# 1. Physical Concepts of the Method

The Mössbauer effect is concerned with the scattering<sup>1</sup> and emission of  $\gamma$ -radiation by atomic nuclei in the condensed phase. It makes use of the probability that the state of a system will remain unchanged when  $\gamma$ -quanta are absorbed or emitted with an energy which is exactly equal to the nuclear transitions energy E<sub>0</sub>. Hence the  $\gamma$ -spectrum J(E) of a Mössbauer source may be represented by the sum of a line J<sub>R</sub>(E) which is displaced due to recoil effects and broadened by the Doppler effect, and a line J<sub>M</sub>(E) with its centre at the energy which is exactly equal to the transition energy, the half-width being close to the natural one -  $\Gamma_{nat}$ . The part of the spectrum J<sub>M</sub>(E) is of particular interest and reveals itself most strikingly when the source and the sample under study are in the solid state. There are many introductory books on Mössbauer spectroscopy which give further details of the fundamental principles of the theory and the technique [1.1-6].

The aim of this Chapter is to briefly familiarize the reader who is not an active practitioner of Mössbauer spectroscopy with the basic concepts of the method. It is intended that this information should be sufficient for the reader to understand the application of Mössbauer spectroscopy to the analysis of surface layers.

## **1.1. General Aspects of Mössbauer Spectroscopy**

The emission probability f and the absorption probability f' of recoilless  $\gamma$ -quanta and the temperature dependence of f and f' are determined by the  $\gamma$ -quanta energy, the mass of the nucleus, lattice vibrations and other properties of the sample. The measurement of f enables the study of atomic vibrations or force constants.

In order to obtain information on chemical bonds of atoms in solids from experimental data, an explicit theoretical relation is needed to associate experimental f (or f') values with the phonon spectrum and the force constants of the crystal. Unfortunately this seemingly rather simple approach produces a number of problems which primarily result from the limited information which is available on the phonon spectra of solids of practical interest. Hence a more general concept of the Mössbauer effect probability may be best developed by use of the time-space correlation function.

The probability of  $\gamma$ -quantum resonant emission with a wave vector <u>k</u> when a nucleus undergoes a transition from an excited state e to the ground state g in a system going

from a state  $\psi_n$  of eigenenergy n to the state  $\psi_n$  of energy  $\eta_o$ , may be written:

<sup>&</sup>lt;sup>1</sup> Only resonant scattering is considered here. If the process is assumed to be isotropic, then the probability of "forward" re-scattering may be neglected. In this sense, any scattering event results in the disappearance of the quantum from the incident well-collimated beam. The process is often referred to as "absorption". Thus, "physically" there is only scattering, still sometimes absorption is spoken of.

$$W(E, \psi_{n}) = \sum_{n} \frac{|\langle g\psi_{n} | H | e \psi_{n} \underline{k} \rangle|^{2}}{|E - E_{0} - (\varepsilon_{n} - \varepsilon_{n}) + i\Gamma/2|^{2}}, \qquad (1.1)$$

where H is the energy operator describing the interaction between the  $\gamma$ -ray and the nucleus in question; and E<sub>0</sub> and  $\Gamma$  are the energy and the full width at half maximum of the excited state, respectively.

Since the interactions of atoms in a solid are very weak as compared to nuclear interactions, the atomic interactions only effect the movement of the centre of mass of a nucleus or atom and do not effect the movement of nucleons in the nucleus. The matrix elements M of operator H may be now represented by the product of two factors

$$M = \langle \psi_{n_0} | \exp (i \underline{k} \underline{r}) | \psi_n \rangle \langle g | a | e \rangle, \qquad (1.2)$$

where <u>r</u> is the radius vector which is characteristic of the position of the nucleus.

The nuclear matrix element  $\langle g | a | e \rangle$  for any changes in the lattice is a common term which may be factorized. It determines the angular dependent properties of emitted or absorbed radiation and the relative intensity of the hyperfine components of the spectrum. The first term of (1.2) describes the momentum transfer of the quantum to the lattice and the resulting change of the phonon spectrum. The term determines the f or f' value and may have an angular dependence of its own. For a cubic crystal where interatomic forces may be assumed to be harmonic, we have

$$f = \exp\left\{\frac{1}{2}k^{2}\overline{x^{2}}\right\}$$
(1.3)

where  $x^2$  is the mean square displacement of the Mössbauer atom from its equilibrium position at temperature T.

The Debye model is most widely used and is assumed irrespective of the lattice symmetry and the number of atoms in the unit cell. Hence, from an observed f value the effective characteristic temperature may be evaluated and compared with the temperatures obtained for the substance by methods such as X-ray analysis or specificheat measurements.

According to the Debye model, the Mössbauer effect probability may be written:

$$f = \exp\left[-\frac{6E_R}{k\Theta}\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} \left(\frac{1}{e^t - 1} + \frac{1}{2}\right) t dt\right],$$
(1.4)

where  $E_R = E_0^2/2Mc^2$  is the recoil energy imparted to an isolated nucleus of mass M; c is the velocity of light;  $\Theta$  is the Debye temperature of the crystal, and k is the Boltzmann constant. For very low and high temperatures (as compared with  $\Theta$ ), expression (1.4) may be written:

$$f = \exp\left[-\frac{3E_R}{2k\Theta}\right]$$
 for T <<  $\Theta$ , (1.5)

$$f = \exp\left[-\frac{6E_RT}{k\Theta^2}\right]$$
 for  $T > \Theta$ , (1.6)

which enables one to further simplify the characteristic temperature determination. The theoretical spectrum of the 129 keV  $\gamma$ -ray of <sup>191</sup>Ir emitted by atom in iridium metal is shown in Fig. 1.0. The Mössbauer spectrometer is sensitive only to the narrow, recoil-free line at zero energy shift, which contains 5,7% of total area under the curve at 4 K for <sup>191</sup>Ir, E<sub>0</sub> = 129 keV.



Fig. 1.0 Absorption cross-section for <sup>129</sup>Ir at 4 and 300 K. The Debye model was used to calculate the lattice vibration.

It is found that when there are several atoms in a unit cell, the Debye model is not adequate, and, apart from three acoustic phonon branches, optical branches also appear. The Mössbauer effect probability is higher if more optical branches determine the oscillation mode of the Mössbauer atom in the lattice. Light atoms, as a rule, vibrate in optical branches. The oscillation amplitude of a heavy atom in the optical branches is determined by the type of interaction of these atoms in the lattice and is significant only when the interaction between heavy atoms is strong.

Using resonance atoms as admixtures to various compounds extends the number of solids in which the Mössbauer effect is observable and this expands the resources of this method even further. Unfortunately the theoretical treatment is much more complicated than compared with the ordinary Mössbauer effect. In such situations it is the oscillations of the admixture atoms which are of the primary interest. At the same time these oscillations cause the translational symmetry to vanish and thus the theoretical treatment becomes rather complicated.

Atoms of the Mössbauer isotope present in a phase are characterized by their f or f' values. These are the important parameters needed for quantitative phase analysis. It has been proved experimentally that for some isotopes even at room temperature the f

values may exceed 0.5 which means that more than one half of the emitted  $\gamma$ -quanta are recoilless with energy equal to the energy of the nuclear transition. These quanta may resonantly interact in the sample under study.

It is unfortunate that there is at present no satisfactory compilation of f-values, although fairly comprehensive information is contained in the annual reference editions of "Mössbauer Effect Data Index" which contains reviews of relevant literature until 1976 and, more recently, in monthly issues of "Mössbauer Effect Data and Reference Journal". On using the results of quantitative phase analysis by Mössbauer spectroscopy, special attention should be paid to the validity of information on the f-values used in the analysis.

