined by Roundmidnight, the fitting module of the MAX package, in the frame of the FEFF EXAFS multiple scattering expansion.

This study takes place in the work carried out by our team on the behavior of these platinum complexes in presence of various halogen and sulfur ligands.

Poster no. PS2.50 - Session 2**X-ray Absorption Spectroscopy of superoxide dismutase isoforms separated on electrophoresis gels**

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Copper,zinc superoxide dismutase (CuZnSOD) is a metalloenzyme involved in 10% of familial cases of amyotrophic lateral sclerosis (ALS), a fatal neurodegenerative disease. ALS causes remain unknown, however a gain of toxic function of CuZnSOD was proposed. This could be related to a deficit in the metallation state of copper and/or zinc in CuZnSOD. These two atoms are essential to this enzyme, Cu being involved in its catalytic activity and Zn stabilizing its three-dimensional structure.

To study such hypothesis, we developed a protocol to separate wild-type and mutant CuZnSOD from protein extracts using polyacrylamide gel electrophoresis by isoelectric focusing in non-denaturing conditions. This technique allows a high-resolution separation without metal losses, metals being non-covalently bound in CuZnSOD. Cu and Zn speciation was then performed for the first time directly on CuZnSOD isoforms separated on electrophoresis gels.

The oxidation state and atomic environment of Cu and Zn were studied using X-ray Absorption Spectroscopy, on the French beamline BM30b/FAME at ESRF (European Synchrotron Radiation Facility). The study of XANES (X-ray Absorption Near-Edge Structure) region of the spectra demonstrated that Zn is as expected in its +II oxidation state and revealed that Cu is present in a mixed redox state of +I and +II in the main isoforms. The study of EXAFS (Extended X-ray Absorption Fine Structure) region of the spectra was also performed, demonstrating the feasibility of EXAFS on proteins separated on an electrophoresis gel. This development could allow to highlight structural differences between isoforms from a protein, and moreover between wild-type and mutant CuZnSOD.

Poster no. PS2.51 - Session 2**Local and electronic structure of sulfur-containing proteinogenic amino acids functionalizing nanoparticles: XANES and DFT analysis**

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Nanoparticles functionalized by amino acids are studied. These are prepared by chemical syntheses. The samples are dispersed in liquid media and the dispersions were sprayed into the ambient atmosphere by using an atomizer. The resulting nanoparticle beam is aerodynamically focused into an interaction region, where it is excited by monochromatic synchrotron radiation. X-ray absorption near edge spectra (XANES) at the S L_{2,3} edge of the sulfur-containing proteinogenic amino acids were measured at the storage ring facility BESSY-II. The XANES spectra near the S L_{2,3} edge were calculated by both the full multiple scattering approach (FEFF8.4 code) and the finite difference method (FDMNES2008 code) within and beyond a muffin-tin approximation. It is shown that inclusion of the non-muffin-tin effects is important for modeling the S L_{2,3} edge XANES spectra of sulfur-containing amino acids and yields even better agreement with the experimental results, if beyond muffin-tin approximation approaches are used.

Density functional theory (DFT), as implemented in the ADF2009 code, was applied for the optimization of the geometry of the sulfur-containing proteinogenic amino acids within LDA and GGA approaches. Several models of exchange-correlation potentials including hybrid ones were tested. The results of DFT optimization were analyzed by a comparison of the XANES spectra calculated for the sets of derived structural parameters with the experimental data. The electronic structure and real space electron density maps for the best structural models of the sulfur-containing proteinogenic amino acids were derived using DFT methodology.

Poster no. PS2.52 - Session 2**Micro XAFS analysis of metallic element containing biological specimens using the polycapillary focusing X-ray optics.**Motohiro Uo¹, and Kiyotaka Asakura²

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Various metallic materials are widely used for medical and dental implants. Erosion and mechanical wearing of metal implants placed in the human body have been reported to be associated with localized and systemic problems. We have been applied the fluorescence XAFS for the analysis of biological tissues which containing the metallic element derived from the implanted materials[1, 2]. However, the metallic elements in the tissues were generally localized in the small region. Then, the polycapillary focusing X-ray optics was applied for the micro-area XAFS analysis for the biological tissues.

The metal implanted animal tissues or metallic element containing pathological specimens were applied for the XAFS analysis. The XAFS spectra were measured at BL-9A of KEK-PF. The incident X-ray was focused the polycapillary (X-ray Optical Systems, USA) into $60\mu\text{m}\phi$ at 10keV. The transmittance was about 20%. For the iron implanted tissue, Fe K-edge XANES spectra similar to that of FeOOH were observed at the surrounding tissue of the implant. The Fe distribution could be also obtained from the absorbance of K-edge with X-Y scanning the specimen.

The bronchoalveolar lavage fluid (BALF) from the patient of pneumoconiosis induced by the tungsten carbide was also analyzed by micro XAFS. The BALF precipitate (smaller than 0.5mm) was dried and applied for the fluorescence XAFS using polycapillary focused X-ray. The W L1-edge XANES spectrum of the BALF precipitate was similar to that of WC. Then, the low concentration WC could be detected from BALF using micro XAFS without excess biopsy.

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Poster no. PS2.53 - Session 2**Using XAFS to identify the proton pathway in proton-translocating membrane proteins: a study on transhydrogenase**Giulia Veronesi¹, Lisa Giachini², Francesco Francia³, Simon J. Whitehead⁴, J. Baz Jackson⁴, Federico Boscherini¹, and Giovanni Venturoli³

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Transhydrogenase (TH) is an enzyme situated in animal mitochondria and bacteria which couples the redox reaction between NAD(H) and NADP(H) to proton translocation across the membrane: $NADH + NADP^+ + H_{out}^+ \leftrightarrow NAD^+ + NADPH + H_{in}^+$. The turnover of the protein consists in the interconversion between an open and an occluded configuration activated by long range ($\geq 30 \text{ \AA}$) conformational changes transmitted from the proton pathway to the redox site upon proton translocation. A complete high resolution structure of TH is still unavailable.

Zn^{2+} inhibits the interconversion between the two states of TH by interfering with the proton translocation [1]. Therefore the characterization of the Zn binding site and its localization can be of great help in tracing the proton pathway, clarifying the catalytic mechanism of the enzyme. In recent years, XAFS studies on inhibitory metal sites have provided useful information about proton pathways in membrane proteins like photosynthetic reaction centres [2] and cytochrome *bc*₁ [3].

We measured the Zn K-edge XAFS spectrum of Zn-incubated TH on the GILDA-BM8 beamline of ESRF. The combination of ab-initio XANES simulations performed with the FDMNES program without muffin-tin approximation, multiple-scattering EXAFS analysis based on Zn^{2+} binding geometries encountered in PDB (Protein Data Bank), and discrimination of putative models on a statistical basis allows us to propose that Zn occupies a tetrahedral site in which first-shell ligands are S atoms from Cys, N from His and O from Asp/H₂O in a 2:1:1 ratio. This result agrees with complementary FTIR spectroscopy measurements, which indicate the presence of His and Asp in the inhibitory site and with mutagenesis studies that proved that βHis91 is located on the proton pathway.

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Poster no. PS2.54 - Session 2**XANES and EXAFS studies of malarial pigment's substitute in reaction with chloroquine in solution.**

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Malaria remains the world's most prevalent vector-borne disease, which causes severe health problem particularly in African and Asiatic countries. The most severe form of malaria is caused by *Plasmodium falciparum* (Pf) parasite. The intraerythrocytic stage of Pf involves hemoglobin proteolysis and detoxify heme into an inert crystalline material, called malarial pigment or hemozoin. The crystal structure of hemozoin has been solved by X-ray powder diffraction in the last years and its synthetic analogue, beta-hematin, was synthesized. The ferriprotoporphyrin IX is believed to be a target for commonly used antimalarial drugs but their interactions are still not understood on molecular level. In presented work we are especially interested in drug-induced perturbations of the structures of soluble beta-hematin-like compound, iron(III) (meso-porphyrin-IX anhydride) called mesohematin. Similarly to its insoluble parent compound, beta-hematin, this compound is also built of dimmers which was confirmed by EXAFS analysis. The XAS measurements on frozen sample of mesohematin in solution were performed at ESRF (station ID26). Pure acetic acid and acetic acid with water of volume ratio respectively 30:1 and 15:1 were used as solvents. The high resolution XANES and EXAFS spectra on iron K-edge enabled us to reveal the differences in local environment of Fe atoms in investigated solutions before and after chloroquine drug addition. The main difference concerns the coordination number of ligand oxygen which is lower in presence of chloroquine for both solutions with water and distance of the same atom which is significantly shorter in solution with less water to acetic acid ratio and drug presence. This work was supported by research grant N20205332/1197 and special project ESRF/73/2006 from the Ministry of Science and High Education.

Environmental**Poster no. PS2.55 - Session 2****Sulfur behavior in silicate glasses by XAS and XES spectroscopies**

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Volcanoes release to the atmosphere large amounts of S gases that influence the backscatter of solar radiation through the formation of sulfate aerosols. The sulfur gaseous emission of a volcano depends largely on the initial S content of the magma and then on the S solubility in the same magma. Solubility, in turn, depends on temperature, pressure as well as the chemical composition and oxygen fugacity of the magma. All these factors affect the chemical state of sulfur and thus its solubility in the magma.

X-ray absorption and emission spectroscopies were applied to the study of silicate glasses from the Kenya Rift Valley. In order to understand the role of sulfur in these systems, information on the geochemical behavior of sulfur is needed. The speciation of sulfur in the glasses, oxidation state and local geometry, are analyzed comparatively by XAS and XES.

The behavior of sulfur in the glasses was accurately determined by using the energy shift of the S K α emission lines, which allowed also to make a quantitative determination of the sulfur species. XANES and K β emission lines also yield detailed information on the local chemistry and structure, and thus help us to understand the geochemical role of S in these systems. We observed that we can follow the evolution of sulfur as a function of controlled formation conditions with respect to pressure, temperature or oxygen fugacity, and determine whether it is present as sulfate or sulfide. In particular we were able to identify the presence of iron in a coordination geometry similar to pyrrhotite as the sulfur ligand in reduced glasses. Furthermore, we investigated the coordination and redox state of iron by means of XANES. By the analysis of the pre-edge and comparison with characterized mineral standards, we determined the coordination and chemical state of iron, which varies with redox state and glass bulk composition and affects the sulfur solubility in the glasses.

Poster no. PS2.56 - Session 2
XAS study on environmental particulate

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The purpose of this work is to study the speciation of Fe and Mn within road dust particles and to further confirm the potential of EXAFS spectroscopy for the study of environmental particulate. Road dust samples were collected on the walls and floor of the ventilation shaft of Traforo del San Bernardo highway tunnel. Only particles with size between 250 – 63 μm and < 63 μm were analyzed.

X-ray absorption spectra were recorded at the European Synchrotron Radiation Facility in Grenoble (France) on the Italian beamline (BM8-GILDA [8]) at the Fe and Mn K-edges. Due to low Mn and Fe concentration (< 100 and < 1 mg/g for Fe and Mn, respectively), measurements were performed in fluorescence yield using a 13-element Ge detector.

Several standard references were measured along with the samples: metallic Fe, FeO, Fe₂O₃, Fe₃O₄, FeCl₃, FeSiO₂, Fe(NO₃)₃, FeSO₄, and metallic Mn, MnO, Mn₂O₃, Mn₃O₄, MnCl₂, MnSO₄. In addition, a standard reference material of road dust (BCR-723) was also analyzed. Principal Component Analysis (PCA) and Least Square Fitting (LSF) [9] were applied on each sample spectrum revealing different species and oxidation states for both Fe and Mn. EXAFS refinements confirmed PCA and LSF results, revealing the structure of the main species associated to the each sample.

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Poster no. PS2.57 - Session 2
S-XANES analysis of sulfur forms in coals and kerogens

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Sulfur X-ray Near Edge Absorption Spectroscopy (S-XANES) has emerged as a powerful tool for speciating sulfur forms in complex carbonaceous solids such as kerogen and coal. S-XANES is also used to collect information about chemical and thermal sulfur transformations in these materials. This technique, used in conjunction with other techniques such as XPS and ¹³C NMR can be used to gain valuable information about sulfur transformations without altering the samples in the process. [1] S-XANES has been performed on Argonne Premium Coal Samples, which are widely used as standards by various coal chemistry researchers. The Premium Coal Sample Program is intended to provide the basic coal research community with the highest quality samples of a limited number (8) of coals for basic research. [3] Measurements of these standards have been re-performed at the Advanced Photon Source beamline 9-BM, which is optimized for low energies XAFS (below 4 keV) and is unique to the APS facility. The data taken at the APS has been compared to the data taken in 1991 at the Stanford Synchrotron Radiation Light Source by M. Gorbaty et al [2]. New insight has been gained into the ability to directly detect the pyritic sulfur content of these samples with XAFS, which has been problematic in the past. Sulfur characterization and analysis methods using spectra from model compounds and selected sulfur data for kerogens and coals taken from the literature is discussed.

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Poster no. PS2.58 - Session 2**A HERFD-XAS study of vanadium oxidation state in titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) from the Bushveld Complex (South Africa)**Amélie Bordage¹, Etienne Balan¹, Christian Brouder¹, Amélie Juhin^{1,2}, Johan de Villiers³, Pieter Glatzel⁴, and Georges Calas¹

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The features of the K-edge X-ray absorption spectrum of transition metal cations occurring at low concentration in minerals provide useful information about their crystallographic and electronic structures. In particular, the energy and relative intensity of pre-edge features depend on the valence state and site symmetry of the absorbing atom. The knowledge of the valence spectral features of an impurity in a structure is particularly relevant to study natural samples, where the impurity may occur under several valence states.

Vanadium is an example of multivalent impurities as it occurs under two redox states (+III and +IV) in titanomagnetites. It makes it a valuable geochemical probe, providing useful information about redox conditions during natural processes, such as the formation of the meter-thick titanomagnetite layers of the Bushveld Complex.

We present a High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy study of natural and synthetic samples of V-bearing titanomagnetite. Compared with conventional XANES measurements in fluorescence mode, HERFD-XAS leads to a significant sharpening of the pre-edge features and can be used to avoid the overlapping Ti fluorescence. The spectra have been recorded on ID26@ESRF, together with that of two references: tsavorite, a V^{3+} -bearing garnet ($\text{Ca}_3\text{Al}_2(\text{SiO}_3)_4\text{V}^{3+}$), and cavansite [$\text{Ca}(\text{VO})\text{Si}_4\text{O}_{10}(\text{H}_2\text{O})_4$] in which V is under the tetravalent state.

The pre-edge features confirm the presence of both V^{3+} and V^{4+} in synthetic and natural magnetite samples, with a ratio depending on the oxygen fugacity. The spectrum of the natural samples is similar to that of the synthetic ones. Variations of the $\text{V}^{4+}/\text{V}^{3+}$ ratio are observed as a function of the stratigraphic height within the main magnetite layer of Bushveld. These variations with depth suggest variations of the redox conditions during the crystallization of the magnetite layer.

Poster no. PS2.59 - Session 2**Speciation of lead in wild flowers from a mining area applying x-ray absorption near edge structure spectroscopy**Gudrun Lisa Bovenkamp^{1,2}, Alexander Prange³, Amitava Roy², Wolfgang Schumacher⁴, and Josef Hormes^{1,2,5}

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Phytoremediation uses a plant's ability to uptake heavy metals from polluted cleanup sites for environmental cleanup. The biological process of plant metabolism of metals, however, is still not well understood and it probably differs between metals. Lead (Pb), one of the most common toxic heavy metals, has low mobility in soil because it is often bound to organic material such as humic substances and has low solubility in the pore water. Still, there are plants that uptake Pb into above ground tissue, sometimes in high concentrations.

Several plants from a lead polluted site near Mechernich/Kall, in the Eifel Mountains, Germany, were investigated for this study using x-ray absorption near edge structure spectroscopy (XANES). Plant parts (leave, stems and roots) along with several reference compounds of Pb (oxides, salts and organic) were measured at the Pb L₃- (13035 eV), L₁- (15860 eV), M₅- (2484 eV) and M₄- (2586 eV) edge. Each edge probes a different electronic environment because of the selection rules.

Even though Pb L₁- and M₅-edges have some advantages, because of physical conditions like life time broadening, compared to the L₃-edge, these advantages do not hold. Pb L₁-XANES spectra show only low sensitivity according to change in coordination and ligand even though L₁ just probes the molecular orbitals of p-character which form most of the bonding of Pb(II) compounds. Pb M_{5/4}-XANES spectra do not show better energy resolution which should be due to life time broadening, because of the limited energy resolution of the beamline at that energy. Further, because of the close proximity of the Pb M_{5/4}-edges to sulfur K-edge high absorption from the sulfur in the plants causes the complete masking of Pb M_{5/4}-edges in samples with low Pb concentration. Although the measurements of the plant samples at sulfur K-edge may show an increase of Pb-S bonding in samples with high Pb concentration.

Poster no. PS2.60 - Session 2**Using XAFS to track iron phase transformations during bacterial respiration**Maxim I Boyanov¹, Edward O'Loughlin¹, and Kenneth Kemner¹*(1) Argonne National Laboratory 9700 S. Cass Ave 60439 Lemont IL USA*

Dissimilatory iron reducing bacteria (DIRB) use Fe(III) minerals as terminal electron acceptors for respiration in oxygen-deficient environments. The type and amounts of Fe(II)-containing DIR products depend on, e.g., the initial Fe(III) phase, the bacterial species, the solution composition, the type and amount of electron donor available, and the presence of electron shuttles. We are investigating DIR transformations to understand the formation of reactive Fe(II) phases that influence uranium speciation in subsurface environments.

In this study, we have identified the initial Fe(III) minerals and the respiratory products during the growth of *Shewanella putrefaciens* CN32 in the presence of a commercial Fe(III) oxide, nominally a nanoparticulate lepidocrocite. After incubation, the starting material changed from a reddish brown rust color to a dark green phase. Acid extraction of the green phase with 0.5 M HCl recovered 85% of the total iron as Fe(II), leaving a solid, acid-resistant phase. The latter phase was identified as nanoparticulate hematite by EXAFS. Using linear combination EXAFS analysis the starting Fe(III) phase was determined to be a mixture of 60% lepidocrocite, 26% ferrihydrite, and 14% hematite. These results, obtained in a mixed-mineral system, are consistent with previous work suggesting that lepidocrocite and ferrihydrite are readily reducible by DIRB, whereas hematite is recalcitrant to bacterial reduction. The XAFS spectrum of the acid-extractable phase in the mixed-phase green product was analyzed by subtraction of the hematite spectral component from the mixed-phase spectrum: XANES indicated an Fe(II) valence state and the EXAFS spectrum was consistent with vivianite, an Fe(II) phosphate mineral. This study demonstrates the utility of XAFS spectroscopy in characterizing dissimilatory metal transformations, particularly in complicated settings such as mixed-phase nanoparticulate minerals in hydrated mineral-bacteria systems.

Poster no. PS2.61 - Session 2**Structural role of europium in silicate glasses**Rita Cicconi¹, Gabriele Giuli¹, Eleonora Paris¹, Werner Ertel-Ingrisch², and Donald B. Dingwell²*(1) Dip. di Scienze della Terra, and Unità CNISM, Università di Camerino, Italy**(2) Dept. of Earth Sciences, LMU, Muenchen, Germany*

This study is focused on the determination of the geochemical behaviour of Europium (Eu) in a set of synthetic silicate glasses, relevant for the Earth Science and ranging from basaltic to granitic composition. Lanthanides or Rare Earth Elements (REEs) are of great interest in geosciences. REEs play an important role as trace indicators of magmatic processes that control the origin and evolution of igneous rocks. In the rocks, the variation of the ratios $\text{Eu}^{3+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ can be used to determine the oxygen fugacity conditions prevailing during mineral formation. The samples have been characterized through Eu L3-edge by X-ray Absorption Spectroscopy (XAS) and the measurements have been performed in fluorescence mode at the ESRF (Grenoble, F). Eu LIII-edge XANES peaks analysis allowed the semi-quantitative assessment of Eu oxidation state. The white line of the Eu-XANES spectra clearly displays two contributions related to the presence of divalent and trivalent Eu with an energy shift of 7-8 eV [1,2]. The evaluation of their intensity ratio allows to determine the $\text{Eu}^{3+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ redox ratio. Detectable variations were observed in the studied glasses as a function of bulk composition, at both oxidizing and reducing condition. In fact, significant changes in the intensity of the two main peaks can be observed when passing from basaltic to granitic compositions, and these changes were interpreted as variations in the $\text{Eu}^{3+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio. Moreover, data obtained from kinetic experiments, clearly show that the equilibrium kinetics for granitic and basaltic composition is very different.

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Poster no. PS2.62 - Session 2
Eu-Fe interaction in silicate melts.

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Synthetic silicate glasses corresponding to a basaltic composition were used to study the dependence of the redox states of multivalent elements (Fe, Eu) on the bulk melt composition, imposed oxygen fugacity and melt temperature. Chemical understanding of oxidation-reduction equilibria in glass forming melts has important technological applications for the production of optical devices, for example, laser glasses and fiber amplifiers. Additionally, Rare Earth Elements (REE) have verified to be effective geochemical indicators, since they are sensitive to igneous processes that operate during magma genesis and evolution (e.g. [1]). Therefore, a complete understanding of transition and REE elements is important for the geochemical and petrological interpretations of magmatic processes and partition properties between melt and crystals. The samples have been characterized through Eu LIII-edge and Fe K-edge X-ray Absorption Spectroscopy (XAS) to study the mutual interactions of Fe and Eu redox couple. Eu LIII-edge XANES peaks analysis allowed the semi-quantitative assessment of Eu redox ratio; literature data report a difference of 7-8 eV between Eu²⁺ and Eu³⁺ in the experimental spectra [2]. This energy shift is evident enough to well differentiate between the two oxidation states and to determine the Eu oxidation state in the glasses under investigation. By Fe K-edge pre-edge peak analysis, we determined also the Fe oxidation state and coordination number by a comparison of pre-edge peak data with those of Fe model compounds allowed to determine Fe oxidation state and coordination number. Either Fe K-edge or Eu LIII-edge analysis indicate that at both oxidizing and reducing condition, in the basaltic composition, the amount of divalent Eu decrease if the amount of Fe increase, confirming a strong interaction between these two elements.

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Poster no. PS2.63 - Session 2
Investigation of heavy metal soil contamination by XAFS.

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Understanding the mechanisms of heavy metal retention on soils and their components is necessary in order to predict the fate and mobility of these environmental contaminants and so to try to preserve environmental quality and health. Basic information such as rates and activation energy of reactions at the soil-water interface can be provided by macroscopic kinetic studies such as batch and stirred-flow methods but they can't yield useful details concerning the reaction mechanism. XAFS spectroscopy, indeed, probes the oxidation state and the local atomic structure around specific elements and therefore can provide important information about the involved mechanisms. The main aim of this study was to use XAS probe to shed light on Ni and Pb speciation in heavy-textured calcareous soils, typical of central Italy and in some of its main constitutive elements. Data revealed that when the contaminant was Ni, precipitation processes occurred mainly via Ni-hydroxide formation and were strongly connected to the presence of organic matter. The investigation of Pb destiny on soil samples excluded the occurrence of co-precipitation suggesting that precipitation products form thanks mainly to the role of oxides and carbonates, that relevantly favour precipitation processes.

Poster no. PS2.64 - Session 2**A XANES study of blue coloured ancient Thai glass samples**Pisutti Dararutana¹, Sorapong Pongkrapan¹, Pornsawat Wathanakul¹, and Narin Sirikulrat²*(1) Gemmology and Mineral Sciences Special Research Unit Kasetsart University 10900 Bangkok Thailand**(2) Department of Physics Faculty of Sciences, Chiang Mai University 50200 Chiang Mai Thailand*

Blue-coloured Ancient Thai Glass (ATG) samples of all typologies from archaeological findings as well as fragments of artifacts were identified for the first time by means of a synchrotron-based technique called; X-ray absorption near edge spectroscopy (XANES) at the Thailand's Synchrotron Light Research Institute with an aim for obtaining information on the cause of visually different shades of blue colour. Besides, the samples were also investigated using spectroscopic techniques such as CIE colour notation system and UV-Vis absorption spectroscopy. Results indicated that the blue coloured ATG samples were the lead-bearing glasses. The presence of copper has attributed mainly to the various shades of blue colouration. The XAS is a powerful yet non-destructive technique for archaeological studies of such ancient glassy materials.

Poster no. PS2.65 - Session 2**Detection of As, Cr and Cd in walnut trees through XAFS.**Jose Alberto Duarte Moller¹, E. Gallegos Loya¹, J. Parra Berumen¹, H. Esparza Ponce¹, R. González-Valenzuela¹, and C. González-Valenzuela¹*(1) Centro de Investigacion en Materiales Avanzados, S. C. Miguel de Cervantes 120, Complejo Industrial Chihuahua 31109 Chihuahua Chihuahua Mexico*

For the heavy metal determination sampling took just two farms with cultivation of walnut, located in the State of Chihuahua, Mexico. Samples from ground, plants, and fruit were taken, properly labeled. Later to the soil samples the quartering method was applied in order to reduce the volume and obtain 5 g the sample to analyze. Samples were dried to 100 °C. XAS experiments were carried out in the Stanford Synchrotron Radiation Laboratory (SSRL).

X-rays absorption spectra of the soil samples that contained As have a similar behavior, displaying the edge of absorption in an energy 11.865 to 11.869 KeV reason why we can assume that it is an As (V) [1,2].

The radial distribution function obtained after applying the Fourier transformation to the absorption spectra, have a distance of first neighbors with a slight variation exists and is in $R=0.19419$ nm to 0.20129 nm which corresponds to the positions As-O [3]. Of similar way for Cd it is observed that all have a similar behavior, displaying the edge of absorption at an energy of 26.71 KeV, the edge of the samples is identically to the edge form of cadmium nitrate and cadmium acetate. It indicates that he is present like Cd (II) .

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Poster no. PS2.66 - Session 2**Pb in naturally irradiated monazites and zircons**Julien Dubraille¹, François Farges², Laurent Gautron¹, Messaoud Harfouche¹, Camelia Borca³ and Daniel Grolimund³*(1) Université Paris-Est Marne-la-vallée 5, bd Descartes 77454 Champs-sur-marne France**(2) Lab. de minéralogie et de cosmochimie du Muséum et UMR CNRS 7202, Muséum National d'Histoire Naturelle, Paris, France and Dept. of Environmental and Geological Sciences, Stanford University, USA**(3) Swiss Light Source, Institut Paul Scherrer, Villigen, Switzerland*

Natural monazite (ideally LaPO_4) and zircon (ZrSiO_4) are often both “enriched” in U and Th. Monazite is resistant to radiation damage but is able to recover from radiation damages caused by minor amounts of U, Th over geological period of times. In contrast, zircon is much more sensitive to natural irradiation. Therefore, the study of those natural surrogates is crucial for better understanding the long-term immobilization of actinides arising from nuclear wastes.

We used bulk and μ -XAFS techniques to evaluate the speciation of radiogenic Pb in those minerals. Pb-L3 edge XANES experiments and μ -XAFS experiments (bulk and μ -focalised) were conducted at 293 K at the SSRL beamline 11-2 and at the SLS beamline X05, respectively; using for both Si(111) monochromators and a 32-element solid state Ge detector. Energetic resolution is ~ 7 eV at 13 keV. Lateral resolution for XAFS experiments varied from ~ 1 mm² (SSRL) to 15 μm^2 (SLS). XAFS spectra were reduced using the XAFS 3.1 package. Ab-initio calculations (FEFF8.4) converged using the HL-DH potentials and tested in a set of Pb-sulfide, oxide, carbonate, phosphate and silicate minerals.

Natural monazites and zircons from various localities and with various degrees of irradiation were studied. Their irradiation degree was characterized using different techniques. XANES spectra show that Pb is “divalent” in all the samples investigated. But large variation in the speciation of Pb has been evidenced from monazites to zircons. In monazite, the ionic radius of Pb is greater than that of its “father” (Th) (1.29 vs 1.05 Å), inducing severe distortions of the structure due to isotopic decay. XANES calculations are consistent with Pb substituting to La in monazite. XANES calculations are underway around Pb in molecular dynamics simulations of a U-bearing ZrSiO_4 ceramic having undergone 4-5 keV cascades along (111).

Poster no. PS2.67 - Session 2**Not all chromates show the same pre-edge feature. Implications for the modeling of the speciation of Cr in environmental systems.**Julien Dubraille¹, and François Farges²*(1) Université Paris-Est Marne-la-vallée 5, bd Descartes 77454 Champs-sur-marne France**(2) Laboratoire de minéralogie et cosmochimie du Muséum national d'Histoire naturelle de Paris and UMR CNRS 7202 and Department of Environmental and Geological Sciences, Stanford University, USA*

The speciation of chromium is often used to evaluate the amount of toxic, mobile, carcinogenic Cr(VI) in materials (soils, glasses, aqueous solutions)[1-10]. In contrast, Cr(III) is considered as less mobile and consequently much less toxic. We studied a variety of compounds showing those environments such as ruby, emerald, Cr-spinel, chromite for Cr(III) while a series of chromates were also studied. Chromates exhibit a variety of polymerization, from orthochromates (such as sodium chromate) to chromic acid (CrO_3). Cr K-edge XANES spectra were collected at the 11-2 beamline (SSRL, Stanford) on SPEAR3 (3 GeV and 100 mA), using Si(220) double-crystal monochromators. Fe K alpha-fluorescence was monitored using a “Lytle” detector. High-resolution XANES spectra were collected with 2 sec/point, 0.1 eV steps from 6500 to 6800 eV (0.1 eV steps in the pre-edge region). XANES calculations were performed using FEFF 8.4, using default conditions. The studied pre-edges for Cr(III) show similar features. Only a greater transition is sometimes observed on the high energy side of the pre-edge. In contrast, that for Cr(VI) increases by a factor of ca. 3 from sodium chromate to CrO_3 , which ab-initio XANES calculations (FEFF8.4) confirms. Pauling’s second rule explains how polymerization enhances polyhedral distortion that had a well-known direct effect on the pre-edge feature intensity but also on its width. This result shows that extreme caution must be taken when simulating a mechanical mixture of Cr(III) and Cr(VI) as Cr-polymerization strongly affects the shape of the pre-edge feature to model to derive the desired respective amounts of Cr(III) and Cr(VI).

Poster no. PS2.68 - Session 2**Determination of the speciation of radionuclides in cementitious materials by micro-XRF/XAS/XRD and STXM**Rainer Dähn¹, Nathalie Macé¹, Dmitry Popov¹, David K. Shuh², and Erich Wieland¹*(1) Paul Scherrer Institut, 5232 Villigen, Switzerland**(2) Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

The safe disposal of radioactive wastes in deep geological repositories is a challenging task. The radionuclide release rate from a deep geological repository can be controlled and reduced by a suitable choice of the engineered and geological barriers. Cement is used to condition the waste materials and for the construction of the engineered barriers. Understanding the binding mechanisms of radionuclides, such as uranium, in the cement matrix enables us to predict their long-term behavior in cement based repositories.

In the past years it has been realized that spectroscopic information on the micro-scale and down to the nano-scale are necessary to gain a mechanistic understanding of the processes governing the binding of heavy metals and radionuclides in cementitious systems. Synchrotron-based micro-XRF, micro-XAS and micro-XRD combined with scanning transmission X-ray microscopy (STXM) were found to be powerful tools for spatially resolved investigations of retention processes in heterogeneous cementitious systems.

In the present study low U(VI) loaded samples (2000 ppm) were used to determine the structural environment of U(VI) sorbed surface complexes, whereas high U(VI) loaded samples (20000 ppm) were used to determine the chemical nature of the U(VI) solubility-limiting phase in the cementitious system. The micro-spectroscopic investigations revealed that the coordination environment of uranium at low U(VI) loadings is mainly uranophane-like. The investigations of the high U(VI) loaded cement samples revealed that uranium mainly precipitated as Ca-uranate phase. The study further demonstrated that STXM is a powerful tool to gain information at the nanometer scale on the distribution and speciation of precipitates forming in the cement system. In conclusion, radionuclide immobilization through the formation of surface complexes and precipitates may reduce radionuclide mobility and ensure their safe disposal in cementitious systems.

Poster no. PS2.69 - Session 2**Speciation of Mg in biologically produced carbonates probed by nanoSIMS and microXANES experiments**François Farges^{1,2}, Anders Meibom¹, Anne-Marie Flank³, Pierre Lagarde³, and Markus Janousch⁴*(1) Laboratoire de minéralogie et de cosmochimie, Muséum national d'Histoire naturelle and CNRS UMR 7202, CP 52, 61 rue Buffon, Paris, France**(2) Dept. of Geological and Environmental Sciences, Stanford University, Stanford, CA 94205-2115, USA**(3) CNRS UR1 Synchrotron Soleil, BP 48, 91192 Gif sur Yvette, France**(4) Swiss Light Source, Institut Paul Scherrer, Villigen, Switzerland*

The Mg/Ca ratio is critical to the formation process of these marine skeletons (1-4). Thanks to nanoSIMS, large Mg/Ca variations have been discovered (5) that correlate well with the skeletal ultrastructure. It has been proposed that these fluctuations are the expression of a transiently stable carbonate precursor phase, referred to as amorphous Mg-carbonate (6). This hypothesis can be investigated by micro-XANES (mXANES) experiments at the Mg K-edge, with the potential of greatly improving the precision by which paleo-environmental information can be derived from structures, with a direct impact on the debate about anthropogenic climate changes.

