Modern Physics
-constituents of matter-

Lecture notes by
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Background

•The idea of matter as constituted by individual particles (called *atoms,* indivisibles) is introduced in modern science first by looking at chemical investigations (reactions that must be associated with well defined proportions of atoms or molecules, Prout, Dalton, Avogadro) and afterwards in electricity looking at the amount of charge (first by Faraday in electrolysis). It was only at the end of the 19th century that became evident that atoms were composed by particles of different charges, and the first optical spectra showing the characteristics of each element in absorbing and emitting light were discovered.

•The central role of the *hydrogen atom* as the simplest atomic system was soon discovered, both by chemical and physical methods. Typical atomic masses as multiples of the hydrogen mass were established. The typical atomic sizes were determined by various methods, by collision techniques with atomic beams (scattering cross-section), thermodynamics (co-volume in Van der Waals equation of state) and by x-ray diffraction.

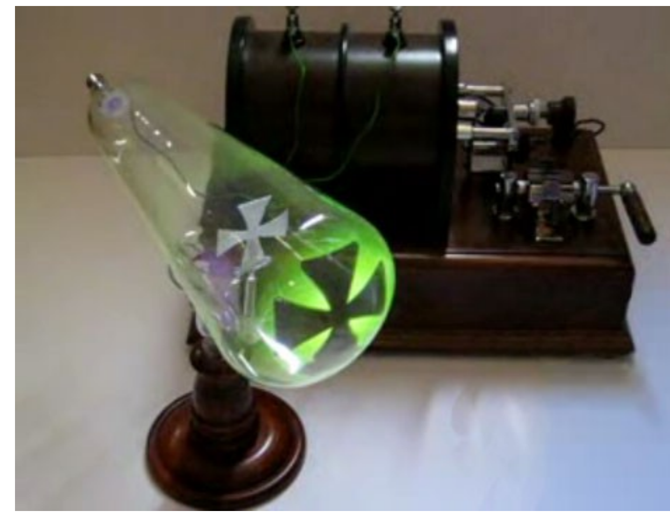
•Evidence for the existence of tiny negative particles, the cathod rays later called electrons were obtained by Thomson, Lenard and many others. It was shown that electrons could penetrate deeply in condensed and gaseous matter and that atoms could be seen like a small planetary system. The realization that small nuclei (10^{-15} m) contained the entire positive charge and almost all the mass of the atoms is due to Rutherford who investigated the scattering of a particles (2+ charged ^{4}He nuclei) emitted by radioactive substances (5 MeV).

The electron

·A fundamental step in our understanding of the atomic structure has been the discovery of the electron, a subatomic particle with a “quantum” of negative charge e. The concept was introduced in chemistry in early 1800 but it was only when Crookes evacuated tubes were available that direct proof of existence of these elementary charges was obtained.

•The key experiments for the electron discovery were performed by J. J. Thomson (Nobel prize, 1906) following the work of many previous scientists (Hittorf, Goldstein, Schuster, Lenard in Germany and Crookes in England) indicating that the “cathod rays” were actually composed by charged particles.

•The basic ideas for the experiment were 1) assessing that the charged cloud emitted by the cathode could not be separated by other effects (luminescence of the glass) possibly due to other kind of rays; 2) assessing whether this cloud can be deflected by an electric field (not only magnetic as it was known); 3) measuring the ratio e/m of the particles composing the cloud.



•Crookes (Maltese) tube during a discharge using a high-voltage Ruhmkorff coil. The profile of the cross-shaped target is projected against the tube face at right by a beam of electrons

Thomson's experiment (I)

Thomson and collaborators devised a series of experiments particularly suited for their aims, using quite sophisticated glass tube assemblies, electrical equipments and pumping systems for the time.

In his first experiment, he investigated whether or not the negative charge could be separated from the cathode rays by means of magnetism. He constructed a cathode ray tube ending in a pair of cylinders with slits in them. These slits were in turn connected to a gold-leaf electrometer. Thomson found that if the rays were magnetically bent such that they could not enter the slit, the electrometer registered little charge.

Whenever the cathode rays were forced to enter the slits the charging was immediately visible (1 sec to alter the potential of a 1.5 μF capacity to 20 V).

The charge was seen to be negative by charging the inner cylinder befor observing the effect of the cathod rays, either with positive or negative charges.

