2. Mössbauer Spectroscopy Based on Detection of Electromagnetic Radiation

There are two types of Mössbauer spectroscopic experiments based on scattering and transmission techniques. Scattering Mössbauer experiments involve either the detection of resonantly scattered γ -quanta or other radiations which are emitted in the process of resonant scattering or immediately after it. The observed effect depends on the spectra of the scattered radiation, on the interaction of the radiation with matter and, to a greater extent than in transmission mode spectroscopy, it depends on the spectrometer design especially on the detector and its' position relative to the sample and the primary beam.

In transmission mode experiments the resonant scattering leads to the sharp attenuation of the radiation intensity registered by a detector, therefore it is sometimes referred to as resonant absorption. The resonant absorption cross section is the total cross section of resonant scattering; the probability of detecting the scattered radiation in transmission spectroscopy may be neglected when the geometrical arrangement is appropriate.

Classical transmission mode Mössbauer spectroscopy is sometimes used in studies of surface layers. Indeed, the analysis of Mössbauer spectra to date has been mainly based on the theory and techniques developed for transmission mode Mössbauer spectroscopy. These problems are dealt with in the first Section of this Chapter, thereafter a concept of scattering channels will be introduced and finally a classification will be given of low-energy γ -quanta scattering in solids. Resonance scattering channels are of prime interest in Mössbauer spectroscopy, hence it is necessary to introduce concepts of resonance fluorescence, coherence, interference and γ - γ correlations.

Based on all these, a theory can be developed of spectral shape and the energy distributions of incident and scattered radiation. Special attention will be paid to backscattering Mössbauer spectroscopy, which is the most promising technique for applied research and industrial applications. Problems of detector design, the evaluation of scattered intensities, and some experimental aspects are given in the last sections of the Chapter.

2.1. Radiation Transmission through Matter

Most surface studies by Mössbauer spectroscopy have been carried out with ⁵⁷Fe and ¹¹⁹Sn nuclides. Most methodology problems for those isotopes have been successfully overcome, hence the information available for ⁵⁷Fe is frequently used in the considerations that follow.

A diagram is given in Fig.2.1 of the nuclear transformations which produce ⁵⁷Fe. The ⁵⁷Mn nuclide decays by β -emission with a half-life of 1.7 min. ⁵⁷Co nuclide also decays by electron capture (EC) with a half-life of 270 d to ⁵⁷Fe. The short half-life period of ⁵⁷Mn makes it practically impossible to use the nuclide in applied research. The Mössbauer 3/2 level with the probability $1/(1 + \alpha)$ decays by the 14.4 keV γ -quantum emission, where α is the total internal conversion coefficient. For the rest of the cases de-excitation of the nucleus is via the emission of conversion electrons followed by rearrangement of the excited atomic shell by X-ray emission and Auger processes. Considering that for approximately 88 cases out of 100, the ⁵⁷Co decay populates the 14.4 keV level a limiting value of 9.55 f Mössbauer quanta per 100 disintegrations of ⁵⁷Co can be obtained [1.24]. The number of the Mössbauer quanta cannot exceed 9.55f and is determined by the source material and the quality of its preparation. For further numerical evaluations ⁵⁷Co will be assumed to be in a rhodium matrix at room temperature and f = 0.77. The yields for γ -quanta of different energies for ⁵⁷Co , ⁵⁷Fe and ¹¹⁹Sn nuclides are listed in Table 2.1. Table 2.2 gives the nuclear characteristics of interest for these Mössbauer nuclei.



Fig.2.1 Decay scheme of ⁵⁷Fe and parent nuclei (from [1.24]).

Mössbauer sources are prepared by introducing the radioactive parent nuclei for the Mössbauer isotope into a substrate with a fairly perfect crystal structure. There are often several parent nuclides of the Mössbauer isotope, but one of them that is mostly used in practice.

E	Intensity [*]			
E KeV	⁵⁷ Co	⁵⁷ Fe	¹¹⁹ Sn	
0.7 (L X-rays ⁵⁷ Fe)		0.2		
3.6 (L X-rays ¹¹⁹ Sn)			5	
6.47 (K X-rays ⁵⁷ Fe)	54	26.3		
14.41	9.55	10.8		
23.87			16	
122	85.6			
136	10.6			

Table 2.1Energies and intensities of photons emitted after resonant excitation of the14.4 keV state of ⁵⁷Fe, 23.8 keV state of ¹¹⁹Sn and decay of ⁵⁷Co.

* The intensities are given per 100 decays of the excited nuclear states.

 Table 2.2
 Nuclear data for the ground and first excited states of ⁵⁷Fe and ¹¹⁹Sn.

	⁵⁷ Fe		¹¹⁹ Sn	
	Ground	Excited	Ground	Excited
	state	state	state	state
The γ-ray	•		•	00.07
energies E (keV)	0	14.41	0	23.87
Half-life		0.098		0.178
(10 ⁻⁶ sec)				
Natural line width				
(neV)	0	4.66	0	25.8
(mm×s⁻¹)		(0.097)		(0.323)
Spin and parity	1/2-	3/2-	1/2+	3/2+
Quadrupole				
moment				
(10 ⁻²⁴ cm ²)	0	+0.20	0	-0.064
Factor g	+0.181	-0.103	-2.09	+0.455
Total internal con-				
version coefficient		8.21		5.1
Natural isotopic				
abundance a (%)	2	.14	8.8	58

The observed effect is determined firstly by the interaction of Mössbauer quanta with matter. The γ -quanta interact not only with the sample under study, but also with the various construction materials used to make detection windows, cryostat windows, collimator and sample holders. The effect may be largely influenced by self-absorption in the source and the saturation absorption due to the finite thickness of the absorber. The correct evaluation of these effects is needed to select the optimum experimental conditions, such as sample and substrate thickness, source - absorber - detector distances and corresponding angles, and concentrations of Mössbauer isotopes in the source and absorber. The evaluation is necessary to carry out a phase analysis, and also to obtain a theoretical equation for the shape of the observed Mössbauer spectra. Some aspects of the passage of the Mössbauer radiation through matter and the dependence of spectrum shapes, line amplitudes and areas on the sample thickness and resonant isotope abundance are given below.

If the source is considered to be a cylinder of a unit cross section (see Fig.2.2), the number of parent radioactive



Fig.2.2 Self-absorption in a Mössbauer source.

nuclei for the Mössbauer isotope in a unit volume of the source n(x) is a function of x only. We can consider that the number of the Mössbauer nuclei in a unit volume of the source, n_s , is constant; f_s is the Mössbauer factor determining self-absorption in the source. If a volume element of a unit cross section with a coordinate x and the thickness dx is taken, the decay of n(x)dx radioactive nuclei produces a flux of γ -quanta dI(x) = Cn(x) dx in the direction close to normal to the source surface (C is a constant). The fraction (1 - f) of the disintegrations occurs with the energy transferred to the lattice, and the fraction f is recoilless. If the energy distribution of the corresponding radiations is $J_R(E)$ and $J_M(E)$, the following normalization conditions may be assumed:

$$\int_{-\infty}^{\infty} J_R(E) dE = 1 - f \; ; \; \int_{-\infty}^{\infty} J_M(E) dE = f \; . \tag{2.1}$$

The particular dependence $J_R(E)$ is of no interest but it should be noted that the centre of gravity of this distribution is shifted by the amount of recoil energy E_R relative to the transition energy E_s in the source. The energy distribution of the Mössbauer γ -quanta $J_M(E)$ may be considered as Lorentzian L(E) with the full half-width Γ such that $\Gamma = \Gamma_{nat}$. Due to the normalization conditions (2.1) $J_M(E)$ may be written as:

$$J_{M}(E) = \frac{f\Gamma_{nat}}{2} \frac{1}{(E - E_{s})^{2} + (\Gamma_{nat}/2)^{2}} = \frac{2f}{\pi\Gamma_{nat}}L(E)$$
(2.2)

Radiation from the layer dx of the depth x of a Mössbauer source is described by the expression

$$dJ(E, x) = [J_{R}(E) + J_{M}(E)]e^{-\mu_{S}(E)x}dI(x), \qquad (2.3)$$

where

$$\mu_{s}(E) = \mu_{s} + \mu_{rs}(E) = \mu_{s} + n_{s}f_{s}\sigma_{s}'(E) , \qquad (2.4)$$

and where $\mu_s(E)$ is the total linear extinction (absorption) coefficient for the source material, $\mu_{xs}(E)$ and $\sigma_s'(E)$ are the linear coefficient and cross section of γ -radiation resonant scattering in the source material, and μ_s is the nonresonant linear absorption coefficient. For a single-line source

$$\sigma_{\rm s}(E) = \sigma_0 L_{\rm s}(E) , \quad \sigma_0 = 2\pi \lambda^2 \frac{2I_{\rm e} + 1}{2I_{\rm g} + 1} \frac{1}{1 + \alpha} , \qquad (2.5)$$

where σ_0 is the maximum cross section of the resonant interaction, $\hat{\chi}$ is the wavelength of γ -radiation, and I_e , I_g are the nuclear spins for excited and ground states. In general, $L_s(E)$ differs from L(E), however, for many sources such as ⁵⁷Co in Rh- or Cr-matrices they may be assumed to be equal. $L_s(E) = L(E)$. Then the energy distribution of γ -radiation from the source (2.3) needs to be integrated over x from 0 to ∞

$$J(E) = \left[J_{R}(E) + J_{M}(E) \right] C \int_{0}^{\infty} n(x) e^{-\mu_{s}(E)x} dx . \qquad (2.6)$$