The speciation of Mg is investigated in various biogenic carbonates from a defined range of phyla and taxonomic groups. mXRF and mXANES spectra were collected at the Mg K-edge using the LUCIA beamline (SOLEIL) hosted at the SLS (Switzerland), operating at 2.4 GeV and 400 mA currents. We used a beryl (10-10) double crystal monochromator and K-B mirrors. Energetic and lateral resolution are ca. 0.5 eV and 10 μ m, respectively. Samples were polished and set into a vacuum chamber while the K-alpha fluorescence of Mg was collected using a Si-drift detector. mXRF maps were collected (1 second/pixel) while mXANES spectra were collected every 0.2 eV (2 s/point). References include brucite (Mg(OH)₂) and dolomite (CaMg(CO₃)₂).

We found that, for each organism studied, hot spots and background spots show same Mg-speciation. However, among biominerals studied, the measured Mg-speciation varies from brucitic-like in some corals (Porites), to dolomitic in others (Bamboo coral and Pinctada shell) to a yet unknown Mg-phase as in the gorgona studied. Identification of the Mg-speciation is still under progress based on the study of numerous model compounds of rare Mg-carbonates (e.g., giorgosite). Ab initio XANES calculations (FEFF8.4)(7) are computed to help determine molecular environments, potentially related to the Mg-anomalies.

Poster no. PS2.70 - Session 2**MicroXANES spectroscopy of sulfur sorbed onto volcanic ashes**François Farges^{1,2}, Hans Keppler³, Anne-Marie Flank⁴ and Pierre Lagarde⁴*(1) Laboratoire de minéralogie et de cosmochimie, Muséum national d'Histoire naturelle and CNRS UMR 7202, CP 52, 61 rue Buffon, Paris, France**(2) Dept. of Geological and Environmental Sciences, Stanford University, Stanford, CA 94205-2115, USA**(3) Bayerische Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany**(4) CNRS UR1 Synchrotron Soleil, BP 48, 91192 Gif sur Yvette, France*

Powders of 4 synthetic volcanic glasses, a silica glass and quartz were equilibrated with SO₂ to get the speciation of S sorbed onto their surface. Those samples mimic the aerosols projected into the atmosphere (warming the stratosphere but cooling the troposphere) during volcanic eruptions. These « ashes » have distinct IR absorbances, in relation of the speciation of their sorbed S, influencing the Earth's climate (pollution, ozone depletion, global cooling) [1].

S K-edge micro-XANES (mXANES) spectra and mXRF maps were collected at the LUCIA beamline (SOLEIL) at the SLS (Switzerland). In addition, various models of S were studied [2-4] with emphasis on the problematic feature near 2480 eV (labeled «PR») either related to S(IV) [5] or S(VI) [6]. Si(111) monochromator (resolution ca. 0.3 eV at 3 keV) were used and K-B mirrors focused the X-ray beam to 3x3 μm². A SDD detector collected the S-Kα fluorescence while total electron yield quick-mXANES spectra (2 mins/spectra) were also collected to monitor photoreduction).

When photoreduction is minimized, SO₂ is sorbed mostly as sulfates but sulfites and elemental S are not excluded. The speciation of S is influenced by the polymerization of the glass probed, its composition and its structure. Despite quartz and silica are similar in composition, large differences of sorption are observed, related to their bulk structure. This indicates that the silica surface is more defective and reactive in the presence of SO₂ than the quartz surface., the large difference in the quantity of sorbed S and its speciation are measured between silica and rhyolite. This suggests that the presence of network modifiers (and/or charge compensating alkali and alkali-earths) increase the number of reactive sites onto the glass surface. But the increase in glass polymerization is less critical on the quantity of sorbed S. However, this influences significantly the speciation of S by increasing S-S bridges (as in elemental S).

Poster no. PS2.71 - Session 2**A metal mixture lowers the reaction temperature of copper chloride as shown using in situ quick XAFS**Takashi Fujimori¹, Masaki Takaoka¹, Yuta Tanino¹, Kazuyuki Oshita¹, and Shinsuke Morisawa¹*(1) Department of Urban and Environmental Engineering, Graduate School of Engineering, Kyoto University C-1-3-463, Katsura, Nishikyo-ku, 615-8540, Kyoto, Japan*

Trace chlorinated organic compounds are generated via thermal processes. Their formation is promoted by copper chloride in solid phase such as fly ash, especially in the post-combustion zone in municipal solid waste incineration. Previously, we reported the chemical state and change of copper chloride in a single model using the in situ quick scan x-ray absorption fine structure (QXAFS)[1]. However, a real solid phase, which is a complex system involving many elements, was not simulated. In this paper, we measured the Cu-K XAFS of a metal-mixture model upon heating to discuss the effect of mixing. The in situ QXAFS technique revealed that the reaction temperature of copper was lower, compared with the single model, when a mixture was measured. The result shows that the formation mechanism of chlorinated organic compounds derived from anthropogenic thermal sources can be described more correctly.

[1] T. Fujimori, and M. Takaoka, Environ. Sci. Technol. in press (2009).

Poster no. PS2.72 - Session 2**Effect of alkali content and oxygen fugacity on the Fe oxidation state in rhyolitic glasses**Gabriele Giuli¹, Maria Rita Cicconi¹, Eleonora Paris¹, Roberto Alonso Mori², Pieter Glatzel², and Bruno Scaillet³(1) *Dip. di Scienze della Terra, and Unità CNISM, Università di Camerino, Italy*(2) *ESRF, Grenoble, F.*(3) *Institut de Sciences de la Terre D'Orleans, UMR 6113 CNRS-UO, Orleans, France.*

The Fe oxidation state, coordination geometry and $\langle \text{Fe-O} \rangle$ distances have been determined by Fe K-edge XANES and EXAFS for a set of sulphur bearing silicate glasses of rhyolite composition in the aim of determining: 1) the effect of bulk composition on the iron oxidation state and local structural environment; 2) the effect of Fe oxidation state on sulphur behaviour in the corresponding magmas/melts. Glass compositions have been chosen so as to represent S-Cl-F bearing rhyolitic magmas with low to high alkali content. These glasses have been equilibrated at a range of different oxygen fugacity conditions typical of magmatic conditions. Comparison of the pre-edge peak data with those of Fe model compounds with known oxidation state and coordination number allowed to determine the Fe oxidation state and coordination number for all the glasses analysed. The $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio varies from 0.25 to 0.80 (± 0.05) in the glasses studied. Moreover, pre-edge peak data clearly indicate that Fe^{3+} can be present in [4] and/or [5] coordination according to the alkali content of the glass, whereas Fe^{2+} is present in [5] coordination units for these compositions. The presence of minor amounts of [6] coordinated Fe cannot be ruled out by XANES data alone. EXAFS derived Fe-O distance in the most oxidised sample indicates that Fe^{3+} is in tetrahedral coordination.

For these glass compositions, going from reducing to oxidising condition results in higher fraction of network forming $^{[4]}\text{Fe}^{3+}$, thus increasing the polymerisation of the tetrahedral network. Alkali content has been found to have a very strongly effect on the Fe oxidation state: at a given oxygen fugacity, Fe oxidation state increase noticeably with increasing alkali content. As Fe oxidation state is known to affect the solubility of S^{2-} species in silicate melts, Alkali content is expected to play a major role together with oxygen fugacity in the S geochemical behaviour in silicate magmas.

Poster no. PS2.73 - Session 2**Sulfur K-edge XANES spectroscopy of the sodalite variety hackmanite**Joerg Goettlicher¹, Alexey Kotelnikov², Natalia Suk², Andrey Kovalsky², Stefan Mangold¹, Ralph Steininger¹, and Jan Stelling³(1) *Forschungszentrum Karlsruhe, Institute for Synchrotron Radiation, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*(2) *Institute of Experimental Mineralogy, RAS, Chernogolovka, 142432, Moscow Region, Russia*(3) *Institut fuer Mineralogie, Leibniz Universitaet Hannover, D-30167 Hannover, Germany*

A hackmanite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl}_2, \text{S})$) containing sample from Lovosero massive (Kola peninsula, Russia) has been investigated by electron microprobe analysis and sulfur K-edge XANES spectroscopy to gain information on the nature of sulfur in its structure. Hackmanite from this location shows an intensive purple color for a couple of seconds after cracking. A reddish tint can be partly reactivated by illumination with UV radiation and X-rays. Electron microprobe data allow two distinguish between two sulfur containing silicate phases which are intergrown on a micrometer scale. Bulk S K-edge XANES spectroscopy will result only in a mixed signal. Thus, μ -XANES spectroscopy (SUL-X beamline of the synchrotron radiation source ANKA) has been used to separate the signals. The S K-edge XANES spectrum of the low grade sulfur phase show a main resonance for sulfate (at 2.481 keV) and a weak resonance at positions for reduced sulfur species. The sulfur rich phase reveals sodalite composition from electron microprobe analysis and is thus assigned to be the hackmannite. Here, S K-edge XANES spectra are characterized by main resonances at positions for reduced sulfur, and additionally by a very sharp and prominent until yet structurally unknown resonance at 2.465 keV. Using this unique resonance that have meanwhile also detected in silicates glasses containing reduced sulfur species the hackmanite distribution in the sample could be mapped. Calculation of XANES spectra has been started and shall help to understand the nature of this resonance.

Poster no. PS2.74 - Session 2**XAS study of uranium binding in a natural, organic-rich soil of an alpine region (Switzerland)**

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Mountain wetlands have been shown to be efficient uranium filters resulting in uranium concentrations of up to 3000 ppm based on dry weight [1]. Extraordinary high concentrations of uranium were found in a natural soil of the alpine region (Dischma valley), in Grisons, Switzerland. The uranium in the soils has a natural isotopic composition and long-lived daughter isotopes of ²³⁴U (e.g. ²²⁶Ra) and ²³⁵U (e.g. ²³¹Pa) which are missing. This clearly points to a process where U is solubilized from a source rock, then migrates with the solution and finally becomes immobilized in organic-rich and water-logged soils.

The goal of this study was to characterize the binding of uranium to the soil matrix and to determine its redox state in order to assess the potential for uranium mobilization. A combination of chemical extraction methods and x-ray absorption spectroscopy was applied to characterize the redox state and binding environment of uranium in the soil.

XANES analysis reveals that uranium is present in both tetravalent and hexavalent states with a dominating U(VI) form. These results are confirmed using chemical extraction methods such as bicarbonate extraction under aerobic and anaerobic conditions [2]. EXAFS revealed that uranium in the soil matrix is octahedrally coordinated with two axial and six equatorial oxygen atoms (respectively at 1.77 and 2.36 Å) indicating a uranyl-like (UO₂²⁺) structure at short range order around uranium. An additional EXAFS signal (at about 3.2 Å), as identified in some spectra, showed that uranium was also bound to a light element such as carbon, phosphorus or silicon. We conclude that U is directly bound to the soil organic matter possibly via an organophosphate/silica complex.

[1] Owen and Otton (1995) Ecological Engineering 5, 77-93.

[2] Schultz (1998) J.1 of Radioanalytical and Nuclear Chemistry 234 (1-2), 251-256.

Poster no. PS2.75 - Session 2**Mechanisms of Zn of bioavailability related to speciation of metal-particulate organic matter associations in polluted soils**

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We present a study about the behaviour of Zn in agricultural soils polluted 100-50 years ago by metallurgical fallout and used nowadays for corn production. Such type of soil concerns an area of several km² around former metallurgical complex in Northern France. Despite the moderated metal amounts of these soils, the metals deposited over the agricultural area still indirectly expose nowadays populations through the food chain. In contrast to the most contaminated industrial site (1-7), these more distant agricultural areas have been less studied. The study was focused on Zn since the presence of this (mobile) element in the upper horizon of the soils after half a century suggests its immobilisation by the soil mechanisms. To evaluate how Zn is associated to POM, Zn K-edge XAFS spectra were collected at 293 K at the SLS on beamlines superXAS and microXAS, using Si(111) monochromators and solid state Ge detectors. Energetic resolution is ca. 2 eV at 9 KeV. Lateral resolution varied from ca. 1 mm² to 15 micron². Spectra were normalized with the XAFS 3.0 software.

We studied different POM size fractions isolated from soils. The largest POM particles correspond to recent leaves or roots fragments. The finest POM particles correspond to decomposition by-products. The results revealed a multiple and heterogeneous speciation of Zn with POM. We observed that little interactions from next-nearest neighbors around Zn. We concluded that most of the Zn tends to be located in the POM matrix as a Zn-organic speciation. We also collected macroscopic EXAFS data on selected intact POM particles probed at the micron scale. The results show that the remaining Zn-distribution related to inorganic (hot-spots), possibly franklinite-type, is minor compared to the Zn-organic speciation. Such observations will help to better understand the mechanisms that regulate the bioavailability and immobilisation of Zn in polluted soils.

Poster no. PS2.76 - Session 2**A XAFS study on the isotopic fractionation mechanism of Molybdenum during distribution between seawater and ferromanganese oxide**Teruhiko Kashiwabara¹, and Yoshio Takahashi¹*(1) Hiroshima University 1-3-1, Kagamiyama, Higashihiroshima, Hiroshima, Japan 739-8526*

The geochemistry of molybdenum (Mo) in the marine environment is widely discussed. In particular, many researches about Mo isotopic fractionation during adsorption reaction onto ferromanganese oxide in seawater are conducted because of its potential for paleoredox proxy. However, adsorption processes are still under debate due to the lack of the structural information of the adsorbed species. In this study, XAFS analyses were performed to reveal the isotopic fractionation mechanisms of Mo during adsorption onto ferromanganese oxide based on the structural information at molecular level.

Adsorption experiments of Mo were conducted under various conditions using synthesized ferrihydrite and δ -MnO₂ as adsorbents. Local structures of adsorbed Mo and Mo in natural hydrogenetic ferromanganese nodules were investigated by XAFS analyses. These measurements were performed at BL01B1 in SPring-8 and at BL-9A in Photon Factory, Japan.

Molybdenum K-edge EXAFS and L_{III}-XANES revealed that adsorbed species of Mo on the surface of ferrihydrite was tetrahedrally coordinated molecule and formed outer-sphere complex, while that on δ -MnO₂ was octahedrally coordinated and formed inner-sphere complex. Additionally, it was also revealed that δ -MnO₂ was the dominant host phase for Mo in the ferromanganese nodules from the comparison of their XAFS spectra. In previous isotopic researches suggested that Mo isotope in seawater are fractionated as a result of incorporation into ferromanganese oxides, exhibiting the enrichment of lighter isotope in ferromanganese oxides. This fractionation can be explained based on the results of this research, that is, due to the structural change from tetrahedral MoO₄²⁻ ion, major species in seawater, into octahedrally coordinated molecule sorbed onto the manganese oxide phase in ferromanganese nodules, which can lead to observed isotopic fractionation.

Poster no. PS2.77 - Session 2**U microxanes investigations of contaminant transformations near bacterial surfaces**Ken Kemner¹, M. Boyanov¹, E. J. O'Loughlin¹, D. Sholto-Douglas¹, K. Skinner-Nemec¹, B. Lai¹, R. E. Cook¹, E. Carpenter², V. G. Harris³, S. D. Kelly⁴, and K. H. Nealson⁵*(1) Argonne National Laboratory 9700 South Cass Avenue 60439 Argonne Illinois United States**(2) Virginia Commonwealth University, Richmond, Virginia United States**(3) Northeastern University, Boston, Massachusetts United States**(4) EXAFS Analysis, Bolingbrook, Illinois United States**(5) University of Southern California, Los Angeles, California United States*

An improved molecular and submolecular understanding of the spatial or configurative chemical interactions between contaminants and biological and geochemical materials is required for better prediction of their fate and transport throughout the environment. The microenvironment at and adjacent to actively metabolizing cell surfaces (approximately 0.1 to 10 micrometers) can be significantly different from ensemble averages of environments across larger spatial scales. Although the behavior/transformations of contaminants in such microenvironments can ultimately affect their macroscopic fates, predicting the behavior of contaminant radionuclides and metals in such microenvironments is currently difficult, because the chemistry of these environments has been difficult or impossible to define. Therefore, information about biogeochemical interactions at/near the microbe-mineral microenvironment is paramount for predicting the fate of contaminants, which is key to the stewardship of contaminated sites. We have performed a number of microXANES (approximately 150 nm spot size) and electron microscopy measurements to characterize the microbiologically-driven (i.e., *Shewanella oneidensis* MR-1) chemical transformations of uranium at microbe-mineral (i.e., lepidocrocite) interfaces. Results that identify both microbial and microbially-mediated chemical transformations of the uranium from a soluble U(VI) valence state to the sparingly soluble U(IV) valence state will be presented.

Poster no. PS2.78 - Session 2**Determination of the relative sulfur speciation in wood and soil samples by sulfur K edge XANES using internally calibrated reference spectra**Daniel Lundberg¹, Ingmar N Persson¹, Gunnar Almkvist¹, and Kristin Boye²

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Sulfur K edge XANES (X-ray Absorption Near Edge Structure) spectroscopy is an excellent tool to determine the speciation of sulfur compounds in complex matrices. This paper presents a method to quantitatively determine the kinds of sulfur species in natural samples using internally calibrated reference spectra of model compounds. Quantitative measurements can only be performed on samples with the sulfur compounds homogeneously separated in the sample at low concentrations, less than 0.3-0.5 %. Samples containing particles are very difficult to determine quantitatively due to high absorption within the individual particles. The method is applied on a wood sample from the historic warship Vasa and a soil sample.

Poster no. PS2.79 - Session 2**XAFS study of Zn in K-T boundary clay**Maki Okube¹, Akira Yoshiasa², Hiroki Okudera³, Akihiko Nakatsuka⁴, and Ritsuro Miyawaki⁵

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Cretaceous-Tertiary boundary (K-T boundary) clays contain relatively high Pt-group element concentration. Zinc anomaly has also been detected in the K-T boundary clays and may have various kinds of information in the asteroid impact and mass extinction at the end of the Cretaceous. In This study, the X-ray absorption fine structure (XAFS) spectra near the Zn K-edge in K-T boundary clays and zinc minerals have been measured in transmission mode and in fluorescence mode using Lytle-type or 19-elements SSD detector at PF BL-12C of Photon Factory in the National Laboratory for High Energy Physics, Japan. The samples for comparison are thirteen species of natural zinc minerals such as, willemite (Zn_2SiO_4), adamite ($Zn_2(AsO_4)(OH)$), smithsonite ($ZnCO_3$), descloizite ($PbZnVO_4(OH)$), hardystonite ($Ca_2ZnSi_2O_7$), franklinite ($ZnFe_3O_4$), gahnite ($ZnAl_2O_4$), scholzite ($CaZn_2(PO_4)_2 \cdot 2H_2O$), zincite (ZnO), wurtzite (hexagonal ZnS) and sphalerite (cubic ZnS). Clear EXAFS oscillations were observed for K-T boundary clays. For local structure analysis, we carried out the parameter fitting with an analytical EXAFS formula expressed by a cumulant expansion up to third order term. The observed XANES patterns can be classified in three large categories. The threshold E_0 energies of oxide groups shift to higher energy compared with those of sulfide group. In the K-T boundary clays, the E_0 energy of Zn agrees well with the values of Zn^{2+} oxide minerals. Additionally, these XANES pattern are characterized by sharp white line peaks. XANES pattern for the K-T boundary clay is similar to those for willemite and adamite. In the K-T boundary clay, zinc occupies the ZnO_4 tetrahedral sites. The obtained Zn-O first nearest neighbor distance of 1.953(3)Å is in agreement with that of willemite (1.990(5)Å) and zincite (1.969(8)Å).

Poster no. PS2.80 - Session 2**Investigation the bark diseases in *Havea brasillensis* using X-ray absorption spectroscopy**

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The X-ray absorption spectroscopy (XAS) technique was used to determine the chemical change of elements induced by bark diseases in *Havea brasillensis* (rubber latex tree). The results show the good sensitivity of XAS to characterize the chemical structure of phosphorus, sulfur, potassium and calcium in healthy and diseased *Havea brasillensis*. The important information for understanding the bark disease involved in sulfur metabolism of plants also was obtained from XAS.

[1] A. Prange, R. Chauvistré, H. Modrow, J. Hormes, H. G. Trüper, and C. Dahl, *Microbiology* 148, 267 (2002).

[2] A. Prange, E. C. Oerke, U. Steiner, C. M. Bianchetti, J. Hormes, and H. Modrow, *J. Phytopathology* 153, 627 (2005).

Poster no. PS2.81 - Session 2**The study of heavy metals removal in wastewater from handcrafted silverware manufacture by natural zeolites**

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The consideration eliminated heavy metal from wastewater to focus attention on identifying efficiency low-cost absorbents and excellent adsorption capacities for various heavy metals. The natural zeolites were applied to remove heavy metal ions from sample aqueous solution, in wastewater from handcrafted silverware manufacture. Many kind of toxic heavy metals such as Cr, Pb, Cu, Zn, Ag, Ni, and S were released from the handcrafted silverware manufacture and become water pollution. These metal ions in wastewater were measured using X-ray fluorescence (XRF) before and after treatment by natural zeolite. The atomic and molecular-level structures of heavy metals absorbed by zeolite were investigated using X-ray adsorption spectroscopy (XAS). Consequently, the natural zeolite is successfully applicable for the removal some heavy metals of wastewater from metal manufacturing. This application would significantly reduce the cost of wastewater treatment with environmentally friendly process.

[1] P. Catalfamo, I. Arrigo, P. Primerano, F. Corigliano, *Journal of hazardous materials* 134, 140 (2006).

Poster no. PS2.82 - Session 2**Elemental transport processes in the upper crust: results from combined spatially resolved XRF, in-situ XANES and Raman spectroscopy on natural fluid inclusion assemblages in miarolitic quartz from the Torres del Paine granite complex**Karen Rickers¹, Volker Lüders², and Jean Cauzid^{3,4}

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Fluid inclusions in minerals can record the chemical composition of fluids causing mineral formation during geological processes. Fluid phase separation can be the principle cause for major variations in fluid composition in many hydrothermal systems. Such variations commonly lead to extreme enrichments of important metals and to the formation of ore deposits. The process of element partitioning is closely linked to the speciation of the element in the different phases. The goal of this study is to characterize ore-forming hydrothermal systems in the upper crust. We have investigated liquid-vapour fluid inclusion assemblages formed by subcritical phase separation in a granitic system because this geological setting is often linked to Cu and Mo ore deposits. The fluids studied here occur as fluid inclusion boiling assemblages hosted in quartz from miarolitic cavities of the barren Torres del Paine granite complex (Chile). Micro-XRF analysis was applied to coexisting fluid and vapour inclusions in order to unravel elemental partitioning during phase separation. It could be shown that Cu and Mo may partition into the vapour phase. Temperature-dependant micro-fluorescence XANES experiments on key elements in fluid and vapour inclusions at temperatures up to 460 °C revealed distinct behaviour for Zn and Cu. While no temperature-dependant speciation changes were observed for Zn, there is strong difference in partitioning of Cu between liquid and vapour. The results of micro-XRF (beamline L, HASYLAB, ID18F & ID22, ESRF) and micro-XANES (ID22, ESRF) in fluid inclusions were complemented by Raman spectroscopy, for additional information on possible ligands for the transport of elements. The results show that differences in elemental speciation may be the driving force for element partitioning during subcritical phase separation and demonstrate the importance of phase separation processes for formation of ore deposit.

Poster no. PS2.83 - Session 2**Structural changes under beta irradiation in an iron-bearing soda lime glass system**Stéphanie Rossano^{1,2}, L. Jean-Soro², B. Boizot¹, F. Farges³, E. Van Hullebusch², J. Labanowski⁴, L. Gouzin¹, J. Linares⁵, J. Grattage⁶, and M. Harfouche⁷

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(6) European Synchrotron Radiation Facility (ESRF) Grenoble Cedex, France

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Ionizing irradiation is known to modify the structure of oxide glasses by inducing a migration of alkalis. This migration induces a decrease of the average Si-O-Si angle, an increase of glass polymerization and the production of molecular O₂. The alkali migration is however decreased when iron is added to the glass composition, due to its multivalent character. In this work, effects of ionizing irradiation on soda lime glasses containing a variable amount of iron are studied as a function of the integrated dose with a multi spectroscopic approach. Environment changes around Fe³⁺ and Fe²⁺ ions are determined with Electron Paramagnetic Resonance (Fe³⁺), Optical absorption spectroscopy (Fe²⁺), Mössbauer spectroscopy and X-ray absorption spectroscopy (XANES and EXAFS). In order to propose quantitative mechanisms the variations in the Fe³⁺/Fe²⁺ ratio as the function of integrated dose has been determined using Mössbauer measurements, chemical methods (ICPMS and colorimetry) and X-ray absorption spectroscopy (pre-edge analysis). While changes on EPR spectra are important as a function of the irradiation dose, Mössbauer and UV-vis spectroscopies do not show significant modifications in the iron ions distribution. The use of complementary methods allowed us to study a large range of glass compositions (from 0.5 to 3 wt% Fe₂O₃) and of irradiation dose. In particular, X-ray absorption spectroscopy allowed the study of small irradiated and diluted samples that cannot be analyzed by the other techniques. First results confirm that a part of the ferric iron is reduced by ionizing irradiation. This reduction is however not sufficient to explain the variation of EPR spectra.

Poster no. PS2.84 - Session 2**Sulfur *K*-edge XANES spectroscopy as a tool for understanding sulfur chemical state in anaerobic granular biofilms**

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When treating sulfate containing wastewaters in full scale up-flow anaerobic sludge bed bioreactors, microbial activity forms residues consisting of a complex mixture of biofilms (also named "granular sludge") and undefined "toxic" inorganic species. These residues contain, among others, iron sulfides. However, highly toxic trace elements (such as Se, Co and Ni) that are contained in these wastewaters appear to show high affinity to iron sulfide precipitates. Hence, *mu*-XRF/XANES experiments are required to better characterize the speciation of S in these biofilms, esp. its "redox states" at the *K*-edge, in order to investigate the fundamental mechanisms involved in sulfate anion assimilation/dissimilation in anaerobic biofilms.

mu-XRF combined with S *K*-edge *mu*-XANES experiments were conducted at the Swiss Light Source (operating at 2.4 GeV and 400 mA injection) on the LUCIA beamline. In addition to the sludges, a large variety of model compounds of S (esp. sulfides) was investigated to find consistencies in the XANES that were used to model each "valence state" of S. Si(111) double crystal monochromators were used as well as K-B mirrors to focus the X-ray beam down to $5 \times 5 \text{ } \mu\text{m}^2$. A Si-drift detector collected the S-*K_{alpha}* fluorescence as a function of incoming energy. The flux on the sample is *sim* 2.1011 ph/s/330mA at 3.6 keV.

The results confirmed that attributing a specific valence to most sulfides is impossible as we measured a continuum of edge shifts from sulfur "–II" to "–I", depending on the electronic structure of S in the probed sulfides. In the sludges, various sulfur hot spots were probed for speciation, despite photo-reduction was sometimes a problem. First, we index the main features of a complex *K*-edge XANES spectra for S(–II) units, S–S bonds, sulfite and sulfate units. Organic sulfur compounds were also shown to contribute significantly to the sulfur species present in the biofilms.

Poster no. PS2.85 - Session 2**Speciation of heavy metals in solidified/stabilized wasteforms**Amitava Roy^{1,2}, Julia Stegemann³, Gregory Merchan², and Qizhi Zhou³*(1) Louisiana State University 6980 Jefferson Highway 70806 Baton Rouge Louisiana USA**(2) J. Bennett Johnsohn, Sr., Center for Advanced Microstructures and Devices, 6980 Jefferson Highway 70806 Baton Rouge Louisiana USA**(3) Julia Stegemann, Department of Civil, Environmental & Geomatic Engineering, University College London, GM-15, Chadwick Building, Gower Street, London WC1E 6BT, UK*

Treatment by solidification/stabilization with cement-based binders is an option for wastes that cannot be prevented or reduced, such as metal treatment sludges from a variety of industries. It is very important that the actual metal species in these sludges be known as the leaching of the metals in ground water, once buried, will depend on the solubility of these species. It will also be of interest to correlate speciation with other engineering properties.

Metal treatment sludges were obtained from three industrial sources. These contained as high as tens of thousands of parts per million of chromium, copper, nickel and zinc. The sludges were mixed with different proportions of portland cement, ground granulated blastfurnace slag, calcium hydroxide (lime), and fly ash to produce solidified/stabilized waste forms.

Even with high metal concentrations in the sludges, X-ray diffractometry showed no trace of any heavy metal crystalline phases. One of the dried wastes appeared very poorly crystalline with minor amounts of calcite and quartz, while others had patterns dominated by calcite.

The K edges of nickel, chromium, zinc and copper were analyzed by X-ray absorption near edge structure (XANES) in the sludge, dried sludge (filter cake), cementitious materials and waste forms, where the waste was incorporated in cementitious matrices.

For the same metal, the speciation was usually very similar in different waste sludges. Chromium XANES showed that the chromium remained in the trivalent form, before and after treatment, confirming leaching tests. For the nickel in the sludge and the waste forms, there is a good match with nickel hydroxide whereas for zinc, the match is good with the double salt zinc carbonate-zinc hydroxide. In general, the speciation of the heavy metals remained unaltered during the treatment process. Among the solidified/stabilized waste forms, the speciation showed differences depending on the composition of the matrix.

Poster no. PS2.86 - Session 2**EXAFS characterization of the structure and stoichiometry of lanthanide-carbonate complexes in aqueous solution**Michel L. Schlegel^{1,2}, V. Philippini³, B. Siboulet⁴, P. Vitorge^{1,2}, and Th. Vercouter¹*(1) CEA, DEN DANS/DPC, F-91191 Gif-sur-Yvette, France**(2) University of Evry, LAMBE, F-91025 Evry, France**(3) University of Nice, LRSAE, F-06108 Nice, France**(4) CEA, DEN, DRCP, F-30207 Bagnols-sur-Cèze, France*

Trivalent actinides (An) and lanthanides (Ln) are present in high level nuclear waste. Migration of these elements in natural systems is controlled in part by complexation with solutions ligands such as (bi)carbonate, a ubiquitous complexant in clay rocks. Thus, correct prediction of Ln (and An) fate in the environment hinges on an accurate description of the molecular structure and stoichiometry of solution complexes between Ln (An) and carbonate.

Solutions of Nd and Lu carbonate freshly prepared by mixing 1 M Na₂CO₃ or K₂CO₃ and an aliquot of Ln stock solutions were filtered and loaded in polycarbonate cells fitted with Mylar windows. EXAFS spectra were recorded in fluorescence detection mode on the INE beamline (ANKA, Karlsruhe). EXAFS data were reduced, and analyzed using standard procedures. Multiple scattering (MS) analyses were performed using FEFF8.

EXAFS data all display a major oscillation typical of Ln coordination by oxygens. Data analysis confirmed the presence of one O shell at 2.50(2) (Nd) or 2.32(2) Å (Lu). These distances compare well with the respective Ln-O distances of the first coordination sphere in pure water. Beyond the first O shell, a second significant FT peak was observed near 3.5 (Lu) to 3.7 Å (Nd). This peak is absent in pure aqueous solutions, and it results from backscattering atoms of carbonate groups coordinated to Ln. Data modelling showed that this peak could be explained only by MS focusing effects between Ln, C and distal O atoms from the carbonate group. Quantitative fitting for Lu yielded 5 C and 5 distal O at 2.75 and 3.95 Å, respectively. The distances are consistent with the formation of bidentate ligands between Lu and carbonate groups, with Ln, C, and distal O aligned. The number of neighboring C and distal O is likely overestimated, due to cumulated uncertainties on the amplitudes of MS paths, yet it clearly points to a number of carbonate groups coordinated to Ln of three or more.

Poster no. PS2.87 - Session 2**Mg structural environment study in silicate glasses by X-ray absorption spectroscopy**Nicolas Trcera^{1,2}, Stéphanie Rossano², Delphine Cabaret³ and Karim Madjer²(1) *Synchrotron Soleil - Saint-Aubin - BP 48 91192 GIF-SUR-YVETTE Cedex, France*(2) *Université Paris-Est, Laboratoire Géomatériaux et Géologie de l'Ingénieur (G2I), EA 4119, 5 bd Descartes 77454 Marne la Vallée Cedex 2, France*(3) *IMPMC, UMR7590, Universités Paris 6 et 7, CNRS, IPGP, Campus de Boucicaut, 140 rue de Lourmel, 75015 Paris, France*

The magnesium is an important alkali-earth in silicate oxide glasses (from a few wt% to around 10 wt% in industrial glasses and up to 30 wt% in natural primitive glasses such as komatiite). Its presence influences largely the glass properties as well as its durability, melting point and seems to play an important role in glass alteration. The link between the physico-chemical properties and the structure is however difficult to make as previous results on Mg environment are still controversial. While NMR studies described the magnesium environment as tetrahedral or octahedral, neutron spectroscopy and X-ray diffraction measurements proposed that magnesium is 5-fold coordinated to oxygen. To help raising these controversies, we have investigated the local environment of the magnesium in magnesio-silicate glasses by using X-ray absorption spectroscopy at the Mg K-edge in simple systems $X_2O-MgO-\alpha SiO_2$ (where X stands for Li, Na, K, Rb and Cs and where α represents the number of silicon oxide) and in more complex glasses. Because it is not straightforward to extract relevant information from glass spectra by a simple comparison with crystalline compounds, we have used *ab initio* XANES calculations based on the reciprocal-space non muffin-tin plane-wave method for glasses of composition KMS2 and KMS3. The XANES calculations have been performed starting from structural models that have been obtained by classical molecular dynamics and relaxed by *ab initio* force calculation. The plausibility of the models has been checked by Bond Valence Calculations. The combination of experiments, Molecular Dynamics and XANES calculations have allowed to prove that magnesium is 4-fold coordinated in K-bearing glasses. By comparison with these calculations, the Mg coordination number in various glass compositions can be estimated.

