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Report:
In order to achieve the aims proposed, the phase diagram of two representative systems Cu_xPd_{1-x} (with x=0.6) and Ag_xPd_{1-x} (with x=0.5) was explored by x-ray absorption spectroscopy (XAS), energy scanning x-ray diffraction (ESXD), and single energy temperature scans under high pressure (HP) and/or high temperature (HT) conditions. Preliminary measurements were performed at HT on samples with x=0.25 and x=0.75 concentrations and on the Ag_xCu_{1-x} alloy under pressure.
This experiment exploited a complex setup involving the Paris-Edinburgh large volume (LV) press for high pressure and high temperature scans. The conventional XAS transmission setup was complemented by a recently developed multi-channel detector collimator (INFM Project-PURS008) for powder diffraction measurements.
The alloys were produced by mixing commercial high purity Ag/Pd, Cu/Pd and Ag/Cu powders in suitable weight ratios for each concentration. The mixture was dispersed in an inert composite α-Al_2O_3-MgO (1:3) matrix in the approximate ratio (1:12), then pelleted and melted in a graphite crucible under high vacuum conditions. After an accurate structural characterization by a laboratory angle-dispersive x-ray powder diffractometer, the final pellets were crushed into a fine powder, and then pressed again into a 1.5 mm cylinder. Each cylinder was directly placed into a graphite cylindrical oven and eventually in a 7 mm Boron gasket for high pressure measurements in a LV setup. A thermocouple has been inserted through the gasket to monitor the temperature, while pressure was measured using the ESXD patterns and the known α-Al_2O_3 and MgO equation of state (EOS).

Two of the samples to be used in the very high temperature regime (T=1200÷1900 K), were mounted without thermocouple. In this case P and T were monitored using simultaneously the EOS of both the pressure markers.

The Ag_5Pd_5 alloy was measured at four different temperatures from RT to above the melting point (T≃1800 K) for pressures in the range 0÷5 GPa. Each sample was subjected to a complex experimental protocol involving cycles of pressurization, ESXD acquisitions, single-energy absorption scans, XAS measurements at both the Ag and Pd K-edges. No solid-solid phase transitions were detected, showing that this alloy keeps its ambient f.c.c. structure up to the melting point in the explored region of the phase diagram. In addition the sudden drop of the absorption at fixed energy points and the disappearance of Bragg peaks from the alloy while rising temperature allowed us to pin the melting point as a function of the pressure.

The Cu_6Pd_4 alloy was subjected to a similar protocol, but the high absorbance of LV samples at low energies does not allow to collect XAS spectra at the Cu K-edge. Measurements were collected in the solid and liquid state (T=300÷1900 K) in a pressure interval 0÷6 GPa.

A transition from a b.c.c CsCl-type ordered structure toward a disordered f.c.c. state upon increasing temperature known at ambient pressure has been detected up to about 2 GPa. The large hysteresis loop in the corresponding single energy absorption scan, (Fig. 1) demonstrates that a metastable disordered f.c.c state is obtained down to 100 K below the transition point, before the nucleation of the b.c.c. phase.

Changes in the local structure of the b.c.c., f.c.c. phases and of the molten alloy are evident both in the near edge region and in the extracted XAFS signals as shown in Fig. 2.

These preliminary results are very promising, showing that a reliable determination of the local structure and phase transition for binary metal alloys is feasible with the experimental techniques developed at BM-29, even under high pressure and extremely high temperature conditions. The collected XAS data are currently under treatment (as new methods for the XAS data analysis of molten binary systems had to be developed) in order to determine the short-range partial distribution functions in a wide P,T range and the local order evolution as a function of both these thermodynamic variables.

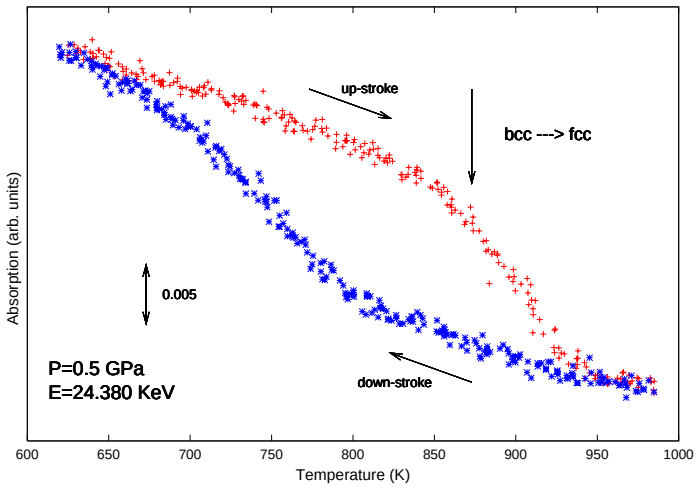

Fig. 1

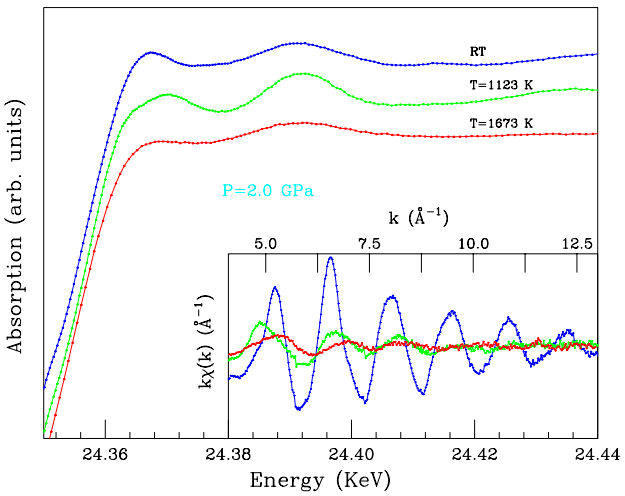

Fig. 2