If the source moves at a velocity v relative to the absorber, the energy distribution is determined by (2.2), where the L(E) Lorentzian is written as:

$$L(E, v) = \frac{\Gamma_{nat}^{2} / 4}{(E - E_{s} - E_{s} v / c)^{2} + \Gamma_{nat}^{2} / 4},$$

$$L(E, S) = \frac{\Gamma_{nat}^{2} / 4}{(E - E_{s} - S)^{2} + \Gamma_{nat}^{2} / 4},$$

$$L(E, \mathcal{E}) = \frac{\Gamma_{nat}^{2} / 4}{(E - \mathcal{E})^{2} + \Gamma_{nat}^{2} / 4},$$
(2.7)

In the last expression the variable has been changed so that

$$\mathcal{E} = \mathbf{E}_{s} + \mathbf{E}_{s} \mathbf{v}/\mathbf{c}$$

Since it is always the relative velocity that is experimentally measured, v (the channel number) is usually given on the abscissa. In theoretical considerations the energy distributions of γ -quanta and intensities of detected radiations are often written as functions of energy E of incident γ -quanta and of parameter S. In theoretical aspects of scattering spectroscopy, especially for multilayer samples, the last of the three expressions (2.7) proves to be extremely useful. In this case the energy distribution of γ -quanta emitted by the moving source is treated as a function of the difference between the variable E, which takes on random values and has a Lorentzian distribution

relative to the transition energy E_s and the energy parameter ${\pmb e}$ which is determined by the spectrometer. To simplify the formulae the energies are usually taken in units of $\Gamma/2$. Since $\Delta \mathsf{E} >> \Gamma$, in usual transmission or scattering experiments, the detector is an effective integrator. Not only does it detect the Mössbauer recoil and recoilless quanta, it also detects the background radiation in the energy region which is incommensurably more than $\Gamma_{\rm nat}$.

When the sample under study is placed between the source and the absorber of thickness d_a, the sample is characterized by the parameters E_a, $\sigma_a(E) = \sigma_r(E) + \sigma_a$, Γ_a , f', n_a, μ_a , the Lorentzian L_a(E), where μ_a and σ_a are the linear absorption coefficient and the cross section for non-resonant interactions, respectively. The intensity of γ -quanta passed through the sample which gives the experimental Mössbauer spectrum is given by the following equation:

$$I(v,d_{a}) = \int_{-\infty} J(E,v) \exp\left[-\mu_{a}d_{a} - L_{a}(E)t_{a}\right] dE ; \qquad (2.8)$$
$$J(E,v) = C\left[J_{R}(E,v) + J_{M}(E,v)\right] \int_{0}^{\infty} n(x) \exp\left[-\mu_{s}(E)x\right] dx ;$$

 $t_a = \mu_r d_a = n_a f' \sigma_0 d_a$.

where t_a is the effective thickness of the sample. It is used as frequently as the linear coefficient of resonant scattering or absorption $\mu_r(E)$ and its maximum value, μ_r without splitting, or μ_r^{i} at a velocity v_i for the split spectrum.

By use of (2.4), (2.8) and the effective thickness t_a an expression for $I(v,d_a)$ can be obtained:

$$I(v,d_{a}) = e^{-\mu_{a}d_{a}} C\left\{ \int_{-\infty}^{\infty} J_{R}(E,v) e^{-L_{a}(E)t_{a}} dE \right\}$$

$$\int_{0}^{\infty} n(x) e^{-\mu_{s}x - L(E) t'(x)} dx + \int_{-\infty}^{\infty} J_{M}(E,v) e^{-L_{a}(E)t_{a}} dE$$

$$\int_{0}^{\infty} n(x) e^{-\mu_{s}x - L(E) t'(x)} dx + \int_{-\infty}^{\infty} J_{M}(E,v) e^{-L_{a}(E)t_{a}} dE$$
(2.9)

where $t'(x) = n_s f_s \sigma_0 x$.

The evaluation of the integral in the first term of (2.9) over energy is based on the fact that the distance between the centres of gravity of the distribution $J_R(E,v)$, and of the resonant scattering cross section $\sigma_r(E)$, is equal to the recoil energy E_R . Since $E_R >> \Gamma$, in the region where $\sigma_r \neq 0$, $J_R(E,v)$ is infinitesimal and the two exponents of the first term describing the resonant scattering are equal to unity. This means that the recoil radiation is virtually resonantly unscattered both in the source and the absorber. Using normalization conditions (2.1) and equation (2.2) and integrating over energy in the first term gives the expression (2.9) in the form:

$$I(v,d_{a}) = C e^{-\mu_{a}d} \left\{ (1 - f) \int_{0}^{\infty} n(x) e^{-\mu_{s}x} dx + \frac{2 f}{\pi\Gamma_{nat}} \int_{-\infty}^{\infty} e^{-L_{a}(E)t_{a}} L(E,v) dE \int_{-\infty}^{\infty} n(x) e^{-\mu_{s}x-L(E)t'(x)} dx \right\}.$$
(2.10)

This is the general expression for the intensity of γ -quanta emitted by the source and passed through a layer of thickness d_a. In transmission mode Mössbauer spectroscopy it is the I(v,d_a) function that determines the line shape.

A source with a uniform distribution of radioactive nuclei: $n(x) = g_1$ if $0 \le x \le d_s$ and n(x) = 0 if $x > d_s$ must now be considered. Integrating (2.10) over x from 0 to d_s and dividing by Cg_1d_s gives the following expression

$$\frac{I(v,d_{a})}{c g_{1}d_{s}} = e^{-\mu_{a}d_{a}} \left\{ (1 - f) \frac{1 - e^{-\mu_{s}d_{s}}}{\mu_{s}d_{s}} + \frac{2 f}{\pi\Gamma_{nat}} \right.$$

$$(2.11)$$

$$\int_{-\infty}^{\infty} \frac{e^{-L_{a}(E)t_{a}}}{\mu_{s}d_{s} + L(E) t'} \left[1 - e^{-\mu_{s}d_{s}} - L(E) t' \right] dE \left. \right\} .$$

If for the source of thickness d_s self-absorption is neglected, i.e. $n_s f_s = 0$, then the intensity of radiation passing through a sample of thickness d_a may be written as:

$$\frac{I(v,d_{a})}{C g_{1}d_{s}} = \frac{e^{-\mu_{a}d_{a}} - e^{-(\mu_{a}d_{a} + \mu_{s}d_{s})}}{\mu_{s}d_{s}} \left[(1 - f) + \frac{f\Gamma_{nat}}{2\pi} \right]$$

$$\int_{-\infty}^{\infty} \frac{e^{-L_{a}(E)t_{a}}}{(E - E_{s} - E_{s} v/c)^{2} + \Gamma_{nat}^{2}/4} . \qquad (2.12)$$

This can be rewritten in the following form:

$$\frac{I(v,d_a)}{Cg_1d_s} = I_R(d_a) + I_M(v,d_a)$$
 (2.13)

where $I_R(d_a)$ and $I_M(v,d_a)$ are the normalized intensities of recoil- and recoilless γ -quanta passed through the layer of thickness d_a . The $I_M(v,x)$ function is very important in scattering experiments. It determines the total intensity of γ -quanta which at a velocity v have reached a layer dx at a depth x. The resonant scattering of a part of this radiation in a layer dx results in emission of radiation from this layer. At $v \to \infty$, we can write

$$\lim_{v \to \infty} \frac{I(v, d_a)}{Cg_1 d_s} = e^{-\mu_a d_a} \frac{1 - e^{-\mu_s d_s}}{\mu_s d_s}$$
(2.14)

It is evident from a comparison of (2.11) and (2.12) that instead of Lorentzian (2.7) and provided $\mu_s d_s \rightarrow 0$, self-absorption in the source allows the energy distribution of the emitted resonant γ -quanta to be described by the following

$$J_{M}^{S}(E,v) = \frac{f\Gamma_{nat}}{2\pi t'} \left[1 - e^{-L(E,v)t'} \right] \frac{L(E,v)}{L(E)}.$$
 (2.15)

It is natural that for a thin source, i.e. when $t' \rightarrow 0$, the shape of the emission line should approach the Lorentzian. From now on it can be assumed that the source is thin, that the line is single and is a Lorentzian. Returning now to (1.36), by use of (2.12) and (2.14) we obtain:

$$\varepsilon(v) = \frac{f \Gamma_{nat}}{2 \pi} \int_{-\infty}^{\infty} \frac{1}{(E - E_{s} - E_{s} v/c)^{2} + \Gamma_{nat}^{2}/4} \left[1 - e^{-L_{a}(E)t_{a}}\right] dE = \int_{-\infty}^{\infty} J_{M}(E, v) \left[1 - e^{-L_{a}(E)t_{a}}\right] dE .$$
(2.16)

