4.3. Diffraction methods

4.3.1. Diffraction methods in the structure investigation of ordered systems

The diffraction methods were already mentioned in Chapter 3 (Subsection 3.11). There were introduced the scattering vector (**s**) ad the atomic scattering functions (f).

The diffraction methods are important in the structure elucidation of liquids and solids. They help in determination of the structure of the ordered or partially ordered systems, the crystal symmetry and the molecular structure.

If the wavelength of a particle (electron, photon or neutron) is comparable to the periodically repeated distances in the crystal, then the crystal behaves like optical grating for electromagnetic waves or particles. They scatters (diffracts) on the crystal lattice.. The waves or particles diffracting in the same direction interfere with one another. Let be the distance between the parallel crystal lattices d, according to Bragg's law

$$2d\sin\alpha = n\lambda \qquad n = 0, \pm 1, \pm 2, \ldots \tag{4.14}$$

n is the order of the diffraction. If n=0, the incident light is scattered in the incident plane (Fig. 4.10). If n>0, it is a back-scattering, if n<0, this is a forward scattering.

A real, three-dimensional lattice can be regarded as the sum of three perpendicular one-dimensional lattices. Each has its own scattering cone.

Supposing the independent particle model, the electric field of scattered wave of the atoms in the crytal cell is

$$E = E_o F(s) \tag{4.15}$$

E_O is the amplitude of the electric wave, and the *structure factor* of the crystal is

$$F(s) = \sum_{j=1}^{N} f_j \exp(isr_j) = \sum_{j=1}^{N} f_j \exp\left[i\left(\frac{h}{d_1}x_j + \frac{k}{d_2}y_j + \frac{l}{d_3}z_j\right)\right] \tag{4.16}$$

h, k and l are the Miller indices and characterize the position of the scattering plane to the coordinates in the unit cell, d_1, d_2 and d_3 are the lattice constants of the unit cell. The unit cell is the smallest part of the crystal wich contains all the repeatable parts of the crystal.

The path diffrence between two scattered waves of distance d is

$$\Delta x = d\sin\vartheta \tag{4.17}$$

The phase difference is

$$\Delta\varphi = 2\pi\frac{\Delta x}{\lambda} = \frac{2\pi d}{\lambda}\sin\vartheta \tag{4.18}$$

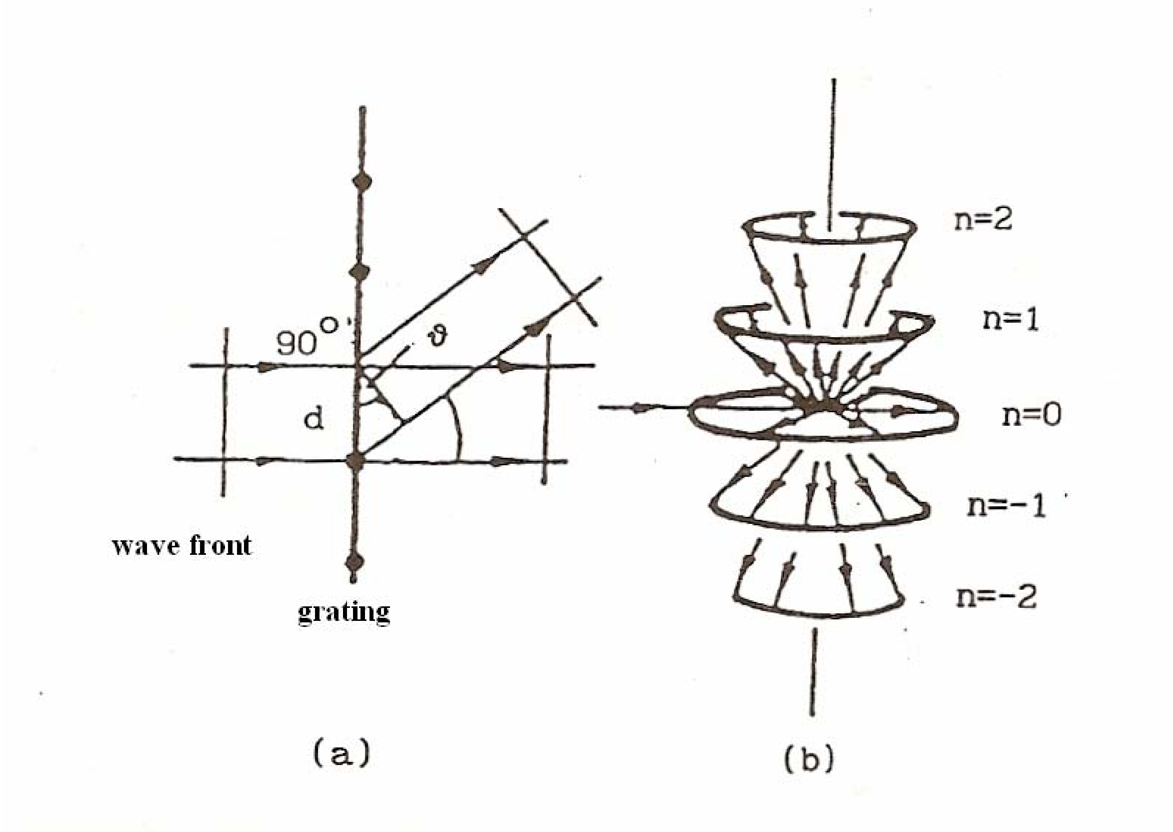


Fig. 4.10

The measured intensities are proportional to the square of F(s). Therefore the phase angle is double, the maximal intensity is observed at

$$\Delta\varphi = 4\pi\frac{\Delta x}{\lambda} = \frac{4\pi d}{\lambda}\sin\vartheta = 2n\pi \qquad n = 1,2,3,... \tag{4.19}$$

Labeling the lattice constants with d_i (i=1,2,3), the atomic dictances from the i-th lattice with d_{ij} (j=1,2,...,N , N is the number of atoms in the unit cell)

$$\Delta\varphi_{ij} = \frac{4\pi\left(d_i \pm d_{ij}\right)}{\lambda}\sin\vartheta = 2n\pi \qquad i = 1,2,3 \qquad j = 1,2,...,N \tag{4.20}$$

Equation 4.20 gives the possibility to determine from the intensity maxima of the diffractogram phase angles, and using them, the lattice constants, and the interatomic distances. However, if the d_{ij} values are very small in comparison with the d_i ones, the intensity maxima become blurred, the measured intensity is the common scattering of some atoms. Therefore some additive equations are necessary for the determination of the d_{ij} values. In this case the diffractograms from the scattering in other directions most be considered.