The consideration so far has not taken into account the dependence of phonon excitation on the direction of the recoil momentum of the nucleus with respect to the crystallographic axes. This must be considered especially when strong anisotropy is observed for laminar crystals. The anisotropy factor f' which is detected for some nontextured polycrystalline samples takes this into account in a phenomenon known as the Goldanskii-Karyagin effect. This enables the extraction of valuable information on solids such as the surface layer structure and texture.

The application of Mössbauer spectroscopy in diverse fields of qualitative and quantitative analysis is based on the ease with which hyperfine interactions can be observed. The information obtained from the Mössbauer spectra may be correlated to other methods by which hyperfine interactions can be examined such as NMR, EPR, ENDOR, PAC (perturbed angular correlations), nuclei orientation and neutron scattering. However, Mössbauer spectroscopy often proves to be experimentally simpler, more illustrative and an efficient method for studying applied problems. The Mössbauer nuclei are ideal "spies" supplying information on both the microscopic and macroscopic properties of solids. The spectrum of  $\gamma$ -rays emitted or scattered by such nuclei, is a source of information on the hyperfine interactions.

Until relatively recently one could measure the  $\gamma$ -rays energy with the inaccuracy  $\Delta E >> \Gamma_{nat}$ . However, since the first work was reported on classic resonance scattering of  $\gamma$ -rays and since the modernization of crystal diffraction spectrometers, it has become possible to significantly increase the energy resolution R ~  $\Delta E/E$  although it is still several orders of magnitude higher than  $\Gamma_{nat}/E$ . That is why  $\gamma$ -spectroscopy initially failed to give information on nuclear energy levels, similar to the information that could be obtained by optical spectroscopy on electronic structure. The direct study of hyperfine interactions by the accurate measurement of  $\gamma$ -rays energy was quite impossible since the energy of hyperfine interactions are of the same order as  $\Gamma_{nat}$ .

The discovery by R.L. Mössbauer made it possible to measure the hyperfine interaction directly. In this Chapter we shall outline the general concepts of Mössbauer spectroscopy in so much as it is necessary to describe the method and its various

applications. In Mössbauer spectroscopy the energy resolution is determined by the natural line width (for <sup>57</sup>Fe  $\Gamma_{nat}$  is equal to 4.8 10<sup>-9</sup> eV). The experimental methods can measure the changes in line positions with an inaccuracy of less than 0.1  $\Gamma_{nat}$ .

# **1.2**. Hyperfine Interactions and Line Positions in Mössbauer Spectra

The energy of a nucleus, as well as of any system of charges and currents, changes upon interaction with an external electromagnetic field by an amount E'. Using classic electrodynamics, the energy may be described by the multipole moments series as:

$$\mathsf{E}' = \mathsf{q}\phi_0 - \underline{\mathsf{p}}\underline{\mathsf{E}}_0 - \underline{\mathsf{\mu}}\underline{\mathsf{H}}_0 - \frac{1}{6}\sum_{i,k=1}^3 \underline{\mathsf{Q}}_{ik} (\partial^2 \phi / \partial x_i \partial x_k)_0 - \dots, \qquad (1.7)$$

where <u>E</u> and <u>H</u> are the electric and magnetic field strength, respectively,  $\varphi$  is the electrostatic potential, q = eZ is the nuclear charge, <u>p</u>, <u>ì</u> are vectors of electric and magnetic dipole moments,  $Q_{ik}$  is the tensor of the electric quadrupole moment. The subscript "o" means that the quantity is that in the centre of the nucleus. The moments of higher orders may be neglected. This is valid if: (i) the velocities of the nucleons are small as compared to the velocity of light; (ii) changes in the external field at nuclear distances are small (the hyperfine anomaly is neglected); (iii) the external field changes the distribution of charges and currents in the nucleus only to a negligible extent. Since nuclei do not have electric dipole moments, the second term of (1.7) is zero and the energy of a nucleus in an external electromagnetic field is determined by the product of the nuclear (q, <u>ì</u>, <u>Q<sub>ik</sub></u>) and electron  $\varphi_0$ , <u>H</u><sub>0</sub>,  $(\partial^2 \varphi / \partial x_i \partial x_k)$ ) factors. In solid state physics and in the applied fields the first factors are supposed to be known.

The classical treatment is insufficient to obtain the positions of the nuclear levels, the relative intensities of the corresponding transitions, and the angular dependence of the emitted radiations and a quantum mechanical approach is needed. As seen from (1.7) the Hamiltonian H, describing the interaction of a nucleus with effective fields, may be represented as a sum of the two Hamiltonians: one for interactions of the nucleus with effective field ( $H_{\rm M}$ )

$$H = H_{\rm Q} + H_{\rm M} \quad . \tag{1.8}$$

The Hamiltonian of the electrostatic interaction is

$$H_{\rm Q} = e \sum_{\rm p=1}^{\rm Z} \phi(\underline{r}_{\rm p}) ,$$
 (1.9)

where  $\underline{r}_p$  is the radius vector of the p-th proton,  $\varphi(\underline{r}_p)$  is the electric potential in the vicinity of the p-th proton, and the summation is over all protons p = 1,...Z. The coordinate system is chosen such that the origin is at the centre of the nucleus and the axes  $x^i$  (i = 1,2,3;  $x^1 \equiv x$ ;  $x^2 \equiv y$ ;  $x^3 \equiv z$ ) are directed along the principal axis of the tensor of the electric field gradient (EFG) acting on the nucleus. Since the external electromagnetic field potential does not change appreciably within the nucleus, and by expansion of (1.9) over the multipoles, we can write

$$\mathcal{H}_{Q} = \sum_{p=1}^{Z} \varphi_{p}(0) + e \sum_{p=1}^{Z} \sum_{i=1}^{3} \left( \frac{\partial \varphi_{p}}{\partial x_{p}^{i}} \right)_{o} x_{p}^{i} + \frac{1}{2} e \sum_{p=1}^{Z} \sum_{i,k=1}^{3} \left( \frac{\partial^{2} \varphi_{p}}{\partial x_{p}^{i} \partial x_{p}^{k}} \right)_{o} x_{p}^{i} x_{p}^{k} + \dots, \quad (1.10)$$

where  $\phi_p(0)$  is the electric potential at the centre of the nucleus due to the p-th proton. The first term in (1.10) displaces the energy of all nuclear levels equally and may be omitted. The second term describes the dipole electric interaction and equal zero (since in the state of a given parity the nucleus has no electric dipole moment).