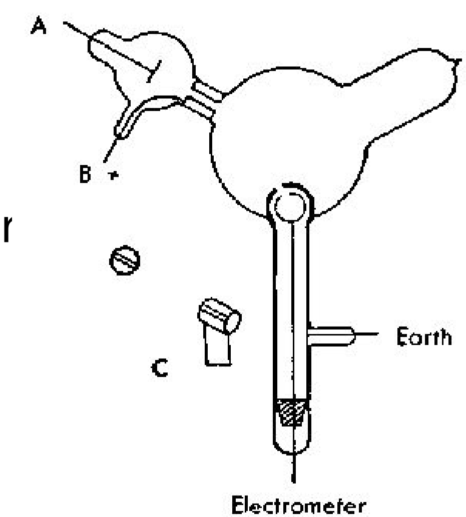
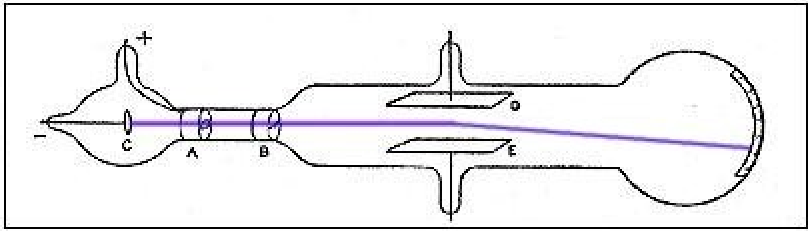


FIG. 1

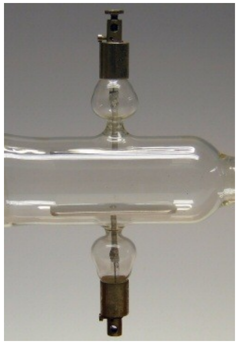
Thomson concluded without any doubt that the negative charge was inseparable from the cathode rays and that the objection about the Nature of cathod rays as ethereal “radiation” (raised mainly by German Physicist), sometimes accompanied by charged particles was not true.

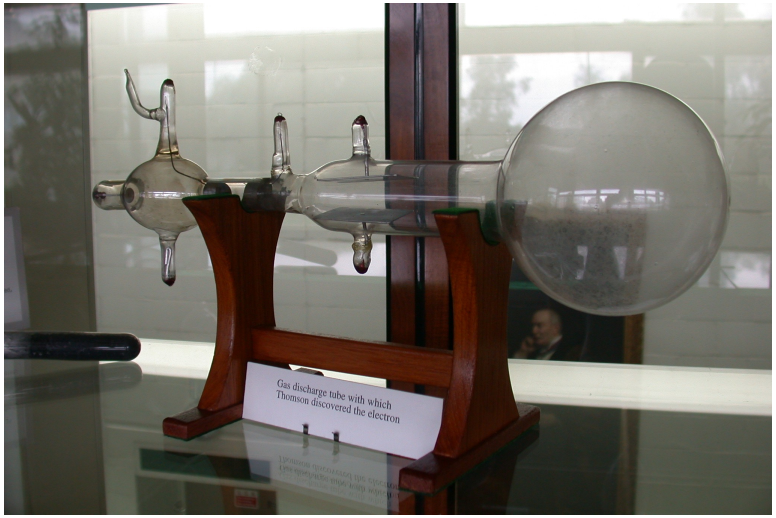
Thomson's experiment(II)

In his second experiment, he investigated whether or not the rays could be deflected by an electric field (something that is characteristic of charged particles). Previous experimenters had failed to observe this, but Thomson believed their experiments were flawed because they contained trace amounts of gas. Thomson constructed a cathode ray tube with a very good vacuum, and coated one end with phosphorescent paint. Thomson found that the rays did indeed bend under the influence of an electric field, in a direction indicating a negative charge.



Thomson and collaborators defined a precise beam of electrons with slits at the anode exit and observed the deflection with a scale depicted at the end of the glass tube at some distance of the plates.





Voltage could be raised up to about 200 V causing large deflections, before the residual gas begin to ionize reducing the effective field in between the plates to zero. When a discharge between the plate was observed the deflection was suddenly eliminated.