There exsits also an other problem, the so-called *phase problem*. It arises from the fact that only the absolute value of the $\exp(isr_j)$ factor is determinable from the diffractogram, its phase not. The problem can be solved either if a heavy atom exists in the cell, or if an atom in the cell is substituted by an other atom that does not change the crystal structure. Sometimes statistical mathematical methods can help estimating the possible phase angle sign.

4.3.2. Methods of X-ray diffraction

The X-ray photons of about 100 pm wavelength scatter on the electrons of the atoms. X-ray diffractograms of powders or of single crystals are measured. The essence of the applied methods are more easily understandable than the mechanism of their developed forms.

The *single crystal* methods have the benefit of the easy choice of the crystal faces. This fact gives the possibility of the easy choice of the direction of the incident X-ray.

1. *Rotating crystal (Bragg's) method.* The crystal is positioned in a goniometer so that one of its crystal axes is the rotational axis (Fig. 4.11a). The incident beam is monochromatic and during one rotation all the reflection planes scatter (Figs. 4.11b and c). The points belonging to the same reflection order are found along the same horizontal line. The detector is classically a cylindric photo film, the modern methods apply crystal detectors or photomultipliers.

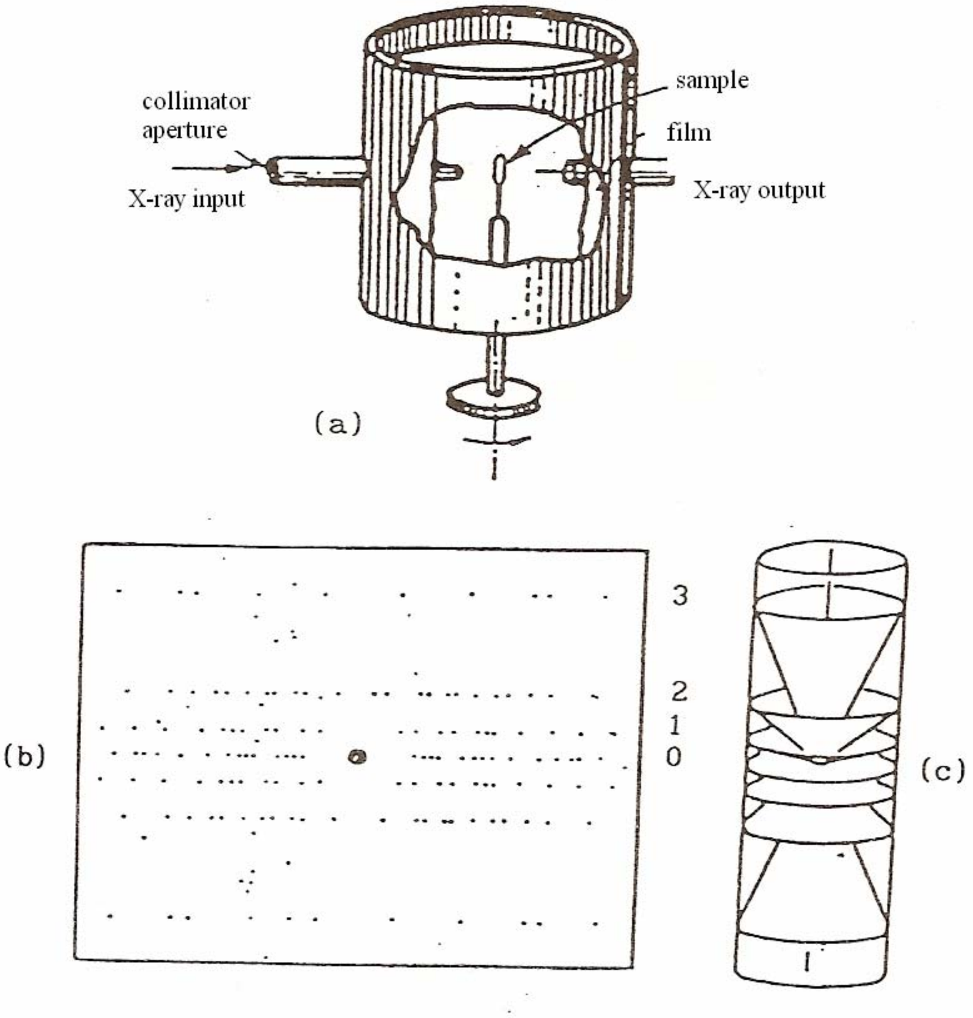


Fig. 4.11

2. *Standing crytal (Laue's) method.* One of the crystal axes of the single crystal are perpendicular to the direction of the incident beam. The X-ray beam is wide-range ("white beam") , about 20-230 pm wavelength. The forward and backward reflections are detected separately on planparallel planar fims (or by photomultipiers) perpendicularly positioned to the incident beam (Fig. 4.12a). The scatterings belonging to the same scattering angle build a ring around the direction of the incident X-ray (Fig. 4.12b). This method is applicable also for very small (1 mm) single crystals.

A crystal lattice behaves like a mirror for one of the incident wavelengths. Therefore the reflected beams have different wavelengths, the different lattices are mirrors for different X-ray wavelengths.