It is the third term that determines the experimentally observed energy change of nuclear levels due to the interaction of the nucleus with external electric fields. For the analysis of experimental data a special method is usually used whereby the same term is added to and subtracted from the right-hand side of (1.10). The result is

$$\mathcal{H}_{Q} = \frac{e}{6} \sum_{p=1}^{Z} \sum_{i,k=1}^{3} r_{p}^{2} \left( \frac{\partial^{2} \varphi_{p}}{\partial x_{p}^{i} \partial x_{p}^{k}} \right)_{o} \delta_{ik} +$$

$$\frac{e}{6} \sum_{p=1}^{Z} \sum_{i,k=1}^{3} (3x_p^i x_p^k - r_p^2 \delta_{ik}) \left( \frac{\partial^2 \varphi_p}{\partial x_p^i \partial x_p^k} \right)_0$$

where  $r_p^2 = \sum_{i=1}^{2} (x_p^i)^2$ . Using the fact that the electrostatic potential  $\phi$  satisfies the Poisson equation  $\nabla^2 \phi = 4\pi \rho_e$ ,  $\rho_e = -e |\psi(0)|^2$  is the charge density at the nucleus (r = 0) and introducing the tensor of nuclear quadrupole moment  $Q_{ik} = \sum_{i=1}^{Z} \left( 3x_p^i x_p^k - r_p^2 \delta_{ik} \right)$  and the EFG tensor,

$$\begin{aligned} & \varphi_{ik} = \sum_{p=1}^{i} (3x_p x_p - I_p \sigma_{ik})^{i} \text{ and the EPG tensor,} \\ & \varphi_{ik} = (\partial^2 \varphi_p / \partial x_p^{i} \partial x_p^{k})_0 \text{ , we can now rewrite (1.9) as} \\ & H_Q = H_\delta + H'_Q = -\frac{2\pi}{3} e^2 \sum_{p=1}^{Z} r_p^2 |\psi(0)|^2 + \frac{e}{6} \sum_{i,k=1}^{3} \varphi_{ik} Q \end{aligned}$$
(1.11)

The nucleus is here considered to be a sphere with a mean-square radius  $\overline{r^2} = \sum_{p=1}^{Z} \overline{r_p^2} / Z$ for the ground state - g and excited state - e. As a rule,  $\overline{r_q^2} \neq \overline{r_e^2}$  and the nuclear

for the ground state - g and excited state - e. As a rule,  $r_g^2 \neq r_e^2$  and the nuclear charge is uniformly distributed inside the sphere. Thus the interaction of the nucleus with the electric fields may be expressed as a sum of two interactions corresponding to Hamiltonians  $H_{\delta}$  and  $H_{Q}$ .

The external electric field acting on such a spherical nucleus does not split the levels but shifts them by the quantity

$$\delta \mathsf{E}_{g,e} = \frac{2\pi}{3} e^2 \mathsf{Zr}_{g,e}^2 |\psi(0)|^2 \ . \ (1.12)$$

The shift due to Coulomb interactions is of the order of  $10^{-12}$  of the transition energy. The value of the shift for every nuclear level depends on the chemical state of the atom. This is characterized by the  $|\psi(0)|_{a,s}^2$  parameter which is the electron density at the nucleus in the absorber (a) or in the source (s). In a Mössbauer spectrum this part of the full electrostatic interaction manifests itself as the chemical isomer shift  $\delta$  [1.8] between the centre of gravity of the emission spectrum of the source and the centre of gravity of the absorber (Fig. 1.1a and b).



Fig. 1.1a, b Energy level shifts for a  ${}^{57}$ Fe nucleus, resulting in the appearance of the isomer shift –  $\delta$  (a); the corresponding Mössbauer spectrum (b).

Thus the transition energy in the source  $E_s$  is different from the energy  $E_a$  in the absorber, either of them being different from the transition energy  $E^0$  for  $\overline{r^2} = 0$ . For a pair of the source and absorber nuclei we may write

$$\delta = \frac{2\pi}{3} Z e^2 (\overline{r_e^2} - \overline{r_g^2}) (|\psi(0)|_a^2 - |\psi(0)|_s^2) .$$
(1.13)

For the first excited level of  ${}^{57}$ Fe  $r_e{}^2 < r_g{}^2$ .

It must be appreciated that in Mössbauer experiments it is not the absolute energy of the  $\gamma$ -quanta which is determined but the energy shift of the nuclear levels. The energy scanning is carried out by the use of the Doppler effect. Therefore the energy parameters ( $\Gamma$ ,  $\delta$ ) are expressed in velocity units, v. If the source moves to the detector with velocity v, the energy of emitted radiation increases by S = Ev/c. For the 14.4 keV transition a change in the source velocity with respect to the absorber of 1 mm/s corresponds to the change in the  $\gamma$ -quantum energy of 4.8 10<sup>-8</sup> eV.

The charge density at the nucleus is mainly determined by s- and only partially by p-electrons. The main effect of the p- and d-electrons and any other electrons shells that do not contribute directly to the electron density  $|\psi(0)|^2$ , is to shield the s-electrons. For example, the addition of a sixth 3d- electron

in the  $Fe^{+3} \rightarrow Fe^{+2}$  transition causes the shielding of the s-electrons to increase. In accordance with (1.13) ferrous compounds give larger positive isomer shifts in the Mössbauer spectra than ferric compounds.

The determination of the scale factor  $(\overline{r_e^2} - \overline{r_g^2})$  in (1.13) is called the isomer shift calibration. The interpretation of isomer shifts in Mössbauer spectra involves the correlation of a given  $|\psi(0)|_a^2 - |\psi(0)|_s^2$  value with the known electronic structure of the Mössbauer atom or the change of the structure resulting from the examination of different samples. It should be noted that it is only one  $10^{-20}$ -th of atomic electrons in a solid that directly participate in the isomer shift; the nuclear parameter  $(\overline{r_e^2} - \overline{r_g^2})$  is of the order of  $10^{-29}$  cm<sup>2</sup>. The isomer shift is four orders of magnitude smaller than the Lamb shift caused by quantization of the electromagnetic field. The measurements of isomer shifts are now carried out by Mössbauer Spectroscopy at the limits of experimental possibility i.e. (R ~  $10^{-13}$ ).

The isomer shift value is often considered to be the main parameter which enables the oxidation state to be identified. However it is often difficult to identify the nature of the phase by the isomer shift alone. For example, approximately similar isomer shifts correspond to a variety of different ferric oxides. Compounds (both sources and absorbers) do exist with especially accurately known isomer shift values. Thus, for Mössbauer studies involving <sup>57</sup>Fe the sources are prepared by introducing <sup>57</sup>Co into chromium, rhodium, stainless steel(SS), palladium- or platinum-foils. Materials such as iron ( $\alpha$ -Fe), sodium nitroprusside (SNP) and potassium ferrocyanide (PFC) are often used as standard absorbers. A diagram of isomer shifts for substances generally used in practice at 298 K is shown in Fig 1.2. The isomer shift is described relative to the centre of the  $\alpha$ -Fe spectrum.

The diagram shows that the energy required for the transition of a  ${}^{57}$ Fe nucleus in SS into the first excited state is less than it would be in platinum. In velocity units the difference is 0.3484 + 0.086 = 0.4344 mm/s. The Mössbauer  $\gamma$ -quanta emitted by a  ${}^{57}$ Co(Pt) source would be too high in energy to be resonantly scattered in SS sample. The maximum resonant scattering would occur if the energy was lowered by application of the Doppler effect. In this case the source and the absorber have to be moved relative to each other. The negative velocity values correspond to the movement of the absorber away from source. Hence for the above example the maximum scattering will be observed at the velocity of - 0.4344 mm/s.