Actinides**Poster no. PS2.88 - Session 2****XANES-derived Sm 4f level parameters in mixed-valent $Sm_{1-x}Y_xS$** Roman V. Chernikov¹, A.P. Menushenkov¹, P.A. Alexeev², V.V. Sidorov¹, and K.V. Klementiev³(1) *Moscow Engineering Physics Institute (State University), Kashirskoe shosse 31, 115409 Moscow, Russia*(2) *Russian Research Center Kurchatov Institute, Kurchatov Sq. 1, 123182 Moscow, Russia*(3) *ALBA-CELLS, 08193 Bellaterra, Barcelona, Spain*

The reasons of occurrence and stabilization of the intermediate valence state in strongly correlated electronic systems such as samarium chalcogenide are still under discussion. Investigation of electronic structure peculiarities can shed light on this question but due to considerable hybridization of samarium 4f-5d levels common methods of electronic structure analysis often give contradictory results. In these conditions direct electronic structure probes based on X-Ray absorption spectroscopy have proved their high efficiency.

We used XANES spectroscopy to determine the parameters of local electronic structure in the mixed-valent yttrium doped $Sm_{1-x}Y_xS$ ($x=0.17, 0.25, 0.33, 0.45$). Temperature dependence of samarium valence was measured in 20-300 K temperature range. Assuming that changes of valence are caused by broadening and shift of the Sm 4f electronic level we have proposed a model that allows to estimate its half-width Γ_f and position $\Delta E=E_F-E_0$. Our calculations show that doping with yttrium leads to the shift of ΔE from 0.12 in $Sm_{0.83}Y_{0.17}S$ to -0.01 in $Sm_{0.55}Y_{0.45}S$. At the same time the least half-width is obtained in $Sm_{0.67}Y_{0.33}S$ that we suppose to be connected with the highest degree of local atomic structure ordering observed in EXAFS experiment.

This work was supported by RFBR grant 08-02-00759a.

Poster no. PS2.89 - Session 2**Investigating the metal-ligand bond in actinide complexes**Clara Fillaux¹, Dominique Guillaumont¹, Jean-Claude Berthet², and Christophe Den Auwer¹

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Understanding the structure and bonding in actinide compounds, from lower to higher oxidation states, can provide fundamental information which is essential for the development of selective extractants for waste management in advanced nuclear fuel cycles. This contribution will describe attempts to characterize the bonding in model actinide complexes through soft x-ray absorption spectroscopy and quantum chemistry calculations. Quantum chemistry and x-ray absorption spectroscopy are two of the few techniques which can potentially probe metal-ligand bonds by giving information about the electronic structure of the complexes.

We are interested in the fundamental understanding of submolecular interactions where the actinide cations are involved in ionic to covalent bonding. In particular, we want to determine the electronic configuration of the atoms by combining experiment and theory. A previous work showed that a coupling between simulations of the experimental spectra and quantum chemical calculations is very fruitful, in order to improve the model describing the final states and better understand the bonding properties of the cation with the ligand.

Hence, we have examined the metal-ligand bond in uranium compounds with various oxidation number. XANES spectra have been recorded both at the uranium L₃ edge and the ligand K edge. The quantum chemistry calculations were used to simulate the experimental XANES spectra and to help its interpretation. From these results, we will discuss the evolution of the metal-ligand bond in the model complexes.

Poster no. PS2.90 - Session 2**Free and silica-gel bound tetraazamacrocycles as complexing agents of actinide cations: a xafs investigation of the solid-state coordination scheme**Lisa Giachini¹, Sébastien Faure², Michel Meyer³, Lé Vi Nguyen^{2,3}, Béatrice Batifol², Hervé Chollet², Roger Guillard³, Christoph Hennig⁴, and Andreas C. Scheinost⁴

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There is a continuous need for processes aimed at the selective uptake of toxic metal ions from dilute wastewaters and industrial process streams. Insofar, solid-liquid extraction processes using chelating agents grafted onto hydrophilic supports are appealing. The Institut de Chimie Moléculaire de l'Université de Bourgogne has designed a series of hybrid organic-inorganic materials for the selective uptake of toxic metal ions, including actinides[1]. These extracting agents are obtained by grafting functionalized tetraazamacrocyclic ligands (cyclen and cyclam derivatives) on the surface of silica-gel beads. In collaboration with the Commissariat à l'Energie Atomique (CEA Center of Valduc), one of these modified gel has been prepared on a semi-industrial scale and used in the final decontamination step of real effluents for removing the residual α -emitters (U, Pu, Am) contained at the sub- $\mu\text{g/L}$ level. This process allowed the successful decontamination of more than 50 m³ wastewaters, with a residual radioactivity level of less than 5 Bq/m³.

We have used XAFS to investigate the coordination scheme of UO₂²⁺ and Pu⁴⁺ cations at the surface of the organic-inorganic hybrid materials. The results show that surface complexes are formed through a combined action between the reactive solid support, namely amorphous silica, and the chelating groups appended on the immobilized ligands[2].

[1] F. Barbette et al., Anal. Chim. Acta 502, 179-187 (2004).

[2] L. Giachini et al., Proceedings of the 5th Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinide XAS 2008), in press.

Poster no. PS2.91 - Session 2**XAFS and HRXES investigations of lanthanide complexes from both the ligand and the metal point of view**Matthias Loeble^{1,2}, Tonya Vitova¹, Melissa A. Denecke¹, and Frank Breher²*(1) Forschungszentrum Karlsruhe, Institut fuer Nukleare Entsorgung, Hermann-von-Helmholtz-Platz 1, 76344 Leopoldshafen, Germany**(2) Universitaet Karlsruhe (TH), Institut fuer Anorganische Chemie, Engesserstrasse 15, 76131 Karlsruhe, Germany*

The separation of actinides from lanthanides is a key step in the partitioning&transmutation strategy for reduction of the radiotoxicity of high-level nuclear waste[1]. To understand the selectivity of existing N-donor ligands for actinide cations over the chemically similar lanthanides, knowledge of electronic structure and bonding between cation and ligand, as well as of the influence of counter anions on the interaction is of crucial importance.

Therefore we have synthesized several tripodal ligands[2] with PS and PO functionalities in their apex. We use XAFS (X-ray absorption fine structure) spectroscopy and HRXES (high resolution X-ray emission spectroscopy) to obtain information on the electronic and structural properties of 3d and 4f metal complexes of these ligands. Studies upon excitation of both, the ligand molecule and the central metal cations are performed, in an effort to gain information from the metal and the ligand point of view.

We present P and S-K edge XANES (X-ray absorption near edge structure) spectra of the ligands and their complex compounds, results of Ln L alpha, L beta HRXES and RIXS (resonant inelastic X-ray scattering) measurements, showing that the cation significantly alters the ligand electronic structure. Complexes of the lanthanide 4f series are characterized by Ln-L3 EXAFS in acetonitrile solution and in solid state. Differences in the coordination environment surrounding the metal cation are observed.

These investigations will be complemented by simulations with the Density Functional Theory based StoBe software package[3], investigations of corresponding 5f complexes and separation/extraction studies in the near future.

[1] A. Geist, K. Gompper, M. Weigl, T. Fanghaenel, Nachrichten – Forschungszentrum Karlsruhe 2004, 36, 97.

[2] I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster, F. Breher, Dalton Trans. 2008, 5836.

[3] StoBe-deMon version 2.1, K. Hermann, L.G.M. Pettersson et al., StoBe Software, 2005.

Poster no. PS2.92 - Session 2**Further study on the evolution of chemical species during electrodeposition of uranium for alpha spectrometry**Maria Elena Montero Cabrera¹, C. G. Méndez¹, D. C. Burciaga-Valencia¹, H. Esparza-Ponce¹, A.M. Beesley², M.E. Fuentes³, M. Rentería-Villalobos¹, A. Reyes-Rojas¹, and L. Fuentes¹*(1) Centro de Investigación en Materiales Avanzados Miguel de Cervantes 120, Complejo Ind. Chihuahua 31109 Chihuahua Chihuahua Mexico**(2) School of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester, M60 1QD, United Kingdom**(3) Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus, Chihuahua, Chih., Mexico*

Alpha spectrometry (AS) has applications in nuclear decay data measurements, environmental, geological and nuclear wastes studies and other works requiring determination of actinide contents. AS sources must be thin and uniform, producing small FWHM to obtain accurate measurements. AS sources produced by electrodeposition consist of a radioactive deposit onto a metallic substrate (cathode of the electrolytic cell). Natural U sources prepared by the Hallstadius method have co-deposited Pt, originated from the dissolution of the anode during the electrodeposition. Sources obtained from natural U hold a large element mass while short half-life-isotopes present scarce mass input that could be practically buried under Pt. Recently [1] have reported a study on the morphology and spatial distribution of the U/Pt deposits with the related chemical speciation of U, using SEM/EDX, XPS and XAFS.

The purpose of this work is to better understand how Pt and U are deposited. Sources have about 5 U atoms/nm. We have obtained new spectra of the U LIII edge XAFS by total electron yield at the beamline 2-3 of the SSRL. Grazing incidence (GI) XRD patterns were obtained at a XPERT-Pro Panalytical diffractometer with Cu K alpha radiation. SEM/EDX and AS studies of the sources were performed for control and correlations. GI-XRD patterns show uniform crystal orientation of Pt, with grains ~ 4 nm; uranyl hydroxide diffraction signals suggest 001 texture of ~ 1 nm grains, i.e. with low crystallization. White line shifts in the XANES spectra indicate different oxidation states of U species in the sources. EXAFS spectra are fitted using Uax-O, U-Oeq, U-H, U-Odis and U-U backscattering paths of uranyl hydroxide. U-Oax-U-Oax-U MS path is included in the fit. U-U path shows low intensity that also may be a result of low crystallization. Uranyl hydroxide fit confirms the Hansen theory about actinide electrodeposition.

[1] A M Beesley et al doi:10.1016/j.apradiso.2009.03.031

Poster no. PS2.93 - Session 2**Analysis of the uranium L3-edge x-ray absorption spectra of some actinides**Galina Borisovna Sukharina¹, Alexander V. Soldatov¹, Olga Batuk², and Melissa A. Denecke³*(1) Southern Federal University, Sorge 5, 344090 Rostov-on-Don, Russia**(2) Moscow State University, Moscow, Russia**(3) Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, Postfach 3640, D-76021 Karlsruhe, Germany*

Recently, great scientific interest stems from suggested use of depleted uranium oxides as engineered barriers in nuclear waste repositories in cases where criticality concerns play a role. This aspect demand detailed investigation of such materials' chemistry, including solubility, sorptive capacity for different radionuclides, ability to form colloidal particles and other related processes.

Schoepite $(\text{UO}_2)_4\text{O}(\text{OH})_6(\text{H}_2\text{O})_6$ and metaschoepite $(\text{UO}_2)_4\text{O}(\text{OH})_6(\text{H}_2\text{O})_5$ are uranium containing minerals, which have been shown to be repository relevant secondary phases in both laboratory experiments and studies of aged SNF. Theoretical simulation of U L3-edge XANES spectra for schoepite and metaschoepite have been carried out by full multiple scattering in real space and finite differences method using programs FEFF8.4 [1] and FDMNES2008 [2]. Our aim is to advance our understanding of bonding and electronic structure in these compounds, which are important factors determining their chemical behavior, as well as to optimize the amount of extractable information from the XANES. In this way we can improve the detection limit of the x-ray absorption method, as the XANES region is more sensitive than the EXAFS regime. We have studied the influence of non-muffin-tin effects on the shape of theoretical U L3 XANES spectra. Results are compared to experimental data measured at the INE-Beamline for actinide research at the synchrotron center ANKA (Karlsruhe, Germany). We also investigate the electronic structure of schoepite. The calculation of uranium partial density of electron state has been accomplished under the top valence band and bottom of conduction band.

[1] A.L. Ankudinov, A.I. Nesvizhskii and J.J. Rehr, Phys. Rev. B 67, 115120 (2003).

[2] Y. Joly, Phys. Rev. B 63, 125120-125129 (2001).

Poster no. PS2.94 - Session 2**High resolution x-ray emission spectroscopy: an advanced tool for actinide research**Tonya Vitova¹, Frank Breher², Boris Brendebach¹, Kathy Dardenne¹, Melissa A. Denecke¹, Alla Lebid¹, Matthias Löble^{1,2}, and Jörg Rothe¹*(1) Forschungszentrum Karlsruhe (FZK), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, D-76021 Karlsruhe, Germany**(2) Universität Karlsruhe (TH), Institut für Anorganische Chemie, Engesserstr. 15, D-76131 Karlsruhe, Germany*

High resolution X-ray emission spectroscopy (HRXES) is becoming increasingly important for our understanding of electronic and coordination structures. Through combination of such information with development of quantum theoretical tools, we can one day hopefully predict reactivity and physical behavior especially of 5f elements. HRXES can be used to remove lifetime broadening by registering the partial fluorescence yield emitted by the sample (i.e., recording a windowed signal from the energy dispersed fluorescence emission while varying incident photon energy), thereby yielding highly resolved X-ray absorption fine structure (XAFS) spectra, which often display resonant features not observed in conventional XAFS. The spectrometer set-up can also be used for a wide range of other experiments, for example, resonant inelastic X-ray scattering (RIXS), which can be used to obtain bulk electron configuration information, in solids, liquids and gases.

A HRXES spectrometer is presently being constructed and commissioned. It will ultimately be made available for use at the INE-Beamline for actinide research at the synchrotron source ANKA at FZK. We present the spectrometer compact, modular design, optimized for attaining a wide range of energies [1]. First measurements of actinides complexed with partitioning ligands both in solid state and in solution will be shown. Results from HRXES studies of their lanthanide counter parts, as well as polarized dependent characterization of a single crystal uranyl system, will be presented too.

[1] The design is based on that originally built by National instruments of standards and technology (NIST): Brennan S, Cowan PL, Deslattes RD, Henins A, Linde DW, (1989) Rev. Sci. Instrum. 60, 2243.

Catalysis

Poster no. PS2.95 - Session 2**EXAFS investigation of Pd metal particles on active carbons, Al₂O₃, and polymers high surface area supports**

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Pd supported on carbons (Pd/C), and Al₂O₃ (Pd/A) are among the most widely used catalysts in highly selective hydrogenation reactions for the synthesis of both fine chemicals (e.g. active pharmaceutical ingredients) and bulk chemicals (e.g. terephthalic acid). Their activity and selectivity toward different molecules is strongly related to the morphology and dispersion of the metal active phase and to its electrostatic interaction with the support. Morphology and dispersion of Pd clusters are strongly dependent on the preparation method, and can be modified acting on different factors, such as: Pd-precursor, support, temperature and pH of the impregnating solution, precipitating agent, reducing agent and method, etc. The investigation of the relationships existing between these variables and the resulting system is consequently the base of a rational construction of more efficient and selective catalysts.

We investigate, by means of in-situ Pd K-edge EXAFS (collected at ESRF, BM26A), TPR, TEM all the steps related with the preparation of Pd/C and Pd/A catalysts, starting from the Pd²⁺ precursor precipitation from solution, through the partial reduction from the basic support, to the chemical reduction from the liquid phase. In all the steps, the samples have been measured in their wet conditions, in order to be as close as possible to the catalysts inserted into the industrial reactor. These results complement those obtained by conventional techniques, investigating the catalysts in dried conditions. For comparison, also a set of Pd/Al₂O₃, and of Pd/polymers samples have been investigated.

The determination from EXAFS data of the fraction of metal Pd in partially reduced samples is critical as the first shell Pd-Pd intensity depends also on the particle dimension. EXAFS data must consequently be supported by TEM XANES and TPR results. This point will be deeply discussed.

Poster no. PS2.96 - Session 2**XAS study on the gold particle size of Au catalysts**

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Supported gold catalysts are very active in catalyzing many types of reactions. Gold particles smaller than 5 nm, in addition to low chlorine residue, are considered essential for the high activity[1]. The support is also reported to play an important role in hydrogenation reactions[2] although this role might be dependent on the reagent, being for some reactions practically negligible. This role can be the one providing a source of hydrogen to the metal sites, or interacting with gold to produce more selective electron-rich gold particles.

This work proposes the XAFS study of gold catalysts prepared using γ -Al₂O₃ as a support. Iron acetyl acetonate, Fe(C₅H₇O₂)₃, was used to surface-functionalize the support in a direct method. The solid was calcinated in order to eliminate the remanent ligands and to form superficial species that we named Fe_xO_y, probably formed by hematite supported on the γ -Al₂O₃. Gold particles were fixed following the direct anionic exchange(DAE) method[3] from HAuCl₄ aqueous solutions at pH 5.

XANES spectra of the modified support and the corresponding gold catalyst were analyzed. At the Fe K-edge, the first prominent signal of both samples appears at 7133.4 eV, and the energy position coincides with that of the Fe⁺³ reference (Fe₂O₃), confirming that Fe is present in its trivalent state. At the Au L_{III}-edge, the catalyst signal appears at 11923 eV, coincident with the Au⁰ profile. Two resonant features, at +21 and +45 eV, above the white line can also be observed, probably associated with isolated and polymeric Au⁺³(OH)₃ species. EXAFS data about Au and Fe atomic distances are also presented and discussed.

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[3] S. Ivanova, C. Petit, V. Pitchon, Appl. Catal. A. 267, 191 (2004)

Poster no. PS2.97 - Session 2**Investigation on the reaction mechanism of C-C coupling mediated by Ni catalyst with in-situ time-resolved XAFS**Hiroyuki Asakura¹, Tetsuya Shishido¹, Kentaro Teramura², and Tsunehiro Tanaka¹*(1) Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan**(2) Kyoto University Pioneering Research Unit for Next Generation, Kyoto University, Kyoto 615-8510, Japan*

We attempted to elucidate the intermediates and reaction mechanism of the C-C homocoupling reaction of aryl halides mediated by the nickel complex Ni(BPY)(COD) (BPY = 2,2'-bipyridine ; COD = 1,5-cyclooctadiene) by means of the in situ time-resolved XAFS spectra and multivariable analysis.

Ni(BPY)(COD) was prepared by injecting BPY/THF solution to a quartz cell containing Ni(COD)₂ with BN windows. Then, 2 eq of chloropentafluorobenzene (^FPhCl) was added to the solution at 323 K and in situ time-resolved XAFS measurements of this reaction solution were performed for 2 hours in the in situ cell holder with the variable temperature controller (Unisoku Co.). In situ Quick XAFS spectra at the Ni K-edge were measured at SPring-8 BL01B1, JASRI, Japan.

In the Ni K-edge XANES spectra, the fast growth of pre-edge peak at 8338 eV was observed immediately after the addition of substrate and then an isosbestic point was obtained for the first 30 minutes and another isosbestic point was obtained for the following 90 minutes. The first change and the existence of two isosbestic points indicate that the reaction consisted of three main steps. The first step is assigned to the oxidative addition of ^FPhCl to the Ni complex. The decay of pre-edge peak at 8338 eV and the growth of white line in the second and third steps suggest that the formation of moderately higher symmetric nickel complexes like Ni(BPY)^FPh₂ and Ni(BPY)Cl₂ by the transmetalation of two Ni(BPY)^FPhCl. To extract each XAFS spectrum of the intermediates like Ni(BPY)^FPhCl of the catalytic reaction, factor analysis was performed to the latter two steps XANES and EXAFS spectra. The structural parameters of the intermediates obtained by a curve fitting for Fourier transform of the extracted spectra are consistent to the proposed intermediates in previous report[1].

[1] T. Yamamoto, S. Wakabayashi, and K. Osakada. J. Organomet. Chem., 428, 223 (1992).

Poster no. PS2.98 - Session 2**Three-dimensional spectroscopy of homogeneous catalytic reactions**Matthias Bauer¹, Stefan Mangold², Benjamin Marchetti¹, and Helmut Bertagnolli¹*(1) Institut für Physikalische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany**(2) Forschungszentrum Karlsruhe GmbH, Institute for Synchrotron Radiation, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*

Multi-dimensional spectroscopy is gaining increasing importance for operando studies of catalytic reactions. However the combination of X-ray absorption spectroscopy with other methods like UV/Vis, Raman and IR [1] in order to study homogeneous catalytic reactions is found rarely [2]. With this contribution, a novel set-up for three-dimensional spectroscopic studies of homogeneous catalytic reactions under realistic laboratory conditions is presented.

The operando set-up that combines XAS, Raman and UV/Vis spectroscopy, allows measurements under defined atmosphere, and different agents can be added in course of the measurements [3].

As a model system, the Cerium-catalyzed hydroxylation of diketons [4] with molecular oxygen was studied. QEXAFS measurements were performed with a time window of 45 seconds per spectrum. The simultaneous registration of dispersive UV/Vis and Raman spectra within a time scale of a few milliseconds allows to monitor possible spectral changes and to gain deeper insights into the reaction. The acquisition of three independent spectra allows the determination of mechanistic details of the hydroxylation reaction. Moreover, Raman spectroscopy delivers information about possible changes in the vibration modes of the ligands.

It will be shown, that three-dimensional spectroscopy can be used to determine the different kinetics of the used diketons and to explain the distinct reactivities by different reaction mechanisms.

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Poster no. PS2.99 - Session 2
EXAFS spectra simulations of catalyst nanoparticles

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Precious metal nanoparticles comprise the active component of a number of supported catalysts. In order to understand the origin of their activity it is necessary to determine their size, shape and extent of interaction with the support. Due to their being small, they are often difficult to characterize. Microscopic techniques such as transmission electron microscopy (TEM) represent the most appropriate technique(s) by which to do so, although it is difficult to obtain a true representation of the sample and can cause sample damage. An alternative technique therefore to characterize these samples is XAFS; a bulk sampling technique which can also be employed to study samples under a range of in situ conditions. To date a number of attempts have been made to determine/predict the influence that the nanoparticle shape/size has on the EXAFS spectra; mainly how these influence the intensity of the peaks of the FT radial distribution function. Whilst useful, such models don't take into account the damping effects on the EXAFS signal amplitude; namely the $1/r^2$ decay of the signal, static and thermal disorder and multiple scattering. This renders previous models limited in their application to real systems. With the advent of reliable theoretical models for simulating EXAFS data we have determined (using the Debye-Waller parameters and multiple scattering contributions from Pt, Au, Ni, Rh and Fe reference foils) theoretical EXAFS spectra for a number of regular stable cluster shapes, such as Spheres (also for a hypothetical hexagonal close packed and body-centred cubic structures), Cuboctahedra, Icosahedra, Half-Spheres and Cylinders. We illustrate the influence of various shapes and their size influences the resultant EXAFS spectra and for both monometallic and bimetallic systems.

Poster no. PS2.100 - Session 2

Promoted platinum catalysts with close contact between platinum and promoter for the selective hydrogenation of cinnamaldehyde

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Precision in catalyst preparation is essential to arrive at catalysts with well defined catalytic properties. A wealth of techniques such as impregnation, precipitation using bases and ion exchange have been applied with varying success. Here we will discuss the preparation of promoted Pt catalysts supported on carbon nanofibers by Reductive Deposition Precipitation (i.e., the deposition of the promoter on a hydrogen saturated metal surface) to achieve a close contact between promoter and the active metal phase. In this study we investigated the platinum-promoter interaction for RDP-prepared, platinum based CNF-supported, bimetallic catalysts using TEM-EDX, XPS and EXAFS. These results will be related to catalytic results using cinnamaldehyde hydrogenation as a showcase. For comparison a catalyst prepared by impregnation was included. To investigate the location and state of Sn in the different catalysts TEM/EDX, EXAFS hydrogen chemisorption and XPS studies were performed. TEM/EDX indicated that for the RDP prepared samples Sn was always in contact with Pt however the resolution was limited and information on an atomic scale could not be obtained. Therefore an EXAFS study was performed (see table 1). For RDP prepared samples a significant Sn-Pt (CN: 5) interaction was found which increased with increasing Sn loading. This Sn-Pt interaction absent in the sample prepared by IWI (CN: 1.6). When a close contact is ensured the activity of the catalysts was increased with a factor of 1.5 and the selectivity toward the desired cinnamylalcohol with a factor of 1.5-2 as compared to the mono metallic catalysts and IWI prepared catalysts. The enhancement of selectivity and activity for RDP prepared samples was also observed for Ga promoted samples thus indicating that this is a general trend for RDP prepared samples.

Poster no. PS2.101 - Session 2**Nanoscale chemical imaging of a catalyst at work using in situ Scanning Transmission X-ray Microscopy**Frank M. F. de Groot¹, E. de Smit¹, J. F. Creemer², H. W. Zandbergen³, and B. M. Weckhuysen¹*(1) Utrecht University Sorbonnelaan 16 3584 CA Utrecht, Netherlands**(2) DIMES-ECTM, Delft University of Technology, 2600 GB Delft, Netherlands**(3) Kavli Institute of NanoScience, Delft University of Technology, 2600 GA Delft, Netherlands.*

Scanning X-ray Transmission Microscopy (STXM), with its current 15 nm spatial resolution and its high chemical speciation potential by using X-ray Absorption Spectra, is an important addition to the field of in situ spectromicroscopy. The main experimental challenge is to overcome the strong attenuation of soft X-rays by the sample and in the gaseous atmospheres. In our studies, we have applied a specially designed nanoreactor [1] which reduced the gas path length to 50 micron. The nanoreactor was used to study the distribution and chemical identity of iron and carbon species in an Fe₂O₃-CuO-K₂O-SiO₂ catalyst during reduction in H₂ [2] and under Fischer-Tropsch Synthesis (FTS) at 523 K [3].

The STXM experiments were performed at beamline 11.0.2 of the ALS in Berkeley and beamline 10ID-1 at the CLS in Saskatoon. Studying the catalyst material during reduction treatment and FTS revealed 35 nm spatial variations in the iron valence and its metal/carbide/oxide nature. After reduction at 623 K, the catalyst material consisted of iron (II) silicates, iron oxide and small amounts of metallic Fe. Both sp² and sp³ hybridized carbon species were observed during FTS, where the sp² species were found near metallic Fe species, indicating the conversion of metallic Fe into iron carbides.

The STXM nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under realistic catalytic conditions opens up opportunities to study many chemical processes taking place on solids.

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[2] E. de Smit, I. Swart, J. F. Creemer, C. Karunakaran, D. Bertwistle, H. W. Zandbergen, F. M. F. de Groot, B. M. Weckhuysen Angew. Chem. 2009, early view.

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Poster no. PS2.102 - Session 2**Structure of catalytically active gold nanoparticles by XAFS spectroscopy**Simon Erenburg¹, Svetlana Trubina¹, Nikolai Bausk¹, Boris Moroz², Alexandr Kalinkin², Valerii Bukhtiyarov², and Sergei Nikitenko³*(1) Nikolaev Institute of Inorganic Chemistry SB RAS, Lavrentiev Ave.3, 630090 Novosibirsk, Russia**(2) Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave.5, 630090 Novosibirsk, Russia**(3) DUBBLE-CRG & ESRF, Grenoble, France*

The catalytic activity of the nanosized gold particles (in contrast to the bulk gold materials) is well established at present. The extraordinary activity of gold particles has been shown for the various catalytic processes such as CO oxidation. Determination of local structure peculiarities, identification of different electronic states in gold particles and their quantitative comparison with catalytic properties should help to identify electronic states of the supported gold which are more active for the catalytic reaction.

A series of Au/Al₂O₃ catalysts prepared by the different procedure and series of model system Au/Si(100), Au/Si(111) differing in the mean Au particle diameter (from 2 nm up to 30 nm) was studied by EXAFS and XANES techniques providing a unique possibility to determine local structural and electronic changes in systems with nanosized gold particles [1]. EXAFS spectra of the AuL_{III} - edges were measured at the VEPP-3 storage ring of the Budker INP (Novosibirsk) and at the DUBBLE beamline of the ESRF (Grenoble).

A gradual reduction of the Au-Au bond length and first shell Au-Au coordination number and an increase in the Debye-Waller factor are observed as the size of supported Au particles decreases. These variations in microstructural parameters of Au nanoparticles are in line with an increase in their catalytic activity in CO oxidation. Fitting the EXAFS spectra measured at low (12 K) temperature on the basis of the harmonic approximation may permit to detect the valuable changes of structural disorder for the smallest Au particles comparatively to the bulk Au metal. For model system some coordination of Au three-dimensional islands and Si- crystal surface was detected for more thin Au "films".

Financial support from the RFBR Program (grant 09-03-00561) is greatly appreciated.

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Poster no. PS2.103 - Session 2**Synthesis and characterization of platinum nanoparticles on single-walled carbon nanotubes**Anatoly I. Frenkel¹, Malka Bromberg¹, Zafar Iqbal², Anitha Pathlolla², Qi Wang¹, Rebecca Segal¹, and Isai Feldman³*(1) Yeshiva University 245 Lexington Avenue 10016 New York NY USA**(2) Department of Chemistry, New Jersey Institute of Technology, Newark, NJ 07102 USA**(3) Weizmann Institute of Science, Rehovot, Israel*

We studied different methods of depositing platinum nanoparticles on single-walled carbon nanotubes (SWNTs) that are potentially efficient electrocatalysts for hydrogen fuel cells. Commercially obtained SWNTs were characterized by Raman Spectroscopy, TEM, EDS, SEM and EXAFS. This multi-technique characterization allowed us to observe metal catalyst impurities (Mo, Co) in SWNTs indirectly (by Raman) and directly (by the other techniques), to choose the best method to remove them, and characterize quantitatively the efficiency of their removal. After purification, we formed a substrate for depositing Pt atoms by synthesizing a "nanopaper": a 10-20 micrometer thick free standing sheet of self-assembled SWNTs. Platinum was deposited onto the nanopaper by electroless deposition. Formation of Pt nanoparticles was verified by XANES and EXAFS. Future plans include investigations of catalytic activity of this system by combined cyclic voltammetry and in situ EXAFS.

Poster no. PS2.104 - Session 2**Study of electrocatalysts atomic structure for application in Proton Exchange Membrane Fuel Cells (PEMFC)**Giorgia Greco¹, A. Witkowska², Y. Soldo^{1,3}, M. Abbas¹, M. Ali¹, R. Gunnella¹, and A. Di Cicco¹*(1) Università di Camerino, via Madonna delle carceri, 62032 Camerino, Italia**(2) Department of Solid State Physics, Gdansk University of Technology, 80-952 Gdansk, Poland**(3) CNRS LEPMI, 1130 rue de la Piscine, 38402 St. Martin d'Hères, France*

The local structure and chemical disorder of a commercially available Pt₃Co nanocatalyst supported on high surface area carbon for proton exchange membrane fuel cells (PEMFC) were investigated. Detailed results of a multiple-scattering (MS) EXAFS double edge (Co *K* and Pt *L*₃) data-analysis of nanocrystalline Pt-Co alloy is presented. EXAFS results on a thin film of Pt-Co [1] has been used as a reference for reliable structural refinement of nanosized systems. Structural refinement of Pt-Co nanoparticles has been performed in combination with electron microscopy and x-ray diffraction, showing the importance of considering the actual size distribution and morphology of the samples. The presence of a Co-Co first neighbour EXAFS signal is shown to be related to the degree of the alloy's chemical disorder. A simple model which takes into account the presence of different degree of chemical disorder is shown to account for changes in the Co-Co, Co-Pt, and Pt-Pt first neighbour coordination numbers, in agreement with experimental data. Moreover, EXAFS spectra have been analyzed accounting for the reduction of the coordination number and degeneracy of three-body configurations, resulting from the measured size distribution and expected surface atom contributions [2]. We discuss also the EXAFS capabilities for evaluating the degree of chemical disorder in this binary alloy. A robust model for the local structure of this nanocrystalline alloy is obtained using EXAFS, x-ray diffraction and TEM Methods and results presented in this work have been found to be successful for a robust structural refinement of biatomic nanocrystalline systems and represent a solid starting point for analyzing subtle structural and dynamical local changes occurring during in situ experiments involving nanomaterials for specific applications like PEMFC.

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Poster no. PS2.105 - Session 2**Insight into the structure of Pd/ZrO₂ during the total oxidation of methane using combined in situ XRD, X-ray absorption and Raman spectroscopy**Jan-Dierk Grunwaldt¹, Niels van Vegten², Alfons Baiker², and Wouter van Beek³*(1) Technical University of Denmark Department of Chemical and Biochemical Engineering, Building 229 2800 Kgs. Lyngby Denmark**(2) Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich**(3) ESRF, Grenoble, France*

Supported palladium particles are presently regarded the most active catalysts in the total combustion of methane under lean burn conditions. They are applied in exhaust catalytic converter systems as well as in catalytic gas turbine combustors. Among the different supported catalysts, Pd/Al₂O₃ and Pd/ZrO₂ have received most attention. Despite much research in this field, the mechanism for methane oxidation is complex and not yet completely understood. Particularly debated are the active species (metallic or oxidized palladium). Additionally, a characteristic hysteresis in reaction rate is observed during heating and subsequent cooling in a methane/oxygen reaction mixture.

In order to gain more insight into the structure of a Pd/ZrO₂-catalyst under relevant reaction conditions we applied X-ray absorption spectroscopy, X-ray diffraction and Raman spectroscopy. These three complementary techniques were combined simultaneously with on-line analysis of the gas composition. During this experiment both information on the short and long range order of Pd(O) was obtained. This allowed investigation of structure-performance relationships during the total oxidation of methane. It was observed that initially Pd is very finely dispersed (no Raman bands typical for PdO, no XRD-reflections and mainly oxidized according to XAS) directly after preparation. Upon heating a sudden reduction (XAS) accompanied by sintering of the Pd-particles (XRD) lead to a significantly lower catalytic activity. During cooling a hysteresis in catalytic activity was found and only when re-oxidation occurred (identified by XAS and Raman) the catalytic activity increased again.