Thomson's experiment(III)

In his third experiment, Thomson measured for the first time the mass-to-charge ratio of the cathode rays by measuring how much they were deflected by a magnetic field and how much energy they carried.

$$\frac{1}{2} N m v^2 = W \,;\, N = \frac{Q}{e} \Rightarrow \frac{m}{2e} v^2 = \frac{W}{Q} \qquad Ne = Q\,;\, \frac{mv^2}{r} = e v * H \Rightarrow \frac{mv}{e} = rH$$

$$\frac{m}{2e} v\, e\, r\, H / m = \frac{W}{Q} \Rightarrow v = \frac{2W}{rHQ}$$

$$\frac{m}{2e} v^2 = \frac{W}{Q} \Rightarrow \frac{m}{2e} \left(\frac{2W}{rHQ}\right)^2 = \frac{W}{Q} \Rightarrow \frac{m}{e} = \frac{2W}{Q\left(2W / QrH\right)^2} \Rightarrow \frac{m}{e} = \frac{(rH)^2 Q}{2W}$$

Looking at these equations we conclude that we can measure m/e by measuring r, H, Q, and W. The radius of curvature was measured by the distances travelled by the electron (namely the collision position with the glass wall) and some uncertainty was due to the spread observed in those positions (segment instead of punctual beam). The uniform magnetic field was provided by two large circular coils and measured by the current circulating in the coils. Q is measured as in experiment (I) (two coaxial cylinders) keeping as short as possible the measurements to avoid discharging in the residual gas. W was measured with a thermoelectric couple Cu-Fe behind the slit of the inner cylinder with known heat capacity (0.003-0.005 cal/K).

Thomson's experiment (results)

The first quantitative results of the 3rd Thomson experiments, performed using three different configurations indicated a m/e ratio for the electron ranging between 0.32×10^{-8} g/C to about 1×10^{-8} g/C ($.32\text{-}1 \times 10^{-7}$ g/emu) depending on the particular set-up used but was not found to depend on the gases present and on the nature of the electrodes..

The current accepted value is m/e = $9.109 \times 10^{-28} / 1.602 \times 10^{-19} = 0.569 \times 10^{-8}$ g/C

An important improvement of the experimental set-up (II) described by Thomson and used to measure again m/e in an independent way is the combination of the application of an electric field and of a magnetic field acting on the same distance path.

This technique is fundamental for further developments in physics (mass spectrometry) and applications (oscilloscope, cathodic tube for tv sets ...).

Applying an electric field: $v_x = cost\, ; v_y = \frac{eE}{m} t \Rightarrow l = v_x t\, ; v_y = \frac{eE}{m} \frac{l}{v_x}$ $\quad tg(\theta) = \frac{v_y}{v_x} = \frac{eE}{m} \frac{l}{v_x^2}$

Applying a magnetic field: $v_x = cost\, ; v_y = \frac{eH_z v_x}{m} t \Rightarrow l = v_x t\, ; v_y = \frac{e H_z}{m} l$ $\quad tg(\phi) = \frac{v_y}{v_x} = \frac{e H_z}{m} \frac{l}{v_x}$

Tuning E, H fields to obtain same deviation angles we obtain: $tg(\theta) = tg(\phi) = \frac{eE}{m} \frac{l}{v_x^2} = \frac{e}{m} \frac{H_{zl}}{v_x} \Rightarrow \frac{E}{v_x} = H_z$

So:

$$tg\,\theta = \frac{e}{m} \frac{H_z}{\frac{E}{H_z}} l = \frac{e}{m} \frac{H_z^2}{E} l \Rightarrow \frac{m}{e} = \frac{l}{tg(\theta)} l \frac{H_z^2}{E}$$

Those measurements gave results in agreement witht the first method ($\sim 1 \times 10^{-8}$ g/C).

Thomson's conclusions

Thomson's conclusions were **bold**: cathode rays were indeed made of **particles** which he called "corpuscles", and these corpuscles came from within the atoms of the electrodes themselves, meaning that atoms are in fact divisible. The "corpuscles" discovered by Thomson are identified with the ***electrons*** which had been proposed by G. Johnstone Stoney. He conducted this experiment in 1897.

He found that the mass to charge ratio was over a thousand times lower than that of a hydrogen ion (H+), suggesting either that the particles were very light or very highly charged. The m/e ratio of hydrogen ions was estimated by electrolysis by measuring the amount of hydrogen produced by a current (1 Faraday = 96.85 kCoulomb per mole). By using an atomic weigth 1.008 (1 mole = 1.008 g) it was known that

$m(H^+)/e = 1.008\ g/\ 96580\ C = 1.044 \times 10^{-5}\ g/C$

So assuming the charge was the same, the ratio between the masses turned to be about ~1830.

Thomson imagined the atom as being made up of these corpuscles swarming in a sea of positive charge; this was his plum pudding model. This model was later proved incorrect when Ernest Rutherford showed that the positive charge is concentrated in the nucleus of the atom.

e/m ratio and mass spectrometry

Thomson's methods and results were used and improved afterwards for determining charges and masses of atomic and subatomic particles.