In <sup>57</sup>Fe Mössbauer spectroscopy the isomer shifts are



Fig. 1.2 Isomer shifts of sodium nitroprusside (SNP), potassium ferrocyanide (PFC) and stainless steel (SS) and  ${}^{57}$ Co sources (chromium, palladium, copper and platinum matrices) relative to the center of the  $\alpha$ -Fe spectrum.

usually quoted relative to  $\alpha$  -Fe. Some works use the centroid of the SNP spectrum. Figure 1.2 enables the necessary conversions to be made. For example, if two spectra of PFC are obtained with the same spectrometer, one using a  ${}^{57}$ Co(Cr) source and the other using a  ${}^{57}$ Co(Pt) source, one spectrum will show a line in the positive velocity region whilst the other will show a line in the negative velocity region. The distance between them will be 0.4944 mm/s. Diagrams of the type shown for  ${}^{57}$ Fe in Fig. 1.2 have also been formulated for other elements [1.9]. For every nuclide there is a compound used as a reference for the standardization of isomer shift data. For example, for tin it is SnTe and BaSnO<sub>3</sub>, for iodine it is CsI, and for neptunium it is NpAl<sub>2</sub>. Let us consider now the second of the above mentioned interactions known as the electric quadrupole interaction and described by the Hamiltonian H'<sub>Q</sub>. By the Wigner-Ekart theorem, tensor components of the nuclear quadrupole moment are expressed through  $\hat{I}_k$  operators of the nuclear spin projection I:

$$Q_{ik} = \frac{eQ}{2I(2I-1)} \left[ \frac{3}{2} (\hat{l}_{i} \ \hat{l}_{k} + \hat{l}_{k} \ \hat{l}_{i}) - \hat{I} (\hat{I} + 1) \delta_{ik} \right].$$
(1.14)

The value of  $Q_{zz}$  when the nucleus is in the state m = I is conventionally called the nuclear quadrupole moment

 $eQ = \langle I,I \mid Q_{zz} \mid I,I \rangle$ . The EFG tensor in the principal axes, taking into account LaPlace's equation is determined by the two independent parameters. Firstly,  $\phi_{zz}$ , commonly called "the electric field gradient" or "the principal component of the electric field gradient tensor" and sometimes denoted as

 $\varphi_{zz} = eq$ ; secondly, by  $\eta = (\varphi_{xx} - \varphi_{yy})/\varphi_{zz}$ , called the "asymmetry parameter", the axes being chosen such that  $|\varphi_{zz}| > |\varphi_{xx}| > |\varphi_{yy}|$  with  $0 \quad \eta < 1$ . The Hamiltonian of the electric quadrupole interaction for the nucleus (with quadrupole moment Q and spin I) may be written as

$$H'_{Q} = \frac{e\phi_{ZZ}Q}{4l(2l-1)} \bigg[ 3\hat{l}_{Z}^{2} - \hat{l}(\hat{l}+1) + \frac{\eta}{2}(\hat{l}_{+}^{2} + \hat{l}_{-}^{2}) \bigg], \qquad (1.15)$$

where the shift operators  $\hat{I}_{\pm}$  are introduced by usual relations  $I_{\pm} = I_x \pm iI_y$ .

In Mössbauer spectroscopy it is necessary to evaluate the eigen values of the  $H'_Q$  Hamiltonian, that is the energies  $E_Q^m$  for the ground state and for the excited state, the transition from which is followed by the emission of a Mössbauer  $\gamma$ -quantum (see Fig. 1.1c). The line positions in Mössbauer spectra are determined by the eigenvalues of the sum Hamiltonian  $H_Q$  for the nucleus in excited and ground states in the source and absorber, i.e. both ä-value and  $E_Q^m$ . The intensity of the lines which provide valuable information on the structure of the surface layers are determined by the eigenvectors of  $H_Q'$  Hamiltonian [1.10].

For the axially symmetric EFG tensor  $(\eta = 0)$  the degeneracy of the nuclear energy levels is not completely split, and the energy depends only on the absolute value of the spin projection. The energy level displacement is given by the following expression:

$$E_{Q}^{m} = \frac{e\phi_{ZZ}Q}{4I(2I-1)} [3m^{2} - I(I+1)], \qquad (1.16)$$

where m is the value of the spin projection onto the quantization axis. For  $\eta = 0$ , the  $E_Q^m$  values may be found by solving a secular equation which has no general analytical solution for I > 2. Hence line intensities and their positions can only be obtained by numerical methods.

For non-textured polycrystalline samples which do not show the Goldanskii-Karyagin effect or relaxation, the quadrupole interaction described by  $H'_Q$  does not shift the centre of gravity of the spectrum  $\sum_{m=1}^{I} E_Q^m = 0$ , that is, the quadrupole



Fig. 1.1c, d The splitting of the excited level of a  $^{57}$ Fe nucleus due to electric quadrupole interaction - (c) and the corresponding Mössbauer spectrum - (d).

interaction conserves energy. For the levels with I = 0 and I = 1/2, the quadrupole interaction energy is zero, since Q = 0. If the nuclear spin is half integral, the quadrupole interaction will cause the levels to be at least two-fold degenerate. If the spin values are integral the level degeneracy for  $\eta \neq 0$  may be completely lifted.

Of special interest in Mössbauer spectroscopy are the transitions between states with spin quantum numbers I = 1/2 and I = 3/2. This is the case for <sup>57</sup>Fe, <sup>119</sup>Sn, <sup>125</sup>Te and many other nuclides. The spectra consist of two lines, the distance between them being equal to:

$$\Delta = \frac{\left| e \varphi_{ZZ} Q \right|}{2} \left[ 1 + \eta^2 / 3 \right]^{1/2} . \tag{1.17}$$

The EFG tensor parameters which are obtained depend on the point group for the nucleus in question rather than on the space group of the entire lattice. However, once the space group and the lattice positions are known, one can determine the point group for all sites by reference to the International Tables for X-ray Crystallography [1.11]. Following to Sternheimer, two primary sources of the EFG may be identified. Firstly, charges on ions surrounding the nucleus

(provided the symmetry of the surroundings is lower than cubic), and secondly, the unfilled valence shells (since filled shells possess a spherically symmetric charge distribution). For free atoms or ions electrons of the unfilled shells do not contribute to the EFG at the nucleus, since the corresponding electronic states are degenerate. If the atom is in a crystal lattice, a component of the EFG at the nucleus ( $\varphi_{zz}$ )<sub>lat</sub> may also be evaluated which is caused by the surrounding ions. The actual EFG at the nucleus is determined by the extent to which the electronic structure of the Mössbauer atom is distorted by electrostatic interactions with external charges. This leads to the so-called "antishielding" effect, which is described by 1 -  $\gamma_{\infty}$  . For iron compounds  $\gamma_{\infty} \cong 10$ . The EFG due to electrons in the unfilled shells ( $\phi_{zz}$ )<sub>val</sub> causes the polarization of the inner filled shells which leads to the appearance of an induced EFG of the opposite sign. This is known as shielding and the shielding effect is taken into account by using the R factor which is equal to 0.25 - 0.30 for iron compounds. The resulting EFG at the nucleus of an ion in a solid may be represented as

$$\phi_{zz} = (1 - R) (\phi_{zz})_{val} + (1 - \gamma_{\infty}) (\phi_{zz})_{lat} . \qquad (1.18)$$

Usually  $(\phi_{zz})_{val} >> (\phi_{zz})_{lat}$ . At low values of the  $\gamma_{\infty}$  factor, the crystal field contribution to the EFG at the nucleus amounts to the electronic term splitting, which in its turn leads to the appearance of  $(\phi_{zz})_{val}$ .