Poster no. PS2.106 - Session 2**Energy dispersive x-ray absorption spectroscopy for studies of catalysts in solution**Gemma Guilera¹, Grigory Smolentsev², Alexander V. Soldatov², Mimi Hii³, Maurizio Benfatto⁴, Mark A. Newton⁵, and Sakura Pascarelli⁵*(1) ALBA-CELLS Edifici Ciències Nord. Modul C-3 central. UAB 08193 Bellaterra, Barcelona Spain**(2) Center for nanoscale structure of matter and Faculty of physics, Southern Federal University, Rostov-on-Don, 344090, Russia**(3) Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, United Kingdom**(4) INFN, Via E. Fermi 40, Frascati 00044, Italy**(5) ESRF, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France*

The millisecond time resolution achieved by Energy Dispersive EXAFS (EDE) and the high stability provided by the unmoved optical components make this technique very attractive to study chemical reactions. In the field of catalysis, in situ EDE experiments have found application in the minutely study of heterogeneous systems [1]. Nonetheless, great progress has been made on the EDE study of the more problematic in situ experiments of catalysts in solution. To reach the aim of understanding the structuro-kinetical changes of homogeneous catalysts under reaction conditions one needs to start from a solid off-line experimentation and supplement it with complementary techniques.

Herein, we will present dynamic and in situ time resolved stopped-flow/UV-Vis spectroscopy/dispersive EXAFS (EDE) experiments, enforced by analytical methodologies such as MXAN code and FitIt program, that have allowed to elucidate the homogeneous oxidative addition process of iodobenzene to [(Ph₃P)₂Pd(dba)], involved in the C-C and C-X bond formation process; and have revealed the intermediate species involved in the homogeneous reaction of hypophosphorous acid on the water-soluble catalyst CH₃ReO₃.

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Poster no. PS2.107 - Session 2**Detailed RIXS studies on Cr(salen) catalysts**

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Salen-type ligands coupled to 3d transition metals are well-known catalysts with a multitude of applications, e.g. alkene epoxidation which is very important in the pharmaceutical industry. Salen ligands can be easily modified and the effect of different substituent on the catalytic activity and (enantio) selectivity is observed. This study looks at chromium complexes with a range of substituted salen ligands and uses Resonant Inelastic X-ray Spectroscopy to probe their detailed electronic structure, as a function of the type of salen ligand (symmetric vs asymmetric) and of substituent.

Initially a series of known reference chromium materials with different oxidation states and geometries was studied, in combination with theoretical modelling, to obtain more fundamental insights in the different features as obtained in Cr K and Cr L XANES spectra, and the Cr 1s3p and 1s2p RIXS, all probing different molecular orbitals in different ways (i.e. reached via different transitions). Angular dependent studies on single crystals have been performed to obtain a detailed picture of the orientations of the different molecular orbitals and a fundamental understanding of the origin of the multiple pre edges observed.

Once the Cr pre-edge features are assigned and their origin known, we use this to look at the more subtle effects of the substituted salen ligands on the electronic structure of chromium. This is useful in understanding the reaction mechanisms occurring, therefore opening up a wide range of catalytic applications for such compounds by controlling the properties of the catalyst through the functionality of the ligand.

Poster no. PS2.108 - Session 2**Nb and Fe K-edges XAFS study on the structure of supported Fe-NbN catalysts**

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Early transition metal (ETM) nitride is attractive as one of the new catalyst material due to the resemblances in physical and chemical properties to those of the group 8-10 metals. We have already demonstrated that introducing a Fe species into a SiO₂-supported Nb oxide precursor (Nb/SiO₂) was able to successfully reduce the nitriding temperature of Nb to 1193 K under a N₂-H₂ gas stream. The conversion from Nb oxide to Nb nitride proceeded around the Fe additive, and hence, the structure of Fe affects the nitriding process. The effect of Fe chemical state on the formation of small Nb nitride cluster was also investigated by XAFS analysis.

Fe-Nb/SiO₂ was prepared by conventional impregnation method using SiO₂, ferrocene acetic acid and peroxoniobic acid as precursors. Nb loading amount and a Fe/Nb molar ratio were regulated to 3 wt% and 0.2, respectively. The nitriding of Nb species into NbN was carried out under N₂-H₂ gas stream in a temperature programmed reaction (TPR) method with a linear rate of 10 K/min up to 1173 K. The intermediate temperature-maintaining (ITM) step was also introduced during the above TPR process. Nb and Fe K-edge XAFS spectra were taken in a transmission mode at BL-NW10A and in a fluorescence mode at BL-12C, respectively (IMSS-PF, Proposal No. 2005G214, 2008G638). XAFS spectra were analyzed by the program REX2000 (Rigaku Co.).

As raising the ITM temperature, Fe species in the Fe-Nb/SiO₂ catalyst was reduced to zero-valent Fe cluster, confirmed by Fe K-edge XANES analysis. Although the Fe-Fe coordination number increased at high ITM temperature, the size of Fe cluster was still small for the ITM temperature of 973 K Fe-NbN/SiO₂ catalyst. The Nb-N coordination number became larger, as higher the ITM temperature. It is concluded that the reduced Fe species effectively assisted the nitriding process of Nb. The effect of Fe cluster size on the NbN formation will be also demonstrated.

Poster no. PS2.109 - Session 2**In situ Quick XAFS studies on the structure of Rh supported on USY zeolites**Kazuo Kato^{1,2}, Kazu Okumura², Takashi Sanada², Takunari Murakami², Shou Ito², and Miki Niwa²*(1) Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan**(2) Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Koyama-cho, Tottori 680-8552, Japan*

Rh/zeolite catalysts are active catalyst in decomposition of N₂O and hydrogenation of CO₂. Previous studies revealed that the acid properties of zeolite influenced on the catalytic performance of Rh. Therefore, structural changes of Rh in different acid-site are important in the catalytic properties. In this study, in order to elucidate the support effect of zeolite, dynamical change of Rh structure was measured by Quick XAFS technique operated under in situ conditions. Rh K-edge EXAFS data were obtained at the beamline BL01B1 of SPring-8. In the atmosphere of H₂, formation of the Rh clusters consist of 13 atoms was observed in H-USY and Na-USY. On the other hand, in the atmosphere of O₂, formation of the highly dispersed Rh oxide was observed in H-USY, whereas, Rh oxide species slightly dispersed in Na-USY. The result shows that the dispersion of Rh oxide species depends on the acid-site of the USY zeolite.

Poster no. PS2.110 - Session 2**EXAFS of lanthanide promoted sulfated zirconia catalysts**Shelly D. Kelly¹, A. S. Y. Chan², George E. Mickelson², Ning Yang³, Simon R. Bare³*(1) EXAFS Analysis 719 Crestview Dr 60440 Bolingbrook IL USA**(2) UOP LLC, a Honeywell Company, Des Plaines, IL 60017 USA**(3) Argonne National Laboratory, Argonne, IL 60439 USA; Present address BURKER AXS Inc., Madison, WI USA*

Increasing the octane value of light naphtha streams through isomerization has been explored by using a range of catalysts including chlorided alumina, sulfated zirconia, and zeolites. Sulfated zirconia (SZ) catalysts are stable, can be used at low temperature, and have activities significantly higher than zeolitic catalysts but are less active than chlorided alumina catalysts. However, the activity of sulfated zirconia can be enhanced with the addition of first row transition metal cations, as first demonstrated by Hsu et al. [1] for the addition of Fe and Mn. There has been a large volume of work documenting the effect of these promoters [2].

It is well known that the addition of lanthanides into zirconia affects many properties including cation diffusion, defect ordering, and oxygen diffusion. Therefore, the effect of lanthanide addition to a SZ catalyst was explored. In this paper the structural characterization of a Tm-promoted SZ catalyst (as representative lanthanide) is presented with the aim of determining if the structural promotion of the lanthanide is similar to that of Mn.

A detailed EXAFS analysis shows that the Tm is not present as a separate Tm₂O₃ phase, or as a tetragonal phase, but instead is present as a distorted cubic phase. These results will be used to interpret the enhanced activity of these promoted SZ catalysts. All of the data indicate the Tm is primarily incorporated into the bulk of the zirconia, and it is not a surface promoter. Through the fundamental understanding of the promoter affect of Tm on the activity of sulfated zirconia allows this stable, low temperature isomerization of light naphtha stream catalyst to be used as a catalyst to increase octane values.

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Poster no. PS2.111 - Session 2**Effect of niobium oxide and oxyphosphate supports on the reactivity of Pt nanoparticles as revealed by electrochemical and in situ XAS analysis**Anna Korovina^{1,2}, Yannick Garsany¹, Albert Epshteyn¹, Karen E. Swider-Lyons¹, and David E. Ramaker^{1,2}*(1) Naval Research Laboratory 4555 Overlook Ave., SW 20375 Washington DC USA**(2) George Washington University Washington DC USA*

Promotion effects have been reported recently for Pt on Nb₂O₅ for the oxygen reduction reaction (ORR) and other fuel cell reactions [1,2,3]. We have found that the electrochemical activity for 1-3 nm Pt is also enhanced when supported on niobium oxyphosphate (NbOPO₄) with Vulcan carbon (VC). In our work, we correlate the ORR activity of Pt on niobium oxide with VC (Pt-Nb₂O₅/VC) and Pt on niobium oxyphosphate with VC (Pt-NbOPO₄/VC) to its physical properties as determined by in situ X-ray absorption spectroscopy (XAS) at the Pt L₃ and Nb K edges. The ORR activity of the electrocatalysts follows the order: Pt-NbOPO₄/VC > Pt-Nb₂O₅/VC > the Pt/VC standard. XAS data is used for the $\Delta\mu$ XANES adsorbate isolation technique to obtain the H, OH and O adsorbate coverage on Pt with potential, and for EXAFS analysis to provide the particle morphology and cluster size. The $\Delta\mu$ results for the Pt L₃ data show that the threshold potential for O[H] adsorption on Pt from water activation moves to higher potentials with increasing electrochemical activity of the electrocatalysts. The lower O(H) coverage on the Pt-NbOPO₄/VC leaves more sites free for the ORR, leading to higher activity. The potential for H adsorption moves to lower potentials for the more active catalysts. At low potentials, H adsorbs not only on the Pt but inserts between the Pt and support as revealed by a non-reversible H adsorption. The EXAFS determined Pt-Osupport bond length of 2.5 Å is apparently sufficiently large to allow this insertion of H, as seen previously in the gas phase. The Nb K-edge data showed no changes with potential. The changes that occur at the Pt L₃ edge with potential are attributed to a metal support interaction or ligand effect imparted by the Nb supports.

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Poster no. PS2.112 - Session 2**XAFS study of nano-structured mono and bimetallic noble supported catalysts**Vladimir V. Kriventsov¹, I.E. Beck¹, I.L. Simakova¹, A. Simakov², E. Smolentseva², B.N. Novgorodov¹, E.P. Yakimchuk¹, V.I. Zaikovskiy¹, D.P. Ivanov¹, A.S. Fedotov³, M.V. Tsodikov³, J.A. Navio⁴, and S.G. Nikitenko⁵, and V.I. Bukhtiyarov¹*(1) Boreskov Institute of Catalysis Pr. Ak. Lavrentyeva, 5 630090 Novosibirsk, Russia**(2) Centro de Nanociencias y Nanotecnologia, UNAM, Ensenada, B.C., Mexico**(3) Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia**(4) Instituto de Ciencia de Materiales, Centro Mixto CSIC-Universidad, Sevilla, Spain**(5) KU Leuven, DUBBLE-CRG & ESRF, Grenoble, France*

Recently a great attention was focused to develop new preparation ways of nano-structured high-disperse mono and bimetallic catalysts with active component having noble metal nanoparticles (with controlled sizes) stabilized on oxide carriers. These catalysts are very promising for various applications, especially for complete oxidation processes concerned with environmental catalysis. Obviously, development of preparation methods for controlling both the particle size and active component structure along with elucidation of key factor contributions to the activity and stability of these catalysts allows to obtain high-effective catalysts and to diminish the noble metal loading as well. Structural studies are very useful to achieve these aims, especially XAFS as a powerful tool to study the local structure and state of the supported nanoparticles of noble metals. This work is devoted to the structural study of genesis of high-disperse mono (Pt, Pd, Au) and bimetallic (Pd-Ce, Pd-Mn, Au-Ce, Pt-Ce) catalysts with active component supported on (Al₂O₃, TiO₂, ZrO₂) oxide carriers by XAFS. The catalysts were prepared by sol-gel from organic and inorganic precursors. All XAFS spectra were recorded at Siberian Synchrotron Radiation Center (SSRC) and European Synchrotron Radiation Facility (DUBBLE, ESRF). The genesis of local structures and state of noble metals for the prepared nano-structured catalysts were studied in detail. It was established that variation of methods preparation caused formation of different types of noble metal nanoparticles (metal, oxide and metal-oxide) located on the oxide surfaces. All possible structural models were discussed. In addition, these nanosystems was studied by the TEM, EDX, XPS and XRD. The data obtained by all methods are in a good agreement.

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Poster no. PS2.113 - Session 2**XAFS study of Pd-M (M=Co, Mn, Zn) catalytic nanosystem prepared from heterobimetallic complexes**

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This work is devoted to the structural study of a high-disperse bimetallic Pd-M (M=Co, Mn, Zn) catalytic nanosystem supported on an oxide matrix by the XAFS. Recently great efforts are devoted to develop new methods of preparation of high-disperse Pd-containing nanosystems stabilized on an oxide matrix, because ones are very promising catalysts for various applications. The main idea of the new approach of synthesis consists in using the heterometallic $\text{PdM}(\mu\text{-OOCMe})_4(\text{OH}_2)$ complex as a precursor to anchor Pd nanoparticles on the surface of oxide support. These complexes, containing Pd and a 3d-metal, such as Mn, Co, Zn are used to anchor Pd containing metal-oxide nanoparticles on the oxide support surface. The samples were prepared by sol-gel method using heterometallic $\text{PdM}(\mu\text{-OOCMe})_4(\text{OH}_2)$ and $\text{Ti}(\text{O}i\text{Bu})_4$. All XAFS spectra of the Zn-K, Co-K, Mn-K, Pd-K edges were recorded at SSRC and ESRF (DUBBLE). The local structure of the prepared samples of catalysts was studied both at the gel stage and after calcination. It was shown that calcination caused formation of the high disperse palladium "oxidizing" nano-phase in which Pd mainly being represented by $\text{Pd}(2+)$ cations. It was found that for the Pd-Co nanosystem, formation of a stable anion sublattice is already finished at the gel stage, and then, after calcination, all structural changes took place for the cation sublattice only, while for the Pd-Mn, Zn catalysts, dramatic structural changes concerning the Mn and Zn local arrangements were observed after calcination of the initial gel. All possible structural models were discussed in detail. In addition, these nanosystems were studied by the TEM and XRD methods. The data of all methods are in a good agreement. This research was supported by RSIA 02.513.3203 contract, RFBR- (080301150a, 080301016a, 090301012a) RFBR-CNRS-080392502a, and RAS Presidium 27.12, 27.13 grants.

Poster no. PS2.114 - Session 2**Effect of ceria on nanoparticulate rhodium catalysts investigated by the array of DRIFTS/MS/EDE**

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Rh metal was implemented as a core component in the so-called three-way automotive exhaust catalyst (TWC) due to its excellent properties such as thermal stability, poison resistance and inert behaviour to react with any support materials [1-3]. These catalysts are often loaded with small amounts of promoter elements such as Ce that enhance their overall catalytic performance and catalyst lifetime [4]. It is therefore desirable to develop new CeO_x -based catalysts with both high redox activity and high thermal resistance.

The combination of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Mass Spectrometry (MS) and Energy Dispersive X-ray Absorption Fine Structure (EDE) techniques in a synchronous, time-resolved manner has been applied to determine the complementary information about structural and kinetic changes of the chemical system throughout CO oxidation in the temperature range between 298 K and 573 K.

The combined DRIFTS/MS/EDE studies have confirmed that CeO_x facilitates the protection of Rh particles against extensive oxidation in atmospheres of air, O_2 and CO. Larger Rh core particles of ceriated Rh catalysts have been observed when compared with undoped Rh samples. The DRIFTS spectrum of CO adsorbed on $\text{Rh/CeO}_x/\text{Al}_2\text{O}_3$ displays a blue shift of linear and bridged CO frequency, which was assigned to the Rh-Ce interaction. Furthermore, ceria doping was found to improve the catalytic activity of promoted Rh catalysts throughout CO oxidation.

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Poster no. PS2.115 - Session 2**Isolated CuCl_2 species hosted in a nanoporous P4VP polymeric matrix: structure and redox activity investigated by in situ XAFS and UV-vis spectroscopies**Carlo Lamberti¹, Mohammed Jasim Uddin¹, Silvia Bordiga¹, Adriano Zecchina¹, and Elena Groppo¹*(1) Department of Inorganic, Materials and Physical Chemistry, NIS Centre of Excellence and INSTM unit, University of Turin, Via P. Giuria 7, I-10125 Turin, Italy.*

In the recent years metal-containing polymers are becoming very attractive owing to their possible applications as catalysts for organic synthesis [1]. In this work, a N-containing polymer, poly(vinylpyridine) (PVP) has been impregnated with CuCl_2 from the liquid phase. The structure and the reactivity of hosted Cu species have been investigated by in situ EXAFS/XANES and UV-Vis spectroscopies. In the as prepared sample, isolated Cu^{2+} are coordinated to two Cu-Cl atoms at $2.287 \pm 0.004 \text{ \AA}$ and are anchored to the polymeric matrix via two Cu-N bonds at $2.03 \pm 0.01 \text{ \AA}$ and complete their octahedral environment with and with two coordinated water molecules [2].

Dehydration results in the loss of coordinated water molecules, while treatment in H_2 at 180°C results in the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction, clearly visible in XANES spectra. Reduced species are isolated molecular CuCl entities ($R_{\text{Cu-Cl}} = 2.149 \pm 0.007 \text{ \AA}$) anchored via a single N atom of a pyridine ring at $R_{\text{Cu-N}} = 1.99 \pm 0.02 \text{ \AA}$ [2].

Exposure to air results to a $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ re-oxidation where Cu^{2+} cations are again anchored to two N atoms of the polymer matrix (at $2.04 \pm 0.01 \text{ \AA}$), exhibit a single Cu-Cl coordination at $2.298 \pm 0.006 \text{ \AA}$ and complete their coordination spheres with three O atoms, probably an O-H group and two coordinate water molecules. The red-ox behavior observed in the $\text{CuCl}_2/\text{P4VP}$ polymeric system [2] is similar to what previously observed in Cu-exchanged zeolites [3].

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Poster no. PS2.116 - Session 2**Potassium promotion effects on metal-support interaction of Ir/ SiO_2 catalysts studied by X-ray absorption fine structure**Zhongrui Li^{1,2}, Wensheng Yan², Liqiu Zheng³, Zhiyun Pan², Qinghua Liu², and Shiqiang Wei²*(1) Nanotechnology Center, University of Arkansas at Little rock, AR 72204, USA**(2) National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China**(3) Department of Physics and Astronomy, Clemson University, SC 29631 USA*

The metal-support interaction of Ir/ SiO_2 catalyst under K-promotion was studied by using X-ray absorption fine structure (XAFS). It was found that the dispersion of Ir nanoparticles on SiO_2 support can be altered by adding K onto SiO_2 surface. The charge transfer between Ir atoms in the clusters and K occurred when the support SiO_2 was promoted with K. Contractions in bond lengths of between 0.5 and 1.2% from bulk metal values were observed from EXAFS data. This work demonstrates that the important role of the promoter K in the tuning of the interaction between Ir nanoparticles and SiO_2 support and usefulness of XAFS in probing the electronic behavior of catalyst nanoparticles.

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Poster no. PS2.117 - Session 2**XAFS study of Ce-enhanced stability of Pt/KL catalyst**Zhongrui Li^{1,2}, Wensheng Yan², Liqui Zheng³, Zhiyun Pan², Yong Jiang², and Shiqiang Wei²*(1) Nanotechnology Center, University of Arkansas at Little rock, AR 72204, USA**(2) National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China**(3) Department of Physics and Astronomy, Clemson University, SC 29631 USA*

The stability of the Pt/KL catalyst can be greatly enhanced by the presence of the rare earth Ce. The analysis of the X-ray absorption edges indicates that some electronic differences may indeed exist in the state of Pt supported on the Ce-KL compared to that on the unpromoted KL zeolite. Although the Pt particle size and location inside the zeolite is very similar in the two zeolites, the presence of the Ce seems to have influence on the electronic potential around Pt, which may be responsible for the observed enhanced stabilization of the small metal clusters. The presence of Ce in the zeolite also greatly affects the reducibility of Pt.

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Poster no. PS2.118 - Session 2**Multidimensional Spectroscopy for the investigation of homogeneous catalytic reactions**Benjamin Marchetti¹, and Helmut Bertagnolli¹*(1) University of Stuttgart Pfaffenwaldring 55 70569 Stuttgart Germany*

In the large field of homogeneous catalysis, palladium-catalyzed cross-coupling reactions play an important role as they allow a wide range of reactants and synthetic conditions and are often used for the preparation of complex molecules or precursors for natural products and pharmaceuticals[1]. So far they have been intensely studied by conventional spectroscopic methods like NMR, XRD or mass-spectrometry[2] and there are a few studies with XAS e.g. [3], but still some important questions about the key steps of the reaction remain unclear since none of these methods provides direct information about the local environment around the metal centre of the catalyst. A powerful tool to bridge this gap is multidimensional spectroscopy. With the combination of different spectroscopic methods, namely XAS, UV-Vis and Raman, it is possible to make a thorough investigation of the catalytic cycle as each method delivers an unique point of view which is in most cases complementary to the other employed methods. In particular the Sonogashira reaction, which is copper-cocatalyzed cross-coupling reaction of alkynes (sp²-carbons) to alkene- or aromatic- halides (sp²-carbons), was investigated with XAS, UV-Vis and Raman. Details on the key steps of the reaction like the structure and the formation of the catalytically active palladium species, the deactivation of the catalyst, etc. will be presented. As an essential result it was found that the active palladium(0) species is linearly coordinated by two phosphine ligands and is formed via coupling of two alkynes, which results in a dialkyne as a side product.

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Poster no. PS2.119 - Session 2**Ethanol oxidation studied by operando XAFS**

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Liquid fuels in proton exchange membrane fuel cells are a good option to enhance the power density and therefore runtime for portable equipment. Ethanol has a number of advantages over hydrogen and methanol, such as its higher energy density, easier handling and availability for the user. However, the direct ethanol fuel cell (DEFC) suffers from an incomplete and slow oxidation reaction. Recent measurements have yielded a better performance with PtRu and PtSn alloys over pure Pt catalyst. To develop catalysts with higher selectivity towards the preferred CO₂ product, an understanding of the reaction mechanisms and their correlation with structure is required.

We have performed XAFS measurements on Pt, PtSn and PtRu catalysts in an operating DEFC. Using the $\Delta\mu$ XANES method, we obtain the relative surface coverage of C- and O(H)-species as a function of potential. From the EXAFS, we extract information about the catalysts' structure. The Pt and PtRu measurements reveal a high coverage of C-species that become oxidized as soon as the $\Delta\mu$ signature of oxygen appears. On PtRu, oxygen formation on the Pt surface and at the Ru islands appears at lower potentials than for the Pt only catalyst. This indicates that both the bifunctional mechanism and the ligand effect play a role in the better performance of PtRu compared to Pt. For PtSn we observe oxygen at all potentials, which may be explained by a bifunctional mechanism involving SnO₂. Furthermore, at all potentials the C-species coverage is lower than for the pure Pt catalyst. This is attributed to a blocking of the higher coordinated sites of the PtSn catalyst inhibiting the C-C bond splitting. As a consequence a higher turnover can be achieved with PtSn, but the selectivity is shifted towards the undesired products acetic acid and acetaldehyde [1].

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Poster no. PS2.120 - Session 2**XAFS study for the formation and deformation process of Ag cluster in the Ag-zeolite A**

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The formation and deformation process of Ag cluster generated in the cavity of Ag-zeolite A have been investigated using Quick XAFS spectroscopy. The Ag-zeolite A was heated under vacuum and atmosphere to several temperature, 300C-500C. The Ag clusters are formed in the β -cage in the cavity. After keeping them 24 hours, the samples are cooled and mixed with air.

(1) In the process that Ag-zeolite was heated to 500C in vacuum, the Ag clusters were formed at 150-230C. In this process, the coordination number of Ag-Ag increases from 1.5 to 3.3. In the cooling process under vacuum to r.t., the coordination number does not change, so Ag clusters are not deformed.

(2) After cooling the sample, the oxygen gas was mixed the sample, Ag clusters are kept but when the air was mixed, Ag cluster was deformed. H₂O in the air plays significant role in the deformation process of Ag clusters.

(3) In the process that Ag-zeolite was heated to 500C atmospheric condition, the Ag clusters were formed at 140-275C. In this process, the coordination number of Ag-Ag increases from 1.5 to 3.3. In the cooling process under vacuum to r.t, the Ag clusters are not deformed.

(4) On the other hand, in the cooling process atmospheric condition, the samples are sealed in the cell to avoid the air (oxygen and H₂O). The sealed sample at 85C and XAFS spectrum was measured after 1 week, Ag cluster was deformed.

Poster no. PS2.121 - Session 2**The ethylene oxychlorination reaction on $\text{MCl}_x\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ ($\text{M} = \text{Li}, \text{K}, \text{Cs}, \text{Mg}, \text{Ce}, \text{La}$) catalysts followed in Operando conditions with Cu K-edge XANES spectroscopy**

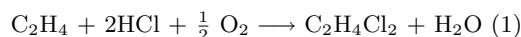
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Nowadays, almost all the world production of PVC is obtained by the polymerization of vinyl chloride (VCM). Ethylene oxychlorination:



reaction is a key step in PVC production.

Oxychlorination reaction (1) is performed at 490-530 K and 5-6 atm in fluid or fixed bed reactors. Commercial catalysts are produced by impregnation of γ -alumina with CuCl_2 (4-8 wt% Cu). Other chlorides are also added in order to improve the catalytic performances making the catalyst more suitable for use in industrial reactors. In particular, KCl is always present in the catalysts used in fixed bed technologies, sometimes together with other alkali-metal chlorides as CsCl, NaCl or LiCl. CeCl_3 and LaCl_3 , added to CuCl_2 and KCl, are also claimed in the patent literature. MgCl_2 is the base additive in the catalysts used in fluid bed processes, where alkali-metal (such as LiCl) or rare-earth-metal chlorides (such as LaCl_3) can also be added.

In the past, some of us have correlated the $\text{Cu}^{2+}/\text{Cu}^+$ ratio with the catalyst activity performing dispersive XANES experiment in OPERANDO conditions [1] at ESRF ID24. A reaction cell [2], ad hoc conceived for transmission XAFS, allowed us to collect time-resolved data while acting on the reaction temperature and on the reactants partial pressures (using gas flow meters). Catalyst activity was monitored with a mass spectrometer that sampled the gas output from the cell. Previous study [1] regarded undoped CuCl_2 and KCl-doped catalysts. In this work we extended the investigation to LiCl-, CsCl-, MgCl_2 , CeCl_3 , LaCl_3 -doped catalysts. We found that KCl- and KCs-doped catalysts work prevalently with Cu in the oxidized state, while the remaining ones works with Cu in the reduced state.

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Poster no. PS2.122 - Session 2**XAFS study on the gold states in the Au/C catalysts at different stages of their preparation**

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Recently nanosized gold deposited on various supports is attracting increasing interest because of its unique catalytic properties. Although carbon is a very promising support for gold in numerous applications, the Au/C catalysts are much less extensively studied probably due to the fact that the methods for obtaining small Au^0 particles on carbon supports from auric complexes just begin to develop.

Here we report the results of XAFS study on the 1-2% Au/C catalysts prepared by the following techniques: (1) deposition of anionic $[\text{Au}(\text{OH})_x\text{Cl}_{4-x}]^-$ complexes from an aqueous $\text{HAuCl}_4 + \text{NaOH}$ solution (deposition-precipitation or DP method which is commonly used for obtaining gold in a dispersed state on oxide supports); (2) grafting of non-dissociated HAuCl_4 from the organic media; (3) adsorption of cationic Au(III) complexes containing N-donor ligands. The Au L_3 -edge XAFS spectra of the unreduced samples suggest that the Au complexes which are deposited from the non-aqueous media HAuCl_4 or hardly reducible $[\text{AuL}_4]^{3+}$ strongly interact with the carbon surface through displacement of the part of parent ligands from the coordination sphere of Au. Upon calcining the samples in hydrogen flow at 300°C, the spectra look like that of Au foil but with the reduced amplitude of EXAFS-oscillations. It means that the anchored gold species are converted into metallic Au particles with a high Au dispersion. The XAFS spectra of the Au/C sample prepared by DP when measuring before and after reduction were similar to each other and to the spectrum of Au foil indicating that the parent $[\text{Au}(\text{OH})_x\text{Cl}_{4-x}]^-$ complexes are reduced by the carbon surface during the deposition step with the formation of course Au crystallites. With all the samples studied, no Au-Au bond length contraction is observed for the supported Au metal particles compared with bulk Au.

Poster no. PS2.123 - Session 2**Time-resolved DXAFS study on redox mechanisms of Pd supported on Al₂O₃**Yasuhiro Niwa¹, Yasuhiro Inada¹, Masao Kimura², and Masaharu Nomura¹*(1) Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Oho 1-1, Tsukuba, Ibaraki, 305-0801, Japan**(2) Advanced Technology Research Laboratories, Nippon Steel Corp., 20-1 Shintomi, Futtsu, Chiba, 293-8511, Japan*

Pd is used as the catalyst for many purposes, such as automobile exhaust purification and steam methane reforming. The efficiency and the feature of the catalyst relate closely to redox state of Pd center on the support. Thus the evaluation of dynamic change of the structure and the electron transfer of Pd during the reaction is very important to understand the catalysis function and to improve the efficiency. In this study, we have carried out the time-resolved DXAFS measurements of the reduction and oxidation processes of Pd to elucidate the reaction mechanism. The reaction mechanisms are revealed by the kinetic analysis of the absorbance change and by the evaluation of the pressure dependence of the conditional rate constants.

The sample used in this work was 3 wt% Pd supported on Al₂O₃. The reduction by H₂ or CO and the oxidation by O₂ at several temperatures were measured by the DXAFS instrument at NW2A beam line (PF-AR, KEK) at the vicinity of the Pd K edge. A Si(511) bent crystal (Laue type) was used as the polychromator with the bending radius of 0.9 m, and a photodiode array was used as the linear detector.

PdO is quantitatively converted to metallic Pd in the reduction reaction with H₂ or CO. The reduced Pd(0) species is oxidized to the initial PdO state by O₂, reversibly. The absorbance is exponentially changed for the oxidation process, indicating that the reaction is first order for Pd. The conditional rate constants are determined by the fitting procedure of the change of the absorbance as the function of time. From the pressure dependence of the conditional rate constants, it is suggested that Pd on Al₂O₃ is oxidized to PdO with O₂ after the formation of the O₂ adducted species with Pd.

Poster no. PS2.124 - Session 2**A XAS study of a low-Pt content electrocatalyst operating in a PEM fuel cell**Emiliano Principi¹, Agnieszka Witkowska², Sonia Dsoke³, Roberto Marassi³, and Andrea Di Cicco^{1,4}*(1) CNISM, University of Camerino, via Madonna delle Carceri 9, 62032 Camerino (MC) Italy**(2) Department of Solid State Physics, Gdansk University of Technology, 80-233 Gdansk, Poland**(3) Department of Chemistry, University of Camerino, I-62032 Camerino (MC), Italy**(4) IMPMC-CNRS UMR 7590, Université P. et M. Curie, 140 rue de Lourmel, 75015 Paris, France*

We present a X-ray absorption spectroscopy (XAS) study of a novel Pt-based catalyst layer (Pt loading 0.1 mg/cm²) operating at the cathode of a proton exchange membrane fuel cell (PEMFC). This innovative catalyst is based on the use of a mesoporous inorganic matrix as a support for the catalyst nanoparticles. The catalytic efficiency thus obtained has been found to be comparable to state-of-the-art electrodes with a Pt load of 1 mg/cm². Due to the very low Pt content, in-situ measurements of its structural properties by XAS are challenging and suitable experimental strategies must be devised for this purpose. In particular, we show that accurate XAS in-situ fluorescence measurements can be obtained using an optimized fuel cell, suitable protocols for alignment of a focused x-ray beam and an appropriate filter for the background signal of the other atomic species contained in the electrode. Details, advantages and limitations of the XAS technique for the in-situ measurements are discussed. Analysis of the near-edge XAS and EXAFS (extended x-ray absorption fine structure) data shows that Pt nanoparticles have a local structure compatible with that of bulk Pt (f.c.c.) and coordination numbers match those expected for particles with typical sizes in the 1.5 nm range. Changes in the oxidation state and in local disorder are found for different applied potentials. The catalyst support, containing W atoms, exhibits a partial reduction upon PEMFC activation thus mimic the catalyst behavior. This indicates a possible role of the mesoporous matrix in favoring the oxygen reduction reaction (ORR) and stimulates further research on active catalyst supports.