An elegant method was developed by Classen (1907) as illustrated in the figure.

The parabola method (E and B parallel) introduced by Thomson (1913) was used and improved for years and is still used for simple mass spectrometry of ions. It allowed to discover the isotopes (Aston 1920).

$$x:[\vec{F}=e(\vec{v}*\vec{B})=\vec{F}_c=m\,v^2\frac{\vec{r}}{r^2}];\ y:[\vec{F}=e\,\vec{E}]$$

$$\ddot{y}=\frac{e}{m}E\Rightarrow y=\frac{1}{2}\frac{eE}{m}t^2=\frac{e}{2\mathrm{m}}E\frac{l^2}{v^2}$$

$$\ddot{x}=\frac{eBv}{m}\Rightarrow x=\frac{eBv}{2\mathrm{m}}t^2=\frac{eBv}{2\mathrm{m}}\frac{l^2}{v^2}=\frac{eBl^2}{2\mathrm{mv}}$$

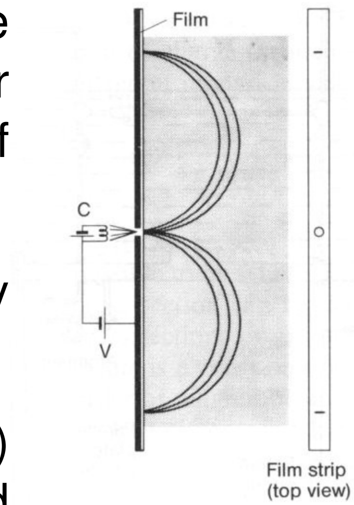


Fig. 6.3. Experimental arrangement for measurement of the specific mass *m/e* of the electron. The electrons are generated at the cathode C and accelerated by the voltage V. They are deflected into circular paths by a magnetic field perpendicular to the plane of the figure and recorded on a film. The direction of the deflection is reversed by reversing the poles of the magnet

$$\vec{F}=-e[\vec{E}+v*B]$$

$$\frac{mv^2}{2}=e\,V\Rightarrow v=\sqrt{\frac{2\mathrm{eV}}{m}};\ \frac{mv^2}{r}=e\,v\,H$$

$$\frac{e}{m}=\frac{2\mathrm{V}}{r^2B^2}$$

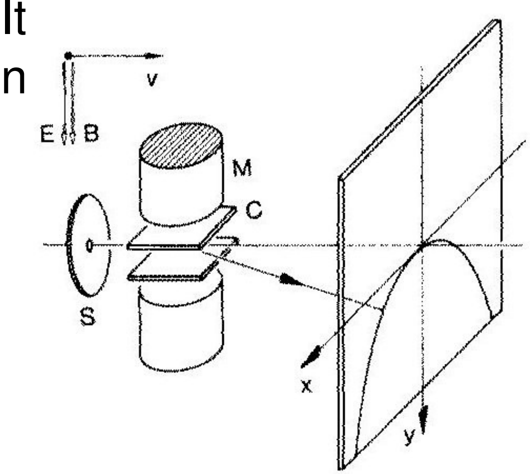


Fig. 3.2. Schematic representation of the parabola method. The ion beam, collimated by the slit S, is deflected by the magnet M and the condenser C in the *x* and *y* directions. Equation (3.5) describes the path of the particles on a catcher screen immediately after exiting from the magnet and the condenser. If the screen is placed at a greater distance, a corresponding distortion of the parabolas due to projection is seen

$$y=2\frac{E}{l^2B^2}\frac{m}{e}x^2$$

mass spectrometry

An example of the application of the parabola method is shown in the figure. Aston, using a more sophisticated (focussed) set-up, determined the composition of naturally occurring Ne isotopes (mass weight numbers A: 20, 21, 22, Z= 10) and suggesting the existence of neutrons. In the Aston spectrometer E and B are perpendicular, and tuning the B field one can focus ions with different velocity (but same m/e) in the same point.