If the resonant scattering cross section $\sigma_a(E)$, as well as $J_M(E,v)$, are characterized by a Lorentzian of natural width, $\Gamma = \Gamma_a = \Gamma_{nat}$, the maximum effect value (v = 0) is given by

$$\varepsilon(0) = f \left[1 - e^{-t_a/2} J_0(it_a/2) \right] = f p(t_a) , \qquad (2.17)$$

where J_0 is the Bessel function of zeroth order, $p(t_a)$ is the function which undergoes a fairly fast saturation on increasing t_a . Integral (2.16) cannot be given in an analytical form, however numerical calculations show that up to $t_a \sim 10$ it is closely approximated by a Lorentzian curve. Its width at half-height Γ_{exp} is a function of the absorber thickness:

$$\Gamma_{exp} = 2 \Gamma_{nat} h(t_a) , \qquad (2.18)$$

where the function $h(t_a)$ may be written as:

$$\begin{split} h(t_a) &= 1 \, + \, 0.135 \, t_a & \text{for } 0 \leq t_a \leq 4 \ , \\ h(t_a) &= 1 \, + \, 0.145 \, t_a \, - \, 0,0025 \, t_a^2 \, \text{for } 4 \leq t_a \leq 10 \, . \end{split} \label{eq:h-tau} \end{split}$$

Mössbauer nuclei in the absorber as well as in the source may be in slightly different conditions due to fluctuations of their local environment. This results in fluctuations of energy of the nuclear transition E_a in the absorber which causes the lines to broaden and change their shape. Nonetheless in many cases the lines may be described by Lorentzian curves whose widths are different from the natural ones:

$$J_{M}(E) = \frac{f\Gamma}{2\pi} \frac{1}{(E - E_{s})^{2} + \Gamma^{2}/4}, \qquad (2.20)$$

$$\sigma_{a}(E) = \sigma_{0}' \frac{\Gamma_{a}^{2}/4}{(E - E_{a})^{2} + \Gamma_{a}^{2}/4}, \qquad \Gamma \neq \Gamma_{a} > \Gamma_{nat}. \qquad (2.21)$$

A relation between σ_0 and σ_0 can be found since the area under the total absorption curve is the sum of individual absorption curves with natural widths. Since the area under a Lorentzian with the amplitude ϵ and the width Γ is $\pi\epsilon\Gamma/2$, we may write $n\pi\sigma_0\Gamma_a/2 = n\pi\sigma_0\Gamma_{nat}/2$, from which it follows that $\sigma_0' = \sigma_0 \Gamma_{nat}/\Gamma_a$;

$$\sigma_{a}(E) = \sigma_{0} \frac{\Gamma_{nat}}{\Gamma_{a}} \frac{\Gamma_{a}/4}{(E - E_{a})^{2} + \Gamma_{a}^{2}/4} = \sigma_{0} \frac{\Gamma_{nat}}{\Gamma_{a}} L_{a}(E) .$$
 (2.22)

 t_a is defined as

$$t_a = \sigma_0 f' n_a d_a \Gamma_{nat} / \Gamma_a . \qquad (2.23)$$

The quantity Γ_a depends on the sample structure. It is only for idealized samples that Γ_a approaches Γ_{nat} . If $\Gamma = \Gamma_a > \Gamma_{nat}$, expression (2.16) may be used as before, and (2.18) is replaced by $\Gamma_{exp} = 2\Gamma h(t_a)$, where t_a is given by (2.23). If $\Gamma \neq \Gamma_a$, the observed line width is given by

$$\Gamma_{\text{exp}} = \Gamma + \Gamma_{a} + 0.27 \sigma_{0} f' n_{a} d_{a} \Gamma_{\text{nat}} , \qquad (2.24)$$

and (2.16) may be rewritten as

$$\varepsilon(\mathbf{v}) = \int_{-\infty}^{\infty} J_{\mathbf{M}}(\mathbf{E}, \mathbf{v}) \left[1 - \frac{\Gamma_{\mathbf{a}}}{\Gamma} \exp\left[-t_{\mathbf{a}}L_{\mathbf{a}}(\mathbf{E})\right]\right] d\mathbf{E} . \qquad (2.25)$$

For not very thick samples ($t_a < 10$) the line is still a Lorentzian, and (2.25) may be written as

$$\varepsilon(S) = f \left[1 - J_0(it_a/2) \exp(-t_a/2) \right] / \left[\left(\frac{2S}{\Gamma_{exp}} \right)^2 + 1 \right] . (2.26)$$

In Mössbauer spectroscopy equations (2.17) and (2.18) are often used to determine parameters f and f'. For a very thin absorber we can write

$$\lim_{t_{a} \to 0} \epsilon(0) = f t_{a} / 2 \quad .$$
(2.27)

However, time-consuming measurements have to be carried out to reach a satisfactory statistical accuracy.

In general σ_0 and Γ_{nat} are known and there are four unknown quantities: f, f', Γ and Γ_a . The dependence of $\epsilon(0)$ and Γ_{exp} on d_a can be measured providing $\Gamma_a = \Gamma$. Thereafter the dependence of Γ_{exp}/Γ on the easily measured parameter $\sigma_0 n_a d_a$ can be plotted. This should be a straight line with slope 0.27 f' and which gives f' immediately [1.14]. The intercept with the y-axis (d_a = 0) is $\Gamma + \Gamma_a$. The dependence of $\epsilon(0)/f$ on t_a can then be plotted.

By the method of least squares the experimental data are approximated by (2.17) which yields f. However, since $J_0(it_a/2)$ is not a rapidly changing function of t_a , the accuracy of the procedure is low. Besides , if $\Gamma \neq \Gamma_a$, the method is more complicated. Similar consistent treatment can be carried out by assuming the lines in the source and absorber to be non-Lorentzian but Gaussian or combinations of the two.

A dependence of e(0) on t_a for the case f = 1 (Fig.2.3) can be obtained by numerical integration of equation (2.17). The dependence when $t_a \ge 0.15$ deviates substantially from linear.



Fig.2.3 Dependences of $\epsilon(0)$ (1) and spectral area (2) on t_a upon detecting the radiation caused by the Mössbauer transition and having passed through the sample of resonant atoms.

For large values of t_a the situation becomes more complicated. The intensity transmitted through a sample falls off rapidly with the sample thickness (2.12), therefore it becomes extremely difficult to observe the limiting $\epsilon(0)$ value accurately at $t_a > 10$. Indeed, it can then only be derived after lengthy measurements. Furthermore, the limiting $\epsilon(0)$ values (Fig.2.3) cannot be reached since equations (2.17) or (2.26) are derived from the sample consisting only of the resonant atoms. Even for monatomic samples having $a \neq 100$ % the photo-effect on non-resonant atoms causes the experimental dependence of $\epsilon(0)$ on t_a to be non-monotonous and to have a maximum at a certain t_a and then to approach zero.

In Mössbauer spectroscopy the shape of the spectrum and its area are the "signals" conveying quantitative information on a phase.

There is a particular shape of the Mössbauer spectrum which corresponds to every given phase or state of resonant atoms. When the shape is known to be Lorentzian, for example, the amplitudes and the line positions are often used as parameters of the signal. The amplitudes of the lines are assumed to unambiguously determine the amount of a given phase in a sample. As can be seen from Fig.2.3, saturation effects can significantly complicate the phase analysis. Furthermore, some experimental features may greatly affects the line amplitudes. That is why it is a good practice to measure the areas under the spectral lines. A dependence is given on t_a of the spectral area obtained by numeric integration of expression (2.16) in Fig.2.3. By definition, the area under the spectrum is:

$$A(t_a) = \int_{-\infty}^{\infty} \varepsilon(v, t_a) dv = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} J_M(E, v) \left[1 - \exp(-t_a L_a(E))\right] dV dE.$$
(2.28)

Taking into account the normalization conditions, we have

$$A(t_a) = f \int_{-\infty}^{\infty} \left[1 - \exp\left[-t_a L_a(E) \right] dE . \qquad (2.29)$$

A significant deviation of this dependence from proportionality occurs at greater thicknesses. The area under the spectrum does not then depend on the line shape and self- absorption in the source, neither does it depend on the cross section of non-resonant interaction in the sample or on the geometry of the experiment or the instrumental line broadening.

The study by transmission Mössbauer spectroscopy of surface layers is of special interest when $t_a \ll 1$. Expression (2.29) is then considerably reduced and due to normalization (2.1) it can be written:

$$A = \pi f t_a \Gamma_a / 2 = \pi f f' n_a d_a \sigma_0 \Gamma_{nat} / 2 . \qquad (2.30)$$

Thus the area under a given line of the spectrum is proportional to f' and the density of Mössbauer nuclei n_a in the phase.