Poster no. PS2.125 - Session 2
Local structure of Cu in Cu/CeO₂ catalysts

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Analysis of EXAFS in metal ion substituted ceria catalysts have shown that though the overall structure remains fluorite type, the local structure around the metal ion is distorted to 4 short and 4 long oxygen bonds instead of 8 equidistant oxygen bonds observed in undoped CeO₂ (G. Dutta et al Chem. Mater. 18, 3249 (2006), G. Dutta et al Catal Lett. 181, 165 (2006), T. Baidya et al J. Chem. Phys. 128, 124711 (2008)). A detailed report on the structure and chemical environment of Cu in Cu/CeO₂ catalysts synthesized by the solution combustion method was published earlier by us (P. Bera et al, Chem. Mater. 14, 3591 (2002)). In the light of above observations the EXAFS of Cu in these Cu/CeO₂ catalysts has been re-analysed and the results are presented here.

Cu K EXAFS in Ce_{0.95}Cu_{0.05}O₂ and Ce_{0.9}Cu_{0.1}O₂ indicate that Cu is incorporated in the CeO₂ matrix. The oxygen cage around Cu ion is distorted with about 4 oxygen ions at 1.94 Å and about 3 oxygen ions at 2.2 Å. The total oxygen coordination number being less than eight indicates presence of oxide ion vacancies. Further, there is a Cu-Ce correlation at about 3.48 Å which is slightly less than Ce-Ce bond distance in pure CeO₂. There are two Cu-Cu correlations at 2.94 Å and 3.54 Å respectively. The longer Cu-Cu correlation again confirms substitution of Cu for Ce in ceria matrix while the shorter correlation is perhaps due to presence of Cu in surface layers.

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Poster no. PS2.126 - Session 2

XAFS studies on a novel water-splitting catalyst with a cobalt-oxo core - Structural model and comparison to the photosynthetic Mn complex

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Efficient water oxidation by low-costs catalysts is prime interest for energy technologies based on H₂ production from water. In photosynthesis, water oxidation is efficiently catalyzed by a manganese complex bound to the proteins of photosystem II (PSII) [1]. Kanan and Nocera recently introduced a water oxidation catalyst using cobalt as the active metal [2]. The cobalt catalyst film (CoCF) is formed on inert cathodes by electrodeposition from aqueous solutions of cobalt, potassium and phosphate salts.

We have approached a characterisation of the amorphous CoCF by XAFS measurements at the K-edges of cobalt (Co), potassium (K) and phosphorous (P) (multi-edge EXAFS analysis). Evaluation of EXAFS data taken at the Co K-edge provides evidence that the Co catalyst film (CoCF) contains interconnected complete or incomplete Co-oxo cubanes; it exhibits limited long-range order only [3]. Potassium ligation to Co-bridging oxygens could result in Co₃K(μ-O)₄ cubanes, in analogy to the Mn₃Ca(μ-O)₄ cubane motif proposed for the photosynthetic Mn complex. The measurements at the K-edges of potassium and phosphorus are in progress.

The similarities in function and oxidative self-assembly between CoCF and the photosynthetic Mn complex are striking. Our study establishes a close analogy also with respect to the Mn-oxo core of the catalyst. We will present a structural model of the promising CoCF catalyst and compare this to models we and others have developed for the Mn₄Ca complex of PSII. Complementary functional studies have been approached to relate the structural results to the catalytic mechanism.

All data has been collected at the KMC-1 beamline of the BESSY (Berlin); we thank Franz Schaefer and Marcel Mertin for support.

[1] Dau H and Haumann M, Coord. Chem. Rev. 2522, 273-295 (2008).

[2] Kanan MW, Nocera DG, Science 321, 1072-1075 (2008).

[3] Risch M, Khare V, Dau H et al. Manuscript in preparation (2009).

Poster no. PS2.127 - Session 2**Sulfur-doping method to promote oxygen reduction reaction over mesoporous titanium oxides: the site structure and operating mechanisms**Yoshiyuki Shibata¹, Kazuki Oka¹, and Yasuo Izumi¹*(1) Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan*

TiO₂ has been applied widely for water and air purification. Because of the greater band-gap than 3 eV, TiO₂ requires UV irradiation which is only 3% of sunlight, to proceed photo-catalysis. Therefore, Many researchers have investigated methods of expanding the photo-response of TiO₂ toward visible light region. Recently, non-metal doping to TiO₂, such as C, N or S anion, was reported to reduce the band-gap. However, the chemical state and responsible site structure have not clarified yet to promote the TiO₂ photo-catalysis most.

In this work, S and/or N-doped mesoporous TiO₂ were synthesized via template method using thiourea (mesoporous SN-TiO₂) and via CVD method with hydrogen sulfide (S/mesoporous-TiO₂). Mesoporous SN-TiO₂ has greater surface area (229 m²g⁻¹) and narrower pore size distribution (2.9 nm) compared to conventional TiO₂. The sulfur sites were characterized using Ti and S K-edge XAFS. The Ti-S bonds were detected at 2.283 - 2.44 Å for mesoporous SN-TiO₂ and S/mesoporous-TiO₂ by Ti K-edge EXAFS for the first time, demonstrating the presence of substitutional anionic S on the O sites in/on TiO₂ matrix. Based on S K-edge XANES, the S amounts of mesoporous SN-TiO₂ and S/mesoporous-TiO₂ were evaluated to 1.7 and 0.77 wt%, respectively. These peak positions were similar to those for TiS₂, supporting anionic sulfur substitution.

In ethanol photo-oxidation with O₂ under visible light, over mesoporous SN-TiO₂ and S/mesoporous-TiO₂, water formation (i.e. O₂ reduction) was promoted by 6.8 and 12 times in contrast to only 2.3 and 1.9 times enhancement, respectively, for acetaldehyde formation. The electron excitation from S impurity level to conduction band and further transfer to O₂ were enabled under visible light, whereas the enough high potential of the impurity S level between the band-gap of TiO₂ was unfavorable to receive electron from substrate.

Poster no. PS2.128 - Session 2**Development of novel preparation method for supported metal catalyst using microwave irradiation**Sayoko Shironita¹, Tomoya Takasaki¹, Takashi Kamegawa¹, Kohsuke Mori¹, and Hiromi Yamashita¹*(1) Osaka University 2-1, Yamada-oka, Suita 565-0871 Osaka JAPAN*

Noble metals, such as Rh, Pt, Pd and Au, were employed in a wide variety of catalytic processes. However, these are one of the most expensive and rare metals in the industrial field. Therefore, the effective utilization of these metals is required. It is necessary to develop new technique to produce small and uniform metal particles. On the other hand, microwave technique for metal nanoparticle synthesis has attracted considerable attention. In this work, nano-sized and uniform metal (Pt, Au) particles were successfully synthesized on Ti-containing mesoporous silica (Ti-HMS) support using microwave irradiation[1]. Ti-HMS was added to the Pt metal precursor solution and irradiated by microwave with stirring. The sample was filtered, dried, calcined, and activated by H₂ (Mw-Pt/Ti-HMS). For comparison, these metal particles were also loaded on Ti-HMS by a conventional impregnation method (imp-Pt/Ti-HMS). The obtained catalysts were characterized by XRD, XAFS, TEM and CO pulse adsorption measurements.

Pt and Au metal particles were successfully synthesized on Ti-HMS support using microwave irradiation, respectively. Pt L_{III}-edge XANES spectra suggested that Pt particles are in metal state. The FT-EXAFS spectra intensity of catalysts prepared using microwave is smaller than that of impregnated catalysts. Evidently, curve-fitting analysis revealed that coordination number (CN) and interatomic distance (R) in the Mw-Pt/Ti-HMS are 6.3 and 2.74 Å, in the imp-Pt/Ti-HMS are 10.2 and 2.78 Å, respectively. It is considered that the prepared particle by microwave is smaller than that of the impregnated one. The Pt metal catalyst prepared by microwave showed the higher catalytic activity than impregnated one for nitrobenzene hydrogenation.

[1] S. Shironita, T. Takasaki, T. Kamegawa, K. Mori, and H. Yamashita, Catal. Lett., in press.

Poster no. PS2.129 - Session 2**Investigation of the ignition and extinction behaviour of the noble metal catalysed catalytic partial oxidation of methane**

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The partial oxidation of methane or natural gas to hydrogen and carbon monoxide can be regarded as the first step to convert natural gas into liquid products such as methanol, DME, or synthetic fuels. Often supported noble metals are used, which were in the present study prepared by flame synthesis. This gives highly dispersed metal nanoparticles and when initiating the reaction a very rapid structural transformation occurs. Hence, in the present study the dynamics of the ignition and extinction of the catalytic partial oxidation (CPO) of methane to hydrogen and carbon monoxide over Pt-Rh/Al₂O₃ and Pt/Al₂O₃ were studied on the subsecond timescale using quick-EXAFS with an oscillating X-ray monochromator located at the SuperXAS beamline at the Swiss Light Source. The experiments were performed in a small fixed-bed capillary reactor. The results show that the structural changes during ignition were significantly faster (a fraction of a second to a few seconds) than during the extinction (several seconds). While the ignition over Pt-Rh/Al₂O₃ occurred at lower temperature than over Pt/Al₂O₃, the structural changes during ignition were significantly faster in the latter case. In addition, a principal component analysis indicates that no intermediate species is found for Rh whereas in the case of Pt a third species is involved. Before the ignition starts the oxidation state of the Pt is already decreasing in both systems as XANES analysis shows. This could be confirmed and further quantified with the Fourier transformation of the EXAFS oscillations. Furthermore, changing oxidation states could be observed for both systems during the active phase when the gas atmosphere was switched from CH₄/O₂ to H₂ and vice versa. The spectroscopic results provide important insight into the dynamics of the catalyst during ignition and extinction of the CPO of methane and demonstrate the application of QEXAFS in catalysis.

Poster no. PS2.130 - Session 2**Chemical state analysis of silver exchanged zeolite catalysts by x-ray absorption and UV-Vis spectroscopies**

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It is well known that hydrogen treatment of Ag⁺ exchanged zeolites or the thermal evacuation above 573 K produces silver cluster inside the pore. Baba et al. found that activity of Ag⁺-zeolites for acid catalyzed reaction was enhanced in the presence of H₂[1]. ¹H-NMR study of Ag⁺-A zeolite (denoted as Ag-A) by their research group suggested that hydrogen treatment at 313 K produces silver hydride species Ag₃-H and the stability depends on the kind of zeolite and the degree of ion exchange[2]. Although formation of triangle Ag₃⁺ cluster was proposed by the ¹H-NMR study, their structural characterization has not been investigated.

In the present Ag K-edge XAFS study, we confirmed that radial structure functions (RSFs) of silver species in Ag-A zeolites (the degree of exchange: 60 or 100

[1] T. Baba, Y. Ono, Zeolites. 7 (1987) 292.

[2] T. Baba, et al., Langmuir 15 (1999) 7894.

Poster no. PS2.131 - Session 2**Combined depth-selective chemical state analysis of nitrogen in visible-light response TiO₂ photocatalyst by XANES and ELNES**Tomoko Yoshida¹, Shunsuke Muto¹, and Eriko Kuda¹*(1) Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University
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In the field of catalytic chemistry, it is crucial to investigate where really works as surface active sites and how, since in solid catalysts different chemical states of the same elements generally coexist and are distributed to a certain depth region. In the present study, we applied a suite of XAFS and depth-selective TEM-EELS to determine the chemical state and optimum concentration of nitrogen most effective for highly-active visible-light responsive photocatalysis.

The optical absorbance in the visible-light region was found to evolve with increasing nitrogen concentration, though the absorbance was not linearly proportional to the photocatalytic activity. The N K-edge XANES spectrum of the active photocatalyst showed a characteristic double-peak around 400 eV, and the XANES spectrum of the inactive photocatalyst a distinct single peak around 401 eV. These features of the XANES spectra were well reproduced by theoretical simulations using the FEFF code based on the model where an O atom in TiO₂ were replaced by N for the active photocatalyst, and that of substitutional NO₂ for the inactive photocatalyst. In the depth-revolved N K-edge ELNES of the active photocatalyst, the double-peak around 400 eV was also observed near the surface region, and the distinct single peak around 401 eV gradually dominated with increasing depth, which reflected the different chemical states of N depending on the local nitrogen concentrations. In addition, quantitative analysis using N, O K-edge and Ti L-edge ELNES of this catalyst revealed that the inactive N-O species start to evolve when the local nitrogen concentration exceeds 1.8 atom%.

NanoStructures**Poster no. PS2.132 - Session 2****Nanocrystal structural analysis of indium oxynitride by exafs**Kittiphong Amnuyswat¹, P.Thanomngam¹, and S.Sopitpan²*(1) College of KMITL Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand and ThEP Center, CHE, 328 Si Ayutthaya Rd., Bangkok 10400, Thailand**(2) Thai Microelectronic Center, National Science and Technology Development Center, Pathumthani, Thailand*

Local structure of indium oxynitride (InON) nanocrystal prepared by reactive gas-timing rf magnetron sputtering technique are under investigation. In this technique, N₂ and O₂ were interchangeably fed into the sputtering system. The feeding time ratio of N₂ and O₂ (N₂:O₂) was varied. It was found that the optical properties of InON thin film depends on this gas timing ratio. Therefore the local structure analysis of the film is needed in order to determine the relation between the gas timing ratio and its optical properties. In this work, InON thin film with 30:0 seconds timing ratio (no oxygen) was analysed for its local structure using X-ray absorption fine structure (XAFS) technique in conjunction with first principle calculation. The XAFS measurement was performed on L3 absorption edge of In atom at the synchrotron light research institute (SLRI), Thailand. The result of the analysis indicates that the local structure of the film is similar to the 4-fold InN structure and there is O atom substitute N atom in the structure. This result is in agreement with the result from Auger electron spectroscopy that there is O content in the film. The O atoms in the film with 30:0 gas timing ratio may come from the remaining O₂ in the sputtering chamber.

Poster no. PS2.133 - Session 2**XAS characterization of embedded Ge nanoparticles: size-dependent trends and changes in shape and phase by ion irradiation**

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By combining XAS and auxiliary techniques we have studied the structural and thermal properties of four embedded Ge NP distributions with mean diameters between 4 and 9 nm. We find for all cases that the NP core is crystalline (diamond lattice) but the surface layers are reconstructed in a bulk-like amorphous structure. This explains the much reduced coordination numbers observed for the second and third nearest-neighbours in the Ge NPs and lends support to the importance of interface effects on the technologically relevant properties. We further observe that structural disorder increases, mean vibrational frequency increases and linear thermal expansion decreases as the mean size of the NP decreases. All trends scale linearly with inverse NC diameter, reflecting the combined effects of surface reconstruction and the surrounding matrix. When irradiated with 5 MeV Si ions ("lower energy" regime), the NPs initially maintain a spherical shape but become completely amorphous at fluences significantly smaller than the needed to amorphise bulk crystalline Ge, as verified from linear combination fits to the XANES region and the evolution of the EXAFS mean square relative displacements. The smaller the NPs, the lowest the amorphisation fluence. At higher fluences, the NPs gradually dissolve in the matrix, with a concomitant increase in Ge-O bonds. Such susceptibility to amorphisation can be explained in terms of the reconstructed surface acting as a nucleation centre for the amorphous phase. A different behaviour is observed when the NPs are irradiated with 185 MeV Au ions ("swift heavy ion" regime), where amorphisation is followed by a change in NP shape. Such change is size dependent: while NPs smaller than 7 nm become rods elongated along the ion beam direction, bigger NPs become oblate spheroids elongated perpendicularly to the beam direction. These results are interpreted in terms of a recently suggested model for the shape change of Ge NPs under irradiation.

Poster no. PS2.134 - Session 2**EXAFS study of Ag nanoparticles in soda-lime glasses**

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Local structure of Ag atoms in Ag nanoparticles of various size in soda-lime glasses has been studied by Ag K-edge XAFS at T=10 K in sample 1 – obtained via ion Na⁺/Ag⁺ exchange and in sample 2 – obtained after annealing of sample 1 [1]. Fourier transform (FT) analysis of Ag XAFS in metallic Ag (reference compound) gives that the Ag-Ag structural parameters for the first shell of the absorbing atom are determined by the single-shell fit, using C₃ cumulant and the k-interval for FT, started from $k_{min} = 7.4 \text{ \AA}^{-1}$, to diminish the effect of the multiple scattering (MS) and the second and more distant shells. The same k-interval was used for the FT analysis of Ag XAFS in samples 1, 2, which permits to separate the Ag-O contribution of Ag ions, connected with two oxygen atoms in these glasses, and to study Ag-Ag contributions of the Ag atoms from the inside (species a) and from the surface (species b) of the nanoparticles. The fits of the Fourier peak of coordinating atoms for the absorbing Ag atoms, performed by the two-shells model, in which the first shell represents Ag atoms in species (a) and the second – in species (b), give the structural parameters for corresponding Ag species in samples 1 and 2, as well as estimates for the relation of the number of Ag atoms inside and on the surface of nanoparticles in these samples. The obtained estimates are in 5 % agreement with the data of TEM investigations [1].

[1] R.Schneider, M.Dubiel, J.Haug, and H.Hofmeister, AIP Conf. Proc. 882, Melville, 743 (2007)

Poster no. PS2.135 - Session 2**Reactivity of iron oxide nanoparticles: existence of a nano-effect on cobalt adsorption?**

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During the last decade, interest in nanoparticles (Np) has grown in environmental sciences because of their exceptional properties that might be exploited to improve water treatment or soil remediation processes. The specific properties of Np, i.e. enhanced adsorption capacity, are often ascribed to the increase of specific surface area (SSA) with decreasing size. Recent studies revealed a real "nano-effect" in term of surface reactivity suggesting different adsorption mechanisms at the surface of Np smaller than 20 nm: e.g. 6 nm maghemite particles adsorb 3 times more As per surface unit than the 20 nm ones [1]. The aim of this work is to study the mechanisms of Co(II) sorption at the surface of nano-maghemite particles (Fe(III) spinel, nMag) ranged between 20 to 6 nm. Sorption isotherms performed on nMag show (i) that the Co removal depends on the particles size (ii) and the highest efficiency of the 6 nm Np to remove Co once normalized by the SSA. The maximum adsorption capacity reaches 25 Co atoms per nm². Such high Co sorption cannot be only explained by a single adsorption layer process.

XAS experiments both at the Co and Fe K-edge were performed using a crystal analyzer spectrometer (CAS) at BM30b beamline (ESRF, France) [2,3]. The high-energy resolution of the CAS enables to get rid of the matrix fluorescence (Fe K-lines at Co K-edge) and to enhance the XANES features. XAS results combined with XRD indicate that adsorbed Co atoms is in the octahedral symmetry. The XANES feature suggests that Co atomic environment is similar to that in CoFe₂O₄ reference compound. This strongly suggests Co diffusion within the octahedral vacancies of the nMag. At the same time, Fe diffusion within the surface tetrahedral vacancies was also observed.

[1] M. Auffan et al., *Langmuir* 24 (7) 3215 (2008).

[2] E. Collart et al., *J. Synchrotron Rad.* 12, 473 (2005).

[3] J.-L. Hazemann et al., *J. Synchrotron Rad.* 16, 283 (2009).

Poster no. PS2.136 - Session 2**XAFS study of the thermal behaviour of gold bulk and clusters**

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Materials showing negative thermal expansion coefficient (NTE) over large temperature ranges are nowadays of great interest for their possible applications. Small nanoparticles show changes in their properties with respect to the corresponding bulk, mainly due to the high surface to volume ratio and to the confinement of electrons in a small volume. In the present paper we report a XAFS study on the thermal expansion coefficient of an Au foil and of Au clusters of very small dimensions ranging from 2.4 nm and 5.0 nm. Their L3 edge has been investigated in the temperature range 20K - 300 K and a very accurate data analysis has been performed taking into account the presence of asymmetry effects. Results on Au bulk compared with X-ray diffraction data, provided detailed information on the local dynamics of Au. Using an original approach based on symmetry considerations, the root mean square amplitude of the vibrations perpendicular to the bond length was directly determined from XAFS data. All clusters showed a thermal trend of the first shell distance significantly different from that of the bulk. The larger clusters were characterized by a reduction of the thermal expansion coefficient with respect to bulk; in the smallest samples the crossover from a thermal expansion to a NTE effect was observed. A simple model, based on the contribution of localized states induced by the finite size of the clusters, qualitatively accounts for the observed behaviour.

Poster no. PS2.137 - Session 2**XAS study of silver nanoparticles formed in phaseolus vulgaris**

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The phytoremediation can be used to recover precious metals like gold, silver, platinum and palladium, indicating that there is a wide opportunity for use it as a remediation technology in mining. The alfalfa alive was used to reduce the silver and forming silver nanoparticles Ag (0).

The phaseolus vulgaris plant (beans) was used to form silver nanoparticles through bioreducción of Ag (I) to Ag (0) in the living plant. Two groups of plants were used. One group of plants grew at garden soil and the other in cotton.

In both cases, a solution of AgNO₃ were added initially in a concentration of 0.01M then, the concentration was changed to 0.1mm. The samples were analyzed with X-Ray Absorption Spectroscopy (XAS) at the Stanford Synchrotron Radiation Laboratory (SSRL) and later with Transmission Electron Microscopy (TEM). Analyzing the media of cultivation in soil and cotton and also in the roots of the plants, silver was found as silver oxide (AgO). In stem and leaves silver was found as Ag(0). The XAS spectras were adjusted for more accurate results. The plant has the ability to reduce the valence of silver and form nanoparticles.

The TEM images show that the average particle size is 18 nm, showing in various forms and a greater number of them in the leaves of plants grown in soil.

Poster no. PS2.138 - Session 2**Structural characterization of bimetallic Ag-Au nanoparticles in glasses**

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Metal nanoparticles embedded in glass have been thoroughly studied because of their specific optical properties. The present work is directed to the fabrication of bimetallic Ag/Au nanoparticles by double ion implantation and to their structural investigation. Ion-implanted samples were measured at the Ag K- and Au L₃-edge at HASYLAB/Hamburg and ESRF/Grenoble, respectively, in fluorescence mode (at 10 and 20 K). The normalized EXAFS spectra of the Ag K-edge exhibit specific effects in dependence on the implanted dose of metal ions. For smaller Ag and Au ion doses (2×10^{16} ions/cm²), there is only a shoulder that can be assigned to nanoparticles. Whereas for doses of 4×10^{16} ions/cm² for subsequent implantation of both ions, a sharp peak similar to that of Ag foil can be detected. The Fourier transformed spectra show Ag-Ag and Ag-O bonds for small ion doses, for high ion doses two different correlations (Ag-Ag and Ag-Au) can be found between 2 and 3 Å. Comparable results were reported for flame sprayed gold-silver nanoparticles [1]. At the Au L₃-edge, the high-dose implantation creates an additional Au-Ag correlation visible in the Fourier transformed spectra too. These results indicate the formation of Ag-Au alloy nanoparticles for high-dose sequential implantation of Ag and Au ions (4×10^{16} ions/cm² in each case) whereas for lower doses the ionic state of implanted ions should exist in the main. Experiments by transmission electron microscopy revealed the formation of smaller homogeneous particles of ~ 5 nm mean size and larger ones of ~ 15 nm that exhibit an internal void, i. e. core-shell particles [2]. However, the EXAFS data prove bimetallic structures for both cases.

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[2] M. Dubiel, H. Hofmeister, E. Wendler, J. Non-Cryst. Solids 354 (2008) 607

Poster no. PS2.139 - Session 2**Growth and structure of Ge-Si nanoclusters encapsulated in silica**

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Group IV semiconductor nanoclusters (NC's) embedded in dielectrics have attracted great attention due to their potential applications in optical and information storage devices. The main challenge posed by the characterization of systems in the nanoscale is the loss of long range order, which hampers the application of the classical crystallography approaches developed for the study of bulk materials. In this sense, XAFS is ideally suited to the study of nanomaterials, due to its local character. In this work, thin films of silicon oxides ($\text{SiO}_{1.8}$) containing $\text{Ge}_x\text{Si}_{1-x}$ ($x=0.6$) NC's were prepared by co-sputtering followed by high temperature annealing. With this method, small particles, with sizes ranging from 1 to 4 nm were obtained. We present results of an extensive characterization of the coalescence of small Ge-Si nuclei, their growth with formation of NC's and subsequent crystallization. Such processes have been followed in detail by high resolution transmission electron microscopy (HRTEM) and synchrotron radiation-based techniques such as X-ray absorption fine structure spectroscopy (XAFS), grazing incidence X-ray small angle scattering (GISAXS) and X-ray diffraction (XRD) which provide information on the short range order, microstructure and long range order, respectively.

The evolution of the size distribution as a function of time and temperature of annealing, the transition from a supersaturated mixture of isolated Ge ions dispersed in silica to a nanocrystalline structure and the critical size and temperatures for crystallization were determined by GISAXS and XRD. XAFS yielded the dependence of average coordination number, bond-length and structural disorder with average NC's diameter. Temperature-dependent EXAFS measurements will be presented and results for the Einstein temperatures associated with Ge-Ge and Ge-Si bonds will be compared to the strain obtained by Raman scattering and XRD.

Poster no. PS2.140 - Session 2

μ -EXAFS, μ -XRD, μ -XRF and μ -PL characterization of compositional gradiented $\text{In}_x\text{Ga}_y\text{Al}_{1-x-y}\text{As}/\text{In}_{x'}\text{Ga}_{y'}\text{Al}_{1-x'-y'}\text{As}$ multi quantum wells electro-absorption modulated laser realized via selective area growth

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In the last years strong efforts have been made to improve the frequency of optical fiber communications. In particular the use of a special kind of integrated optoelectronic device called Electro-absorption Modulated Laser (EML) [1] allows to communicate at long distances at 10 Gb/s or higher: this is based on a Multiple Quantum Well (MQW) Distributed Feedback Laser (DFB) monolithically integrated with an MQW Electro Absorption Modulator (EAM).

To grow on the same InP substrate these two structures we used Metal Organic Vapor Phase Epitaxy combined with Selective Area Growth (SAG) [2], a particular growth technique based on the fact that deposition doesn't occur on semiconductor areas covered by SiO_2 stripes. This means that reactive species coming from the gas phase are enriched by those coming from the mask in the neighborhood of it, resulting in a variation in composition and thickness of the $\text{In}_x\text{Ga}_y\text{Al}_{1-x-y}\text{As}$ quaternary alloy grown near (SAG region) and far (field region) from the mask. The SAG region will host the DFB laser, while the field region will host the EAM.

The variation in the chemical composition takes place in the micrometrical scale. Laboratory μ -photoluminescence proves the effectiveness of the SAG technique in modulating the MQW energy gap along SAG and field regions. To obtain space-resolved structural information we used the X-ray microbeam available at the ESRF ID22 beamline. Combining μ -EXAFS, μ -XRD and μ -X-ray fluorescence we obtained information about the spatial variation of the growth thickness and of the chemical composition. In particular we estimated the width and the mismatch of the barrier and the well in the MQW structures and the Ga-As bond length.

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[2] M. Gibbon et al., Semicond. Sci. Technol. 8, 998 (1993).

Poster no. PS2.141 - Session 2**Shape and structural changes induced in embedded Pt nanocrystals by swift heavy ion irradiation**

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The effects of swift heavy ion irradiation (SHII) on embedded Pt nanocrystals (NCs) were investigated by transmission electron microscopy (TEM), small-angle x-ray scattering (SAXS) and x-ray absorption fine structure (near edge (XANES) and extended (EXAFS) regions). Pt NCs were formed in amorphous SiO₂ by ion implantation and thermal annealing. Spherical NCs with mean diameters of ~ 8 nm and ~ 14 nm were irradiated with Au ions in the energy range 27-185 MeV, with fluences ranging from 2×10^{12} to 2×10^{15} cm⁻². Upon irradiation, NCs larger than an energy dependent threshold diameter changed shape, becoming rods with the major dimension aligned parallel to the incident beam. In contrast, NCs smaller than the threshold diameter decreased in size but remained spherical. Coincident with elongation, NC dissolution was also observed by means of SAXS measurements, which show a decrease in the total NC volume with increasing energy deposited into the matrix. XANES analysis revealed the presence of Pt-H bonding in samples annealed in forming gas at 1200 and 1300 °C, yet the H content decreased upon SHII at a NC-size dependent rate. EXAFS analysis showed a size dependent bond length contraction for unirradiated NCs, from which a surface tension was calculated. Upon irradiation, structural parameters like coordination number, bond-length and mean-square relative displacement were strongly influenced by the Pt-H bonding and NC dissolution.

Poster no. PS2.142 - Session 2**Local atomic and electronic structure around copper atoms in ferromagnetic AlN:Cu nanorods**

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Ferromagnetic nanorods AlN with 5 at.% of copper [1] were studied using synchrotron based x-ray absorption spectroscopy above Cu K and L₃ edges. This material has important semiconducting properties from nanostructured AlN and new ferromagnetic properties induced by intrinsically nonmagnetic copper dopants. The main problem in interpretation of ferromagnetic properties is that it is not easy to obtain exact position of doping atoms in a host lattice and local atomic structure around them. X-ray absorption spectroscopy is a unique tool for solving this problem. Advanced analysis of XANES [2] allows extracting parameters of local atomic geometry around absorbing atom with high degree of accuracy.

This work is devoted to the investigation of the copper doping atoms neighborhood in host AlN lattice during AlN nanorods growth. We utilize both XANES and EXAFS spectroscopy of copper K-edge. XANES of Cu L₃ edge is used for confirmation of supposed ideas from Cu K-edge. X-ray absorption spectra were simulated using finite difference method beyond muffin-tin approach. Magnetic properties of the point Cu defects in AlN host lattice and small free copper clusters were estimated using full potential linear augmented plane-wave approach. Theoretical simulations of experimental spectra clearly identify a formation of small copper clusters inside AlN lattice. Average size of the clusters was estimated to be less than 10 Å (from analysis of both XANES and EXAFS regions of spectra). Calculation of magnetic properties for different copper point defects in AlN host lattice and free copper clusters show induced spin magnetic moments on copper atoms in AlN matrix and intrinsic spin magnetic moments of free copper clusters.

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[2] - Smolentsev G., Soldatov A.V., Feiters M.C., Phys.Rev.B 75, 144106 (2007).

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Poster no. PS2.143 - Session 2**(Co, Cu)-codoped ZnO dilute magnetic semiconductors studied by XAFS**

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X-ray absorption fine structure (XAFS) technique was employed to study the local structure around and the effect between Co and Cu ions in $\text{Zn}_{0.95-x}\text{Cu}_x\text{Co}_{0.05}\text{O}$ ($x=0, 0.02$) dilute magnetic semiconductors (DMSs) prepared by sol-gel and pulsed laser deposition methods. The Co *K*-edge XAFS results unambiguously indicate that the doped Co ions are located at the substitutional Zn sites for all the samples. In contrast, the Cu *K*-edge XAFS analysis combined with XRD results reveals that the doped Cu ions are separated to form the phase of CuO compound and incorporated into the ZnO lattice for the samples calcined at 1073 K and sintered at 1473K, respectively. While for the film samples, the metallic Cu is precipitated. We find that the effects of Co and Cu ions are relatively independent in the low concentration regime for the samples prepared under the same conditions. The results provide an experimental guidance in the synthesis of the codoped ZnO based DMSs.

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Poster no. PS2.144 - Session 2**EXAFS study of tellurium nanoparticles**

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Trigonal tellurium (t-Te) has a chain structure with two-fold coordinated covalent bonds. The hybridization between lone-pair orbital and antibonding orbital in adjacent chain brings about interchain interactions which affect intrachain covalent bonds. Twofold coordinated chains, much like those in t-Te, exist even in the nanoparticles, but covalent bonds or intrachain interactions are stronger than those of t-Te as shown by a shorter bond length and higher Einstein temperature[1]. We report the size dependence of the structural parameters of the Te nanoparticles.

Layers of Te and NaCl were deposited, and samples of Te nanoparticles isolated in NaCl matrix were obtained. Samples are represented by their average thickness of the Te thin films. EXAFS measurements for Te *K*-edge (31.8 keV) were carried out at the NW10A of PF-AR.

Figure shows the size dependence of the intrachain first neighbor (1NN) coordination number (*N*) and distances (*r*). Almost values of *N* are same as that of t-Te except 0.5 nm-thick-films. This independence of *N* with the sample thicknesses implies that the twofolded covalent chains are preserved even in the nanoparticles. The atomic distance *r* is same as that of t-Te in the thicker samples, but it shortens with decrease of the sample thickness below 10-nm-thick films. The bond distance of the 0.5-nm-thick films is 0.047 Å shorter than that of t-Te. These results show that the basic structure, that is, two-folded chains is preserved, but the covalent bond strengthened below the 10 nm-thick-films. This is confirmed by Einstein temperatures which are obtained with temperature dependence of Debye-Waller factors.

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Poster no. PS2.145 - Session 2
EXAFS study of bismuth nanoparticles

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Rhombohedral bismuth has a layer structure and the Bi atoms are incorporated into two-dimensional networks of puckered six-fold rings. The bondings between the three-fold co-ordinated Bi atoms are mainly covalent. Raman-scattering measurements of bismuth nanoparticles suggest a phase transition from semimetallic rhombohedral Bi nanocrystalline to semiconducting amorphouslike nanoparticles with decreasing size[1]. We report the size dependence of the structural parameters of Bi.

Layers of Bi and NaCl were deposited, and samples of Bi nanoparticles isolated in NaCl matrix were obtained. The samples are represented by their average thickness of the Bi thin films. EXAFS measurements were carried out for Bi L₃-edge at BL-12C of the Photon Factory (PF)-KEK.