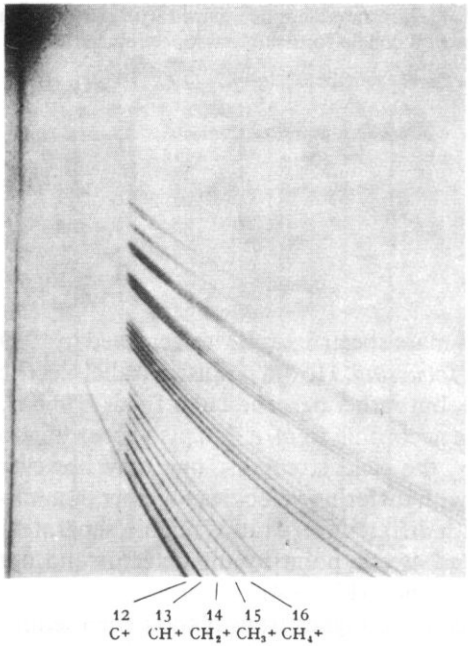


Fig. 3.3. Separation of a mixture of hydrocarbon ions with the Thomson parabola method. For calibration, one uses ions of known mass. The intensities of the individual parabolic sections correspond to the relative amounts within the mixture of the ions which produced them. [Photo after *Conrad* from W. Finkelnburg: *Einführung in die Atomphysik*, 11, 12th ed. (Springer, Berlin, Heidelberg, New York 1976) Fig. 12]

Modern mass spectrograph using various focussing techniques to improve signal and mass resolution. Quadrupole (electric) high-frequency mass filters provides better separation of masses.

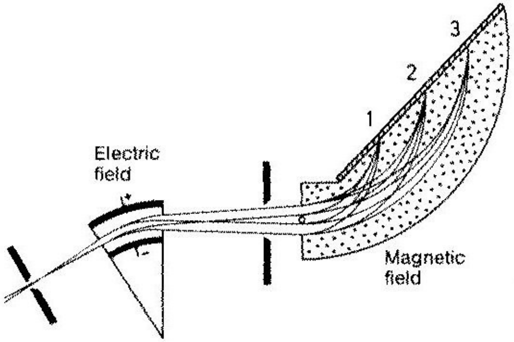


Fig. 3.4. A focussing mass spectrograph as designed by *Aston*. The points 1, 2, and 3 denote the points at which three types of particles with three different values of m/e are collected

Table 3.2. Isotopic composition of neon. The values of A_{rel} given were not determined with the parabola method, but rather, with the precision quoted, by the use of a double-focussing mass spectrometer

$^{20}_{10}Ne$	90.92%	$A_{rel} = 19.99244$
$^{21}_{10}Ne$	0.26%	$A_{rel} = 20.99385$
$^{22}_{10}Ne$	8.82%	$A_{rel} = 21.99138$

Electron charge (Millikan)

Knowledge of the e/m ratio by Thomson's experiments called for independent measurements of the fact that a quantum of charge “e” actually exists.* Millikan (1911) accomplished this task in a famous series of experiment on the dynamics of oil droplets under the action of gravity, of an electric field and of the bouyancy into the fluid (air) and friction in air (Nobel prize 1923).

The experiment needed to be performed in a very accurate way, taking into account all of the source of possible errors.

The oil droplets were naturally charged (by friction for example) in a first version of the experiment, while charges could be induced by x-rays in a second one.

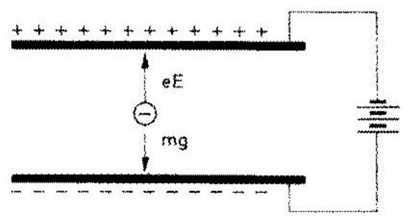


Fig. 6.1. Principle of the Millikan oil-drop experiment for measuring the charge of the electron. A negatively charged oil droplet experiences the force neE, where n is the number of elementary charges on the droplet; the graviational force mg acts in the opposite direction