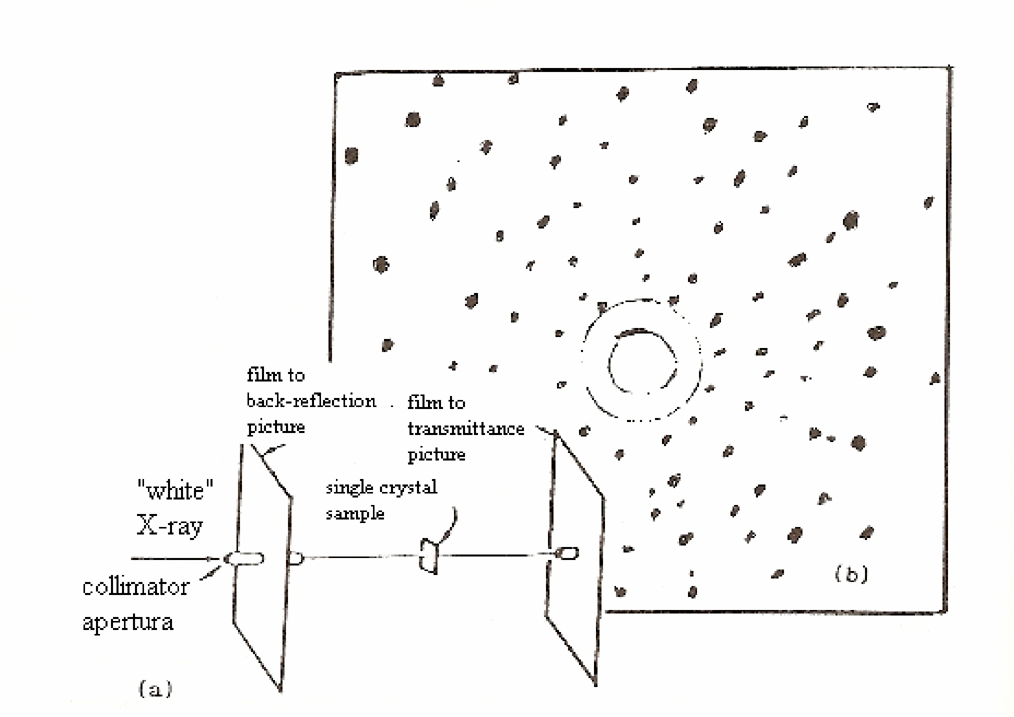


Fig. 4.12

Powder (Debey-Scerrer) method. The powder is filled in a small capillaric tube. This is irradiated with a monochromatic X-ray (Fig. 4.13). Every crystal has its own reflections. Since the small crystals in the powder are disordered, the reflections from all reflecting planes are observable. The identical reflections of several crystals build a conal surface. The axis of the cone is the direction of the incident beam, its half apex angle is the double of the scattering angle. The cylinder-like film of the moving photodetector observes the intersection of the cone and the cylinder.

The modern measuring instruments called *diffractometers* use moving detectors. In this case is very important the reproducibility of the experiment. The films registrate all the reflections in the same moment while the diffractometers scan the points of the diffractogram one after the another. Either the detector or the sample is moved during the measurements. Proportional scalers or scintillator detectors are used for detection.

The X-ray diffraction is applicable also to the structure determination of liquids with structure (e. g. colloid solution).

The diffractograms are *applicable* to the determination of the crystal structure, to the molecular structure in the crystal, the detection of the different phases in the crystal. In powder samples the grain sizes are measurable, the polycrystalline character is detectable.

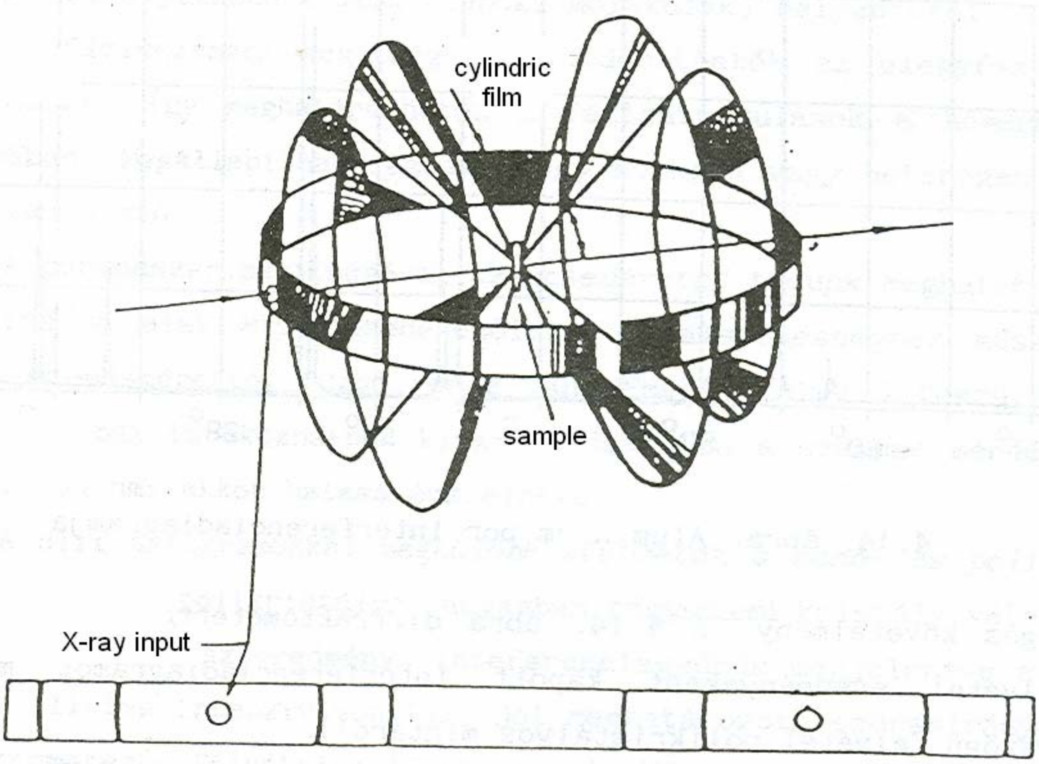


Fig. 4.13

4.3.3. Methods of electron diffraction

The theory of gas phase electron diffraction was presented in Subsection 3.11.3 . The most important difference between the X-ray and the electron diffractions is the higher intensity of the beam source in the latter case. The applied accelerating voltage is 10 -10^6 V that corresponds to about 300 - 1 pm wavelength. If the accelerating voltage is lower than 1 kV this is low electron energy diffracton (LEED), between 1 and 10 kV it is called of medium energy, at voltages higher than 10 kV this is of high energy (HEED). For the measurements high vacuum is necessary.

The method is suitable for the investigation of surface layers. Their optical orientation (their texture), crystal stucture and grain size can be measured.

The HEED is applyed mostly in reflection (RHEED) applying an electron beam with an incident angle nearly to the friction direction. Therefore the scattered electron beam gives information on a very thin surface layer (1 μm or less). In transmission only very thin layers (only of thickness of some atom layers) are measurable.

The LEED measurent is possible with nearly perpendicular electron beams and so gives information also about the deeper structure of the surface.