The phase analysis from a fairly well resolved spectra requires no special treatment and (2.29) holds even when there is instrumental line broadening. Indeed, the addition of the noise velocity u_n to the average velocity of the source results in an additional energy change of γ -quanta Eu_n/c. The distribution function for noise may itself depend on the average velocity v. If $p(u_n, v)$ is defined as the probability that at a given average velocity the actual velocity is between $v + u_n$ and $v + u_n + du_n$, the normalized function can be expressed

$$\varepsilon(\mathbf{v}) = \int_{-\infty}^{\infty} d\mathbf{u}_{n} \int_{-\infty}^{\infty} p(\mathbf{u}_{n}, \mathbf{v}) J_{M}(\mathbf{E}, \mathbf{v}, \mathbf{u}_{n}) \left[1 - \exp(-\mathbf{L}_{a}(\mathbf{E})\mathbf{t}_{a})\right] d\mathbf{E}$$
$$= \int_{-\infty}^{\infty} J_{M}^{*} (\mathbf{E}, \mathbf{v}) \left[1 - \exp(-\mathbf{L}_{a}(\mathbf{E})\mathbf{t}_{a})\right] d\mathbf{E} ,$$

where

$$J_{\mathbf{M}}^{\star}(\mathbf{E},\mathbf{v}) = \int_{-\infty} p(\mathbf{u}_{\mathbf{n}},\mathbf{v}) J_{\mathbf{M}}(\mathbf{E},\mathbf{v},\mathbf{u}_{\mathbf{n}}) d\mathbf{u}_{\mathbf{n}}$$

The area under the spectrum is given by an expression which is analogous to (2.29):

$$A = f^* \int_{-\infty}^{\infty} [1 - e^{-L_a(E)t_a}] dE$$

where

$$\mathbf{f}^{*} = \int_{-\infty}^{\infty} d\mathbf{v} \int_{-\infty}^{\infty} p(\mathbf{u}_{n}, \mathbf{v}) J_{\mathbf{M}}(\mathbf{E}, \mathbf{v}, \mathbf{u}_{n}) d\mathbf{u}_{n} .$$

ω

If the distribution function does not depend on v the equation is reduced, f = f, and the area under the spectrum is not affected by noise. If the noise distribution function does depend on v, the area depends on the line shape of the source. Hence it follows from (2.29) and (2.30) that for the simplest case of single lines the area under the spectrum depends only on f, f', Γ_a and $n_a d_a$.

Up to now we have assumed implicitly the detector to register only the γ -rays of the Mössbauer transition. In practice this is not so because of the background noise. In transmission experiments there are three sources of the background: i) γ -and X-rays of higher energies which may be Compton-scattered before reaching the detector; Bremsstrahlung produced outside the detector may contribute to this, too; ii) High-energy γ -and X-rays having lost only a part of their energy in the detector; iii) X-rays that are not distinguished by the detector from the Mössbauer quanta.

The relative intensity of the background also increases sharply as the thickness of the absorber increases. The experimentally observed effect is given not by (1.36) but by the following

$$\varepsilon_{\exp}(v) = \frac{I(\infty) - I(v)}{I(\infty)} \frac{I(\infty)}{I(\infty) + I_{back}} = p \varepsilon(v) . \qquad (2.31)$$

There is analogous relationship for the relative area under the spectrum

$$A_{exp} = pA$$
 . (2.32)

The background coefficient p is always less than unity. Usually the difficulties in determining p do not permit the absolute measurement of f by the above method. Furthermore, the measured f-value may also be lower since the Mössbauer quanta may lose a part of their energy as a result of the Compton effect. This effect is more significant with detectors of poor resolution.

With the exception of emission Mössbauer spectroscopy, work can be performed with standard sources with f-values which are provided with the details of this source. Otherwise f-values are determined using the "black" absorber which completely resonantly absorbs only the Mössbauer radiation [1.15,16].

Mössbauer spectroscopy requires a knowledge of the absolute values and ratios of the cross sections of both resonant and non-resonant processes. For ⁵⁷Fe in transmission experiments it is the 14.4 keV γ -quanta interaction which is of interest as it also is in scattering experiments together with the 6.46keV X- rays. In both theoretical and practical studies of the interaction of radiation with matter the appropriate absorption coefficients are expressed in different units. Thus, the atomic absorption cross sections σ_e are expressed in [cm²] or barn [10⁻²⁴cm²] per atom; the linear scattering (absorption) coefficients μ expressed in [cm⁻¹]; and the mass absorption coefficients μ^m in [cm²g⁻¹]. For an element they are related by the following expression:

$$\mu = \mu^{m} \rho = \sigma_{e} \rho N / A , \qquad (2.33)$$

where ρ is the density, N is Avogadro number, and A is the mass number.

Theoretical aspects of Mössbauer spectroscopy use the interaction cross section per atom whilst for transmission experiments the mass absorption coefficients are preferred and, in scattering experiments, the linear scattering coefficient is used. A review of cross sections for the interaction of electromagnetic radiations in the energy range of interest can be found in [1.17,2.1]. For the Mössbauer 14.4 keV radiation and an iron absorber the following values apply: $\sigma_0 = 2.56 \ 10^6 \ barn/atom$,

 $\sigma_a = 5.9 \ 10^3 \ \text{barn/atom}, \ \mu_a = 0.0504 \ \mu\text{m}^{-1}$ and $\mu^m = 64 \ \text{cm}^2 \ \text{g}^{-1}$. It is sometimes of convenience to use the quantities of the following type to quantify the non-resonant absorption length

$$1 = \mu_a^{-1} . (2.34)$$

It shows, for instance, that a 18 mm thick iron foil will attenuate the 14.4 keV non-resonant γ -quanta by a factor e. Figures 2.4 and 2.5 depict the calculated dependence of the 14.4 keV γ -quanta and the 6.46 keV X-rays intensities on the filter thicknesses for some frequently used substances.



Fig.2.4 Intensity dependence of the 14.4 keV 57 Co γ -quanta on the filter thickness.

It is now possible to consider two iron absorbers with ⁵⁷Fe abundances of 2.14 % and 90 %, with f' = 0.67 for iron [2.2] and H_{eff} = 33.0 Tesla. If v = v₀, v₁, v₂, v₃ be the relative velocities at which the source line $J_M(E,v)$ excites the centre of the spectrum and the first, second and third line in it, intensity ratios can be assumed to be 3:2:1:1:2:3. The maximum value of the linear resonant absorption coefficient for a line whose partial intensity is k_i may be written as:

$$\mu_r^i = n_a f' k_i \sigma_0$$
 .

(2.35)



Fig.2.5 Intensity dependence of the 6.46 keV K-X-rays on the filter thickness.

In subsequent discussions of spectral simulations we shall use the hypothetical substance non-magnetic iron ($H_{eff}=$ 0). The values of the linear resonant scattering coefficients for iron and the hypothetical substance are given in Table 2.3.

Table 2.3

Linear coefficients of resonant scattering $\mu_r(cm^{-1})$ at room temperature for α -iron and non-magnetic iron.

a, %	H _{eff} = 33. Tesla				$H_{eff} = 0$
	V ₀	V ₁	V2	V3	V ₀
2.2	2	790	527	263	3160
90	83	32 800	21 900	10 900	131 000

Notes: 1. v_0 , v_1 , v_2 and v_3 for α -iron correspond to the spectrum centre and to line I, II, and III, respectively. 2. Linear coefficient of non-resonant absorption of the 14.4 keV γ -rays in α -iron are $\mu_{\rm ph}$ = 497.5, $\mu_{\rm R}$ = 5.75 and $\mu_{\rm C}$ = 0.71 cm⁻¹ for the photoeffect, Rayleigh scattering and the Compton effect, respectively.

The dependences of the γ -quanta intensity (E₀ = 14.4 keV, f = 0.77) on thicknesses of the "non-magnetic iron" absorber are shown in Fig.2.6 whilst Fig.2.7 shows similar dependences for α -Fe absorbers. Curves 1 and 4 are obtained for the source line at resonance with the first line of the sextet. The difference between the curves is caused by the different abundances of ⁵⁷Fe in the absorber.



Fig.2.6 Intensity dependence of the 14.4 keV γ -quanta from a ⁵⁷Co(Rh) source (f = 0.77) on the thickness of a sample of non- magnetic iron (f' = 0.7, δ = 0) at room temperature: 1 - resonant and non-resonant interactions are accounted for, a = 2.14 %; 2 - beam of non-resonant γ -quanta; 3 - beam of resonant γ -quanta, a = 90 %.

An examination of the results presented in Figs.2.6 and 2.7 enable an evaluation of the amount of substance needed to obtain a required effect, and also the optimum thickness of the windows and substrates. In particular, from curves 2 and 3 in Fig.2.6 it follows that the maximum $\epsilon(0)$ value in transmission experiments cannot exceed the value of f. Indeed, at a \rightarrow 100 %, only the non-resonant γ -quanta will pass through an absorber whose thickness is ~ 0.4 µm and $\epsilon(0) \rightarrow f$.



Fig.2.7 Intensity dependence of the 14.4 keV γ -quanta from a ⁵⁷Co (Rh) source on the thickness of a sample of metal iron at a constant velocity of the source. 1 and 5 are for v = v(1), 2 - for v = v(0), 3 - for v = v(3), 4 - for v = v(2); a = 2.14 % for 1, a = 90 % for 2 - 5.

2.2. Low-energy γ -quanta Scattering

There are various scattering channels of incident Mössbauer radiation, including the channels which give conversion electrons as opposed to γ -quanta. It is important in transmission Mössbauer spectroscopy, that if the secondary scattering is not taken into account every resonant scattering leads to the attenuation of the transmitted intensity, i.e. to absorption. Neither the type of the scattering channel nor the interaction of the scattered radiation with matter are of any significance here. Of primary interest in scattering experiments are the types of the scattering channels, their probabilities and the properties of the scattered radiation.

Let us divide all the scattering channels into two groups. The first group includes scattering channels yielding γ -quanta. Scattering channels of the second group correspond to all other possible interaction processes. As in transmission experiments, in a scattering geometry γ -quanta are detected but the background is caused by different processes. The main process competing with resonance interactions in the transmission mode experiments is the photoelectric effect (see Table 2.3). The Compton effect is to be taken into account when the source emits high-energy γ -rays in addition to the Mössbauer radiation.