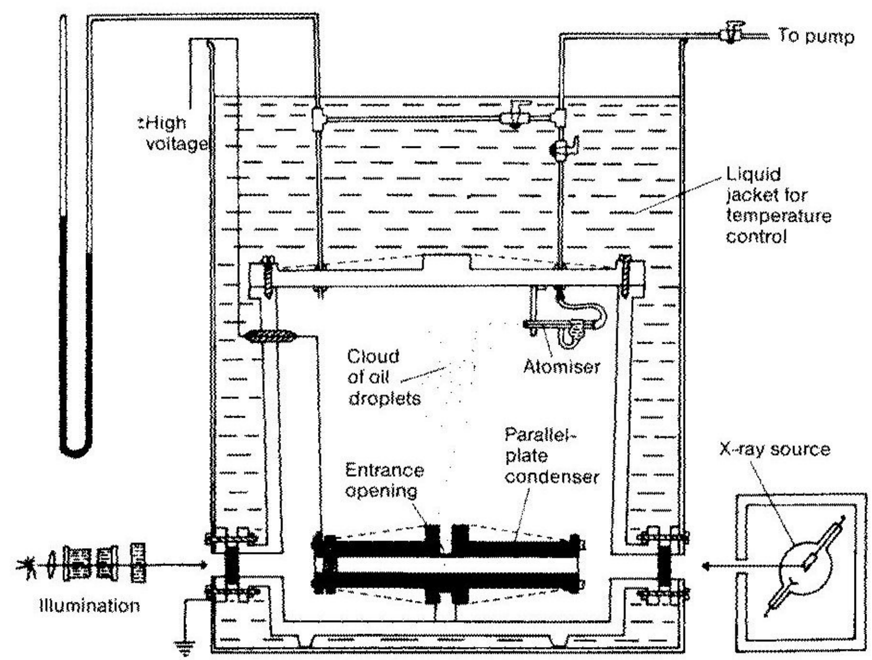


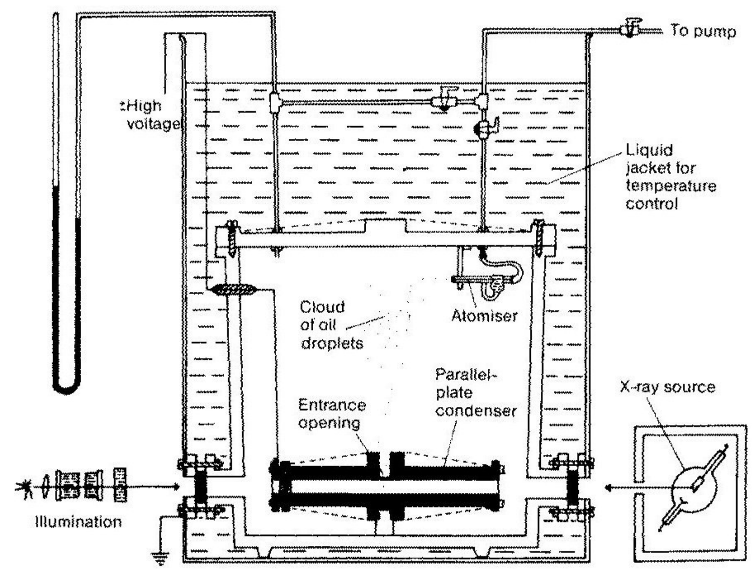
Fig. 6.2. Experimental arrangement of *Millikan* from Phys. Rev. **2**, 109 (1913). The oil droplets, which are formed by the atomiser, can be charged or discharged by irradiation with x-rays

*At that time mainly inferred by electrolysis through the Faraday constant F: q =F/N, F=96.5 kC*mole.

Electron charge – II -

Observation of the falling spherical oil droplets, emitted by an “atomizer” and passing through a hole into a capacitor (voltage 3-8 kV) was performed using a short-distance telescope allowing a precise measurements of timing over short distances (fraction of mm). Timing obviously depended on charges deposited onto the droplets, ranging usually from 1 to hundreds, and sudden variation of state of motion was recorded upon increasing or decreasing the charge by (multiples of) e. The chamber was filled by dust-free clean air under controlled pressure (1-15 atmosphere) and temperature conditions (engine oil bath 40 l).

The measured elementary charge was 4.93×10^{-10} esu (statCoulomb), later corrected by Millikan into $4.78\ 10^{-10}$ esu. The main source of error was the viscosity of air (calculated assuming a Stokes law $F = 6\pi\eta r v$ - η is the viscosity coefficient, r is the radius of the oil drop, but the value of η had to be reconsidered and the Stokes law was found inaccurate for small r).



The current accepted value is (1statC=3.3356×10^{-10} C)

$e=4.802\ 10^{-10}$ esu = $1.602\ 10^{-19}$ C.

Atomic structure

At the beginning of the 20th century our understanding of the atomic structure was about to clarify, mainly due to the discovery of the electrons (negatively charge) as individual particles and of the nuclei (positive) studied by Rutherford (1911) by ion scattering.