The method is also applied for the determination of the structure of liquids.

4.3.4. Methods of neutron diffraction

Since the neutron does not have charge but have magnetic moment it can magnetically interact with the electrons.

Neutrons of thermal distribution are applied. They can be polarized, parallelized and according their wavelengths they can be resolved by a special monochromator.

In liquid phase the molecular motions become observable. In solid state the most important application is the investigation of magnetic structures (lantanides, actinides and their alloys). Biological sytems are also investigated. This is very usful since the cross-section of the hydrogen scattering is very high in comparison of other elements, while the same is in the case of the X-ray diffraction very low.

4.4. Spectroscopic methods

4.4.1. X-ray photoelectron spectroscopy (XPS)

It is similar to the UPS (see Subsection 3.6.6, Fig. 3.51). The application of X-rays results internal ionization. Li, Cu and Zr L_α so far as Mg, Al, Ti, Cr and Cu K_α radiations are applied in high vacuum, their energies are in the ragion of 800 - 8000 eV.

The results contain the internal ionization energy (see the energy levels of nitrogen at the desciption of the UPS). The method is applied for the investigation of surface layers. The penetration depth of the electrons is called the depth where 63 % of the electrons have the energy to leave the surface yet.

From the point of view of chemistry the chemical shift is important: sensitivity to the effect of the chemical environment and to the strength of the chemical bond. Fig. 4.14. is the XPS of the azide ion, Fig. 4.15 is this for uracyl.

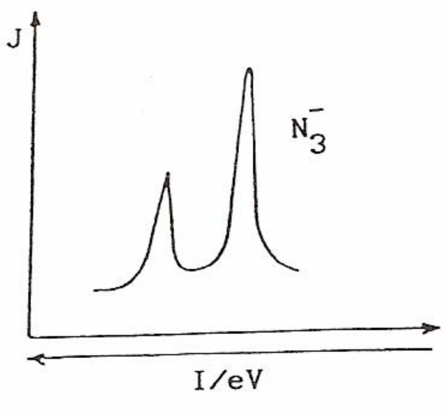


Fig. 4.14

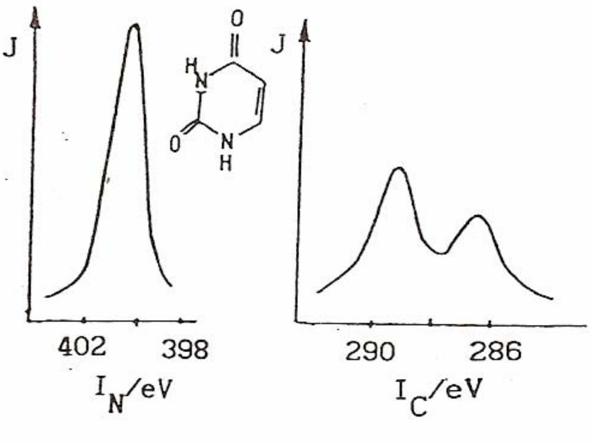


Fig. 4.15

4.4.2. Auger-electron spectroscopy (AES)

It is based on the Auger effect (Fig. 4.16). An internal electron will be ionized by a high energy electron (in high vacuum), K shell. The electron gap will be filled by an electron from a higher level of the atom, L_1 subshell.. The energy decrease of this electron can be appear as a photon (X-ray fluorescense) or can be used for the emission of a second, so-called Auger electron (from L_2 subshell). This last is the Auger effect.

The AES is a method for surface investigation. The depth of the investigable surface depend on the energy of the electron beam. This is characterized by the "free path" of the electrons in the layer, this is the path where the average kinetic energy of the electron decreases to the e-th part of initial one.

The necessary electron energy is 1-10 keV. They can be focused on the area of μm magnitude.

The detection is the separation of the Auger electrons by their velocities. A retarding electric field is applied. Here the electrons have to overcome a repulsing electric field.

The chemical shift of the Auger effect is result of the same effects as in the case ot the XPS.

Fig. 4.17. shows the AES of carbon in different environment, Fig. 4.18 shows the diffusion of the Ag through a thin Au layer (time dependence). The intensities are given as the differential quotient of the number of electrons (N) to the energy (E).