In scattering Mössbauer spectroscopy the processes competing with Mössbauer scattering are the Compton effect, Rayleigh scattering and classical resonant scattering of γ -rays [2.3]. Non-resonant scattering of γ -rays occurs on free or bound electrons.

The maximum energy change is for the electrons which are assumed to be free, i.e. in Compton scattering. The minimum energy E' for the backscattered γ -quantum is given by $E_{b}^{'} = E /(1 + 2\beta)$, where β is the ratio of the incident γ -quantum energy to the rest energy of the electron. For low-energy quanta the energy change is small. Thus, for ⁵⁷Fe E' = 13.6 keV. Ordinary detectors cannot discriminate the quanta backscattered due to resonance from the Rayleigh scattering and Compton scattering. Typical energy losses for the Compton effect are of the order of $10^{2} - 10^{4}$ eV. Compton scattering may or may not influence lattice vibrations, but the energy losses may be neglected since they are several orders of magnitude less than the energy transferred to the electron.

Rayleigh scattering is the scattering of γ -quanta from atomic shells and is completely analogous to X-rays scattering which leads to diffraction from the crystal lattice. Hence, there is no ionization or excitation of the atom. Rayleigh scattering occurs on atomic shells and the energy may or may not be transferred to the lattice. Hence, Rayleigh scattering is either elastic or inelastic. In scattering spectroscopy, as opposed to transmission mode experiments, Rayleigh scattering may play an important role. Interference between Rayleigh and resonant scattering results in series of interesting effects and allows a deeper insight into composition and structure of the substance. Phase analysis for even relatively simple samples may prove to be incorrect if the contribution of Rayleigh scattering is not taken into account. This is discussed in more detail in Chapt.4.

It is now necessary to examine the dependence of the Rayleigh scattering cross section on the γ -ray energy, the scattering angle and the atomic number Z of the scatterer. The Rayleigh scattering of high-energy γ -rays results in more than three-quarters of the scattered radiation within a cone of angle θ_0 [2.4]

$$\theta_0 = 2 \arctan \left[2.6 \ 10^{-2} \ Z^{1/3} \ \beta^{-1} \right]. \tag{2.36}$$

The scattering cross section for this radiation at $\theta \rightarrow 0$ is approximately proportional to Z² and independent of E. Thus, inside the cone classical X-ray elastic scattering occurs, and the cross section can be found from tables, e.g. [2.1].

At scattering angles $\theta > \theta_0$ the cross section falls off rapidly and is given by [2.4]:

$$\sigma_{\rm R} = 4.33 \ 10^{-33} \left[\frac{Z}{\beta} \right]^3 w'(\theta) \quad [cm^2/sr],$$
 (2.37)

 $w'(\theta) = \frac{1 + \cos^2 \theta}{\sin^3 \theta/2}$

For the 145 keV Mössbauer transition in ¹⁴¹Pr $\theta_0 = 40^\circ$, and the backscattering cross section can be evaluated from formula (2.37). If the γ -transition energy is less than 40 keV, the formula is inappropriate. Indeed, for E = 40 keV and Z = 26 (Fe), (2.36) gives $\theta_0 = 170^\circ$. At these and lower energies, the photon wave length is of the order of an atomic radius and the angle dependence is determined not by (2.37) but by the atomic form factors. In backscattering Mössbauer experiments involving ⁵⁷Fe and ¹¹⁹Sn the Rayleigh scattering mainly contributes to the background if there is no Compton scattering of higherenergy radiation. Indeed, from Table 2.3 it can be seen that for the 14.4 keV γ -quanta $\mu_R = 5.75$ cm⁻¹ and the probability of Compton scattering is 8 times lower than for Rayleigh scattering.

The main processes of γ -rays scattering in solids for energies bellows 200 keV will be classified provided that scattering of γ -rays, whose energy is equal to the binding energy of atomic electrons, is not considered. Within this classification (Table 2.4) scattering processes are divided

Table 2.4

Classification of γ -ray scattering processes in solids.

Type of	Classification of γ-ray scattering processes			
Scattering	Fur	Fundamental classification		
		coherent	recoilless	elastic or
				quasi-elastic
Nuclear elastic	resonant		Nonrecoilless	inelastic
and		incoherent	recoilless	elastic or
Rayleigh	non-resonant			quasi-elastic
			nonrecoilless	inelastic
			recoilless	inelastic
Compton	non-resonant	incoherent		
			nonrecoilless	inelastic
Nuclear			Recoilless	energy-shifted
inelastic	resonant	incoherent		
			nonrecoilless	inelastic

primarily into resonant and non-resonant ones [2.5]. Resonant scattering occurs on nuclei if the energy of a γ -quantum is close to the γ -transition energy. Non-resonant scattering is the scattering by electrons. Both resonant and non-resonant scattering may be elastic or inelastic, coherent and incoherent. Elastic scattering is a process which results in no energy change of the scattered quantum.

A change of γ -quanta energy may occur in resonant scattering as a result of recoil. Typical energy changes are of the order of 10^{-2} eV. If resonant scattering is recoilless it may still be inelastic since, after scattering, the nuclear quantum state may change and the energy of the scattered γ -quantum will differ from the energy of the incident quantum by the value of the ground level splitting. Typical energy changes are about 10^{-8} eV. Only Mössbauer spectroscopy allows the observation of inelasticity in this type of scattering. Finally, different scattering channels may be coherent or incoherent. Coherence is the property of several stochastic processes characterizing their ability to strengthen or weaken each other. Even inelastic processes may be coherent.

In addition to the classification based on physical processes occurring in scattering, another classification is possible based on the energy resolution of the method used. An example of this classification is given in the right-hand column of the Tab. 2.4. In accordance with the classification, quasi-elastic scattering is the scattering where energy losses due to recoil are of the same order as Γ_{nat} . Energy shifted scattering is the scattering where the recoil energy is not transferred to the solid at the moment of scattering, but the energy of scattered γ -quantum differs from that of the incident quantum by a fixed amount which is determined by hyperfine interactions. We end this classification of scattering processes by noting that every scattering process has its own angular distribution.

The greatest advantage of scattering experiments as opposed to transmission mode experiments is that they may involve a significantly smaller background contribution. This has applications when observing the effect in relatively high-energy transitions [2.6]. A typical experimental arrangement is shown in Fig.2.8. The source is assumed to be a point source and a tungsten shield is used to shield the detector completely from direct γ -rays of the source. Such an axially symmetric backscattering arrangement ensures a higher efficiency and is convenient for low temperature measurements. Indeed, for a scatterer of ¹⁴¹PrO₂ at 20 K and a source of ¹⁴¹CeO₂ at 18 K (E₀ = 145 keV) the signal-to-background ratio is found to be 0.20, whereas for the equivalent transmission experiment the ratio would not exceed 0.01.

The gain in the observed effect is caused by the fact that in idealized scattering experiments only the radiation from the scatterer is detected; the direct radiation of the source is not registered by the detector neither is the radiation scattered by surroundings. If there are no γ -quanta with energies higher than

the Mössbauer transition energy the radiation from the scatterer consists of three components: Mössbauer, Rayleigh and Compton. The last one can be discriminated if the incident quanta energy is sufficiently high. If there is no hyperfine splitting in both the source and the scatterer then for a thin scatterer consisting of the resonant isotope only the observed effect will satisfy the relation:

$$\varepsilon \leq \frac{1}{2} f f'(d\sigma_M / d\omega)(d\sigma_R / d\omega) , \qquad (2.38)$$

where $d\sigma_M/d\hat{u}$ is the differential cross section for Mössbauer scattering at resonant energy; and $d\sigma_R/d\hat{u}$ is the differential cross section for Rayleigh scattering.



Fig.2.8 Scattering Mössbauer experiment in an axially symmetric geometry [2.6]. γ_1 and γ_2 are the angles of incidence and the scattering angle respectively; <u>k</u>₀ and <u>k</u>_f are the wave vectors of γ -quanta.

For $^{141}\mbox{Pr}$ the ratio of the differential cross sections turns out to be 70400, and (2.38) takes the form

(2.39)

In transmission mode geometry ε is always less than or equal to f'. In scattering geometry the situation is different. For a hypothetical scatterer of ¹⁴¹Pr with f' of only 0.01 %, the effect due to (2.39) may be 3.5 times larger than f' [2.6].

The Rayleigh and Compton scattering cross sections taken per Mössbauer atom are usually many orders of magnitude less than the maximum cross section for resonant scattering by the atom. However, it should not be concluded that Mössbauer scattering makes the main contribution to the observed intensity of the scattered radiation. Indeed, Rayleigh or Compton scattering will arise from all atoms of all elements in the sample under study and will not depend on the isotopic composition. In contrast, the Mössbauer effect is observed on the isotope only. Even if the sample is monatomic, a factor a/100 must be introduced where "a" is the percent abundance of the resonant isotope. For natural iron this will lower the maximum value of the resonant scattering cross section by a factor of about 45. The hyperfine splitting, in its turn, lowers the maximum possible cross section value for Mössbauer scattering in the sample. It should be noted that if γ -quanta scattering from iron is observed which corresponds to the absorption maximum for the third or the fourth line, a factor f'/12 should be introduced in the expression for the scattered cross section. There are some other reasons for lowering the maximum value of the Mössbauer scattering cross section and these are outlined below.