The Hamiltonian for the interaction of the magnetic dipole moment of a nucleus with the effective magnetic field  $\underline{H}_{eff}$  acting on it may be written

$$H_{\rm M} = -g_{\rm I} \,\mu_{\rm n} \,\underline{\rm I} \,\underline{\rm H}_{\rm eff} \,, \tag{1.19}$$

where  $\mu_n$  is the nuclear magneton,  $g_l$  is the gyromagnetic ratio, <u>l</u> is the nuclear spin operator (the quantization axis coincides here with the direction of <u>H</u><sub>eff</sub>). The degeneracy of the nuclear levels is completely split. Figure 1.3 depicts the splitting of the nuclear energy levels and the corresponding Mössbauer spectrum. The shift of the levels is determined by the expression

$$E_{M}^{m} = -g_{I} \mu_{n} m H_{eff}$$
(1.20)

The number of lines in a spectrum is given by the selection rules for the given transition multipolarity. In <sup>57</sup>Fe, where the transition multipolarity of interest is M1,  $m_e - m_g = 0, \pm 1$ , and out of eight possible transitions in H<sub>eff</sub> only six are present

(Fig. 1.3a).



Fig. 1.3a, b Effect of the magnetic dipole interaction on energy level splitting in <sup>57</sup>Fe: a) energy level diagram in the field  $H_{eff} \neq 0$ ,  $\phi_{zz} = 0$ ; b) corresponding Mössbauer spectrum.

The contributions to the effective magnetic field in, for example, iron alloys arise from:

(i) The Fermi contact field:

$$\underline{H}_{c} = \frac{8}{3}\pi\mu_{B}\sum_{s}\left\{\left|\psi^{s}_{\uparrow}(0)\right|^{2} - \left|\psi^{s}_{\downarrow}(0)\right|^{2}\right\},\qquad(1.21)$$

where  $\mu_B$  is the Bohr magneton. The summation of the spin-up and spin-down densities at the nucleus is over all filled s- shells of the atom. The polarization of the filled s-shells of the atom caused by the exchange coupling of these s-electrons in magnetically ordered compounds of 3d-elements, results in the appearance of a magnetic field at the nucleus with the direction of the field being opposite to the atomic magnetic moment. In  $\alpha$ -Fe such spin polarization of the ion core results in H<sub>c</sub> = - (35.0 - 38.0) Tesla.

(ii) The magnetic coupling between the nuclear spin I and

the orbital momentum L of electrons of the atom, when the LS- coupling occurs:

$$\underline{H}_{L} = -2\mu_{B} < 1/r^{3} > < \underline{L} > , \qquad (1.22)$$

where the angular brackets denote averaging. For  $\alpha$ -Fe the H<sub>L</sub> contribution is (+5.0 ÷ +7.0) Tesla.

(iii) The direct contribution of the atom's magnetic moment <u>S</u>  $\mu_{\rm B}$ :

$$\underline{H}_{D} = -2\mu_{B} < \frac{3r(\underline{S} \underline{r})}{r^{5}} - \frac{S}{r^{3}} > , \qquad (1.23)$$

which corresponds to the classical dipolar interaction with the nuclear magnetic moment. This contribution is zero for an ideal cubic lattice.

(iv) The externally applied magnetic field  $H_{\circ}$  which gives rise to Lorentz and demagnetizing fields, the total field upon saturation being in the order of 1.0 Tesla.

(v) The dipole field  $H_d$  produced by the resulting moment of 3d-electrons of neighbour atoms.  $H_d$  does not usually exceed 1.0 Tesla. In the cubic lattice of  $\alpha$ -Fe  $H_d$  is zero since the fields of neighbouring atoms are quenched.

(vi) The field resulting from the contact interaction of the nuclear magnetic moment with the field of 4s-conduction which is also polarized by the total spin of 3d-electrons. The evaluation of the contribution of the 4s-conduction electrons is the most uncertain.

It is very often that all the three interactions i.e. the electric monopole-, magnetic dipoleand electric quadrupole- interaction occur simultaneously. In terms of the principal axis of the EFG tensor the Hamiltonian of the combined interaction may be written

$$H = \frac{eQ\phi_{zz}}{4l(2l-1)} \left[ 3\hat{l}_{z}^{2} - \hat{l}(\hat{l}+1) + \eta / 2(\hat{l}_{+}^{2} + \hat{l}_{-}^{2}) \right] - g_{l}\mu_{n}H_{eff} \left[ I_{z}\cos\theta + \frac{1}{2}(\hat{l}_{+} + \hat{l}_{-})\sin\theta\cos\theta + \frac{1}{2i}(\hat{l}_{+} - \hat{l}_{-})\sin\theta\sin\phi \right]$$
(1.24)

where  $\theta$ ,  $\phi$  are the polar and azimuthal angles specifying the magnetic field direction acting on the nucleus in the chosen axes system. If the quadrupole interaction is small as compared with the magnetic interaction ( $E_Q^m << E_Q^m$ ), a correction to the interaction energy may be applied using the first-order perturbation theory for a nondegenerate spectrum. For the case of an axially symmetric EFG tensor ( $\eta = 0$ ) the level positions are given by the following expression:

$$E_{M}^{m} = -g_{I}\mu_{n}mH_{eff} + \frac{eQ\phi_{zz}}{4I(2I-1)} \left[3m^{2} - I(I+1)\right] \frac{3\cos^{2}\theta - 1}{2}$$
(1.25)

The splitting of the energy levels and the corresponding Mössbauer spectrum are shown in Fig. 4 a and b. If the z-axis





Fig. 1.3c, d. c) Energy level splitting diagram with combined hyperfine interactions ( $E_Q^m << E_M^m$ ) for <sup>57</sup>Fe; d) corresponding Mössbauer spectrum.

of the axially symmetric EFG is parallel to the magnetic field ( $\theta = 0$ ), the hyperfine structure is described by (1.25).

It follows from expression (1.25) that equidistant sublevels are shifted due to the quadrupole interaction. Provided  $\varphi_{zz}$  is positive the sublevels |3/2, ±3/2> shown in Fig. 1.3c are shifted by an amount  $E_Q^m = \Delta/2$  to higher energies

and the sublevels  $|3/2, \pm 1/2\rangle$  are shifted to lower energies. The sublevels are not equidistant. This results in an asymmetric magnetically split Mössbauer spectrum as depicted in Fig. 1.3d. For the more general case there is a dependence of the sublevels shift on the angle  $\theta$ .

It is necessary to distinguish the proper constant of the quadrupole interaction  $\Delta = eQ\phi_{zz}/2$  for a nucleus in the state with the spin I = 3/2 from the constant  $\Delta(\theta) = \Delta(3 \cos^2\theta - 1)/2$  which is directly obtainable from the Mössbauer spectrum (see (1.25)). If  $E_Q^m \sim E_M^m$ ,  $\eta = 0$  and  $\theta \neq 0$  then due to the operators  $I_{\pm}$  and  $I_{\pm}^2$  in the Hamiltonian (1.24) the wave-functions  $\ddot{o}_m$  describing a nuclear state with a definite spin projection m into the z-axis are not the eigen-function of that Hamiltonian. The wave functions of the nuclear state with energies given by the roots of the secular equation

 $Det (H_{mm'} - \varepsilon \delta_{mm'}) = 0$ (1.26)

will be a superposition of  $\varphi_m$  functions at different m (H<sub>mm'</sub> is the matrix element of the Hamiltonian *H*). The superposition will cause the relative line intensities of the Mössbauer spectrum to be different from these characterizing a pure magnetic interaction. This effect may also give rise to the appearance of additional lines in the Mössbauer spectrum.

### **1.3. Relative Intensities of Spectral Lines**

The previous sections have presented a discussion of the hyperfine interaction parameters and the Mössbauer effect probabilities f (f') which enable the characterization of compounds and phases. These factors determine the line positions in the spectrum and the total area under the spectrum. In Mössbauer spectroscopy the line shape for atoms in definite positions and in the absence of relaxation phenomena is of Lorentzian form. The relative line intensities in the spectrum of a given phase and the radiation polarization also convey important information on the properties of the sample under examination. The correct interpretation of the experimentally observed intensity ratios gives information on the macroscopic structure of the sample, i.e. its spin texture. In the case of poorly resolved spectra recorded from textured samples, an incorrect account of line intensity ratios may lead to errors in the determination of hyperfine parameters and thereby to incorrect analysis of the data.