It is difficult to obtain EXAFS functions for Bi-L₃ edge, because the large oscillation structure exists around 4 Å⁻¹. While it is usual to extract EXAFS oscillations from the edge, we restrict the extracting region in the range above 4.0 Å⁻¹. Figure shows obtained EXAFS functions of the 0.5 nm- and 300 nm-thick films. We obtained good quality of EXAFS functions up to high wavenumbers. The Fourier filtered EXAFS functions were fitted by a nonlinear least-squares method to the theoretical function within the frame of a one-shell model with Bi-Bi pairs including third order cumulant. The atomic distance of the 0.5 nm thick films is about 0.006 Å shorter than that of the crystalline Bi. Breaking of interlayer correlation may induce shortening of the atomic distance.

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Poster no. PS2.146 - Session 2
State-selective monitoring of heterogeneity of gold and platinum nanoparticle catalytic sites related to fuel cells

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Au nanoparticles are active for low-temperature CO oxidation only supported on TiO₂ and of particle size 3 nm. Pt nanoparticles in polymer electrolyte FCs must contact with active carbon to conduct e^- , with wet polymer to conduct H^+ , and with fuel gas. It is highly difficult to analyze each site structure at the interface of 2 or 3 phases under catalytic conditions [1,2]. State-selective XAFS is only one method to clarify this heterogeneity.

Au L α_1 emission corresponded to Au(0)/(I) for Au/TiO₂ catalysts using fluorescence spectrometer equipped with Ge(555) crystal [1] set at SPring-8 37XU. Next, Au L₃-edge XAFS spectra for Au δ^- and Au δ^+ were obtained by tuning to Au L α_1 peak top-5.2 eV and peak top+5.2 eV, respectively. The spectra were similar to data generated by FEFF8.2 for Au interface site models in contact with surface O and Ti atoms of anatase TiO₂(001), respectively. The 2p-5d transition peak in the former spectrum was suppressed. Due to tune energy difference, absorption edge shifted by 8.6 eV in CO, but the shift was 11.4 eV in air. The extra shift in air was only observed for Au particles of mean particle size 3 nm, not for greater Au particles, suggesting Au δ^+ -O₂ δ^- species as reaction intermediate at the interface of Au and Ti [1].

Pt L β_1 emission energy was tuned for Pt L₂-edge XAFS of Pt-C electrodes on Nafion. 2p-5d peak intensity change and absorption edge shifts were detected. The efficiency of 3-phase interface at Pt can be evaluated based on independent monitoring of Pt δ^- in contact with electrons from C, Pt⁰ in nanoparticles, and Pt δ^+ in contact with H⁺ from Nafion/H₂ or O₂ δ^- in air.

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[2] Izumi et al., *Mater. Lett.* **61**, 3833 (2007).

Poster no. PS2.147 - Session 2**XAFS study of local atomic structure in CoPt nanoparticles**

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CoPt₃ is a bimetallic magnetic material which is synthetically produced either in alloy form having in this case a fcc structure with a lattice constant of 3.85 Å, or in a core-shell structure. CoPt₃ is widely studied due to its magnetic properties and application in data-storage media, sensors and read heads. Another reason for interest in this system is its use for catalysis. From synthesis by wet chemistry, the nanoparticles are surrounded by a shell of organic ligands. In order to study these nanoparticles, they are generally deposited on substrates like Si wafers by dip or spin coating or Langmuir-Blodgett techniques. Such nanoparticle films often exhibit a well-ordered hexagonal arrangement. The internal atomic arrangement of the nanoparticles remains unclear. The changes in bond lengths and atomic coordination, e. g. by decreasing crystalline quality or oxidation are concerned. In order to investigate changes of the bond lengths and of the atomic coordination of Co and Pt atoms in CoPt₃ nanoparticles the Near Edge X-ray Absorption Fine Structure (NEXAFS) and Extended X-ray Absorption Fine Structure (EXAFS) were used.

The XAFS spectra were measured around the Co K absorption edge (7.709 keV) in fluorescence mode at the HASYLAB, beamline E4, using a Si(111) double crystal monochromator and a one pixel HPGe detector. The experimental XANES spectra were analysed by comparison with spectra calculated by FEFF8 code. The EXAFS data were analysed using the Athena and Artemis program. The analysis proves that the CoPt nanoparticles have chemical disordered fcc structure with a lattice constant of 3.81 Å and a stoichiometry of about 1:1. The result of the analysis will be discussed in details.

Poster no. PS2.148 - Session 2**Structural origin of magnetic anisotropy in CoPt₃(111) epitaxial nanostructured alloys**

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The perpendicular magnetic anisotropy (PMA) observed on Co_xPt_{1-x} nanostructures makes them good candidates for applications on high density magnetic storage devices. An interesting behaviour has been reported on CoPt₃(111) grown on WSe₂(0001) substrate by molecular beam epitaxy. In these systems the weak van der Waals interactions between the adatoms and the Se atoms forming the topmost hexagonal plane of the substrate, lead to epitaxially grown nanostructures which depict drastic enhancement of ordering kinetics and PMA for growth temperatures well below 420K.

Preliminary RHEED (reflection high energy electron diffraction) and XRD (x-ray diffraction) measurements have shown that the nanostructures formed at room temperature (RT) have a chemically disordered fcc structure. Raising the deposition temperature (T_d) above 400K, the L1₂-type long range order appears and PMA vanishes.

Polarized XAFS measurements allow probing the local structural anisotropy related to the out-of-plane easy magnetization axis responsible for the PMA. In particular, it has been possible distinguishing the structural features parallel and perpendicular to the substrate plane by accurate Co K-edge XAFS data analysis, performed including single and multiple scattering contributions up to the fourth neighbour shells. A short range structural anisotropy has been observed by XAFS in the sample prepared at RT, in contrast with the disordered long range structure found by RHEED and XRD. This anisotropy, characterized by preferential Co-Co correlations parallel to the film plane, disappears in the samples deposited at $T_d=700$ K. To understand the reason of such Co segregation, CoPt₃ nanostructures were grown on NaCl(001). In these samples the local (XAFS) as well long range (XRD) structural features are definitively isotropic demonstrating the relevance of the substrate in determining the structural anisotropy then the magnetic response of these nanoparticles.

Poster no. PS2.149 - Session 2**XAS studies of nanostructured $V_2O_5nH_2O$ obtained in hydrothermal conditions**Valmor Roberto Mastelaro¹, W. Avansi¹, C. Ribeiro², and E. R. Leite³*(1) Instituto de Física de São Carlos - Universidade de São Paulo, São Carlos São Paulo Brasil.**(2) Embrapa, Empresa Brasileira de Pesquisas Agropecuárias, São Carlos, SP, Brazil.**(3) LIEC - DQ/UFSCAR, Universidade Federal de São Carlos, São Carlos, SP, Brazil.*

In the last decade, nanostructured vanadium oxide compounds have attracted much interest due to their chemical and physical properties. Among the various vanadium oxide compositions that can be obtained, vanadium pentoxide V_2O_5 possesses a unique set of properties because its structure is composed of two-dimensional layers that can be used as an intercalation compound. This work reports a systematic structural study of the synthesis of $V_2O_5nH_2O$ nanoparticles using the vanadium peroxide route by a template-free hydrothermal method without the addition of organic surfactant or inorganic ions. The variation in the electronic and local atomic structure was checked by X-ray absorption spectroscopy (XAS). HR-TEM technique was used to study the modifications in the morphology of nanoparticles. The XANES and the EXAFS part of the absorption spectra were measured at the V K-edge using the D08B-XAFS2 beam line at the Brazilian Synchrotron Light Laboratory (LNLS). HR-TEM analysis shows the formation of $V_2O_5nH_2O$ orthorhombic phase in the nanowire and nanorod forms which was developed by the dehydration of $V_2O_5nH_2O$ monoclinic phase. XANES results show that the dehydration process and the resulting change observed in the structure of the as-synthesized samples did not alter the oxidation state of vanadium in the samples with $V_2O_5nH_2O$ orthorhombic phase when compared with the precursor. Nevertheless, the $V_2O_5nH_2O$ monoclinic phase showed the presence of a mixed valence of vanadium atoms. The local structure around the vanadium atoms in the samples with $V_2O_5nH_2O$ monoclinic phase displayed a higher degree of symmetry within the VO_5 square pyramid structure, albeit with a more disordered medium range order than that of the samples containing $V_2O_5nH_2O$ orthorhombic phase. The analysis of EXAFS spectra are in good agreement with XANES results.

Poster no. PS2.150 - Session 2**Copper nanoclusters deposited on a surface: local atomic and electronic structure**Victoria Mazalova¹, Alexander Soldatov¹, Kazuhisa Tamura², and Hiroyuki Oyanagi³*(1) Southern Federal University 5, Sorge st. 344090 Rostov-on-Don Russia**(2) Synchrotron Radiation Research Center, Quantum Beam Science Directorate, JAEA, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198 Japan**(3) AIST, Tsukuba 305-8568, Japan*

The metal/semiconductor interface has been a subject of intensive studies because of its importance in modern nanotechnology and scientific interests such as investigation of the mechanism of energy band bending. To fully understand the deposition process, it is important to know the local structure of the substrate and the deposited layer on an atomic scale. X-ray absorption fine structure (XAFS) analysis is a leading technique for studying of the local atomic and electronic structure of atoms with high sensitivity even at the surface without a long-range order. We have investigated the structure of electrochemically deposited Cu on GaAs(100) with various coverages using XANES (X-ray Absorption Near Edge Structure) and EXAFS (extended X-ray absorption fine structure) techniques.

Experimental Cu K-XANES spectra of Cu/p-GaAs(100) for various coverage were obtained at the Photon Factory (Japan). The interatomic distances and coordination numbers were calculated by means of EXAFS analysis. The experimental Cu K-edge XANES of Cu nanoclusters deposited on GaAs surface have been analyzed on the basis of full potential calculations of XANES in a combination with DFT geometry optimization. Our investigation has showed that Cu nanoclusters were characterized by a shorter Cu-Cu bond length than that of the bulk fcc Cu were formed when the surface coverage of the Cu overlayer was less than 0.25 monolayer. Cu atoms in small nanoclusters were coordinated with the O atoms. At higher coverage the Cu microclusters grow with a fcc structure.

Poster no. PS2.151 - Session 2**Growth process of Ag triangular nanoplates observed by in situ XAFS**Haruno Muruyama¹, Naomi Hashimoto¹, Hideki Tanaka¹*(1) Chuo University 1-13-27 Kasuga Bunkyo-ku 112-8551 Tokyo Japan*

Geometric controls of anisotropic nanocrystals have been widely studied to develop nanomaterials since the properties depend on their shapes. Especially, Ag triangular nanoplates have attracted attention in order to apply it to catalysts. Though synthesis methods of the Ag triangular nanoplates have been studied, growth process of the triangular plates has not been well understood. In this work, we investigated growth process of the Ag triangular nanoplates by in situ XAFS measurements. The Ag triangular nanoplates were synthesized by photo-induced reduction of silver nitrate ethanol solution in the presence of PVP at room temperature. During the synthesis reaction, the products were sampled at every hour. Structures of the samples were analyzed by Ag K-edge XAFS, XPS and UV-vis absorption spectroscopy. The samples were deposited onto a collodion-coated Cu grid, and then the shapes were observed by using scanning transmission electron microscopy.

By photo-irradiation of 4 h, EXAFS oscillation of the sample, which was similar to that of Ag metal, was obtained. The bond distance for Ag-Ag bonds of the sample was 0.29 nm, which was the same with that of Ag metal. On the other hand, the coordination number for Ag-Ag bonds of the sample was 9, which is lower than that of Ag metal as 12. The coordination number increased with increase of the photo-irradiation time. By photo-irradiation of 12 h, the coordination number for Ag-Ag bonds was grown to 12. The shapes of the sample were sphere with the diameter of 2 nm at photo-irradiation time for 4 h, and triangular nanoplates with the edge length of 60 nm at photo-irradiation time for 12 h, respectively. Moreover, the color analysis of Ag ions showed that the reduction reaction went to completion by 4 h of photo-irradiation. The results show that small spherical nanocrystals were produced at the beginning of photo-induced reduction and then the Ag triangular nanoplates were grown by aggregation of the small Ag nanoparticles.

Poster no. PS2.152 - Session 2**The calculated XANES K-spectra of all elements of (10,0) nanotubes**Igor Yakovlevich Nikiforov¹, B.V. Gabrelian¹, A.A. Lavrentyev¹, I.Ya. Nikiforov¹, and J.J. Rehr²*(1) Don State Technical University Gagarin sq. 1 344010 Rostov-on-Don Russia**(2) University of Washington, Seattle, WA98195, USA*

Using the cluster version of the multiple scattering theory with the FEFF8 code [1] the XANES K-spectra of zinc, sulfur, selenium and tellurium in nanotubes and clusters were calculated. The nanotubes were imitated by structures of growing sizes: from 40 to 120 and 200 atoms. But the bulk systems were modeled with clusters with the same radius as of nanotubes, of 87 atoms. The XANES of K-spectra of Zn and chalcogenides for nanotubes constructed from 120 and 200 atoms coincide with each other. Because of that we conclude, that model of 120 atoms is good enough to represent the infinite nanotube. The calculated K-spectra for clusters were compared with the experimental data for corresponding crystals. The satisfactory agreement between calculated and experimental data was obtained.

Poster no. PS2.153 - Session 2**Local structure around gold atoms in Au/Sn core/shell system studied by X-ray absorption fine structure**Zhiyun Pan¹, Kuai Yu², Yingmei Li², Yi Xie², Tao Yao¹, Zhi Xie¹, Wensheng Yan¹, Zhihu Sun¹, and Shiqiang Wei¹*(1) National Synchrotron Radiation Laboratory & School of Nuclear Science and Technology, University of Science and Technology of China, Hefei 230029, People's Republic of China**(2) Department of Nanomaterials and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, P. R. China*

Au-Sn bimetallic nanoparticles synthesized by adding different amount of tin salts to the Au colloidal solution were investigated by x-ray absorption fine structure (XAFS). The Au L₃-edge XAFS spectra demonstrate the sequential formation of the stable Au/AuSn core/shell, AuSn, AuSn/AuSn₂ core/shell and AuSn₂ nanoparticles with increasing of the amount of Sn. The EXAFS fitting results show that the contents ratios of each component in Au/AuSn and AuSn/AuSn₂ core/shell nanoparticles are 28% : 72% and 25% : 75% respectively. The bond lengths of Au-Au and Au-Sn pairs in core/shell nanoparticles elongate 0.02~0.07 Å compared with those in pure nanoparticles. We consider that the lattice mismatch between the core and shell phase is mainly reduced by elongation of the bond lengths in both phases.

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Poster no. PS2.154 - Session 2**Resonance in XAFS of finite-size systems encapsulated in fullerenes and carbon nanotubes**Andrey Alexeevich Pavlychev¹, and X. O. Brykalova¹*(1) St. Petersburg State University Ulianovskaia, 1 198504 St. Petersburg Russia*

Resonance features in X-ray absorption and inner-shell photoemission spectra provide a sensitive probe of local electronic and atomic structures in matter. In the present work XAFS of composite systems such as endohedral molecules confined in fullerene (M@C₆₀) and one-dimensional crystalline structures encapsulated in single-wall-carbon-nanotubes (1D@SWCNT) are examined and discussed. Resonance photoemission from 1D@SWCNT in directions perpendicular to the translation vector **z** attracts our main attention. The double barrier optical potential approach successfully applied to X-ray absorption in molecular units bound in van-der-Waals clusters [1,2] is used. The internal potential barrier describes scattering of 1s photoelectron on atoms within the endohedral molecule or the crystalline structure whereas the external barrier describes scattering on carbon atoms embodied in the fullerene or the nanotube. Applicability of this approach to 1s photoemission from 1D@SWCNT is examined. The performed calculations predict that in addition to the shape and confined resonances new window-like resonances appear. These “windows” are associated with resonance tunneling of the photoelectron through the composite system in directions perpendicular to **z**. The “windows” as well as multielectron excitations play substantial role in NEXAFS. The computed and experimental data are compared to reveal the “windows”. The link of the “windows” with atomic structures of M@C₆₀ and 1D@SWCNT is discussed in more detail.

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Poster no. PS2.155 - Session 2**Analysis of local structure of Ru_{1-x}Ni_xO₂ electrocatalytic materials**Valery Petrykin¹, Katerina Macounova¹, Marina Makarova¹, and Petr Krtíl¹*(1) J. Heyrovsky Institute of Physical Chemistry, Doležalkova 3, 18223 Prague, Czech Republic*

Nanocrystalline RuO₂ based materials doped with 3d transition metals demonstrate selectivity towards chlorine evolution in the electrolytic chlorine and oxygen production [1]. While electrolytic chlorine production is the most convenient technology for the generation of this industrially important chemical, oxygen forms as an undesired by-product of water electrolysis. Therefore, control of electrocatalytic properties of the anode materials and their selectivity are of practical importance. At the same time understanding of the nature of “active sites” for both oxygen and chlorine evolution is limited due to the lack of structural information on the doped RuO₂ materials.

In this work we carried out structural characterization of Ru_{1-x}Ni_xO₂ (0 < x < 0.3) samples using EXAFS data at Ru-K and Ni-K edges. Analysis of EXAFS spectra and local structure refinement revealed: a) for low Ni concentration (x < 0.1) the material's structure can be interpreted in terms of Ni substitution for Ru in RuO₂, and Ni tends to occupy metals sites along the diagonal of rutile unit cell. The deviation of site occupancy from the statistically expected value indicates possible tendency of Ni towards clustering; b) for Ru_{1-x}Ni_xO₂ materials with x > 0.1 Ni content, local structure around Ni can not be explained solely in terms of substitution, and one should assume formation of defects with rock salt motif in the vicinity of Ni ions. Such defects may be similar to shear planes, which are common for the oxygen deficient rutile crystals in the TiO_{2-d} system. The packing of atoms in these defect layers is characterized by higher metal-metal coordination numbers. Thus, found aggregation of Ni in the Ru_{1-x}Ni_xO₂ materials may indicate preferential location of Ni atoms in the vicinity of such shear planes.

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Poster no. PS2.156 - Session 2**Depth-resolved probing of the chemical state of buried nanolayers using the example of various TiO_x** Beatrix Pollakowski¹, and Burkhard Beckhoff¹*(1) Physikalisch-Technische Bundesanstalt Abbestr. 2-12 10587 Berlin Germany*

Probing non-destructively buried nanolayers, photon-in photon-out spectroscopy provides an approach to study properties of materials beyond the information depth of other methods. Grazing incidence x-ray fluorescence in combination with near-edge x-ray absorption fine structure (GIXRF-NEXAFS) investigation enables a depth-resolving analysis of thin layer stacks with respect to both elemental composition and speciation. The strength of the x-ray standing waves (XSW) field strongly affects the mean penetration depth of the incident beam and can consequently tune the information depth of the emitted fluorescence radiation in a way that it varies from a few to several hundreds of nanometers.

The sample system investigated first consists of several 10 nm titanium nanolayers oxidized to different extents and buried below a preserving 5 nm carbon layer, which was investigated in the PTB laboratory at BESSY II using monochromatized undulator radiation and absolutely calibrated instrumentation [1, 2]. Initial results confirm the speciation potential, appropriate angular corrections [3] based upon parallel XSW simulations allow for a constant mean penetration depth. The measured Ti- $L_{3,2}$ absorption spectra exhibit different bonds and oxidation levels, e.g. TiO , Ti_2O_3 and TiO_2 , providing information comparable to that from other methods suited for near-surface layers. The full potential of this method is expected for double layer systems consisting of a titanium oxide (TiO_2 or Ti_2O_3) and metallic titanium layer.

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Poster no. PS2.157 - Session 2**Local atomic and electronic structure of $\text{ZnO}:\text{Mn}$ films and core/shell nanorods $\text{ZnO}/\text{ZnO}:\text{Mn}$.**O. E. Polozhentsev¹, V. E. Kaidashev¹, E. M. Kaidashev¹, and A. V. Soldatov¹.*(1) Southern Federal University 5 Zorge st. 344090 Rostov-on-Don Russia*

Investigation of the local atomic and electronic structure of thin films $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ and nanoscale core/shell structures (nanorods $\text{ZnO}/\text{film Zn}_{0.9}\text{Mn}_{0.1}\text{O}$) have been performed.

Theoretical analysis of x-ray absorption near edge structure (XANES) has been applied to study peculiarities of local atomic and electronic structures. Experimental Zn and Mn K-edge XANES spectra of the studied materials have been measured at the synchrotron radiation facility SIBERIA-2 (Kurchatov Center of Synchrotron Radiation and Nanotechnology, Moscow) and at laboratory spectrometer Rigaku, Research Center for Nanoscale Structure of Matter, Southern Federal University, Rostov-on-Don, Russia.

The structures are synthesized with high pressure pulsed-laser deposition (PLD) method. Synthesis and growth of the studied structures have been considered in detail for the determination of Mn embeddings and impurities in ZnO host lattice. Their distributions crucially influence on magnetic and electronic properties and therefore the different positions (such as substitutional site, interstitial site, clustering and secondary phase) in the host lattice have been considered.

Theoretical analysis of experimental XANES data have been carried out using a self-consistent, real space multiple scattering method (FEFF8.4 code) and a finite difference method (FDMNES2008 code). Band structure calculations have been performed with Wien2k-08 code. Local structure parameters have been refined using multidimensional interpolation approach on the basis of XANES fitting (Fitit2.0 code). Principal Component Analysis (PCA) (realized in Fitit2.0 code) have been used to determine the concentrations of different secondary phase compounds in the spectra of studied compounds.

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Poster no. PS2.158 - Session 2**Grazing incidence diffraction anomalous fine structure spectroscopy of Ge/Si nanostructures and molecular dynamics structural models**Maria Grazia Proietti¹, N. A. Katcho², H. Renevier³, M.I. Richard⁴, V. Favre-Nicolin⁵, and G. Bauer⁶

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Ge/Si nanostructured systems, as domes, super-domes, pyramids are widely investigated, as a natural evolution of the GeSi compounds which are still of great interest as a model system for semiconductor solid solutions [1]. Grazing Incidence Diffraction anomalous Fine Structure (GIDAFS) is an emergent technique in the field of nanostructures characterization. We have recently shown that combination of DAFS spectroscopy, and Multiwavelength Anomalous X-Ray Diffraction (MAD) provides a unique tool to investigate the structural properties of nanostructures [2]. Strain, chemical composition, atomic intermixing, can be determined thanks to the chemical contrast mapping of reciprocal space provided by MAD, and to quantitative analysis of DAFS oscillations giving information on the local environment of the resonant atoms (chemical selectivity) selected by diffraction (spatial selectivity). We present recent results on different Ge/Si nanostructures, showing different morphologies depending on growth conditions. On one side, we have performed quantitative analysis of DAFS oscillations. On the other side we propose theoretical simulations of MAD and EDAFS oscillations performed on an island+substrate model (~20 million atoms) calculated by means of a Paralell Molecular Dynamics calculations [3,4]. This novel theoretical approach, both improves the EDAFS and MAD interpretation. It provides new insights and perspective and gives a stronger impact to this powerful experimental technique.

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[4] <http://lammps.sandia.gov>**Poster no. PS2.159 - Session 2****XANES and EXAFS studies of manganese incorporated into novel mesoporous aluminophosphate thin film**Mojca Rangus¹, Nataša Novak Tušar^{1,2}, Iztok Arčon^{2,3}, Saša Cecowski¹, Gregor Mali¹, and Venčeslav Kaučič¹

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Transition-metal (Me) functionalized mesoporous aluminophosphate (AlPO) and silicoaluminophosphate materials (SAPO) have been widely investigated as heterogeneous catalysts due to their hydrothermal stability and high catalytic activity[1]. MeAlPO and MeSAPO as powders have attracted attention as acid, base and redox heterogeneous catalysts. As thin films, these materials also have potential in optics and electronics. Recently, the detailed preparation and structural characterisation of thermally stable mesoporous cubic AlPO as a thin film was reported for the first time[2].

We functionalized the above mentioned mesoporous cubic AlPO structure with silicon and manganese. MnSAPO was prepared by using Pluronic F127 block copolymer (EO₁₀₆PO₇₀EO₁₀₆) as a structure directing agent by Evaporation-Induced Self-Assembly (EISA) procedure on a thin film obtained by the dip coating method. The local environment of manganese was investigated by XAS (X-ray Absorption Spectroscopy). XANES and EXAFS results of the MnSAPO thin film show that there are Mn³⁺ and Mn²⁺ cations present in the MnSAPO framework in almost equal amounts. In MnSAPO thin film there are Mn cations coordinated to four oxygen atoms, which are not all equally distant from manganese. This indicates that Mn ions are located in distorted tetrahedral environment. This suggests the presence of framework manganese and thus catalytically active acid and redox sites are expected.

We acknowledge financial support of DESY and the European Community Contract RII3-CT-2004-506008 (IA-SFS) and access to synchrotron radiation facilities of HASYLAB for XAS measurements.

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Poster no. PS2.160 - Session 2**Order effect of Au nanoparticles on forest SWCN studied by NEXAFS.**Felix G. Requejo¹, J.M. Ramallo-Lopez¹, L. Zhang², and D.E. Resasco³*(1) INIFTA Diag. 113 y 64. (1900) La Plata, BA, Argentina.**(2) Pacific Northwest National Laboratory, Richland, WA. USA.**(3) University of Oklahoma. Norman, OK, USA.*

Aligned Single Wall Carbon Nanotubes (SWCN) have a great interest because of their potential applications in many fields[1]. In order to optimize their use in different applications in catalysis, nanoelectronics, optics or nanobiotechnology, it becomes interesting to functionalize their surface with metal nanoparticles (NPs). However, attention should be paid to the order of the CNT after the addition of the NPs. In this work, we studied the order of vertical and horizontal aligned-SWCN functionalized with gold NPs by two different methods through carbon K-edge XANES spectroscopy[2] using linearly polarized x-rays. Gold NPs were introduced to the SWCN by evaporation of gold and by dipping in a solution of thiol-capped Au NPs. Through the peaks attributed to the dipolar transition of core level 1s electrons into C-C π^* and C-C σ^* states in the conduction band we found that a decrease in the order of the vertical-aligned SWCN after the addition of gold by both methods takes place. However, the order of the SWCN can be recovered after a fast annealing. No such effect is observed for horizontal-aligned SWCN which may indicate a weaker interaction between the side walls and the metal NPs.

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Poster no. PS2.161 - Session 2**Structural nanoscale characterization of (Ga,Fe)N and (Ga,Fe)N:Si by x-ray absorption spectroscopy**Mauro Rovezzi¹, F. D'Acapito¹, A. Bonanni², A. Navarro-Quezada², Bogdan Faina², Tian Li², and Tomasz Dietl³

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One of the most controversial issues of today's materials science is the origin of ferromagnetic behaviour persisting above room temperature in semiconductors doped with transition metals and rare earths. Until recently, many misleading assumptions and conclusions have been caused by a lack of proper correlation between fabrication parameters and structural characterization at the nanoscale. In fact, in a recent study [1] we have demonstrated experimentally that combining synchrotron radiation tools like x-ray diffraction and absorption with high-resolution transmission electron microscopy is possible to control magnetic ions aggregation into the semiconductor host lattice.

In this contribution we focus on a systematic investigation by x-ray absorption fine-structure (XAFS) spectroscopy in Fe-doped as well as Fe and Si-co-doped films grown by metalorganic vapour phase epitaxy. The analysis of the extended-XAFS data shows that depending on the growth conditions, Fe atoms either occupy Ga substitutional sites in GaN or precipitate in the form of *epsilon*-Fe₃N nanocrystals, which are ferromagnetic and metallic. Precipitation can be hampered by reducing the Fe content, or by increasing the growth rate or by co-doping with Si. The near-edge region of the XAFS spectra provides information on the Fe charge state and shows its partial reduction from Fe⁺³ to Fe⁺² upon Si co-doping.

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Poster no. PS2.162 - Session 2**Analysis of the structure of amorphous and nanocrystalline materials using valence-to-core x-ray emission spectroscopy**Olga Safonova¹, J.M.M. Millet², and V.A. Safonov³*(1) SNBL at ESRF, 6 Rue Jules Horowitz, 38043 Grenoble, France**(2) Institut de Recherches sur la Catalyse et Environnement de Lyon, Claude Bernard Lyon 1-2 avenue A. Einstein, 69626 Villeurbanne, France.**(3) Department of Electrochemistry, Faculty of Chemistry, Moscow State University, 119991 Moscow, Russia*

Novel materials often involve very small particles and amorphous structures where no long-range order exists. To characterize such materials element-specific characterization techniques are important. Valence-to-core X-ray emission spectroscopy (XES) has shown to be very useful for the analysis of the local structure of 3d metals [1]. In the present work valence-to-core XES spectra were measured for a number of reference compounds of V, Cr, Fe, Co, and Ni. Good agreement of the experimental results with the full multiple scattering calculations forms the basis for a detailed analysis of the first coordination shell of transition metals. The unique opportunities of valence-to-core X-ray emission spectroscopy (XES) in combination with XRD, XAS, and XPS for material chemistry and catalysis will be illustrated by two examples. In the first study valence-to-core XES was used to confirm the presence of Cr-C, Fe-P, Co-P, Ni-P, and Ni-B bonds in the bulk structure of electrochemically deposited amorphous metal coatings. The XRD measurements have shown that these solids before annealing at high temperatures do not have any long-order crystalline structure. In a second case the structure of V-Al mixed amorphous oxide catalyst under in situ conditions of acrylonitrile synthesis from propane was studied. Using valence-to-core XES we observed that bulk vanadium atoms are reduced during the catalytic process. However, significant nitridation (i.e. the integration of nitrogen in the first coordination shell of vanadium in the bulk structure), which was discussed in literature, was not confirmed. The results obtained by in situ valence-to-core XES and ex situ surface XPS allowed us to conclude that both surface and bulk oxygen species are active in the catalytic process of acrylonitrile production, whereas the reactive nitrogen species are mainly present on the surface of this catalyst.

[1] P. Glatzel, U. Bergmann, *Coord. Chem. Rev.* 249, 65 (2005).**Poster no. PS2.163 - Session 2****Effects of capping agent on cobalt nanoparticles**Luisa Sciortino¹, Alessandro Longo², Francesco Giannici¹, and Antonino Martorana^{1,2}*(1) università degli studi di palermo, dipartimento di chimica inorganica ed analitica**(2) Istituto per lo studio dei materiali nanostrutturati, CNR, Palermo*

Cobalt nanoparticles have attracted considerable interest because of their applications in memory devices. The properties of nanoparticles are closely dependent on their size, shape and structure[1] that are affected by the synthetic process.

During sample preparation the presence and the nature of a capping agent play a crucial role. For this reason the knowledge of the changes induced by the capping agent on the morphology of nanoclusters is essential[2]. In this work we synthesised cobalt nanoparticles using different capping agents (TOA, ODA, stearic acid) by two different routes: thermal decomposition[3] and SMAD techniques[4].

A combination different synchrotron radiation techniques: SAXS, high-resolution XRD and EXAFS was used in order to investigate the Co nanoparticles formation. The characterization was carried out with no sample pre-treatment in order to obtain information about the electronic and geometric structure and morphology. EXAFS data allowed to investigate the ability of the capping agent to protect clusters from oxidation. Moreover, the capping agent influences the coalescence process and nanoparticles size was investigated by SAXS and EXAFS. XRD data showed very complex patterns due to the presence of both fcc and hcp phases and, therefore, a high-resolution XRD technique was required. The two close-packed structures exhibited high lattice disorder due to the presence of stacking faults[5]. Results indicate that a good cluster size control is possible by using different synthesis conditions.

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Poster no. PS2.164 - Session 2**Structure evolution of free NaCl clusters with size: X-ray absorption spectroscopy analysis.**Valentina Shmatko¹, Galina Yalovega¹, and Alexander Soldatov¹*(1) Department of Physics, Southern Federal University, Sorge 5, Rostov-na-Donu, 344090 Russia*

The investigation of the local structure of the free NaCl clusters presented here has been done on the basis of advanced theoretical analysis of experimental XANES data, obtained previously. Here, we report a study of local atomic and electronic structure of free NaCl clusters as the function of the cluster size. Theoretical analysis Na K-edge XANES spectra for the free clusters containing 8, 18 and 72 atoms and bulk has been carried out by both a self-consistent full multiple scattering method (FEFF8.4 code) and advanced approach beyond muffin-tin approximation - finite difference method (FDMNES 2008 code). Density function theory (DFT) calculations (ADF2008.1 code) and MOPAC preoptimization have been applied to obtain the optimized geometry for these objects. Structure of crystal NaCl fragments was used an initial point of calculation. Strong decreasing of interatomic distances and deviation of atomic structure from the structure of a bulk NaCl crystal was observed in the nanoclusters. The shape of free clusters, containing 18 and 72 atoms is more close to spherical form. The theoretical analysis of XANES spectra for all investigating clusters, including all nonequivalent positions of atoms has been carried out. Use muffin-tin potential gives satisfactory results for ionic clusters NaCl, when is applied (z+1) approach, but essential redistribution of intensity of peaks is observed. Better agreement of experimental and theoretical data was obtained non-beyond the muffin-tin approximation. Densities of states (DOS) for NaCl clusters and crystal NaCl have been calculated and it was found that the energy band gaps (HOMO-LUMO gaps) are differ for optimised structure and crystal NaCl fragments.