In general, the classical resonance scattering should be accounted for. This arises from a partial overlap of emission and absorption γ -ray spectra which are significantly broadened by thermal motion of atoms in the source and the absorber. The centres of gravity of such spectra are shifted relatively to the transition energy E₀ in opposite directions by an amount equal to the recoil energy E_R. As a rule, classical resonance scattering does not change the shape and intensity of Mössbauer scattering spectra, since the process cross section is small and practically unchanged in the energy region used in Mössbauer spectroscopy.

2.3. Resonance Fluorescence and Interference Effects

The principles of resonance scattering of γ -rays have been detailed in the well known monograph of W. HEITLER [2.7]. The scattering of electromagnetic radiation of an energy very close to that E₀ of the scattering system was called resonance fluorescence. An important feature of the process is that the cross section on resonance is significantly larger than for any other scattering process and that the phase of the scattered radiation is definitely shifted. The shift is significant in the vicinity of resonance. On passing through the resonance the shift changes from $\pi/2$ to 0 at E << E₀ and to π at E >> E₀.

It was shown by W. Heitler that for an individual process of resonance fluorescence the energy E' of the emitted photon should not differ from energy E of the absorbed photon by more than the ground state width. For scattering Mössbauer spectroscopy involving stable ground states and no level splitting due to hyperfine interactions the energy of the scattered quantum is equal to that of the incident quantum within the ground-state width. If a beam of monochromatic γ -quanta of energy E which is close to the resonance energy E₀ is directed onto a resonant scatterer, the scattered radiation will be also monochromatic with energy E, as opposed to Lorentzian with linewidth Γ which is the case for an emission line.

Resonance fluorescence is a single coherent quantum process if there are no external perturbations. In a stationary case, it cannot be regarded as two subsequent unrelated processes of absorption and emission because the nucleus would not "remember" which γ -quantum had been absorbed and the relative probability to emit a γ -quantum of energy E would be given by a Lorentzian distribution of width Γ with a maximum at energy E₀. For resonance fluorescence the scattered wave is coherent with the incident radiation. Its phase is shifted relative to the phase of the incident wave. Fundamental results for the development of resonance scattering theory for nuclear physics were obtained by LAMB [2.8] who developed a theory of resonance absorption of neutrons by nuclei bound in the crystal lattice. This theory was used by R. Mössbauer to explain his experiments on resonance γ -quanta scattering by nuclei in solids.

All Mössbauer scattering experiments show two types of dependence. The first type concerns the angular dependences of the scattered radiation. As a rule, the intensities are measured depending on either angles γ_1 and γ_2 for the incident and outgoing radiation or on the scattering angle θ . The experimental arrangement for the particular case of the scattering angle $\theta = \gamma_1 + \gamma_2 = 90^\circ$ is shown in Fig.2.9. The angular dependence is determined by the parameters of the nuclear-excited and -ground levels as well as by other parameters of the sample such as the vibration spectrum, the crystal structure, texture, the resonant isotope abundance and hyperfine interactions. The intensity is considerably dependent on the collimation of the incident and scattered radiation, as well as on interference with Rayleigh scattering even at $\theta = 90^\circ$ if the transition is not M1.

The second type of dependence is evident in various spectra. Most of the Mössbauer spectra are obtained by methods similar to those used in transmission experiments, i.e. by detection of all γ -quanta scattered by the sample at different Doppler velocities. Sometimes a more sophisticated experimental arrangement is used, allowing the energy spectrum of recoilless γ -rays at fixed Doppler velocity to be examined.

The analysis can be approached by considering the elastic scattering from an atom in a crystal where the divergences of incident and scattered radiation are small. It is initially necessary to consider the interference effects on the scattered



Fig.2.9 Experimental geometry for scattering $\theta = \gamma_1 + \gamma_2 = 90^\circ$, allowing the simultaneous recording of the transmission spectra (detector 1) and scattering spectra (detector 2). γ -radiation is incident at an angle γ_1 within the solid angle d ω onto the sample under study of thickness d_a.

electromagnetic radiation with a wavelength of about 1 Å by a single atom. Rayleigh scattering by atomic electrons always produces interference, since the distance between electrons in an atom is also about 1 Å. The interference processes are accounted for by means of the atomic form factors. If this radiation is resonantly scattered by a nucleus, elastic Mössbauer scattering may occur and there will also be interference between incident and scattered radiation. Thereafter, the resonantly scattered radiation may interfere with the radiation scattered by electrons of the atom. Finally, Mössbauer scattering gives a specific interference which occurs if the hyperfine splitting is of the order of $\Gamma_{\rm nat}$.

The problems related to Rayleigh scattering and atomic form factors are described in most textbooks on X-ray diffraction. We shall start with the interference effects taking place on resonant scattering. A theoretical problem is to derive an expression for the elastic resonant scattering amplitude F_r , where all the experimental conditions are taken into consideration. For a given transition multipolarity, F_r will depend on the parameters of levels or sublevels of the initial and final nuclear states, on the direction of the quantization axis, on the energy of the incident γ -quantum, and on the wave-

vectors of the incident and scattered radiation and on the polarization vector. If these parameters are fixed, the scattering amplitude is the sum of partial amplitudes corresponding to all intermediate excited states. When the incident radiation is a mixture of multipoles, each of the partial amplitudes will contain contributions from each multipolarity.

The amplitude of the elastic nuclear resonance scattering for which the nuclear spin projection on the quantization axis changes as $m_g \to m_e \to m_g$, may be written [2.9,10] in the following form:

$$\mathcal{F}_{\mathbf{r}} = \operatorname{aC} \frac{\Gamma_{\gamma}}{2k_{0}} \sum_{n} \frac{\left(\psi_{n_{0}} \mid e^{-i\underline{k}_{f}\underline{r}} \mid \psi_{n} \right) \left(\psi_{n} \mid e^{i\underline{k}_{0}\underline{r}} \mid \psi_{n_{0}} \right)}{E - E_{0} - (\varepsilon_{n} - \varepsilon_{n_{0}}) + i\Gamma/2} \quad .$$

$$(2.40)$$

where the values of \emptyset are the crystal wave functions, **e** describe their energy eigenvalues, C is a factor depending on polarization or multipolarity, E is the energy of an incident γ -quantum, \underline{k}_0 and \underline{k}_f are the wave vectors of incident and scattered γ -quanta; $E_0 - i\Gamma/2$ is the resonance energy, Γ_{γ} is the partial width for de-excitation of the nuclear level by emission of a γ -quantum, $\Gamma_{\gamma} = \Gamma/(1 + \alpha)$. The nuclear matrix element, which depends on the multipolarity of the γ -transition and determines the nuclear part of the angular dependence for the scattered radiation, is factorized and included in C.

The terms "collision time" and "scattering length" are sometimes used in the theory of resonance scattering (see [2.9]). In Mössbauer spectroscopy the collision time, which is proportional to Γ^{-1} , is by several orders of magnitude longer than the lattice vibration periods. There is no correlation here between the initial $\underline{r}(0)$ and final $\underline{r}(t)$ positions of the atom and the process is considered in terms of slow collisions. Some times one speak about "slow scattering". Despite this the scattered wave remains coherent with the incident one. The quantity

$$\Gamma_{\gamma} / 2k_0 [E - E_0 - (\mathbf{e}_n - \mathbf{e}_{n0}) + i\Gamma/2]$$

in the expression for the scattering amplitude (2.40) is the free-particle resonance scattering length [2.9]. In the centre- of-mass system the energy $E - (\mathbf{e}_n - \mathbf{e}_{n0})$ corresponds to this scattering length. Summation in (2.40) causes the main contribution to be made by the term with $n = n_0$. Therefore, for the elastic resonance scattering of γ -quanta we have

$$\mathcal{F}_{\mathbf{r}} = C \frac{\Gamma_{\gamma}}{2k_0} \frac{\left(\psi_{\mathbf{n}_0} | e^{-i\underline{k}_{\mathbf{f}}\underline{\mathbf{r}}} | \psi_{\mathbf{n}_0}\right) \left(\psi_{\mathbf{n}_0} | e^{i\underline{k}_0\underline{\mathbf{r}}} | \psi_{\mathbf{n}_0}\right)}{E - E_0 + i\Gamma/2}$$

which, for a cubic isotropic crystal, reduces to:

$$\mathscr{F}_{\mathbf{r}} \simeq \mathbf{a} \frac{\Gamma_{\gamma}}{2k_0} \frac{\exp(-k_0^2 \overline{\mathbf{x}^2})}{\mathbf{E} - \mathbf{E}_0 + \mathbf{i}\Gamma/2} . \tag{2.41}$$