In the absence of relaxation effects and saturation arising from finite sample thickness, the intensity of a spectral component is determined by the nuclear transition characteristics (see Fig. 1.1d and 1.3). The most important of these are the spin and the parity of the excited and ground

states of the Mössbauer nuclei, the multipolarity of the transition, and the direction of the wave vector  $\underline{k}$  of the  $\gamma$ -quanta emitted with respect to a chosen direction which is specified, for example, by the magnetic field or by the electric field gradient which causes the nuclear level degeneracy to be lifted.

This may be considered in terms of the expressions which determine the Mössbauer transition intensities for <sup>57</sup>Fe (the magnetic dipole transition M1). The probability P of the occurrence of a nuclear transition of multipolarity M1 from a state  $|I_em_e\rangle$  to a state  $|I_qm_q\rangle$ , equals

$$P(I_{g}m_{g}1M, I_{e}m_{e}; \theta, \phi) = |G(m_{e}, m_{g})|^{2} F_{L}^{M}(\theta, \phi)| < I_{g} ||1|| |I_{e}\rangle|^{2}, \qquad (1.27)$$

where  $\theta, \phi$  are the polar and azimuthal angles determining the direction of emitted  $\gamma$ -quanta in the coordinate system defined by the magnetic field direction,  $M = m_e - m_g$ ;  $G(m_e, m_g) = \langle I_g m_g LM \mid I_e m_e \rangle$ , are the Clebsh-Gordan coefficients;  $\langle I_g \mid \mid 1 \mid \mid I_e \rangle$  is the reduced matrix element which does not depend



Fig. 1.4 Polar angles  $\theta$  and  $\phi$ , defining the wave vector <u>k</u> of the emitted  $\gamma$ -quantum. The quantization axis z is parallel to H<sub>eff</sub>.

on the quantum numbers  $m_g$ ,  $m_e$ . The angular function  $F_L^M(\theta, \phi)$  is determined only by the transition multipolarity. The intensity

of the Mössbauer line is proportional to the product of the Clebsh-Gordan coefficients and the  $F_L^M(\theta,\phi)$  functions. The information for M1 (L = 1) and E2 (L = 2) transitions (which are of special interest in Mössbauer spectroscopy) and which occur between levels with  $I_e = 3/2$  and  $I_g = 1/2$  is given in [1.3].

Situations in which the purely magnetic hyperfine splitting of nuclear levels in the sample or the axially symmetric EFG tensor ( $\eta = O$ ) correspond to radiation from an axially- symmetric oriented initial state. For an unpolarized axially symmetric source the angular distribution of  $I_i$  of the Mössbauer spectral components takes the following form: (a) for the electric quadrupole interaction:

 $I_{1}(\theta) \quad (\pm 3/2 \rightarrow \pm 1/2) = 3/2 \quad (1 + \cos^{2}\theta)$  $I_{2}(\theta) \quad (\pm 1/2 \rightarrow \pm 3/2) = 1/2 \quad (5 - 3 \cos^{2}\theta) \quad (1.28)$ 

(b) for the magnetic dipole interaction:

```
\begin{split} I_{1}(\theta)(+3/2 &\to +1/2) &= I_{6}(\theta)(-3/2 \to -1/2) = 9/4(1 + \cos^{2}\theta) \\ I_{2}(\theta)(+1/2 \to +1/2) &= I_{5}(\theta)(-1/2 \to -1/2) = 3 \sin^{2}\theta \qquad (1.29) \\ I_{3}(\theta)(-1/2 \to +1/2) &= I_{4}(\theta)(+1/2 \to -1/2) = 3/4(1 + \cos^{2}\theta) \end{split}
```

The corresponding plots of angular dependence of the intensities of the spectral components are given in Fig. 1.5. Equations (1.28) and (1.29) should be obeyed for nonpolarized source and a thin single crystal absorber if the isotropic factor f does not depend on  $\grave{e}$ . By these equations the direction of the magnetic field <u>H<sub>eff</sub></u> or of the EFG axes may be determined.

For an ideal thin single crystal the line intensity ratio for the electric quadrupole interaction ( $\eta = 0$ ) is

$$R_{g} = \frac{I_{1}}{I_{2}} = \frac{1 + \cos^{2}\theta}{5/3 - \cos^{2}\theta} \quad .$$
(1.30)

For the magnetic dipole interaction:

$$R_{\rm m} = \frac{I_{2,5}}{I_{3,4}} = \frac{4(1 - \cos^2\theta)}{1 + \cos^2\theta} , \qquad (1.31)$$

The situation is more complicated if both the magnetic dipole-



Fig. 1.5 Angular dependences of relative intensities of the hyperfine structure components for the  $I_e$  = 3/2,  $I_g$  = 1/2 transition in  $^{57}\text{Fe:}$  a) for electric quadrupole interaction,  $\eta$  = 0, the quantization axis is the direction of the principal EFG axis, b) for magnetic dipole interaction, the quantization axis is the direction of  $H_{\text{eff}}$ ,  $\theta$  is the angle between the radiation direction and the quantization axis.

and electric quadrupole-interactions are present. For a polycrystalline absorber with a random orientation of crystallites with a cubic symmetry the intensity ratios are described by  $R_g = 1$ ,  $R_m = 2$ , as a result of averaging over all directions.

The effect of anisotropy of atomic vibrations in solids causes not only the Mössbauer effect probability f to be anisotropic in single crystals, but may also lead to anisotropy in f for non-textured polycrystalline samples consisting of

randomly oriented crystallites. Such anisotropy in polycrystallites caused the values  $R_g$  and  $R_m$  to deviate from those described above. Similar deviations may be caused by texture, that is by a preferred orientation of crystals in a polycrystalline sample. To identify the origin of line asymmetry in a spectrum of polycrystallites as a result of either texture or the Goldanskii-Karyagin effect it is necessary to evaluate the effect of each of these phenomena on the Mössbauer spectra. Since the study of spin texture is described in detail in Sect. 5.3, only the Goldanskii-Karyagin effect is considered at this stage.

The expression for the Mössbauer effect probability (1.3) can be rewritten in the following form:

$$f = \exp(-\langle (\underline{k} \ \underline{u})^2 \rangle)$$
, (1.32)

where <u>k</u> is the wave factor of the incident  $\gamma$ -quanta; <u>u</u> is the displacement vector of an atom from its equilibrium position. Although the crystal here is anisotropic we assume, as before, that the Debye model is appropriate, and that there is a certain characteristic temperature  $\Theta_D$  which is analogous to the Debye temperature. The exponent of (1.32) may be written as a function of polar angles  $\theta$  and  $\phi$ :

$$\langle (\underline{\mathbf{k}}, \underline{\mathbf{u}})^2 \rangle = \mathbf{k}^2 \left[ (\overline{\mathbf{x}^2} \cos^2 \varphi + \overline{\mathbf{y}^2} \sin^2 \varphi) \sin^2 \theta + \overline{\mathbf{z}^2} \cos^2 \theta \right].$$