The electron is considered a structureless point-like particle (as shown by high-energy scattering experiments). The "classical" radius of the electron can be found imposing that the energy of its electrostatic field (assumed to be that of a spherical capacitor) is equal to its rest mass:

$$E = m_0 c^2 ; E = \frac{1}{2}\frac{e^2}{C} = \frac{1}{2}\frac{e^2}{2\pi\epsilon_0 r_{el}} \Rightarrow r_{el} = \frac{e^2}{4\pi\epsilon_0 m_0 c^2} = 2.8\,10^{-15}\,m$$

The radius of atoms nuclei, containing almost the entire mass of the atom and a charge Ze, as found by Rutherford, was of the same order of magnitude (10^{-15} m). Nuclei were shown later to have an inner structure made by charged protons and (neutral) neutrons, both composed by other fundamental particles called quarks (having fractional charges 1/3e, 2/3e, but they are always bonded to form integer charges).

A simple calculation for condensed matter show that the average dimension occupied by an atom in solid systems is quite bigger. For metallic Cu, atomic weight A=63.546 g/mole, density ρ at room temperature 8.94 g/cm3 we find: Volume per mole V_m=A/ρ= 7.108 cm^3. The average interatomic spacing results then to be: $d_{int} = (V_m/N)^{1/3} = 2.277\ 10^{-10}$ m (Ang.)

Atomic structure as seen by x-ray diffraction

Early after the discovery of the x-rays, scientists were using them to investigate matter in various ways. C. G. Barkla (Nobel Prize 1917) and others showed the properties of transmission and excitation of matter by using x-rays, identified as electromagnetic radiation at very short wavelength (in the range around 10^{-10} m).

The experiments in 1912 of M. Von Laue, (Nobel 1914) Friedrich and Knipping and of W. L. and W. H. Bragg (Nobel 1917) showed unambiguously that crystalline matter was able to produce interference patterns on x-ray beams.

The basic experiment showing the reflection of x-ray radiation from crystalline specimens provided:

1) the direct proof that crystals are built up of discrete entities, the atoms

2) the lattice constant of crystals, so a direct measure of the interatomic distances in a crystal, being in the 10^{-10} m range (subatomic particles are instead below 10^{-15} m, matter is thus pretty empty!)

3) the wavelength of x-ray radiation

The exact derivation of the interference conditions can be obtained using a tridimensional atomic arrangement and the incoming and outcoming electromagnetic waves (Laue/Ewald construction). A simplified picture showing a relationship with lattice planes is due to Bragg.

Bragg reflections

A typical set-up for diffraction can be seen in the figure. When a single-crystal is shined by a polychromatic x-ray beam a certain number of spots, corresponding to well-defined reflections of x-rays of given wavelength is obtained.

Experiments of this kind were performed for many crystals. X-ray diffraction can be regarded as a reflection of x-ray radiation by a specific set of lattice planes at well-defined scattering angles.

Each set of plane is distinguished by spacing, orientation and atom density on the planes.

As shown in the figure each atom belonging to a plane is a source of an elementary scattered wave, interfering with all the others generated by the other atoms.

The condition for constructive interference is simply given by imposing that the difference in the optical path (Δ) must be equal to a multiple of the wavelength:

$$n\,\lambda = 2d\sin\theta$$

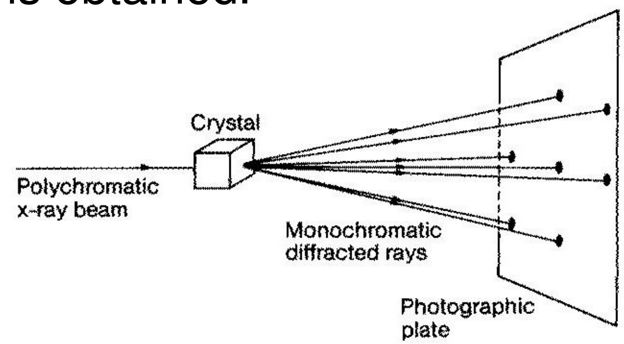
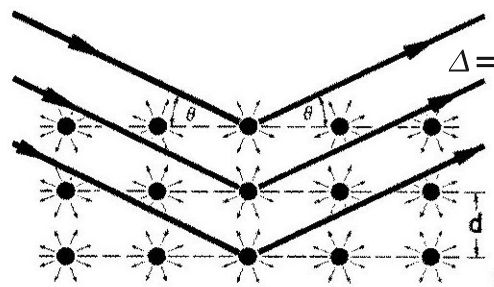