The nuclear transition energy in (2.40) in the presence of hyperfine splitting depends on the quantum numbers m_g and m_e . Let us assume that the initial and final nuclear states for a γ -transition are the eigen states of the angular momentum operators, and denote them by $|I_e m_e \rangle$ and $|I_g m_g \rangle$ respectively. The theory of angular momenta can be used to evaluate the matrix elements for the transition. To obtain an expression for the amplitude F_{coh} of the coherent resonance scattering of γ -quanta, it is necessary to sum the amplitudes F_r over all m_e values and to average the result over initial spin states m_g . The plane wave representation of the wave function is transformed into the spheric wave one. The amplitude $F_{coh}^{k_0\sigma_1 \rightarrow k_f\sigma_2}$ of the elastic resonant scattering of a γ -quantum with energy E and polarization σ_1 , incident in the direction k_0 on a nucleus whose spin projection to the quantization axis z is m_g , and scattered in the direction k_f with polarization $\sigma_2 = \pm 1$ for right- or left-hand circularly polarized waves and axially symmetric hyperfine interactions, is written [2.9, 11] as:

$$\mathcal{F}_{coh}^{\underline{k}_{0}\sigma_{1} \rightarrow \underline{k}_{f}\sigma_{2}} (E) = \frac{\Gamma_{\gamma}}{4k_{0}} \frac{2L+1}{2I_{g}+1} f_{1}f_{2}(\sigma_{1}\sigma_{2})^{\Delta(\pi)}$$

$$\sum_{\substack{D_{K\sigma_{2}}^{L^{*}}(\hat{z} \rightarrow \hat{k}_{f}) \quad D_{K\sigma_{1}}^{L}(\hat{z} \rightarrow \hat{k}_{0}) \mid G(m_{e}, m_{g}) \mid^{2}}{E - E_{0}(m_{g}, m_{e}) + i\Gamma/2}, \quad (2.42)$$

where $K = m_e - m_g$. For an atom in an isotropic crystal the probability amplitudes of the Mössbauer effect are:

1

$$f_{1} = \exp \left\{ -\langle (\underline{k}_{0}, \underline{u})^{2} \rangle / 2 \right\} ; f_{2} = \exp \left\{ -\langle (\underline{k}_{f}, \underline{u})^{2} \rangle / 2 \right\}$$

where <u>u</u> is the displacement vector of an atom from equilibrium. The parity conservation for the system "nucleus - γ -quantum" leads to the following selection rule for the transitions between the two states of parities π_e and π_g : $\Delta(\pi) = (-1)^L$ and $(-1)^{L+1}$ for EL and ML transitions, respectively. For M1 transitions $\Delta(\pi) = 1$. The transformation of the angular momentum eigen-functions from the \hat{z} coordinate system, where spins of the excited and ground nuclear states are quantized, into the \hat{k}_0 or \hat{k}_f coordinate system connected with the propagation direction of the γ -quantum, is determined by special rotation functions - the D functions which are rotation matrices of the angular momentum eigenfunctions. The D-functions give the angular dependence of polarization and intensities of transmissions with energies E₀(m_g,m_e).

If a scatterer is an isotropic substance then, for an M1 transition and in the absence of hyperfine splitting the expression for the coherent resonant scattering amplitude

 $\mathbf{F}_{coh}^{\underline{k}_{0}\sigma_{1}\rightarrow\underline{k}_{f}\sigma_{2}}$ (E) is reduced to:

$$\mathscr{F}_{coh} = \frac{a}{4k_0} \frac{2I_e + 1}{2I_g + 1} f' D^1 \sigma_2 \sigma_1 (k_f \longrightarrow k_0) (\sigma_1 \sigma_2)^{\Delta(\pi)} \frac{\Gamma_{\gamma}}{E - E_0 + 1\Gamma/2}.$$
(2.43)

The approach presented here may be compared with other ways which have been used to derive the expression for the nuclear resonant scattering amplitude [2.12,13].

In parallel with the nuclear resonant scattering it is necessary to also consider Rayleigh scattering. If Rayleigh scattering is elastic the phase shift equals π . For the elastic scattering channel there will be two corresponding coherent (although phase-shifted) scattering processes, the Mössbauer and Rayleigh. The amplitude of the total elastic scattering of a γ -quantum of energy E turns out to be a sum of the Mössbauer amplitude F_r and the Rayleigh F_R . The energy distribution J(E,S) of the scattered γ -radiation (at S = const) may differ substantially from that of the incident one.

Let γ -radiation with the energy distribution L(E) be incident on a sample. Let us measure energy in units of $\Gamma/2$. If there are no hyperfine splittings the energy distribution of γ -radiation after elastic scattering by an atom in an isotropic crystal may be written as [2.14-16]:

$$J(E,S) \sim \frac{1}{(E^{2} + 1)} \left\{ \frac{C_{2}^{2} f_{1}f_{2}}{(E - S)^{2} + 1} + C_{3}^{2} f_{R} - \frac{2C_{1}C_{2}C_{3} (E - S) \sqrt{f_{R}f_{1}f_{2}}}{(E - S)^{2} + 1} \right\},$$

$$f_{R} = \exp \left\{ - \langle ((\underline{k}_{0} - \underline{k}_{f}) \underline{u})^{2} \right\} / 2,$$

$$(2.44)$$

where f_R is the Debye-Waller factor, C_1 is a constant that accounts for different scattering by nuclei and electrons of differently polarized quanta, C_2 is a constant, which is proportional to the resonant scattering length of a γ -quantum by a nucleus exactly in resonance, C_3 is a constant, which is proportional to the Rayleigh scattering length [2.15].

Each of the three terms in (2.44) has its own energy dependence. The energy distribution J(E) of the scattered radiation, corresponding to every term in (2.44) at S = 5, is given in Fig.2.10. For the calculations it may assumed that $C_3\sqrt{f_R} = C_2\sqrt{f_1f_2} = 1$. Two lines of equal widths are observed in the spectrum resulting only from resonant scattering (Fig.2.10a). Their amplitudes and areas are determined by convolution of the emission and scattering spectra. The large distance between the centres of the spectra means that the amplitudes of the lines are only 4 % of the scattering line amplitude in resonance, i.e. at S = 0. The Rayleigh scattering spectrum intensity in Fig.2.10c effectively coincides with the emission spectrum. As seen from Fig.2.10a and c at S = 5 it is the Rayleigh scattering that mainly contributes to the elastic scattering process. The interference term (Fig.2.10b) becomes zero for the γ -quanta energy corresponding to resonance in the scatterer. When the γ -quanta energies are greater than the resonant energy in the scatterer the interference term increases the total intensity of the elastically scattered radiation whereas for lower energies the total intensity is decreased.

The Mössbauer effect allows the observation of the energy distribution of the scattered γ -radiation when resonance detectors are used. However, such experiments are time consuming. In conventional Mössbauer spectroscopy the radiation detector usually serves as an energy integrator. It detects all γ -radiation of a given velocity which reaches the detector from a scatterer. It is now necessary in a way similar to that used



Fig.2.10 Contributions to the energy distributions of the radiation elastically scattered by a single atom of an isotropic crystal: a) - resonant scattering, b) - the interference term, c) - Rayleigh scattering. S = 5 $\Gamma_{nat}/2$. γ -Ray energy is in units of $\Gamma_{nat}/2$.

to analyze the separate spectral components (Fig.2.10), to analyze separately the radiation intensities resulting from the resonant scattering process, the Rayleigh scattering process, and the interference effects. As seen in Fig.2.11a the intensity of Rayleigh scattering is independent of S. Indeed, since it is not a resonant process, the energy change of the γ -quanta by an amount greater than, say a million natural widths, will not significantly change the cross section for scattering by electrons. The intensity of the resonantly scattered radiation (Fig.2.11b) follows the usual Lorentzian curve, whilst the contribution of the interference term (Fig.2.11c) to the total intensity of the scattered radiation takes the form of a dispersion curve. The maximum radiation intensity changes which arise from interference occur at S = $\pm \Gamma$.



Fig.2.11 Partial contributions to the total radiation intensity as a function of the energy parameter S. a) - resonant scattering, b) - the interference term, c) - Rayleigh scattering.

The dependence of three terms in (2.44) on the scattering angle θ are determined in the first instances by the angular dependences of the scattering processes. The electric dipole interaction in Rayleigh scattering leads to an angular dependence of the form (1 + $\cos^2 \theta$)/2. For the magnetic dipole transition, resonance scattering has an angular dependence of the same type, but the polarization of the magnetic and electric radiation components differ by 90° and the interference term in this case contains the angular factor $\cos\theta/(1 + \cos^2\theta)$. Thus, for a scattering angle of 90°, the interference term for M1- transitions vanishes. The Debye-Waller factor for Rayleigh scattering is anisotropic even for an isotropic crystal. It also causes the line shape I(S) to depend on θ . It is significant that all these dependences are smooth, and a change of the scattering angle, say by 1°, will not lead to an appreciable change of the line shape or the intensity of the scattered radiation.