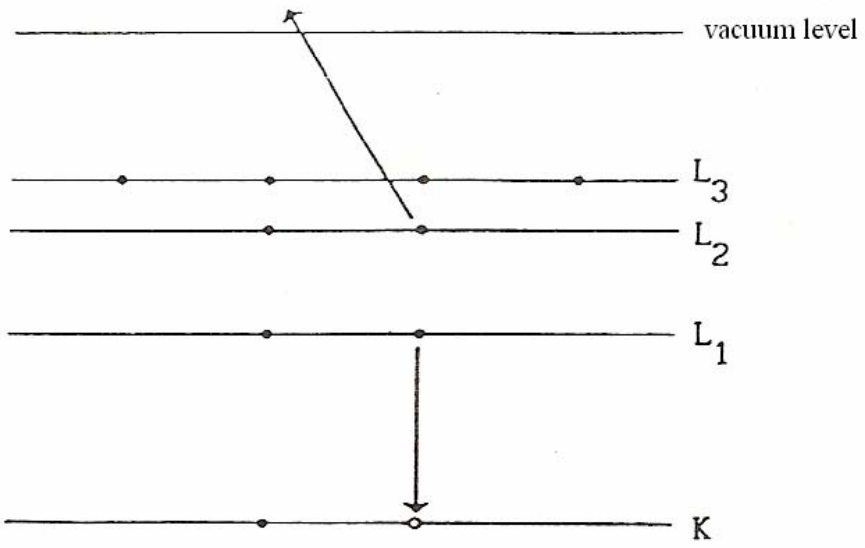


Fig. 4.16

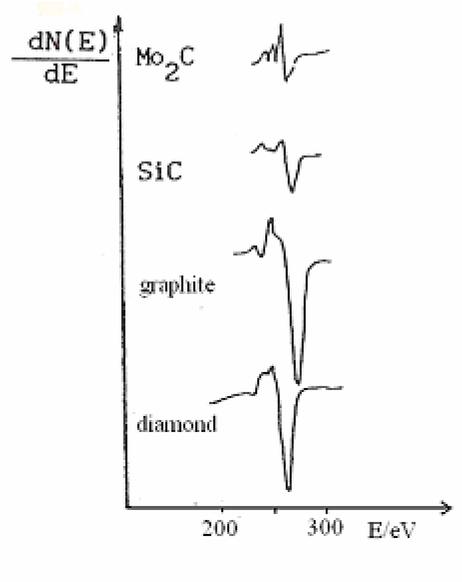


Fig 4.17

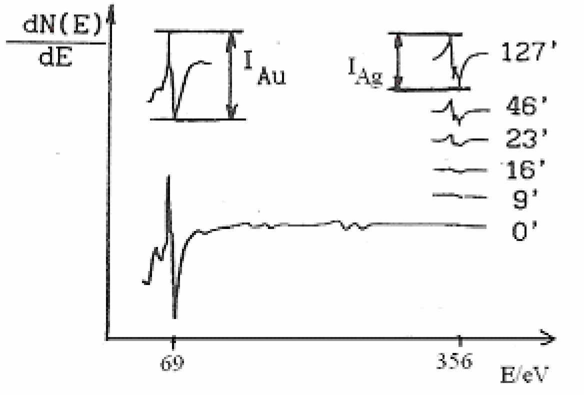


Fig. 4.18

4.4.3 Secundary ion emmission mass spectrometry (SIMS)

The basic concept is the following. High energy ions (1-100 keV) bomb the surface of the solid body in high vacuum. This primary ions (e.g. Ar^+ ionized with electron beam), penetrates the surface in the depth of some atomic layers (some 10 nm). In between they lose their kinetic energy and increase that of the surface atoms. This energy initiates a cascade and as a result a collision wave reaches the surface (Fig. 4.19). The energy of the wave ionizes some atoms on the surface. On the surface also contaminants, adsorbed molecules are found.

The aim is either the cleaning of the surface or the determination of the surface composition (Fig. 4.20, SIMS of a Se surface). Pulverizing the sulface by drilling, also the depth is investigable (Fig. 4.21, depth compositon function of a Fe-Ni alloy).

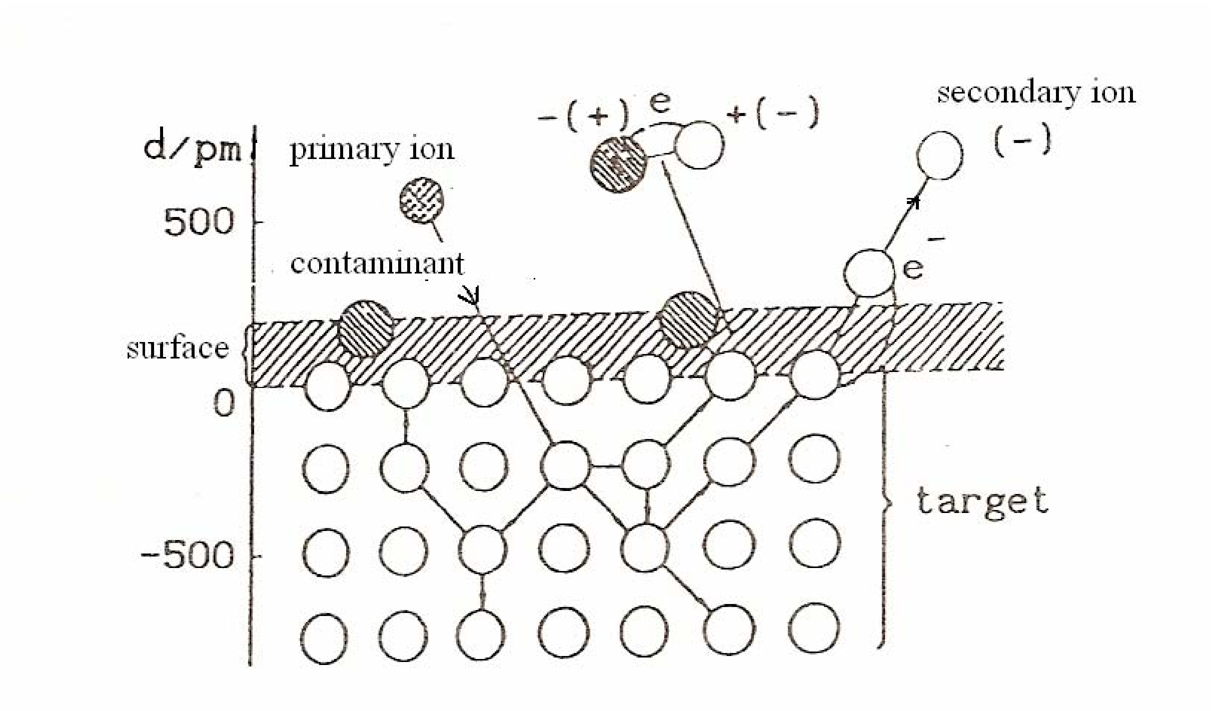
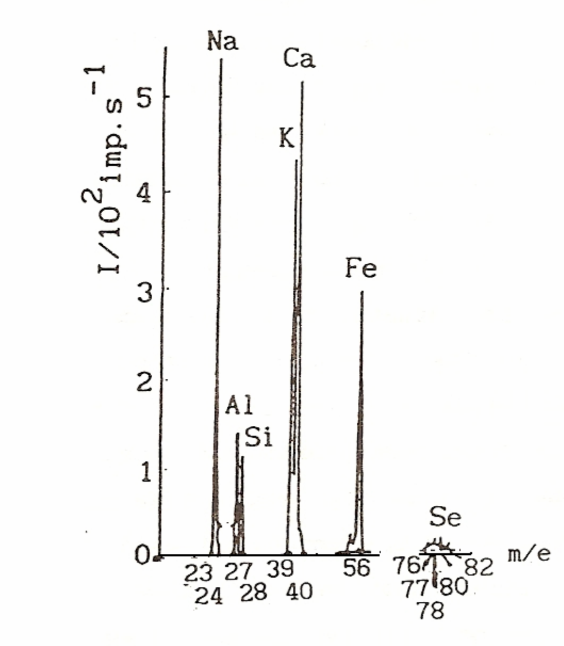