For the axially symmetric factor f, that is, if  $x^2 = y^2$ :

$$f(\theta) = \exp(-k^2 \overline{x^2}) \exp(-a \cos^2 \theta) , \qquad (1.33)$$

where  $a = k^2 (\overline{z^2} - \overline{x^2})$  is a certain real;  $\overline{x^2}$  and  $\overline{z^2}$  are the mean square amplitudes of the atomic vibrations which are parallel and normal to the principal EFG axis or to H<sub>eff</sub>. When the electric quadrupole interaction  $\eta = 0$  for a polycrystalline absorber with a random orientation of crystallites with an anisotropic factor f, R<sub>g</sub> 1 and is written

$$R_{g} = \frac{\int_{0}^{\pi} (1 + \cos^{2}\theta) \exp(-a \cos^{2}\theta) \sin\theta \, d\theta}{\int_{0}^{\pi} (5/3 - \cos^{2}\theta) \exp(-a \cos^{2}\theta) \sin\theta \, d\theta} , \qquad (1.34)$$

when analyzing the experimental data it is often convenient to examine the dependence of  $R_g$  on the  $W_{x}$ - or  $W_z$ -parameters, which are characteristic of anisotropy of atomic vibrations in a lattice:

$$W_{x} = \frac{\overline{z^{2}}}{\overline{x^{2}}} = 1 + \frac{a}{k^{2} \overline{x^{2}}}, W_{z} = \frac{\overline{x^{2}}}{\overline{z^{2}}} = 1 - \frac{a}{k^{2} \overline{z^{2}}}.$$
 (1.35)

Suppose that a crystal whose  $\Theta = 300$  K, is at room temperature. For <sup>57</sup>Fe (k = 7.28 Å) hence  $\overline{x^2} = 8.76 \ 10^{-3} \ \text{Å}^2$  corresponds to the Debye temperature.

Following to [1.12] it is possible to consider a situation when the crystal is not axially isotropic  $(\overline{x^2} = \overline{y^2} \neq \overline{z^2})$ . In this case  $k^2 \overline{x^2} = 0.465$  and  $R_g$  values may be described by the parameter  $W_x$ . The requirement of  $W_x > 0$  limits the allowed values of parameter "a" in expression (1.33) to a -0.465. Value of a < -0.465 may be realized only in terms of another model for the vibration spectrum, which is described by the parameter  $W_z$ . In this situation  $k^2 \overline{z^2} = 0.465$  and the experimentally observed  $R_g$  values are determined by the parameter  $W_z$ .

The R<sub>g</sub> values found at room temperature and evaluated as functions of W<sub>x</sub>(W<sub>z</sub>) for solids with characteristic temperatures of 200, 300 and 400 K are shown in Fig.1.6 a. Each curve in Fig. 1.6 corresponds to a family of crystal lattices of the same characteristic temperature but of different anisotropy. If  $\overline{x^2} = 2\overline{z^2}$ , then two cases are possible in which W<sub>x</sub>= 0.5, or W<sub>z</sub> = 2 each having its own a-value (1.33). For the characteristic temperature of 300 K R<sub>g</sub> equals either 1.053 or 1.067 for the two cases. From Fig. 1.6 it follows that increasing the sample temperature (or decreasing  $\Theta$ ) causes an increase to be observed in the line asymmetry. In the case of the magnetic hyperfine splitting the anisotropy of the f factor may also manifest itself in a deviation of the line intensities ratio from R<sub>m</sub> = 2. The room temperature dependence R<sub>m</sub> on W<sub>x</sub>(W<sub>z</sub>) for polycrystalline samples with characteristic temperature of 200, 300, and 400 K is shown in Fig. 1.6b.



Fig. 1.6 a. Dependences of the line intensity ratios (at room temperature) -  $R_g$  on the ratio of the mean square displacements  $W_x(W_z)$  or the parameter  $a = k^2 \left( \overline{r_z^2} - \overline{r_x^2} \right)$ .



Fig. 1.6b Dependences of the line intensity ratios (at room temperature) -  $R_m$  on the ratio of the mean square displacements  $W_x (W_z)$  or the parameter a.

Hence, to observe the factor-f anisotropy a mechanically isotropic polycrystalline sample should be used. For such a sample the intensity ratios of the components in the Mössbauer spectra will not depend on the angle between the incident direction and the surface of the sample. The observation of such a dependence reflects texture effects. It should be noted that Mössbauer spectroscopy is sometimes the only experimental method suitable for the study of texture. A quantitative examination of spin texture requires the investigation of the effect of the anisotropy of the f-factor on the Mössbauer spectra.

#### 1.4. Experimental

It is important to consider some problems which are associated with the Mössbauer experiment. To observe the Mössbauer effect and to obtain a spectrum the radiation from a Mössbauer source should be directed onto the sample under study. The Mössbauer spectrum is a measure of the dependence of the total intensity of radiation I(v) registered by a detector in a definite energy region on the relative velocity v of the source.

A schematic diagram of a Mössbauer experiment and the spectrum is shown in Fig. 1.7 [1.3]. If both the source and the absorber are characterized by single lines of natural width  $\Gamma_{\rm nat}$ ,  $\delta$  being zero the spectrum will show maximum absorption at v = 0. In this situation the resonant absorption of the ã-quanta is maximized, and the intensity (I(0)) registered by the detector is minimized (Fig. 1.7c). When the source moves at a certain velocity v, the emission line  $J_M(E)$  is displaced relative to the absorption line  $J^a(E)$ . The overlap then decreases and the intensity registered by the detector increases. Finally, at a certain velocity, which may be considered to be infinitely large (v =  $\infty$ ), the spectrum overlap becomes so small that any further increase in velocity will not result in a significant increase in relative intensity. This value of intensity may be described as  $I(\infty)$ . The fact that the line shapes of the source and absorber are described by Lorentzians causes the experimentally observed line for a thin absorber to be Lorentzian, and its half-height width is the sum of the line widths of the source and the absorber.

A typical device for accumulating the Mössbauer spectrum is the multichannel analyzer (MCA) where the count rate is a function of the channel number of MCA. Each channel corresponds to the energy of the  $\gamma$ -quanta with a definite (and often equal) dwell time for the accumulation of information. The count rate is normalized relative to the off-resonance count rate. Hence, for transmission mode Mössbauer spectroscopy relative intensities are always less than one (or 100%). In Mössbauer scattering experiments relative intensities always exceed 100% and can reach several hundred percent in the case of electron detection from



Fig. 1.7 Schematic illustration of the experimental arrangement (a), used to obtain a Mössbauer spectrum (c) for a single Lorentzian line both in the source and in the absorber (b).

samples with a high abundance of the resonant isotope. Each channel number corresponds to a definite value of the Doppler velocity. It is most often that the  $-v_{max}$  value corresponds to the first channel and the  $+v_{max}$  value to the last (N-th) channel. The velocity increment  $\Delta v = 2v_{max}$  /N then corresponds to one channel.

The quality of a Mössbauer spectrometer is determined by how accurately the modulation of the  $\gamma$ -quanta energy follows

the chosen mode of movement e.g. sine or triangle. This modulation is primarily determined by the movement of a vibrating plunger which causes the source to move at a velocity v relative to the absorber. The v values should exactly correspond to the channel number of the accumulating device. Usually for the v(t) function one of the periodic laws of movement is used (Fig.1.8).



Fig.1.8 Velocity v and position s of the vibrating plunger of a Mössbauer spectrometer: a) parabolic movement, b) double parabolic movement, c) sine movement.