Poster no. PS2.165 - Session 2**Structural characterisation of Pt₃Co nanoparticles as a function of the temperature**Yvonne Soldo^{1,2}, G. Greco², M. Minicucci², L. Olivi³, A. Cognigni³, and A. Di Cicco²*(1) CNRS-LEPMI 1130 rue de la Piscine 38402 St. Martin d'Hères France**(2) Università di Camerino via Madonna delle Carceri 62032 Camerino Italy**(3) ELETTRA, Sincrotrone Trieste S.C.p.A. Strada Statale 14, Km 163.5 Basovizza 34012 Trieste - Italy*

It has been shown that Pt₃Co nanoparticles used as a catalyst for cathode of Proton Exchange Membrane Fuel Cells (PEMFC) enhance oxygen reduction reaction (ORR) activity even by a factor two compared to Pt nanoparticles [1]. Surface Pt segregation by high temperature annealing, enriching Pt on extended Pt alloy surfaces, is one possible strategy in order to increase ORR activity. It is then important to investigate structural modifications induced on nanostructured platinum-cobalt alloys by thermal treatment. Moreover, an order-disorder phase transition is expected near 1000 K [2]. We have performed an EXAFS study on commercial E-TEK Pt₃Co nanoparticles up to 1073 K, both at Pt L_{III} and Co K edges. TEM (Transmission Electron Microscopy) and XRD (X-ray diffraction) measurements have also been used in order to have more complete information about structural evolution induced by thermal treatment. As expected, nanoparticles agglomerate after heating. Significant contraction of the cobalt-cobalt first neighbour distance is observed at high temperature: such decrease is irreversible, as it is pointed out by the measurements performed after going down to room temperature (RT). This is not the case for platinum-platinum interatomic distance, whose value at RT after heating is stable. Complete EXAFS, XRD and TEM results will be presented.

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Poster no. PS2.166 - Session 2**Formation, irradiation and modification of Co nanoparticles**

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We combined XAS and complementary techniques to study Co nanoparticle (NP) formation, irradiation and modification. NPs were formed in silica by ion implantation and thermal annealing with the NP size and phase governed by the fabrication conditions. Samples were then irradiated with 9-185 MeV Au ions.

The size distributions of the as-formed spherical NPs were measured with transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS). XANES and electron diffraction showed NPs of size smaller than 5 nm were HCP while those larger than 12 nm were FCC. An HCP/FCC mixture was apparent for intermediate sizes.

EXAFS revealed a NP size-dependent bondlength contraction resulting from surface-curvature-induced capillary pressure. With a liquid-drop model, we then determined the NP surface tension which exceeded that of the bulk. Einstein temperatures were calculated from temperature-dependent EXAFS measurements with NP values greater than that of the bulk, approaching the latter as the NP size increased. We attribute this increase to an upward shift in the VDOS resulting from capillary pressure.

Low-energy irradiation of small NPs yielded an amorphous-like inter-atomic distance distribution consistent with our calculations using a melt-and-quench model. In the bulk, quench rates sufficient to produce amorphous material cannot be achieved. We suggest the encapsulating amorphous matrix stabilized the amorphous Co phase.

High-energy irradiation of large NPs induced a stress-driven FCC-to-HCP phase transformation (XANES) followed by a spherical-to-rod-like shape transformation (TEM and SAXS), the latter driven by molten ion track formation in the matrix. With XANES, we also evaluated the ion energy and fluence dependence of NP dissolution in the matrix. In summary, complementary methods have been used to probe the properties of Co NPs subjected to ion irradiation, demonstrating novel non-bulk-like transformations in both phase and shape.

Poster no. PS2.167 - Session 2**XANES study on Mn-doped SiC magnetic thin films**

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X-ray absorption near edge structure (XANES) is used to study the local structure around Mn ions in the Mn-doped 3C-SiC thin films with the Mn concentration of 0.005 and 0.18 prepared by molecular beam epitaxy. The XANES spectra of the Mn₄Si₇ compound and Mn ions located at the substitutional sites of Si and C atoms in SiC lattice are theoretically calculated. The results indicate that the experimental XANES spectra of Mn ions are well reproduced by the one of Mn₄Si₇ compound, and no substitutional Mn ions at the Si or C site exist in the SiC host. Furthermore, the Mn₄Si₇ nanocrystalline grains were found to be dispersed in the SiC host, which are the major origin of the ferromagnetism in the Mn-doped SiC DMSs.

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Poster no. PS2.168 - Session 2**NEXAFS investigation of crystal phase of HfO₂ films**E. Yu. Taracheva¹, E. O. Filatova¹, A. A. Sokolov¹, A. A. Ovchinnikov¹, K. M. Lysenkov¹, D. E. Marchenko²*(1) St.-Petersburg State University Ulyanovskaya 1 198504 Saint-Petersburg Russia**(2) BESSY, Albert Einstein Str. 15 D-12489 Berlin Germany*

HfO₂ films of 5 nm thick deposited by two methods (ALD and MOCVD) and film of 100 nm thick prepared by ALD method were studied near OK-absorption edge. OK-absorption spectrum in HfO₂ is formed by transitions from the O1s atomic orbital to the system of unoccupied hybrid MO: e_g , t_{2g} , a_{1g} and t_{1u} .

It has been established that sensitivity of OK-absorption spectrum to the crystal phase is specified by two groups of parameters. The main critical parameter controlling ordering is relative intensities of components e_g and t_{2g} . The second parameter is presence or absence of components related with transition to the a_{1g} and t_{1u} .

Studying of films of the same thickness, but synthesized by different methods has allowed to establish following laws. Both films have similar e_g/t_{2g} intensities ratio (e_g is more intensive than t_{2g}). At the same time in the spectrum of film prepared by MOCVD the e_g feature has the narrow and sharp shape and the a_{1g} and t_{1u} features are well-expressed. But in the spectrum of film prepared by ALD the a_{1g} and t_{1u} features are practically not visible. One can conclude that the film synthesized by ALD is amorphous and the film prepared by MOCVD has the explicit signatures of crystal structure.

Studying of the film of 100 nm thick prepared by ALD method specifies:

- 1) e_g/t_{2g} intensity ratio is inverse in comparison with this ratio in a thin films studied
- 2) e_g component is split in a result of Jahn-Teller effect that is characteristic of 7-fold coordinated monoclinic phase
- 3) The structures connected with transitions to a_{1g} and t_{1u} MO are well-expressed. One can conclude that the film is crystallized mainly in monoclinic phase.

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Poster no. PS2.169 - Session 2**Al K edge XANES analysis of Al doped ZnO thin films**Miki Tatsuro¹, Masaki Ueda¹, Shin-ichi Nagamatsu¹, Tatsuro Miki¹, Takashi Fujikawa¹, Masako Sakamaki¹, Takehisa Konishi¹, and Masatoshi Sakai²*(1) Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage, 263-8522 Chiba, Japan**(2) Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage, 263-8522 Chiba, Japan*

We report on a local structural analysis of Al doped zinc oxide based on a real-space multiple scattering calculation of Al K-edge XANES spectra. Measured Al K-edge XANES spectra[1] of this system show systematic changes as a function of the dopant concentration.

The overall trend of the observed spectra is qualitatively reproduced by the substitutional site model, only when some of the neighboring Zn sites are assumed to be occupied by dopant atoms. This suggests that the doped Al atoms are not uniformly distributed and have a tendency to aggregate in the ZnO matrix. Hence, existence of small α -Al₂O₃ -like clusters also cannot be excluded at the higher Al concentrations.

In addition, another result of calculations employing the interstitial 4- or 6-fold coordinated sites model showed that high concentration of the interstitial 6-fold coordinated Al is not likely.

We attribute the lowering of the electronic conductivity at heavy doping to suppression of impurity band formation due to the observed nonuniform distribution of dopants.

[1] M. Sakamaki et al., in preparation.

Poster no. PS2.170 - Session 2**Structural characterization of cobalt nano-clusters obtained through template controlled synthesis**

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Physical properties of metallic nanoparticles are strongly dependent on their size and the interaction of the surface ions with capping agents also plays a determinant role. Therefore, in order to understand the physical properties of nanoparticles their size, size distribution and surface interactions must be strictly controlled. The template-controlled synthesis strategy represents a valuable method to obtain monodispersed metallic particles; recently cross-linked polymers have been used successfully. These synthetic routes offer several advantages over other methods (i.e. colloidal synthesis), in fact properly choosing the pore sizes of the resins they allow tuning the particle size down to the nm scale with narrow (monochromatic) particle size dispersion. Moreover they provide minimal interaction with the support, good resistance to oxidation and prevent particle aggregations and interparticle interactions. We present here a detailed EXAFS characterization of template controlled Co nanoparticles prepared using different resin templates. Nanoparticles were also investigated by TEM, HR-TEM showing sharp size distribution in 1-2 nm range. Magnetic response has been also probed by VSM. Co K edge XAFS measurements were performed as a function of temperature from 25 K to room temperature in order to highlight anomalies in thermal expansion coefficient originating from electron localization effects.

Poster no. PS2.171 - Session 2**XAFS study of host-guest supramolecular assemblies - cucurbit[8]uril and Cu(II) complex**

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The family of cucurbit[n]urils (CB[n]) - macrocyclic cavitands consisting of several glycoluril fragments interconnected by methylene bridges - is interesting due to their unique features, in particular, their ability to have "calibrated guests" [1]. Creation of supramolecular inclusion compounds on the basis of CB[n] makes it possible to produce catalytically active systems in a CB[n] matrix. The aim of this work is to prepare samples of CB[8] with "copper guests" (Cu(acac)₂; [Cu(en)₂(H₂O)₂]²⁺; [Cu(cyclam)]²⁺) and to study copper location after next treatment of the synthesized inclusion compounds such as annealing at 200 - 330°C in H₂.

EXAFS and XANES spectra of the CuK- absorption edges have been measured at the VEPP-3 storage ring of the Budker Institute of Nuclear Physics (Novosibirsk, Russia). Cu atoms local arrangement has been determined using the fitting procedure for $\chi(k)k^2$ in the photoelectron wave-number range from 3.0 Å⁻¹ to 12 Å⁻¹. The CuK EXAFS and XANES spectra of the system have been measured at different stages of their treatment to determine the composition of Cu closest environment, coordination numbers and interatomic distances.

It has been found out, that Cu-Cu bonds appear in CB[8]+Cu(acac)₂ samples annealed in hydrogen at 250°C [2] unlike the other samples ([Cu(en)₂(H₂O)₂]²⁺; [Cu(cyclam)]²⁺) in which annealing at 330°C leads to decomposition of the complexes in the intracavity of the cavitand and occasionally of CB[8] itself, with possible formation of various copper fragments.

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Poster no. PS2.172 - Session 2**In situ time-resolved XAFS study on the formation and phase separation of supported Pt-Sn bimetallic nanoparticles**Yohei Uemura¹, Yasuhiro Inada², Mizuki Tada³, Akira Yagishita², Masaharu Nomura², and Yasuhiro Iwasawa^{1,4}*(1) The University of Tokyo 7-3-1 Hongo, Bunkyo-ku 113-0033 Tokyo Japan**(2) KEK-PF, 1-1 Oho Tsukuba, 305-0801 Ibaraki Japan**(3) Institute for Molecular Science, 5-1 Higashiyama Myodaiji Okazaki 444-8787 Aichi Japan**(4) The University of Electro-Communications, 1-5-1 Chofugaoka Chofu-shi, 182-8585 Tokyo Japan*

We have exploited the dynamic formation and phase separation processes of Pt-Sn bimetallic nanoparticles supported on γ -Al₂O₃ and SiO₂ by in situ time-resolved XAFS. Pt-Sn bimetallic nanoparticles have received much attention as catalysts for reforming of hydrocarbons, anode in fuel cells, etc. The addition of Sn to Pt catalysts improves deactivation of Pt catalysts in hydrocarbon reforming processes due to much less coking by their alloying, and in fuel cell systems because a Pt-Sn bimetallic anode is tolerant to poisoning by impurity carbon monoxide in hydrogen. The catalytic property of Pt-Sn bimetallic nanoparticles is referred to the electronic states near the Fermi level and the redox property, which are relevant particularly to the behavior of fuel cell electrodes. Thus, in the present study dynamic behaviors of supported Pt-Sn bimetallic nanoparticles in reduction and oxidation processes were characterized by in situ quick XAFS and dispersive XAFS (DXAFS) at Pt L_{III}-edge and Sn K-edge.

In situ Quick XAFS and DXAFS revealed that Pt-Sn bimetallic nanoparticles were formed within 30 s by reduction with H₂ (p_{H₂} = 20 kPa) at 400 °C. It took more than 10 min to finish oxidizing Pt atoms included in Pt-Sn bimetallic nanoparticles with O₂ (p_{O₂} = 20 kPa) at 400 °C, while Sn atoms included in the Pt-Sn nanoparticles were oxidized completely within 5 min. Pt and Sn atoms in the nanoparticles were oxidized in different time scales, respectively.

Microstructural information and phase separation in the Pt-Sn bimetallic nanoparticles will be discussed.

Poster no. PS2.173 - Session 2**MnSb inclusions in the GaSb matrix grown by MBE**Anna Wolska¹, Krystyna Lawniczak-Jablonska¹, Marcin T. Klepka¹, and Janusz Sadowski^{1,2}*(1) Institute of Physics PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland**(2) Lund University, MAX-Lab, Lund SE-221 00, Sweden*

Heterostructures consisting of metallic ferromagnetic layers deposited on semiconducting materials are potentially useful for spintronics applications. Among them, these created by introducing ferromagnetic inclusions in a semiconductor matrix seems to be very promising. It requires preparing the system in such a way that small ferromagnetic nanoparticles are immersed in the semiconductor host lattice. Such a composite material could be considered as a good semiconductor filled with nanomagnets providing a built-in magnetic field. In order to obtain materials with desired magnetic properties, it is reasonable to start with inclusions with a Curie temperature above room temperature. One of the candidates is MnSb. It was showed that Curie temperature for bulk MnSb is equal to 587 K and for the MnSb layers reaches even 620 K. This indicates that MnSb can be a good compound to form nanoinclusions ferromagnetic above room temperature.

In order to form the MnSb inclusions several MBE processes were tested. Different kinds of substrate as well as growth temperatures were examined. The EXAFS technique was used to monitor the location of Mn in the layers. Depending on the applied growth conditions Mn atoms were found in different positions in the GaSb lattice (in several cases in position of Sb atoms). Finally we succeed in the formation of the GaMnSb layers with MnSb inclusions on two types of substrates: GaAs(111)A and GaSb(100). The substrates temperature during growth was kept at 720 K. EXAFS analysis confirmed that the local structure around Mn atoms in these layers was close to that of the MnSb reference powder. The existence of MnSb inclusions was combined with the magnetic properties of the samples.

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Poster no. PS2.174 - Session 2**Magnetic nature of Co dopants in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods studied by XAFS**Tao Yao¹, Wensheng Yan¹, Zhihu Sun¹, Zhiyun Pan¹, Yuanyuan Li¹, Yi Xie², and Shiqiang Wei¹*(1) National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P.R.China**(2) Department of Nanomaterials and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, P. R. China*

Fluorescence X-ray absorption fine structure (XAFS) technique is used to study the local structures around Co ions in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0.01 \leq x \leq 0.15$) dilute magnetic semiconductor nanorods which were synthesized by a solvothermal method. The Co *K*-edge XAFS spectroscopy reveals that, at low Co concentration ($x \leq 8\%$), the doped Co ions are substantially incorporated into the ZnO host lattice. However, at higher Co doping concentration ($x \geq 10\%$), only part of the Co ions enter the lattice of the wurtzite and the others exist in the form of a Co_3O_4 phase. From the obtained Co–O coordination number, we can estimate that the solubility limit of Co ions in ZnO for our nanorods is about 0.08. The magnetization measurements of Co-doped ZnO nanorods show the intrinsically paramagnetic characteristic, which suggests the intrinsically paramagnetic properties for the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods with a perfect structure.

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XMCD**Poster no. PS2.175 - Session 2****Magnetic anisotropy of induced orbital magnetic moments in As 4p states**Adam Freeman^{1,2}, K. W. Edmonds², N. R. S. Farley^{2,3}, R. P. Campion², A.W. Rushforth², G. van der Laan^{1,3}, F. Wilhelm⁴, A. Rogalev⁴, C. T. Foxon², and B. L. Gallagher²*(1) Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK**(2) University of Nottingham, Nottingham, NG7 2RD, UK**(3) STFC Daresbury Laboratory, Warrington, WA4 4AD, UK**(4) European Synchrotron Radiation Facility, BP220, 38043, Grenoble, France*

Dilute magnetic semiconductors (DMS) which exhibit robust carrier-mediated ferromagnetism have great potential for applications in spintronics[1]. The anisotropic magnetic and transport properties of (Ga,Mn)As are closely related to lattice symmetry and strain, due to the strong spin-orbit interactions of the carrier subsystem.

We investigate this coupling in (III,Mn)As films using x-ray magnetic circular dichroism (XMCD) at the K-edge of Mn, As and Ga. The samples studied were unstrained freestanding (Ga,Mn)As films and strained (In,Ga,Mn)As films on InP substrates. Both materials exhibit a distinct dichroism at the Mn and As K-edges, and weakly at the Ga K-edge. Orbital magnetic moments are calculated using the XMCD orbital sum rule. The Ga 4p shell orbital moment is an order of magnitude less than that of As, showing that the valence band holes are predominantly As-like. The hole density, estimated by magnetotransport, indicates an orbital magnetic moment per hole of $\sim 0.2\mu_B$.

A striking anisotropy of the As orbital moment is found for in-plane and perpendicular directions in the strained films, mirrored by the bulk magnetic anisotropy seen by SQUID magnetometry. Previous studies indicate that the Mn 3d magnetic moments in (Ga,Mn)As are virtually isotropic [2]. The Mn K-edge consists of both 1s to 4p and 1s to 3d transitions. On-site p-d hybridization allows the stronger 4p transitions to dominate, yielding a positive XMCD. This indicates the Mn 4p orbital moment is antiparallel to the bulk magnetization, opposite to that of the 3d states - a valuable insight into the Mn-As hybridization in these materials. Moreover, we show direct experimental evidence of a magnetic impurity coupling to the orbital moment of the semiconductor host, confirming that the As 4p holes give the dominant contribution to the magnetocrystalline anisotropy in DMS.

[1] T. Dietl et al, Science, 287 1019 (2000)

[2] K. W. Edmonds et al, Phys. Rev. Lett. 96, 117207 (2006)

Poster no. PS2.176 - Session 2**Multiple scattering approach to XMCD for Bi doped Gd iron garnet**Ikuko Hojo¹, Shin-ichi Nagamatsu¹, Takashi Maruyama¹, Hiroshi Maruyama², and Takashi Fujikawa¹

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We have studied Bi XMCD in BiGd-IG(Bi doped Gd Iron Garnet) by using the relativistic multiple scattering calculations. BiGd-IG is well known as magnetic-optical material because it strongly enhances Faraday rotation in visible and near-infrared regions with increase of Bi. According to Shinagawa *et al.*, these effects are related to the charge transfer transitions in iron-oxygen molecular complexes modified by covalent mixing of Bi 6p orbitals with oxygen 2p orbitals due to large spin-orbit interaction in Bi[1]. The XMCD analysis is suitable for such studies to understand the interesting behavior; it is important to understand the local magnetic and electronic structure around absorption atom Bi.

We have studied the effect of the nonmagnetic atoms such as Y and Ga substituted for Gd and Fe sites around Bi. XMCD spectra for some substituted models have been calculated and analyzed in comparison with the experimental spectra for the sample $(\text{Gd}_{0.97}\text{Y}_{0.9}\text{Bi}_{1.14})(\text{Fe}_{4.15}\text{Ga}_{0.85})\text{O}_{12}$. The substitution changes XMCD spectra mainly in absorption edge. The results show that the substitution around Bi is crucial to obtain good agreement with the observed XMCD spectra. We have also studied the dependence of the spin polarization of the Bi 6p states, assuming that Bi has the parallel/ anti-parallel magnetic moment to the Gd spin polarization. The calculated result shows that Bi has very small magnetic moment at most.

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Poster no. PS2.177 - Session 2**Magnetic Circular Dichroism effects in the Resonant Inelastic X-ray Scattering at the K pre-edge of 3d transition metal ions: an outlook**Amélie Juhin^{1,2}, Frank M. F. de Groot¹, Christian Brouder², Philippe Saintavirt², and Pieter Glatzel³

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Transition metal elements play an essential role in physics (magnetic materials, superconductors), chemistry (catalysis) and geophysics (*3d* elements are major constituents of the Earth and planets). Properties such as magnetism, catalytic activity and optical absorption are governed by the *3d* orbitals, which can be probed by X-ray spectroscopies at the K pre-edge ($1s \rightarrow 3d + 4p$ transitions), such as Resonant Inelastic X-ray Scattering and X-ray Magnetic Circular Dichroism. Compared with the $L_{2,3}$ edges ($2p \rightarrow 3d$ transitions), the smaller interaction between the core-hole and the *3d* orbitals enables to make a more direct connection to the ground state properties. However, XMCD effects are very small, due to the absence of spin-orbit coupling in *1s* core-hole. This drawback has so far hampered the interpretation of XMCD at the K-edge.

Our project to couple XMCD and RIXS spectroscopies at the K edge of *3d* ions will be discussed. Preliminary calculations performed on divalent Co in the multiplet approach show that large XMCD effects are visible, both in the $1s2p$ RIXS ($K\alpha$ fluorescence) and also directly in the pre-edge structure when measured with a high-resolution fluorescence detector. These theoretical simulations suggest that RIXS-MCD could be used in the future to measure magnetic polarization of the *3d* orbitals, with bulk sensitivity, high energy resolution, and the possibility to study samples in demanding environments such as high-pressure cells.

Poster no. PS2.178 - Session 2**Local magnetic structure around Bi in optical isolator Bi-doped rare-earth iron garnet**Hiroshi Maruyama¹, T. Matsumoto^{1,*}, N. Ishimatsu¹, N. Kawamura², T. Hanai³, and K. Shirai³

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Optical isolator is one of the most essential devices for optical communication. To realize wavelength division multiplexing optical communication system, Bi-doped rare-earth iron garnets BiR-IG have been regarded as an indispensable material because of larger Faraday rotation in visible and infrared regions.

In BiR-IG the Faraday rotation is remarkably enhanced with increasing Bi dopant. This effect has been explained that Bi 6p-orbitals covalently mixed with O 2p-orbitals are crucial for the enhancement of charge transfer transitions in Fe-O molecular orbitals. However, there have been no direct evidence for this explanation. To examine this mechanism, we have recorded X-ray magnetic circular dichroism (XMCD) at the Bi $L_{1,2,3}$ -edges.

Sample of $(\text{GdYBi})_3(\text{FeGa})_5\text{O}_{12}$ powder was prepared from the crystal of practical isolator. XMCD experiment was made at SPRING-8 BL39XU. The spectrum was recorded using the helicity modulation method in transmission mode under $H=0.6\text{T}$ at RT. The Bi $L_{2,3}$ -XMCDs were measured in the wide range of $-70\text{ eV} \leq (E - E_0) \leq 400\text{ eV}$.

The Bi L_1 -XMCD shows a featureless profile with a weak intensity. It is likely that the Bi 6p-states are not notably polarized. In contrast, the Bi $L_{2,3}$ -XMCDs show an oscillatory structure extending to the higher energy range up to about 250 eV above E_0 . It is noted that the Bi 6d-states are strongly polarized and hybridized with the ligand O 2p-states. And the dichroic periodicity is clearly different from that of the EXAFS oscillation. To analyze local magnetic structure around Bi ions, the Fourier transform was carried out the magnetic EXAFS. As a result, magnetic radial-distribution function shows a prominent peak at ca. 2.98 Å, which corresponds to the Bi-Fe atomic pairs. The Bi 6d-states are significantly polarized in BiR-IG instead of the Bi 6p-states in literature.

Poster no. PS2.179 - Session 2**Multiple-scattering approach to Co $L_{2,3}$ -edge XMCD of $\text{C}_{60}\text{-Co}_x$ granular magnetic thin films**Shin-ichi Nagamatsu¹, Takashi Maruyama¹, Yoshihiro Matsumoto², Seiji Sakai², Toshihiro Shimada³, and Takashi Fujikawa¹

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Spin-transport properties in complexes of organic molecules and magnetic transition metals have been discussed to apply spintronics devices in recent years. The local magnetic structures near the magnetic transition metals play important roles in the spin-transport properties. The $\text{C}_{60}\text{-Co}$ granular magnetic thin films show large tunnel magnetoresistance (TMR). The properties depend on the Co contents and low Co content systems exhibit the large TMR properties. The Co $L_{2,3}$ -edge XMCD spectra are observed through $\text{C}_{60}\text{-Co}_x$ granular magnetic films. In order to study the local magnetic structures nearby the Co sites, we have used a fully-relativistic multiple-scattering theory [1]. The main features of the local atomic structure of novel $\text{C}_{60}\text{-Co}_x$ complex mixtures have been studied using density functional theory [2]. The calculated XMCD spectra show main features of observed spectra and strongly depend on the local atomic structures. We clarify the Co-C bonds and discuss the local magnetic structures of nearby atoms.

Reference

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Gas-phase

Poster no. PS2.180 - Session 2**XAS at GaPh BL@ELETTRA: studies of the electronic properties of atoms and molecules of transition metals in vapour phase.**

Monica de Simone¹, Antti Kivimaki¹, Marcello Coreno², Kevin C. Prince³, Piero Decleva⁴, G. Fronzoni⁴, Mauro Stener⁴, Paola Finetti⁵, and Sergio D'Addato⁶

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Acquaintance of atomic and molecular effects at the nanometer and micrometer level is becoming more and more important in technologically relevant condensed matter. Therefore a detailed view of the macroscopic properties of highly correlated systems such as metals, both of main block and d and f blocks, requires a thorough knowledge of their electronic properties. Starting from this point of view, since the beginning of our experimental activity we are developing a program of research utilizing the analysis of synchrotron radiation excited phenomena in VUV range on system containing metal atoms of increasing complexity: atoms, molecules and complexes of metals.

In particular X-ray absorption structures near the ionization threshold are closely related to the local electronic structure around the atom in which the excitation take place and contain the most significant information on the low-lying unoccupied states of the system. Theoretical calculations relate each excitation energy to a virtual state whose nature (valence or Rydberg) can be defined, and yield oscillator strengths which are connected with the composition of the unoccupied orbitals, mapping in particular the dipole-allowed atomic site component of the molecules.

Poster no. PS2.181 - Session 2**Experimental and theoretical investigation of photoabsorption in TiCl_4 , VOCl_3 and CrO_2Cl_2 in the 3p region**

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At variance with 2p excitations, XAS studies of the 3p energy region are very scarce. While 2p hole makes resonances to appear mainly below threshold, and to interact weakly with the continuum, the large autoionization rate of 3p-3d excitation is much more complex to describe and probes the discrete-continuum interaction. Beside the interest in a quantitative understanding of the basic process, the spectral range, with photoelectron kinetic energies around 50 eV, may make it a sensitive probe for surface science studies. Although qualitatively understood, the theoretical description of this region is quite difficult, because of the interplay of several strong interactions: 3p-3d Coulomb and exchange interaction, chemical bonding and orbital splitting, discrete-continuum interaction. These give rise to a structured resonance which spans some tens of eV across the threshold. Similar studies of molecules can elucidate the influence of chemical bond formation, covalency, and change in metal oxidation state.

A study of 3p-edge of 3d metals has been performed at Elettra on free TiCl_4 , VOCl_3 and CrO_2Cl_2 and very recently a theoretical approach, the continuum TDDFT method [1], has been extended to such systems, and an initial calculation on TiCl_4 has been presented [2]. While calculations on the other two molecules are underway, data for TiCl_4 show a very good agreement except for a sharp structure at the resonance, which is absent in the experiment. Similar agreement is observed with other experimental results [3-5], supporting the possibility that the large difference among the theoretical calculation and the experimental data can be due to more subtle reasons worth to be deeply investigated.

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[3] B. E. Bursten et al., Inorganic Chem. 33 (1994) 5089

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Poster no. PS2.182 - Session 2**Size dependence of $L_{2,3}$ branching ratio and 2p core hole screening in X-ray absorption of transition metal clusters**

Konstantin Hirsch¹, Jochen Rittmann¹, Marlene Vogel¹, Vicente Zamudio-Bayer¹, Andreas Langenberg¹, Philipp Klar¹, Jürgen Probst¹, Robert Richter¹, Fabian Lofink¹, Thomas Möller¹, Bernd von Issendorff², and Tobias Lau¹

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Only very recently the first X-ray absorption spectra of size-selected free clusters could be recorded [1], marking an important breakthrough on the way to a detailed study of the local electronic structure of isolated nanoparticles. To achieve this aim, size-selected metal cluster cations were accumulated and studied in a linear ion trap. For the 3d transition metals Ti, V, Cr, Mn, Fe, Co, and Ni an atomic multiplet structure is only present up to the trimer, while tetra- and pentamers already show bulk-like line shapes. The $L_{2,3}$ branching ratio and the L_3 X-ray absorption onset, however, evolve over a much larger size range. Our analysis shows that the evolution of the $L_{2,3}$ branching ratio in 3d transition metals is independent of their effective 2p spin-orbit splitting and can rather be attributed to size-dependent electron delocalization and core hole screening effects. Furthermore, we show how spectral features in $L_{2,3}$ X-ray absorption of bulk transition metals can now be traced back to their atomic origin.

[1] J.T. Lau, K. Hirsch et al., Phys. Rev. Lett. 101 153401 (2008).

Poster no. PS2.183 - Session 2**Geometry of small krypton clusters revealed by site dependent peak shifts in inner-shell spectroscopies**

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We report surface site dependent core level absorption and photoemission, arising from different numbers of the nearest neighbor atoms. This provides specific information on the surface geometry of the small krypton clusters. This work goes beyond previous EXAFS work, where mostly the bulk properties of small rare gas clusters were probed[1]. The experiments were performed at the soft x-ray undulator beamline BL3U at UVSOR-II. X-ray absorption spectroscopy (XAS) spectra were obtained in the Kr_2^+ yield. Core-to-Rydberg transitions can be described by a Rydberg electron and a core-ionized atom. The ionic core is stabilized in clusters by induced polarization (PL) of the surrounding atoms. This stabilization effect results in different redshifts, dependent dominantly on the number of the nearest neighbor atoms, as observed by X-ray photoelectron spectroscopy (XPS)[2,3]. On the other hand, the Rydberg electron interacts in clusters with electrons of the surrounding atoms due to short-range exchange interaction (EX). This results in a blueshift of the low-lying Rydberg states in XAS[3]. The energy shift (ΔE) in XAS of clusters is derived from the competition between the redshift by PL and the blueshift by EX . We can change the size and principal quantum number of the Rydberg orbital as a function of photon energy. This provides information on the radial distribution of clusters by analyzing the blueshift of different Rydberg orbitals. We will also discuss the RAS (resonant Auger spectroscopy) spectra, showing that the Rydberg electron is bound to a doubly charged ion. These results are compared to XAS spectra, where the Rydberg electron is bound to a singly charged ion.

[1] S. Kakar *et al.*, Phys. Rev. Lett. 78, 1675 (1997).

[2] T. Hatsui *et al.*, J. Chem. Phys. 123, 154304 (2005).

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Poster no. PS2.184 - Session 2
EXAFS of diatomic molecules

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Intramolecular interference of ejected and scattered photoelectron waves depends on zero-point molecular motion, molecular motions in final state and changes in equilibrium geometry due to ionization. Special emphasis is put on extended oscillations in intensity of 1s-ionization in diatomic molecules. Within the VDFN model [1,2] the intensity of individual vibration v' -bands is presented as $I_{v'}(h\nu) = I_0 \sin(2kR^+(v') + \Phi(k))$, $h\nu$ is the photon energy, k is the photoelectron wavenumber. $\Phi(k)$ is independent on molecular vibrations, $R^+(v')$ is the characteristic interatomic distance [2]: $R^+(v') = R^+(v' = 0) + v'\Delta$. Here $R^+(0) = \frac{1}{2}(R_e + R^+)$ and $\Delta = \hbar^2/(\mu\omega(R_e - R^+))$, where μ and ω is the reduced mass and the vibration spacing. R_e and R^+ are equilibrium distances in ground and ionized states.

Conventionally far from the threshold the relative intensity $I_{v'}/I_0$ is regarded as independent on $h\nu$ and coincident with the sudden limit. However, the ratio oscillates [2]

$$\frac{I_{v'}(\nu)}{I_0(\nu)} \propto \frac{4v'kF(k)\Delta}{3R^+(0)^2} \sin(2kR^+(0) + \Phi(k)) \quad (1)$$

F is the backscattering amplitude. These oscillations appear exclusively for Franck–Condon transitions. Comparison of the calculated oscillations for CO with the high-resolution experimental spectra confirms the link between EXAFS and geometries in the ground and ionized states. Perspectives in high-resolution EXAFS-spectroscopy of free and bound molecules are discussed. Combination of the Fourier transformation techniques and the Franck–Condon analysis of vibration transitions is regarded as a promising tool for precise determination of the spectroscopic parameters of core-ionized molecular states.

[1] Mistrov D A, De Fanis A, Kitajima M, et. al. PRA 68 (2003)022508

[2] Pavlychev A A, Mistrov D A J.Phys.B 42 (2009) 055103

Poster no. PS2.185 - Session 2

Soft x-ray absorption spectroscopy of amino acids in the gas phase

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Amino acids possess a very flexible skeletal structure, which allows them to adopt various shapes at low energies, for instance at laboratory temperatures or just above. These different shapes of the same molecule are known as conformers, and this flexibility combined with hydrogen bonding are the fundamental phenomena on which protein folding is based. The near edge x-ray absorption and photoemission spectra of eight amino acids in the gas phase have been measured at the carbon, nitrogen and oxygen K edges, and compared with theoretical calculations [1-4]. The nitrogen 1s photoemission spectra show clear evidence of the effect of conformational isomerism, and conformers with OH...N hydrogen bonding between the hydroxyl and amino groups are distinguishable from other isomers with internal hydrogen bonds, such as NH...O. Quantitative estimates of the relative populations of these two classes of conformers have been made, and compared with published predictions of relative energies. Effects of isomerism on the NEXAFS spectra are more difficult to detect, and calculations show that this is in part due to compensating effects in the electronic structure. Conformational differences tend to change the energy of both the core level and the unoccupied orbitals, so that the transition energy does not vary much between conformers. The present spectra at the carbon K edge are similar to those of condensed amino acids, but the nitrogen and oxygen edge spectra are very different.