Fig. 2.7. X-ray diffraction from a single crystal after *von Laue*; schematic of the experimental arrangement. X-radiation with a continuous distribution of wavelengths (polychromatic or white x-radiation) is diffracted by a single crystal. The conditions for interference from a three-dimensional lattice yield constructive interference at particular directions in space and at particular wavelengths. One thus observes interference maxima, which correspond to certain discrete wavelengths (monochromatic x-radiation)



$$\Delta = AB + BC - AE = 2AB - AE = \frac{2d}{\sin(\theta)} - 2\,AD\cos(\theta)$$

$$AD = \frac{d}{\tan\theta} \Rightarrow \Delta = \frac{2d}{\sin\theta}(1-\cos^2\theta) = 2d\sin\theta$$

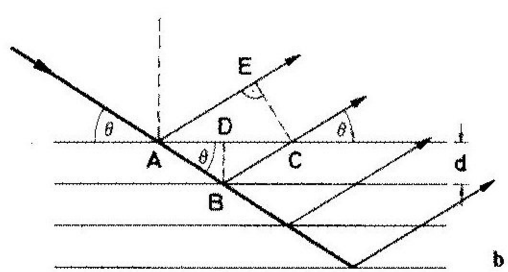


Fig. 2.9 a, b. Derivation of the Bragg Law of Reflection. The horizontal lines symbolise lattice planes, from which the incident x-radiation arriving at angle θ is scattered. **a)** Each atom of a lattice plane acts as a scattering centre. **b)** The derivation of the Bragg condition for the reflection of x-radiation from a lattice plane

X-ray diffraction methods

Besides the Laue method with polychromatic radiation (useful for single crystals), other methods were devised using monochromatic radiation by Bragg for single crystals (interference conditions fulfilled rotating the crystal at well defined angles), and by Debye/Scherrer for powdered/polycrystalline samples.

A typical Debye-Scherrer set-up showing many lattice planes of MgO is shown in the figure.

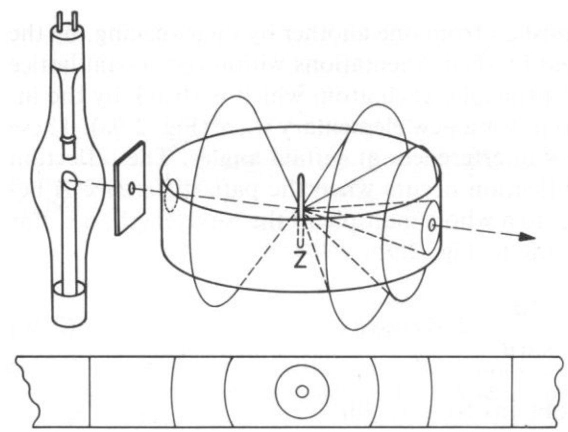


Fig. 2.10. Debye-Scherrer method: x-ray diffraction of monochromatic x-radiation by a polycrystalline sample *Z*. On the film, the intersections of the diffraction cones from the various families of lattice planes appear as rings

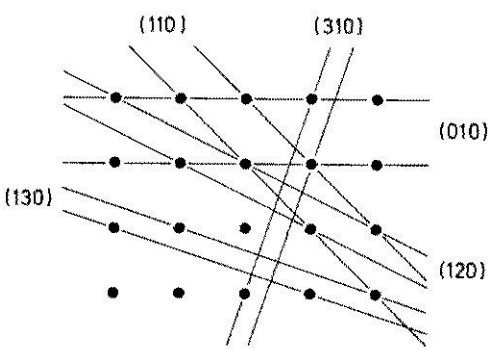


Fig. 2.8. Simple cubic lattice with several lattice planes. These are characterised by the *Miller Indices*. The spacing between two parallel lattice planes decreases with increasing Miller indices

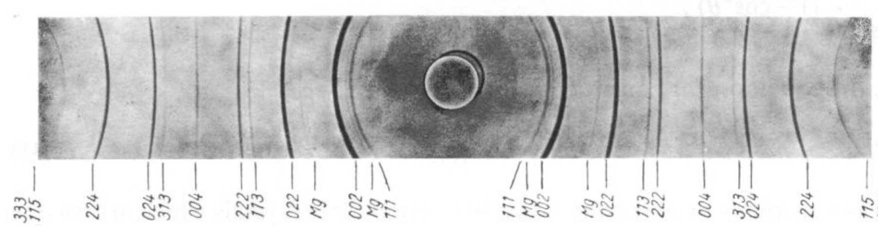


Fig. 2.11. Debye-Scherrer diagram of MgO [from Gerthsen, Kneser, Vogel: *Physik*, 13th ed. (Springer, Berlin, Heidelberg, New York 1978) Fig. 12.37]