Fig. 4.19



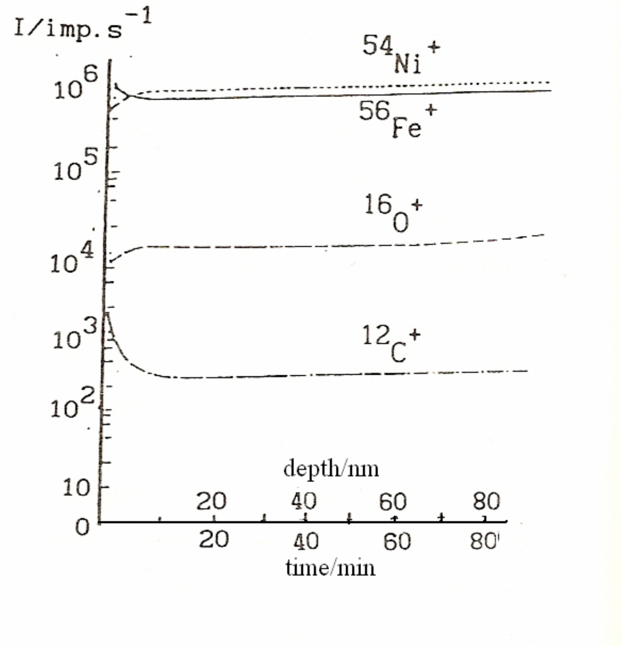


Fig. 4.20 Fig. 4.21

4.4.4. Mössbauer spectroscopy

If one want to excite an atomic nucleus it is necessary to irradiate it with a γ-ray having the energy difference between two energy levels of the nucleus. If a nucleus absorbs a γ-photon the nucleus recoils (this effect exists also applying smaller photons but is negligible). Mössbauer found, that if the nucleus is inbedden in a crystal then the absorption is recoilless. Not all nuclei are Mössbauer ones. The most important ones are ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{151}Eu,

^{119}Ir. The widly used nucleus is ^{57}Fe since it shows the effect also at room temperature. For all other nuclei low temperature is necessary. Since the ^{57}Fe nucleus has a low half-time, the ^{57}Co nucleus is applied instead. From this the ^{57}Fe is generated with a half-time of 270 days. The decay of ^{57}Fe follows two ways (Fig. 4.22).