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[2] O. Plekan et al., Chem. Phys. Lett. 442 (2007) 429.

[3] O. Plekan et al., J. Phys. Chem. A 111 (2007) 10998.

[4] V. Feyer et al., J. Phys. Chem. A 112 (2008) 7806.

Poster no. PS2.186 - Session 2**XANES spectroscopy of sulfur in the gas phase generated from elemental sulfur and pyrite**Alexander Prange^{1,2}, Annette Summers Engel³, and Josef Hormes^{2,4,5}*(1) Niederrhein University of Applied Sciences, Microbiology and Food Hygiene, Rheydter Strasse 277, 41065 Moenchengladbach, Germany**(2) Louisiana State University, Center for Advanced Microstructures & Devices (CAMD), 6980 Jefferson Hwy, Baton Rouge, LA 76806, USA**(3) Louisiana State University, Department of Geology and Geophysics, E305 Howe-Russell, Baton Rouge, LA 70803, USA**(4) University of Bonn, Institute of Physics, Nussallee 12, 53115 Bonn, Germany**(5) University of Saskatchewan, Canadian Light Source Inc. (CLS), 101 Perimeter Road, Saskatoon, SK, Canada S7N 0X4*

Hydrogen sulfide, elemental sulfur (S^0), and polysulfides are some of the most reactive inorganic S species in the biogeochemical sulfur cycle. Gradual thermal changes induced during burial of S-containing solids in sediments can force the emission of sulfur gases (e.g. S_2 - S_8) in varying quantities and compositions. However, the movement of sulfur gases into, out of, or through sedimentary systems has been difficult to measure due to a paucity of suitable techniques to monitor species changes. Therefore, we developed a heating cell to measure gas phase XANES spectra at low X-ray energies (e.g. P, S and Cl-K-edge) at CAMD. In separate experiments, S^0 and pyrite were used as model geochemical systems. These minerals were heated incrementally from room temperature to 400°C and the spectra of the gaseous species recorded at the sulfur K-edge. As there are limited comparable XANES spectra for sulfur gases known to date, for the moment we rely on theoretical chemistry and chemistry to interpret the reactions. Our results do not indicate a “zoo” of sulfur containing molecules (at least, only a few species dominate) in both systems. For example, there is indication that only one sulfur gas compound is generated from pyrite. For elemental sulfur, there is some indication that the sulfur ring opens, causing the formation of a chain-like S structure (probably with negatively charged ends) and the emission of a small sulfur molecule. These first results impact our understanding of sulfur gas dynamics in sedimentary processes.

Poster no. PS2.187 - Session 2**X-ray absorption spectroscopy reveals high symmetry and electronic shell structure of transition metal doped silicon clusters**Jochen Rittmann¹, Marlene Vogel¹, Konstantin Hirsch¹, Philipp Klar¹, Andreas Langenberg¹, Fabian Lofink¹, Robert Richter¹, Jürgen Probst¹, Vicente Zamudio-Bayer¹, Thomas Möller¹, Bernd von Issendorff², and Tobias Lau¹*(1) Technische Universität Berlin - IOAP, Hardenbergstr. 36, 10623 Berlin, Germany**(2) Fakultät für Physik, Universität Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany*

Size selected transition metal doped silicon clusters have been studied with resonant 2p x-ray absorption spectroscopy. For VSi_{16}^+ , the spectrum is dominated by sharp transitions and reveals a highly symmetric silicon cage and a high degeneracy of its electronic states. In spite of the different number of valence electrons, nearly identical local electronic structures are found at the dopant atoms in $TiSi_{16}^+$, VSi_{16}^+ , and $CrSi_{16}^+$. The experimental data can be understood in the spherical potential model. Charge transfer to the silicon cage leads to a local $3d^0$ configuration of the transition metal dopant, quenching the magnetic moment. Our findings are further corroborated by the fact that the local electronic structure of the dopant atom is unchanged when replacing the Si_{16} cage by Ge_{16} . Because of its closed electronic shell structure, the exceptional stability of VSi_{16}^+ can be linked to spherical aromaticity according to the $2(N+1)2$ rule. The data indicate strongly interlinked electronic and geometric properties: While the transition metal atoms impose a geometric rearrangement on the silicon cluster, the interaction with the highly symmetric silicon cage determines the electronic structure of the transition metal dopants.

Poster no. PS2.188 - Session 2**Resonant and direct 2p photoionization spectroscopy of size-selected free silicon clusters**

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X-ray absorption spectroscopy of size selected clusters has become feasible with the use of ion traps to increase target density and absorption length [1]. Here we present first results on 2p X-ray absorption of size selected pure Si_n^+ ($n = 5-92$) clusters. Cluster size dependent changes in the electronic and geometric structure can be deduced from the spectra, and the gradual evolution of the bulk 2p X-ray absorption spectrum can be followed. Compared to metal clusters [1], this evolution extends over a much larger size range in silicon.

Since direct 2p photoionization is associated with a specific ion yield channel, direct and resonant photoionization can be distinguished, giving access to core level photoionization thresholds of size selected clusters. We will present first results and compare the size dependence of the 2p photoionization threshold to the image potential model. In contrast to valence band photoionization of neutral clusters [2], the prolate-compact shape transition does not lead to changes in the 2p core-level binding energies [3].

[1] J. T. Lau, J. Rittmann, T. Möller, B. v. Issendorff, et al., Phys. Rev. Lett. 101, 153401 (2008).

[2] K. Fuke, K. Tsukamoto, F. Misaizu, M. Sanekata, J. Chem. Phys. 99, 7807 (1993).

[3] J. T. Lau, M. Vogel, T. Möller, B. v. Issendorff, et al., in preparation.

Poster no. PS2.189 - Session 2**Inner-shell excitation and fragmentation processes of acetic-acid clusters at the oxygen K-edge**

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In order to investigate inner-shell electron excitation and induced chemical processes of strongly hydrogen-bonded (HB) molecular clusters, time-of-flight (TOF) fragment-mass and excitation spectra of deuterium-labeled acetic acid-d (AAD) have been studied under the effusive and cluster conditions. The experiments were performed using a cluster-beam machine [1] connected to a high-resolution plane-grating monochromator at the c-branch of BL27SU in the SPring-8 facility. Cluster beam was generated by supersonic expansion of AAD/He mixtures through a $\phi 50 \mu\text{m}$ nozzle, whereas effusive gas was prepared by direct introduction of neat AAD through a $\phi 1/16'$ i.d. stainless-steel tube. With $(1s_{CO}-\pi^*_{CO})$ excitation at 532 eV, sample TOF spectra of AAD clusters were compared with those of free molecules. Intensity enhancement of the CH_3CO^+ fragment and growth of the mixed-cluster cations, $(\text{M})_n\text{D}^+$ and $(\text{M})_n\text{CH}_3\text{CO}^+$ could be ascertained in the cluster beams, where AAD molecule is denoted by M. The stable production of CH_3CO^+ upon $(1s_{CO}-\pi^*_{CO})$ excitation can be interpreted as being due to the π^*_{CO} orbital that has an antibonding character both between carbonyl C and O, and carbonyl C and hydroxyl O atoms. The production of $(\text{M})_n\text{D}^+$ is attributed to the deuteron (proton) transfer process within the clusters made up of a stable dimer-unit with doubly-bridged HBs. Under the cluster beam stagnation conditions up to $P_0=0.2 \text{ MPa}$, the maximum size of $(\text{M})_n\text{D}^+$ with $n \leq 5$ could be identified. The $(\text{M})_n\text{CH}_3\text{CO}^+$ production clearly shows that a local fragmentation channel as previously proposed for the formic-acid (FA) clusters [2] are also realized in the present AAD clusters.

[1] Y. Tamenori et al., J. Electron Spectrosc. Relat. Phenom. 144-147, 235 (2005).

[2] K. Tabayashi et al., J. Chem. Phys. 125, 194307 (2006).

Poster no. PS2.190 - Session 2**Site- and state-selective dissociation of methyl-trifluoroacetate observed in core-electron excitation at the oxygen K-edge region**Kiyohiko Tabayashi¹, Takeshi Yamanaka¹, Tomoé Maruyama¹, Chié Harada¹, and Hiroaki Yoshida^{1,2}(1) *Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526 Japan*(2) *Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, Japan*

The site- and state-selective reactions following inner-shell excitation have been fundamental subjects for the isolated [1,2] and condensed [3] molecular systems. Here, we studied core-electron excitation and fragmentation of methyl-trifluoroacetate at the O K-edge, and found the site- and state-selective reactions that occur effectively in the isolated molecular condition. The experiments were carried out using a cluster-beam apparatus [4] placed at the beamline BL-6 of the HiSOR facility in Hiroshima University. Total-ion-yield spectra were obtained in the effusive molecular beam. The band peaks were assigned based on the comparison with other esters [1,2] in the O K-edge. Using time-of-flight spectroscopy, branching ratios of the CH_3^+ and HCO^+ production were measured at the $1s(\text{O}-\text{CH}_3) \rightarrow \sigma^*(\text{O}-\text{CH}_3)$ and $1s(\text{O}-\text{CH}_3) \rightarrow \sigma^*(\text{C}-\text{OCH}_3)$ transitions. Since product CH_3O^+ is known to be a transient species that spontaneously dissociates into $\text{HCO}^+ + \text{H}_2$, the CH_3^+ and HCO^+ production reflects the valence characters of the first core-excited states. The results suggest that the state-selective bond scissions take place after the spectator Auger transition via two-holes/one-electron states. The site- and state-selective dissociation mechanisms will be discussed in comparison with those of other esters [1-3] in the isolated and condensed conditions.

[1] H. Yoshida et al., unpublished work.

[2] R. Kawasaki et al., J. Nucl. Sci. Technol., Suppl. 5, 19 (2008).

[3] M.C.K. Tinone et al., J. Chem. Phys., 100, 5988 (1994).

[4] K. Tabayashi et al., AIP Proceedings, 879, 1788 (2007).

Related Phenomena**Poster no. PS2.191 - Session 2****Low-kinetic energy photoelectron diffractions for C 1s and O 1s electrons of free CO molecules in the EXAFS region**Jun-ichi Adachi¹, Masakazu Yamazaki¹, Takahiro Teramoto², Yasuyuki Kimura¹, Akira Yagishita^{1,2}, Misato Kazama³, Yusuke Ohori³, and Takashi Fujikawa³(1) *Photon Factory, IMSS, KEK 1-1 Oho 305-0801 Tsukuba Japan*(2) *Department of Chemistry, School of Science, The University of Tokyo, Japan*(3) *Graduate School of Integrated Science, Chiba University, Japan*

Photoelectron diffraction phenomena have been used to determine material structures, in particular, for the surfaces, the interfaces and the adsorbed molecules. However, conventional such measurement techniques cannot be applied to free molecules because of the thermal molecular rotation. In order to investigate the electron scattering phenomenon as a fundamental quantum process, it requires the measurement without any effects from the substrates and/or the surrounding environments. Recently, we have developed a spectrometer that records velocity-map images of both photoelectrons and fragment ions ranging the whole solid angles. This spectrometer (Coincidence velocity-map image spectrometer; CO-VIS) enables us to measure molecular-frame photoelectron angular distributions (MFPADs) with kinetic energy (KE) of up to about 150 eV, which opens a study on the elementary process of low-kinetic energy photoelectron diffraction for free molecules. We have measured MFPADs from carbon 1s and oxygen 1s levels of CO molecules from KE 50 eV to 150 eV. A strong modulation as a function of the kinetic energy of the photoelectrons was observed in the intensities for the backward scatterings, whereas the intensities for the forward scatterings gradually increased, then became nearly constant over KE \sim 100 eV. Multiple scattering calculations with a muffin-tin potential qualitatively reproduced the experimental results. The present results may be considered as the observation of low-energy photoelectron diffraction pattern involving the modulations in EXAFS spectra. Moreover, simulation calculations with some restriction in the scattering theory were performed to explain intuitively the origins of the patterns of the MFPADs.

Poster no. PS2.192 - Session 2**Electron energy loss near edge structure of ‘n-diamond’: a study to determine the structure of carbon in new phase**Mehrdad Dadsetani¹, Dirk Lamoen², and John Titantah²*(1) Department of Physics, University of Lorestan, Khoramabad, Iran**(2) TSM, Department of Physics, University of Antwerp, Groenenborgerlaan 171, Belgium*

New crystalline phases of a given material are interesting because they correspond to a different bonding arrangement, and new properties can be expected. Three possible structural models (fcc, rhombohedral and glitter) of carbon in the new phase, namely, ‘n-diamond’, are proposed on the basis of observed electron diffraction patterns, Raman spectroscopy and Electron Energy Loss Near Edge Structure (ELNES). In all these publications, n-diamond with the strong diffraction reflexes forbidden ((200), (222) and (420)) for the diamond crystal lattice constant close to that of diamond was obtained. In fact, the electron diffraction from such a phase is very similar to that from fcc, tetragonal and rhombohedral phases.

In the present study, LAPW calculations are performed to determine the crystal structure of carbon in the new phase ‘n-diamond’ within the framework of density functional theory. We have calculated the K-edge ELNES of carbon in three possible structures (glitter, rhombohedral and fcc) predicted by others. The results presented here were obtained by adopting the fast electron beam convergence semiangle of 1.87 mrad and the collection semiangle was set to the magic value of 3.01 mrad. The core hole calculations have been carried out by reducing the occupancy of the core level corresponding to the observed edge. The ELNES is then calculated on the atom where the core hole was introduced. Relativistic effects were considered for both core and valence electrons. The use of supercell avoids interaction between neighboring core holes.

Comparing our results with the experimental ones, we find that glitter and fcc phase of carbon can not explain the measured ELNES spectrum, and that the rhombohedral phase is the only phase whose ELNES compare well with it. In order to check the reliability of our calculations for the analogous results obtained for the diamond, graphite and amorphous carbon are included in this work.

Poster no. PS2.193 - Session 2**A resonant Auger study of the ethylene molecule**Roberto Flammini¹, P. O’Keeffe¹, L. Avaldi¹, O. Kudelich², A. Moise², V. Feyer², R. Richter², K. Prince², and M. Satta³*(1) CNR-IMIP Istituto di Metodologie Inorganiche e dei Plasmi, Area della Ricerca di Roma 1 00016 Monterotondo Scalo (RM) Italy**(2) Elettra Sincrotrone Trieste, Strada Statale 14, 34012 Basovizza, Trieste, Italy**(3) CNR-ISC Istituto dei sistemi complessi, Via dei Taurini 19, 00185 Rome, Italy*

Resonant Auger electron spectra are obtained by measuring the electrons emitted after excitation of an inner shell electron to an excited state below the ionization threshold. When the core hole is filled by an outer electron, either the electron in the excited state or another valence electron can be emitted. In the former case the decay is named “participator” Auger decay and this process leaves the molecule in a singly charged 1h-1p state. This is the case of the X 1b_{3u}⁻¹ state (²B_{3u}) of ethylene. In this work, this state has been studied at several photon energies which correspond to different members of the C-C and C-H vibration series of the excited neutral molecule. The resonant Auger spectra of ethylene have been measured with a total experimental energy resolution of about 140 meV. This value is larger than the core-hole lifetime (90 meV) but smaller than the vibrational spacing (C-C) of the π^* electronic excited state of the neutral molecule (200 meV). The ground state vibrational structure of the ionized molecule (X state, ²B_{3u}) has been observed for the first time in a resonant Auger spectrum.

At each excitation energy a different coupling among the vibrations of the neutral excited and final ionic states is observed. Due to the occupation of the antibonding π^* orbital the molecule undergoes a distortion and pyramidal geometry is preferred to the planar conformation [1]. The distribution of the vibrational intensities of the ground state of the ion changes depending on the group of vibrational modes excited in the π^* orbital. This is rationalised in terms of different molecular configurations of the ethylene ion.

[1] Köppel et al. J. Chem Phys 106, 4415 (1997)

Poster no. PS2.194 - Session 2**Soft x-ray resonant scattering in highly stoichiometric magnetite**J. Garcia¹, G. Subias¹, V. Cuartero¹, J. Herrero-Martin², J. Blasco¹, M. C. Sanchez¹, and F. Yakhou²*(1) Instituto de Ciencia de Materiales de Aragon, CSIC-U. de Zaragoza P. Cerbuna 12 50009 Zaragoza Aragon Spain**(2) European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex 9, France.*

Soft x-ray resonant scattering (SXRS) has recently developed into a powerful technique for investigations of magnetic, charge and orbital ordering. Fe_3O_4 , displays a highly complex low temperature structure that has been claimed to be charge and orbital ordered. Debate still rages over this interpretation, including recent SRXS studies. We report here SRXS measurements on single crystal of highly stoichiometric Fe_3O_4 (Verwey transition at $T_V = 123.5$ K) at both O K-edge and Fe L-edges of the (0,0,1/2) and (0,0,1) reflections (in cubic notation) of the low temperature phase. Resonant scattering intensity was observed at the Fe $L_{2,3}$ and O K edges for the (0,0,1/2) reflection and at the Fe L_1 -edge for the (0,0,1) reflection. The energy, azimuthal angle and temperature dependence was explored. The (0,0,1) reflection is active in the $\sigma\sigma$ channel while the (0,0,1/2) reflection is in the $\sigma\pi$ one. The (0,0,1) reflection is observed at energies below the Fe L_1 edge, confirming that this reflection is permitted while the (0,0,1/2) reflection is forbidden and intensity is only observed on resonance. The resonant and non-resonant signals simultaneously disappear at T_V for the two studied reflections. This result indicates that the associated electronic anisotropy of the Fe d, Fe p and O p-states are controlled by the lattice distortions. Therefore, these resonant reflections can be analysed as anisotropy of the tensor of susceptibility (ATS) reflections. The (0,0,1) reflection appears due to the different anomalous atomic scattering factors of the octahedral B1 and B2 sites in the Pmca setting. This can be interpreted as a very small charge disproportion of about 0.1 electrons between these two Fe atoms. On the other hand, the (0,0,1/2) reflection is mainly sensitive to the local distortions around the different Fe (tetrahedral and octahedral) and O atoms.

Poster no. PS2.195 - Session 2**A hard X-ray photon-in photon-out study of the electronic structure in Mn(III) complexes**Pieter Glatzel¹, Javier Herrero-Martin¹, Alessandro Mirone¹, Jochen Geck², Joaquin Garcia³, Vittal Yachandra⁴, Junko Yano⁴, Yulia Pushkar⁴, Thomas Weyermüller⁵, and Johannes Messinger⁶*(1) ESRF 6 Rue Jules Horowitz 38043 Grenoble France**(2) Institut für Festkörper-und Werkstofforschung, 01171 Dresden Germany**(3) Instituto de Ciencia de Materiales de Aragón (CSIC-Universidad de Zaragoza), E-50009 Zaragoza (Spain)**(4) Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA**(5) Max-Planck Institute for Bioinorganic Chemistry, Stiftstr. 34-36, 45470 Mülheim, Germany**(6) Department of Chemistry, Umeå University Linnaeus Väg 6 (KBC huset) 90187 Umeå, Sweden*

The formal oxidation state of Mn can vary between II and VII. This wide range of oxidation states makes Mn a versatile ion taking a fundamental role in many fields of natural sciences. Mn is, for example, found at the center of photosynthetic water oxidation and gives rise to colossal magnetoresistance in manganites. An oxidation from Mn(II) to Mn(III) is particularly important because the half filled $3d^5$ shell is opened with dramatic changes in the electron-electron interactions and the local symmetry. This can be directly observed in the Mn K absorption pre-edge. The absence of multiplets enables to derive the crystal field splitting from the pre-edge in Mn(II) systems with local octahedral symmetry. However, strong electron-electron interactions and Jahn-Teller distortions in Mn(III) systems result in a complicated splitting of the valence shell energy levels and thus a complex spectral shape of the pre-edge.[1, 2]

We present polarization and spin dependent X-ray absorption studies on Mn(III) single crystals and compare spectra from solid state systems with coordination complexes. We find considerable quadrupole contributions to the absorption pre-edge. We argue that intra-atomic electron-electron interactions predominantly shape the pre-edge and not interactions between neighboring Mn atoms. This is in contradiction to previous studies.[3, 4] The difficulties when attempting a theoretical interpretation of the pre-edge are addressed. We furthermore demonstrate how polarization dependent X-ray emission and absorption studies allow separating electronic from structural changes.

[1] F. Farges, Phys. Rev. B, 71 (2005) 155109.

[2] P. Glatzel, et al., J. Am. Chem. Soc., 126 (2005) 9946.

[3] H. Hayashi, et al., Phys. Rev. B, 73 (2006) 5.

[4] Q. Qian, et al., Phys. Rev. B, 68 (2003).

Poster no. PS2.196 - Session 2**Hard X-ray spectroscopy determination of the electronic structure in titanium molecular systems**Janine Cathy Swarbrick Grattage¹, Kristina Kvashnina¹, Tsu-Chien Weng¹, and Pieter Glatzel¹*(1) European Synchrotron Research Facility (ESRF) 6, rue Jules Horowitz, BP 220 38043 Grenoble Cedex 9 France*

Titanium phthalocyanines, such as TiPcCl_2 and TiPcO are of interest in many applications including photovoltaic devices, photoreceptors and organic electronics. Understanding the electronic structure of these molecules is vital for exploiting their properties for different applications. We have studied the electronic structure of three titanium-containing molecules using different hard X-ray techniques to probe the occupied and unoccupied electronic structure of the Ti atom.

Ti K-edge X-ray absorption near-edge spectroscopy (XANES) is used to map the unoccupied states of the atom. The pre-edge region gives information on the p- and d-like density of states (DOS) and thus the bonding and symmetry around the atom being studied. K-beta X-ray emission spectroscopy (XES) can be used to probe the occupied states; in particular the K-beta satellite lines just below the Fermi level contain information about the nature of the ligands bonded to the Ti atom. XANES and XES satellite line spectra can be modelled using several methods; however, for molecular complexes the calculations often do not faithfully reproduce the spectra, due to Fermi level positioning, inclusion of appropriate crystal field effects, and treatment of the core hole amongst other factors.

New and powerful spectroscopy techniques are currently being developed. Beamline ID26 at the ESRF can record resonant inelastic X-ray scattering (RIXS) spectra. RIXS is a powerful technique which can be used to selectively access the electronic transitions possible and plot them on a 2-D map. In this study we used valence band RIXS to study transitions close to the Fermi level. The electronic structure for the molecules studied varies significantly, and in certain cases optical excitation peaks in the range 0-6eV are observed. Using valence band RIXS to study molecular complexes is a new and exciting method which will provide valuable insight into the electronic properties of molecular materials.

Poster no. PS2.197 - Session 2**Probe for spin- and valence-selective XAFS spectroscopy: Eu L_{γ_4} emission**Hisashi Hayashi¹, Naomi Kawamura², Masaichiro Mizumaki², and Toshiro Takabatake³*(1) Japan Women's University 2-8-1, Mejirodai, Bunkyo-ku 112-8681 Tokyo Japan**(2) SPring-8, JASRI, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan**(3) Graduate School of Advanced Science of Matter, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8530, Japan*

Eu L_{γ_4} emission spectra of EuS, EuF_3 , EuCl_3 , and Eu_2O_3 were measured using a multicrystal, multidetector spectrometer. Splitting of the Eu L_{γ_4} band was observed in the EuS spectra and attributed to exchange interactions between Eu 5p and Eu 4f. It was shown that because of this splitting, the Eu L_{γ_4} emission could be used for performing spin-selective measurements. This emission exhibited a large chemical shift (~ 5 eV), depending on the valence state of a compound. The applicability of this emission to valence-selective X-ray absorption fine structure spectroscopy was demonstrated through partial fluorescence yield measurements performed on a 1:1 mixture of EuS and Eu_2O_3 and on a valence-fluctuating compound $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$.

Poster no. PS2.198 - Session 2**Theoretical study of focusing and double slit effects in x-ray photoelectron diffraction**Misato Kazama¹, Masakazu Yamazaki², Jun-ichi Adachi², Akira Yagishita², and Takashi Fujikawa¹*(1) Graduate School of Science, Chiba University, Yayoi-cho 1-33, Inage, Chiba 263-8522, Japan**(2) Photon Factory, Institute of Materials Structure Science, KEK, Oho 1-1 Tsukuba, Ibaraki 305-0801, Japan*

X-ray photoelectron diffraction (XPD) is widely used as a tool of surface and near-surface structural analyses. The ejected electrons are strongly scattered in the forward direction which is called *forward focusing effect*. In XPD analyses direct structural information is obtained by using this effect. In the case of XPD from AB_1B_2 system, where atom A is an emitter, two strong peaks are expected in forward direction from A to B_1 and from A to B_2 because of the forward focusing effect. Besides that, however, we can observe a peak in the bisecting direction, which is due to the interference between these two scattering waves; it can be referred as *double slit effect*. In particular when the angle between AB_1 and AB_2 is small, the double slit effect can be dominant in comparison with the forward focusing effect. We numerically study the relative importance of these two effects for different conditions. We calculate, for example, O 1s XPD spectra from sulfur dioxide and study the energy dependence.

Poster no. PS2.199 - Session 2**Resonant Inelastic X-ray Scattering of Rare Earth Systems**Kristina Kvashnina¹, Sergei Butorin¹, and Pieter Glatzel¹

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Rare earth systems were studied using X-ray Absorption spectroscopy (XAS) and Resonant Inelastic X-ray scattering (RIXS). The use of synchrotron radiation made possible to obtain valuable information on the electronic structure of Cerium and Ytterbium compounds. Weak and forbidden quadrupole 2p-4f transitions in RIXS spectra were found to be sensitive to the oxidation states in different rare earth systems. Experimental results were analyzed by means of atomic multiplet calculations.

Poster no. PS2.200 - Session 2**Resonant x-ray scattering at the forbidden reflections in Mn³⁺ perovskites REMnO₃ (RE:La and Tb)**M. C. Sanchez¹, G. Subias¹, V. Cuartero¹, J. Garcia¹, J. Blasco¹, J. Herrero-Martin², K. Hatada³, and C. R. Natoli³

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Resonant x-ray scattering (RXS) of forbidden reflections in Mn³⁺ perovskites was initially attributed to orbital ordering coming from the Jahn-Teller effect of Mn³⁺. We carried out an accurate experimental and theoretical study of the forbidden reflections in two isomorphous compounds, LaMnO₃ and TbMnO₃. The two samples show an orthorhombic Pbnm structure with Mn surrounded by nearly tetragonal-distorted oxygen octahedron. The RXS experiments were undertaken at the ID20 beamline at the ESRF around the Mn K-edge of the (h,0,0), (0,k,0) and (0,0,l) (h,k,l=3,5) forbidden reflections. All the reflections show a resonance only in the $\sigma \pi$ channel. The observed resonant intensities exhibit a $\sin^2 \phi$ azimuthal dependence, characteristic of dipolar transitions. The (h,0,0) and (0,k,0) reflections have identical energy dependence while the resonance at the (0,0,l) reflections has its maximum and its rising edge slightly shifted to higher energies and the intensity is lower. These differences are even more pronounced in the case of TbMnO₃. The origin of the two types of reflections (related to two different non-zero non-diagonal elements of the scattering tensor) is explained within the multiple scattering theory considering structural distortions beyond the oxygen atoms. We calculated the two non-diagonal elements of the scattering tensor using the MXAN code to investigate the behaviour of the electric quadrupole moment. We found that its principal axes are not constant with the photon energy so there is not direct correlation between RXS and quadrupolar charge distribution in the ground state for Mn atoms in these perovskites. This is confirmed as approximating the principal axes along the Mn-O bonds and using experimental f' and f'' components determined from polarized XANES spectra along the a, b and c crystallographic axes in the untwined TbMnO₃ does not reproduce the experimental results.

Poster no. PS2.201 - Session 2**K _{β} emission spectra of dinitrosyl iron complexes**Tsu-Chien Weng¹

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Nitric oxide (NO) plays key roles in mammalian biology as an important biological signaling molecule and regulator. Dinitrosyl iron complexes (DNICs) have been known to exert NO bioactivity under physiological and pathological conditions. The thiolate groups coordinated to the Fe(NO)₂ motif also play the key role in modulating the NO-releasing ability and stability of DNICs by tuning the electronic structure of DNICs.

DNICs containing the various ligation modes [O,O]/[S,S]/[Se,Se]/[O,S] were recently synthesized. The K _{β} x-ray emission spectroscopy (XES) analysis indicated the presence of Fe species with one unpaired electron. The 1s2p RXES spectrum of DNIC-SPh reveals the electronic configuration of Fe to be [Ar]4s²3d⁵.

Roussin's red esters (RREs) are the dimeric form of DNICs, considered to perform the similar role as DNICs. The electronic structure of the anionic dimeric DNICs [Fe(μ -SR)(NO)₂]²⁻ (R = Et, Bu) is described as [Fe⁺(·NO)₂]⁹⁻-Fe⁰(·NO)₂]¹⁰⁻ in resonance. The K _{β} XES spectra of both neutral and anionic RREs were collected.

Poster no. PS2.202 - Session 2**Magnetite at low temperature: Resonant Inelastic X-ray Scattering (RIXS) at the Fe K-edge**Max Wilke¹, Wolfgang A. Caliebe², and Pavel Machek³*(1) Helmholtzzentrum Potsdam - GFZ, Telegrafenberg, 14473 Potsdam, Germany**(2) HASYLAB at DESY, Notkestr. 85, 22603 Hamburg Germany**(3) Institute of Physics, Cukrovarnicka 10, 16253 Prague Czech Republic*

At room temperature, magnetite (cubic inverse spinel structure, $Fd\bar{3}m$ s.g.) shows metal-like electrical conductivity, which discontinuously drops by two orders of magnitude below ca. 120 K (T_V , [1]). This is due to a first-order phase transition, where the cubic structure is distorted to monoclinic symmetry (Cc s.g.). Proposed models for this metal-insulator transition (MIT) are: charge ordering on the B-sublattice at the transition; a conductivity mechanism involving electron-phonon coupled states, which are not present below T_V (e.g. [2], [3], [4]). Lately, a combination of weak charge order and orbital order of the t_{2g} states invoked by local electron interactions, that affect the electron-phonon interactions were used to explain the MIT [5], [6]. Here, RIXS experiments have been performed at HASYLAB, beam line W1 using a Si(111) double-crystal monochromator. The emission spectra were recorded using an in-vacuum crystal spectrometer in Rowland-circle geometry. Spherically bent Si(440) and Si(531) crystals were used as analyzer. We have performed 1s3p as well 1s2p RIXS measurements well below and above T_V on a sample of synthetic magnetite powder to probe any difference present in the electronic states. Neither 1s3p nor 1s2p RIXS spectra reveal any difference between the two phases. X-ray emission spectra excited in the pre-edge of the K-edge (excitations to the 3d-like orbitals) are identical. Our observations are consistent with earlier EXAFS data [3] and the models proposed by [5], [6].

[1] E.J.W. Verwey (1939) *Nature* 144, 327.[2] N.F. Mott (1979) *Adv. S.S. Phys., Festkörperprobleme* 19, 331.[3] G. Subias et al. (2005) *Physical Review B* 71, 155103.[4] G.K. Rozenberg et al. (2006) *Physical Review Letters* 96, 045705.[5] P. Piekarczyk (2007) *Physical Review B* 76, 165124.[6] J. Schlappa et al. (2008) *Physical Review Letters* 100, 026406.**Poster no. PS2.203 - Session 2****A new instrument for the study of soft X-ray absorption edges with hard X-rays: Inelastic X-ray Scattering at PETRAIII**Max Wilke¹, Wolfgang A. Caliebe², Frank U. Dill², Jochen Geck³, and Christian Sternemann⁴*(1) Helmholtzzentrum Potsdam - GFZ, Telegrafenberg, 14473 Potsdam, Germany**(2) HASYLAB at DESY Notkestr. 85, 22603 Hamburg, Germany**(3) Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany**(4) Institute of Physics/DELTA, University of Dortmund, Maria-Goeppert-Mayer-Strasse, 44221 Dortmund, Germany*

PETRAIII is a new third-generation synchrotron radiation source at DESY [1]. In one of the straight sections, a 10m-long undulator is installed, which will be used for nuclear resonant scattering and non-resonant inelastic x-ray scattering (IXS) for the study of electronic excitations with energy resolutions of 50meV and 500meV, respectively. The IXS-spectrometer is a backscattering Rowland-circle spectrometer with two analyzer systems, which consist of 9 and 12 analyzers, respectively. The analyzer systems are installed at low (9) and high (12) scattering angles in order to measure spectra at low and high momentum transfers simultaneously, if applicable. Each system has 3 (2) high-resolution analyzers (30meV) in the center, and 6 (10) (300meV) around those. The detector is a low noise, high spatial resolution area-detector.

The applications of the instrument are the study of low-energy electronic excitations like valence band excitations, collective excitations (plasmons), and low-energy absorption edges with energies below 1.5 keV under extreme conditions, where these excitations cannot necessarily be measured with direct methods. One planned application is research at high pressure and high temperatures. This instrument can be used to measure absorption spectra of elements like Na or Si in a laser-heated diamond anvil cell, which is not possible with soft x-ray absorption spectroscopy.

[1] Balewski K et al., PETRAIII: A Low Emittance Synchrotron Radiation Source, Hamburg (2004)

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