In parabolic movement the velocity change is with period T, following the saw tooth law. For practical reasons this law of movement is the most convenient although the vibrating plunger is hardly able to drive in such a fashion. Indeed, from the expansion of the velocity signal in the Fourier series

$$v(t) = {2v_0 \over \pi} \sum_{k=1}^{\infty} {(-1)^{2k+1} \over k} \sin {2k\pi t \over T}$$

where  $v_0$  - is the maximum velocity value, it is seen that a large number of harmonics are needed to be reproduced without distortion. Furthermore, the corrections are difficult to make for the various geometry effects that may lead to substantial distortions of the observed spectrum.

Double parabolic movement allows the avoidance of the geometry effects by permitting the convolution of the two resulting mirror spectra. It is then easier to achieve linearity here over the entire range of the velocities since the movement is represented by a smaller number of harmonics. If for the parabolic movement the amplitude ratio of the first harmonic to that of the third is 3, double parabolic movement gives a ratio of 25. This is very desirable since for a better generation of the reference signal a deep negative feedback can be used. Phase shifts accumulated within the system including the vibrator may lead to the feedback becoming positive for the higher harmonics and this is a potential cause of self-excitation. It is evident that in this mode of velocity change a deeper negative feedback can be used to generate a more accurate reference signal generation. In addition, the double parabolic mode gives no pulse forces.

The sine movement is also often used when the reference signal contains only one harmonic. An exceptionally high quality for the entire system can be reached when working at the resonant frequency of the vibrator which in turn raises the vibrator power. A disadvantage of this mode is the nonlinear velocity scale of the Mössbauer spectrum. For the linear conversion a computer or a microprocessor can be used. A classical Mössbauer spectrometer consists of four parts: (i) the drive which controls the vibrator movement; (ii) the detector; (iii) a multichannel analyzer for spectra storage and for the drive unit control; (iv) a computer for mathematical evaluation of the stored spectra, and a device to get the information in a required form. A new generation of spectrometers are now available. The main difference between the first- and second- generation spectrometers is the use of a microprocessor and large scale integrated circuits (LSIC's) in the new equipment. Such development offers the following benefits: i) the use of a function generator in the driving device which enhances the capabilities of the spectrometer; ii) the substitution of the multichannel analyzer by a dedicated unit; iii) the use of a microprocessor instead of the computer to evaluate the Mössbauer spectra. When the Mössbauer spectrum is being recorded the  $\gamma$ -quanta

from a source interact with the sample. The main types of interaction with matter of  $\gamma$  -quanta in the energy range of interest are the photoelectric effect, the Compton effect, Rayleigh scattering and resonant scattering. The Mössbauer experiment may be in transmission mode, where  $\gamma$ -quanta are detected or be a scattering experiment where any radiation which follows the resonant scattering is detected. The typical experimental arrangements are presented in Fig.1.9.

In both types of experiments the probability of the effect f' can be evaluated from the observed resonance effect magnitude a(v). For transmission geometry a(v) is determined by the following relation:

$$\varepsilon(\mathbf{v}) = \frac{\mathbf{I}(\mathbf{\omega}) - \mathbf{I}(\mathbf{v})}{\mathbf{I}(\mathbf{\omega})} . \qquad (1.36)$$

Of utmost interest are a(v) value at  $v_i$  (i = 0, 1, ...), corresponding to the maxima of resonant scattering. For unsplit lines in both the source and absorber the intensity on resonance is I(0).

Expression (1.36) is true in the absence of background radiation. To evaluate the possible magnitude of the effect one needs to know the energies and relative intensities of various  $\gamma$ -quanta groups per 100 disintegrations of the parent nucleus, all the relevant cross sections for the  $\gamma$ -quanta interaction with matter, and the value of the f' parameter characterizing the recoilless  $\gamma$ -quanta in the sample under study. Theoretical considerations of the f' factor in transmission spectroscopy, including the contribution of various experimental conditions, have been given in [1.13-18]. Scattering experiments permit the detection of conversion electrons in addition to  $\gamma$ -rays, X-rays, Auger electrons and even photons which follow resonant scattering. An important advantage of scattering experiments is that they enable an estimate of the thickness of the layer of the substance under examination.

Mössbauer scattering spectra obtained by detection of the  $\gamma$ -quanta or X-rays emitted out of the bulk of a material, convey information on the layer with a depth which is determined by the total linear absorption coefficient  $\mu(E)$ . The values of  $\mu(E)$  for  $\gamma$ -rays and X-rays are generally different, therefore the Mössbauer spectra correspond to the layers which are different in depth from one to several  $\mu$ m. The interaction of electromagnetic radiations with matter gives no correlation between the  $\gamma$ -quanta or X-ray energy and the depth of the layer through which they have passed. By ignoring any resonant re- scattering the direction of the resonantly scattered quanta may be considered unchanged up to the moment of their interaction with matter.

Mössbauer scattering spectra obtained by detection of conversion electrons or Auger electrons, provide information on substantially thinner layers. This type of spectroscopy is called Conversion Electron Mössbauer Spectroscopy (CEMS). There are definite relations between the energy of detected electrons and the depth of the layer through which they have passed. If



Fig.1.9 Experimental arrangements and Mössbauer spectra for a  ${}^{57}$ Co (Cr) source and an absorber of á-Fe: a) transmission geometry, b) scattering geometry with the detection of - or X-rays, c) backscattering geometry with the detection of X-rays and electrons. 1. source at a velocity v, 2. sample, 3. detector.

these relations are used the depth selective analysis of the surface layers can be performed. The use of CEMS for quantitative measurements requires a good knowledge of the interaction of electrons with matter over an energy ranging from several hundred eV to several tens of keV. The problems encountered are extensively considered in [1.19-23], but so far there is no comprehensive theory of the interaction of such electrons with matter.

Although the Mössbauer effect is not observed for all elements (see Table 1.1) [1.24], for those which do have a Mössbauer active isotope such as iron, tin, dysprosium and many others, Mössbauer spectroscopy compares favorably as a versatile method by which important information can be obtained.

Table 1.1 Mössbauer periodic table.

IA	1			Fe <sup>2</sup>	∕ nu Mċ	mber össbai	of ol Jer t	oserve ransiti	ed ons									rare gases
H	IIA	. ,	/	nu	mber o	of isot		A IV	4 V/	A VIA	A VII	AHe						
LI	80			Mà ha	issbau Is beer	ier effe i obse	8	C	•	ı 0	F	Ne						
Na	Mg	IIIB IVB VB VIB VIIB VIII IB IIB										3	1 S	i F	> s	c	I Ar	
<mark>к</mark>	Ca	Sc	TI	v	Cr	Mn	Fe	e C	0 N	",	Çu	Z	n <sup> </sup> G	G G	e <sup>2</sup> A	s S	e Bi	r Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	R	u <sup>2</sup> R	n P	d	Ag	c	d lr	າ <sub>ເ</sub> S	n <sup>2</sup> S	<b>ь</b> <sup>1</sup> , т	e   1	<sup>2</sup> X e <sup>2</sup>
Cs	ٰ B مٰ	,La'	Hf	Ta	<b>w</b> <sup>7</sup>	Re	_0 :	6   Ir	· <sup>4</sup> ⊢	<b>2</b>	Au	Н	g   T	I P	b B	i P	0 A	t Rn
Fr	Ra	Ac		<b>Se</b>	Pr	1 d F	<b>`</b> m	5 m 6	Eu	G	° d	ть'	D y ⁴	, H 0 '	Er 5	, Tm <sup>1</sup>	Yb 5	Lu'
			1	Γή	Pa	ע ĭ  ִו	Np	຺຺ຏ຺	_Am	C	m f	3 K	C 1	Es	Fm	Mđ	Νo	LW

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