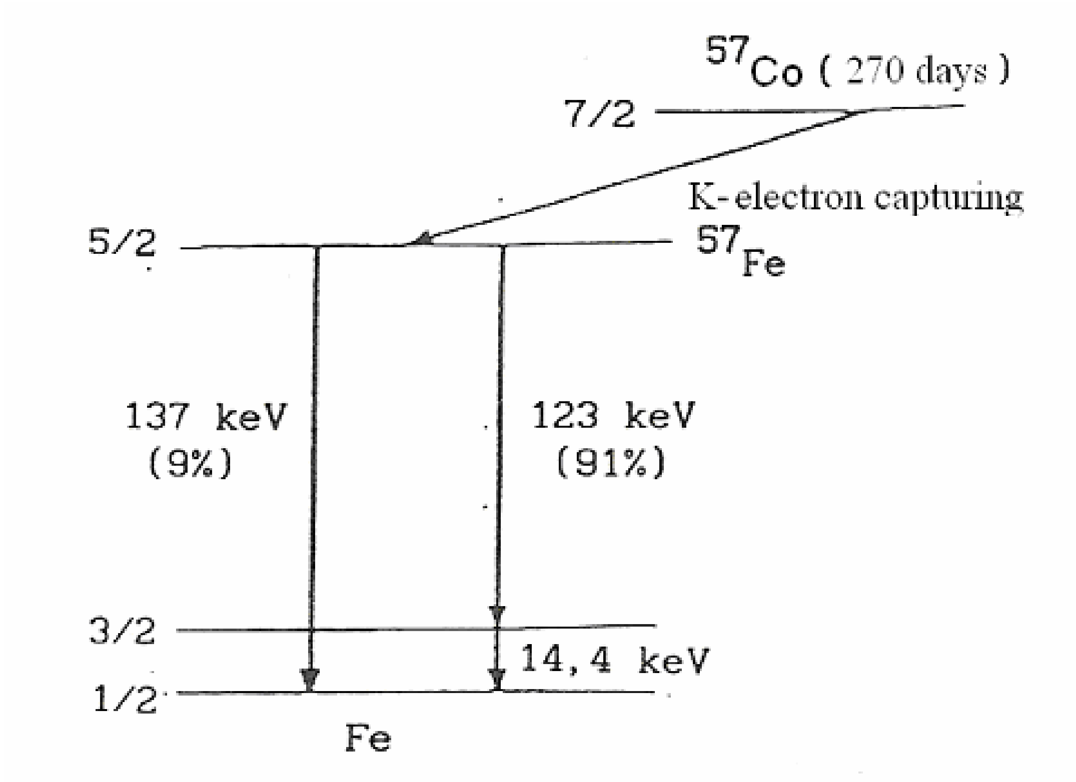


Fig. 4.22

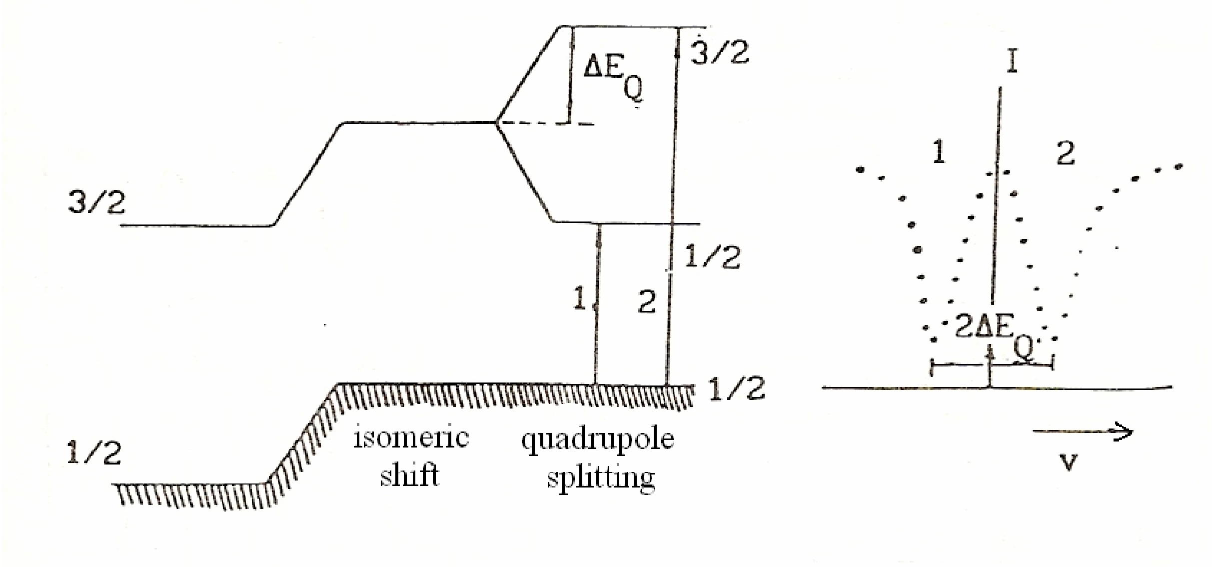


Fig. 4.23

The Mössbauer spectra are recorded as function of the velocity. Namely, the wave source has a constant frequency that will be shifted with moving either the source or the sample (Doppler effect). There are two different types of shifting in the Mössbauer spectrum.

1. *Isomeric shift*. It depends on the difference between the radii of the excited and ground state nuclei and the probability of the s electrons on the place of the nucleus.

2. *Quadrupole splitting*. If the spin quantum number of the excited nucleus is higher than 1/2 the charge distribution in the environment of the nucleus is no more symmetric (quadrupole moment exsists) and if there exsists an inhomogenous electric field (effect of ions, lattice effect) then the degenerated levels split (Fig. 4.23).

Fig. 4.24 presents isomeric shift and the hyperfine splitting of ^{57}Fe according to the values of the nuclear magnetic quantum number and the possible transitions and the temperature dependence of the fine structure of ^{57}Fe. Mössbauer spectrum. Fig. 4.25 presents the Mössbauer spectra of some Fe compounds: a. clean metal Fe, b: $FeSO_4$, c: $FePO_4.7H_2O$, d: $K_4[Fe(CN)_6]$, e: $K_3[Fe(CN)_6]$, f: $Na_3[Fe(CN)_5NO]$

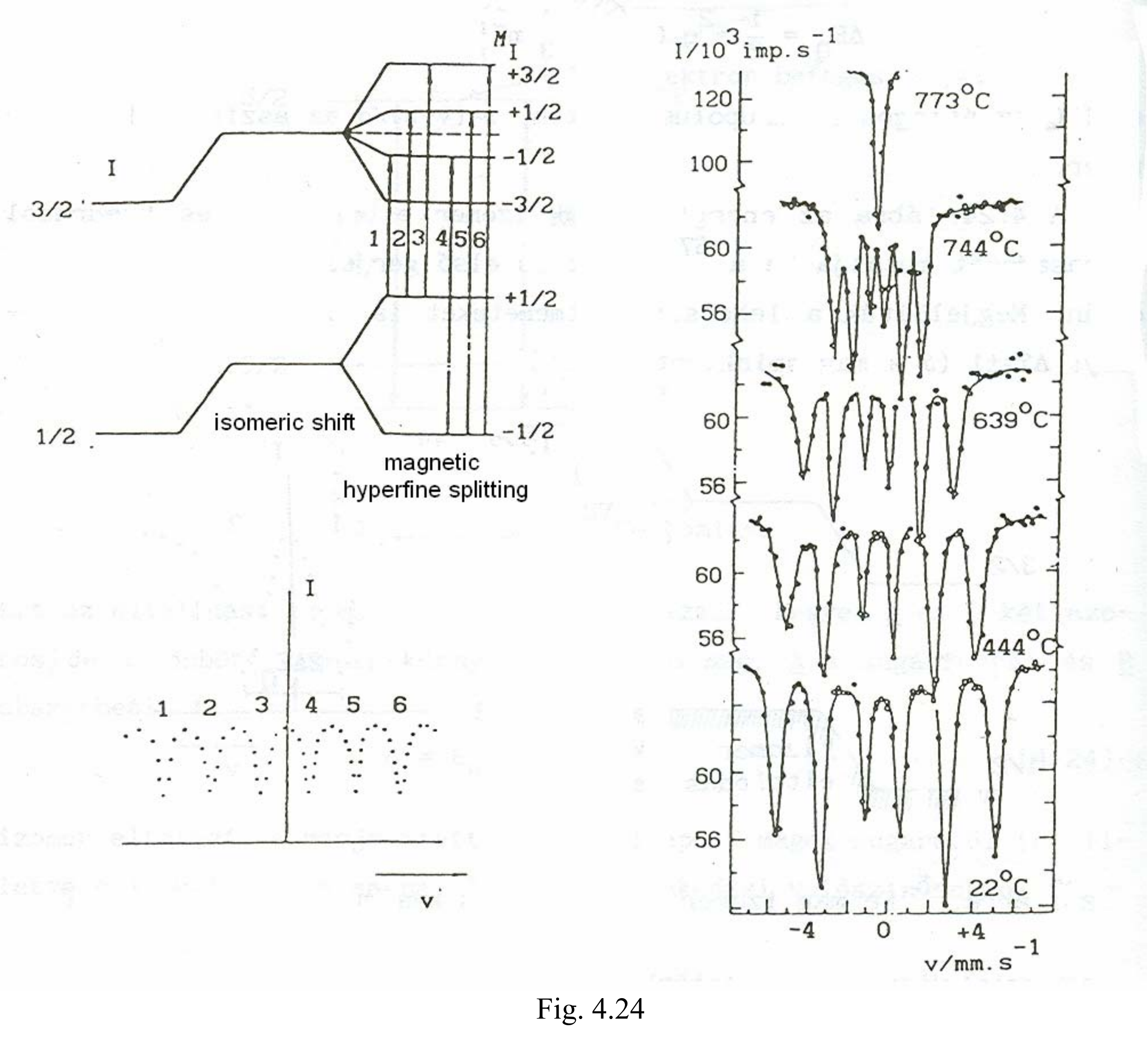


Fig. 4.24

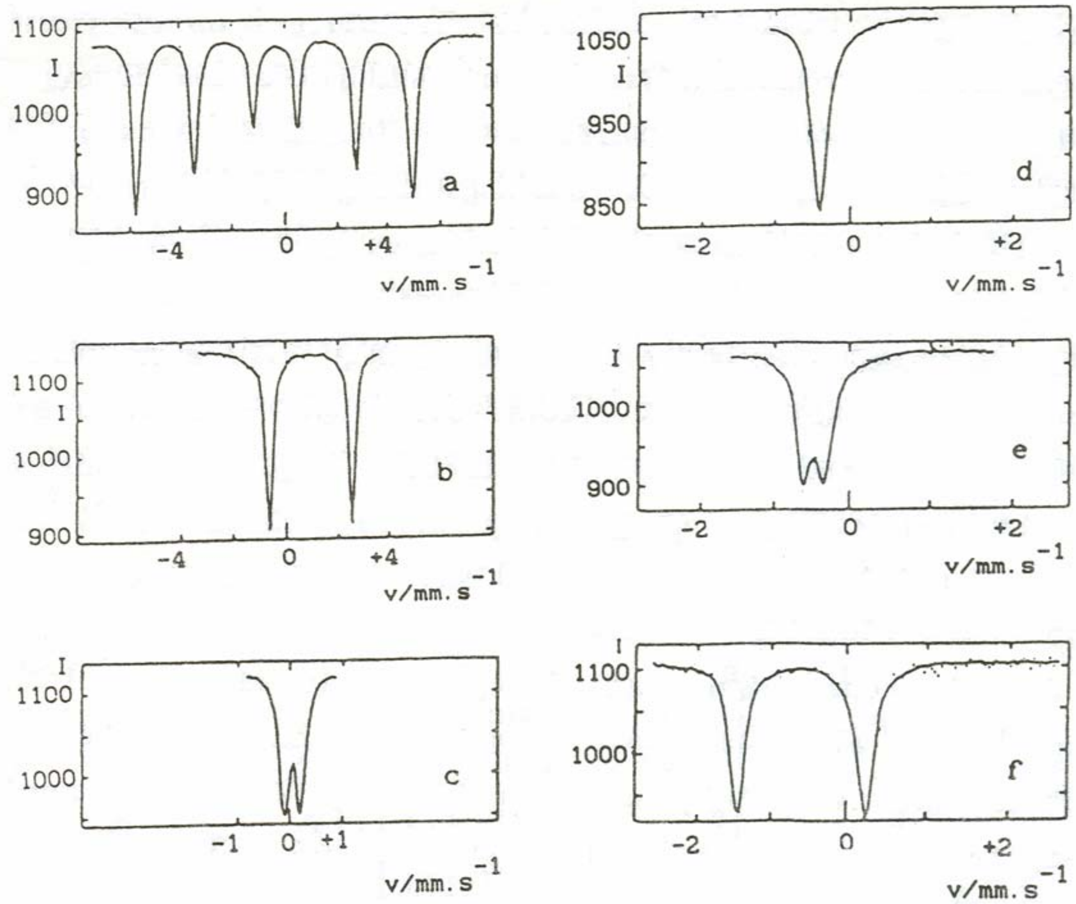


Fig. 4.25

4.4.5. Vibrational spectroscopy in condensed phases

The vibtrational spectra of condensed matters are more or less distorted by inter- and intramolecular interactions.

The reason of the *intramolecular interactions* may be the interaction of polar substituent groups, e.g. hydrogen bond, charge transfer, dipole-dipole interaction. Diluting the solutions with apolar solvents, the spectrum does not change.

In contrary, the *intermolecular interactions* between the solute molecules will change with dilution since the average distance between the solute molecules increases. The solute solvent interaction remain, but its probability decreases.

The interaction appears in the spectra in several forms, in shifts of the bands (in both directions), in change of the band intensity, in the shape of the band and also in the rise of new bands or vanishing of bands.

The shape of the liquid phase bands (the band profile) reflects the energy distribution as effect of the intermolecular interactions. The Fourier transformation of the band profile gives information about the lifetime of the excited state.

The hydrogen bond can form a new band, see the IR spectrum of neat aniline (Fig. 4.26).

The vibrational spectra of the crystals contain further bands practically below 250 cm^{-1}. The crystal vibrations appear in this region. They are collective vibrations of the entire crystal. If the unit cell of the crystal contains s molecules, the molecule with N atoms has 3sN degrees of freedom. 3s(N-6) of them are molecular vibrations. Further 6s-3 are optical vibrational modes of the crystal and may be present in the infrared and Raman spectra (according to the symmetry relations). The remaining 3 are so-called acoustic modes and are not present in the vibrational spectra.

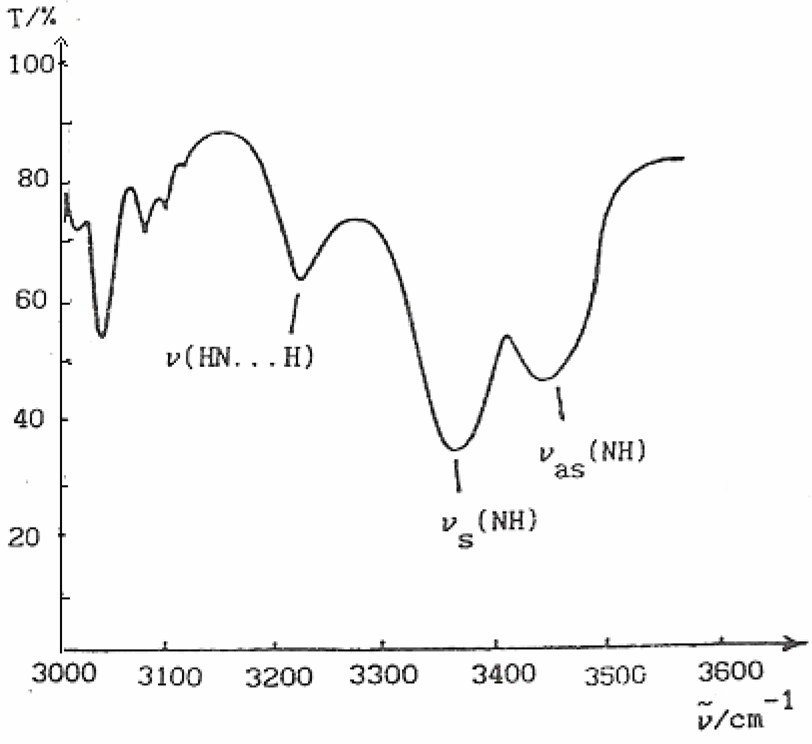


Fig. 4.26