Apart from the interference effects mentioned above, interference is possible as a result of scattering by sublevels of magnetic or electric hyperfine structures [2.17]. To an inci-

dent γ -quantum of any energy E there correspond different (and, in general, nonzero) amplitudes for scattering by all transitions of the hyperfine structure. Hence interference should occur which will manifest itself in an asymmetry of the energy distribution of the scattered radiation. If the scattering atom is in an ideal polycrystal the γ -radiation scattered into the solid angle dù' as a result of the Mössbauer effect can be written in the following form:

$$\frac{dI_{r}(v)}{d\omega'} \sim \sum_{k,m_{g}} P_{k}(\cos\theta) \left\{ \sum_{m_{e}} B_{k}(m_{g},m_{e},m_{e}') \frac{\Gamma_{nat}^{2}}{[v(m_{g},m_{e})-v]^{2} + \Gamma_{nat}^{2}} + \sum_{m_{e},m_{e}'} \frac{B_{k}(m_{g},m_{e},m_{e}') [v(m_{g},m_{e})-v] [v(m_{g},m_{e}')-v]}{\left[[v(m_{g},m_{e})-v]^{2} + \Gamma_{nat}^{2}\right] \left\{ [v(m_{g},m_{e}')-v]^{2} + \Gamma_{nat}^{2}\right\}} \left\{ \frac{\left[v(m_{g},m_{e})-v(m_{g},m_{e}')\right]^{2} + 2\Gamma_{nat}^{2}}{\left[v(m_{g},m_{e})-v(m_{g},m_{e}')\right]^{2} + 2\Gamma_{nat}^{2}} \right\} , (2.45)$$

where I_e , I_g , m_e and m_g are the spins of the excited and ground nuclear states and their projections onto the quantization axis respectively. The coefficients $B_k(m_g,m_e,m_e)$ depend on quantum properties and the transition multipolarity. The Legendre polynomials $P_k(\cos\theta)$ describe the dependence of the separate spectral intensities on the scattering angle. The subscript k takes all even integral values from zero to the minimal 2L and $2I_e$ values, where L is the highest multipolarity of the transition. It should be recalled that k = 2 for the M1 transition. $v(m_g,m_e)$ is the Doppler velocity at which the line is observed corresponding to the γ -transition $E_o(m_g,m_e)$. The second term (in braces) in (2.45) takes into account the departure of the line shape from Lorentzian as a result of interference between scattering by different sublevels. The interference amplitudes $B_k(m_g,m_e,m_e)$ contribute to the intensity at resonance.

The relative contribution of the interference term to the total intensity of the scattered radiation is determined by the energy of hyperfine interactions. It has been calculated [2.18] that for Mössbauer scattering at an angle of 135° in the transition $I_g = 0$, $I_e = 1$ and in the presence of magnetic hyperfine interaction the relative contribution of the interference term in (2.45) does not exceed 1 % for $\underline{\mu} \ \underline{H}_{eff}/\Gamma_{nat} = 5$ and rises to 5 % as this ratio decreases to 0.5.

Interference effects are observed on scattering from a real sample and not from an isolated atom. Interference effects were observed for the first time on scattering from a polycrystalline α -Fe foil (a = 65 %) using ⁵⁷Co in α -Fe γ -ray source [2.19]. Interference led to a slight asymmetry of the resonant scattering peak. The asymmetry agrees with a classical model of scattering by a damped resonator [2.20]. In this model resonant scattering is in phase with Rayleigh scattering when the incident radiation energy is above resonance but is in antiphase when below resonance and is in quadrature when on exact resonance. The use of Bragg reflections in single-crystal scatterer permits a substantial reduction in the contribution from incoherent scattering. The interference pattern in this case may be unambiguously connected with the crystallographic and electronic structure. It is therefore important that Mössbauer diffraction from single-crystal scatterers should be considered.

An analysis of interference effects on scattering by single crystals can be carried out in a similar manner to the above consideration of scattering from an isolated atom. The observed pattern is a sum of the three contributions: Rayleigh scattering, nuclear resonant scattering and interference between Rayleigh and nuclear scattering. The reader interested in Rayleigh scattering from single crystals is referred to textbooks and numerous monographs on X-ray diffraction. In addition, there are reviews, e.g. [2.5] and a monograph on coherent Rayleigh scattering of Mössbauer radiation [2.21]. We restrict ourselves here to a note on the fact that the scattering from crystals requires that the structure factors be used instead of the atomic form factors and that the absorption of the scattered radiation should be always taken into account. A correct estimation of the contribution by Rayleigh scattering to the total intensity of the scattered radiation is important when attempting to find the optimum geometry for the scattering of relatively hard radiations.

The detection of Rayleigh scattering of Mössbauer radiation enables samples which do not contain resonant nuclei to be studied. For this purpose a Mössbauer absorber must be placed between the scatterer and the detector. The absorber then serves as an analyser of the scattered radiation. The elastic Rayleigh scattering amplitude can be evaluated by measuring the difference between the intensities at a velocity corresponding to the isomer shift of the source relative to the analyzer, and the intensities at a very large velocity.

The measurement of a continuous velocity scanning experiment enables the Mössbauer spectrum to be obtained which provides more information about the sample. Detecting elastically and inelastically scattered γ -quanta with a resolution of ~ $10^{-7} - 10^{-9}$ eV allows the study of the effect of the low energy phonons on scattering. Experiments on thermal neutrons scattering require an energy resolution of better then 10^{-6} eV. The

technique is extremely convenient for studies of phase transitions, ordering phenomena, and dynamic effects, including diffusion. The angular dependence of the intensity of the elastically scattered radiation provides information on the static radial distribution function, and the inelastically scattered radiation gives information on diffusion and thermal motion.

Let us consider now coherent resonant scattering by single crystals [2.22,23]. The interaction of the scattered radiation with the sample material has a significant influence on the shape of the spectrum. The observed pattern will be a result of the competing resonant absorption and coherent scattering processes. The resonant absorption cross section in a monatomic scatterer is determined by the forward coherent elastic scattering amplitude, i.e. for $\underline{k}_0 = \underline{k}_f$

$$\sigma_{a}(E) = -\frac{4}{k_{0}} J_{m} \boldsymbol{F}_{coh} (\underline{k}_{0} = \underline{k}_{f}) = a\sigma_{0} f' L(E) . \qquad (2.46)$$

 F_{coh} has been taken from equation (2.43) which was derived for an isolated scattering atom. This is fairly well justified for a polycrystalline scatterer. For a single-crystal scatterer, scattering by other atoms must be taken into account. Inserting the F_{coh} amplitude corresponding to the scattering by one atom into (2.46) when \underline{k}_0 is within a Bragg angle results in an underestimation of the total scattering cross section.

The coherent resonant scattering amplitude determines the scattering cross section. To obtain it, the squared F_{coh} modulus must be calculated, integrated over all angles and then summed over all polarizations

$$\sigma_{coh}(E) = a^2 \frac{\sigma_0}{3} \frac{1}{1+\alpha} \frac{2I_e + 1}{2I_q + 1} f'^2 L(E) = p\sigma_a(E) .$$

The p-factor, which determines the cross section ratio for the competing processes, is always less than unity. Thus, for example, for an α -⁵⁷Fe scatterer the coherent scattering cross section is less than 2 % of the total resonant scattering cross section. Using the results obtained above, it is easy to find the total differential resonant (elastic and inelastic) scattering cross section of γ -rays. If there are no diffraction effects on scattering, then

 $\frac{d\sigma_r(E)}{d\omega}\!=\!\frac{\sigma_a(E)}{4\pi}\frac{1}{1\!+\!\alpha}~.$

Resonant absorption leads to the incident radiation reaching deeper layers of the scatterer to have a different spectral composition. To evaluate the radiation intensity which is elastically scattered by an isotropic sample of thickness d, one should use an expression of the following type:

$$I(S) = \int_{-\infty}^{\infty} \int_{0}^{d} J(E,S) \ F(E,S,x) \ dE \ dx \ , (2.47)$$

where a change of the spectral composition of the incident and scattered radiation is taken into account using a certain function F(E,S,x). For J(E,S) expression (2.44) may be used. On diffraction the expression for the spectral shape is significantly more complicated and in the case of interference between the resonant scattering and Rayleigh scattering the spectrum is generally a combination of peaks (intensity maxima) and dips (intensity minima).

The directions of Mössbauer diffraction, when the hyperfine splitting is absent, coincide generally with the θ_{hkl} directions of Rayleigh coherent scattering. However, the angular dependence of diffraction line intensities from nuclear scattering and Rayleigh scattering are different. Since the Debye-Waller factor decreases with the scattering angle it is necessary to use large scattering angles in order to increase the contribution of nuclear diffraction to the total spectrum. Sometimes, when there are several atoms in a unit cell, the Rayleigh scattering amplitudes from the atoms in the unit cell may compensate each other. This has made it possible to observe for the first time the pure Mössbauer diffraction from the (080) plane in a single crystal of potassium ferrocyanide K_4^{57} Fe(CN)₆·3H₂O [2.14]. Since the Rayleigh scattering amplitude from other atoms of the unit cell, a Bragg peak is observed at resonance whereas there is no peak at positions far from resonance.

When the hyperfine splitting is present the diffraction pattern caused by resonant scattering is substantially complicated. The line intensities of Mössbauer scattering then manifest an azimuthal dependence in contrast to Rayleigh scattering. The polarization of a scattered γ -ray is then determined not by scattering angle as in Rayleigh scattering, but by the mutual orientation of the axes system for the hyperfine interactions and \underline{k}_{f} . Thus the coherent resonant scattering by nuclei, whose hyperfine interaction axes' orientations are different, leads to a different polarization. The interference of the waves with these different polarizations within a unit cell gives spectra which contain information on structure, both the hyperfine interaction axes orientation, and the relative positions of nuclei in the unit cell. The azimuthal dependence leads to the necessity of using structure matrices [2.11] instead of the scalar scattering amplitudes (see (2.41, 43)) for the analysis of scattering by a unit cell in terms of polarization transformations.

The periodic repeat of lattices and numbers of resonant atoms which give rise to scattering and diffraction lines may give different effects in resonant and Rayleigh scattering. The scattering by a magnetic sublattice in a simple antiferromagnetic with the spins up means that the nuclei of another sublattice do not participate in the coherent scattering. When the nuclear level degeneracy is completely lifted as a result of a magnetic dipole interaction the purely nuclear maxima resulting from Mössbauer diffraction may be detected. This has been observed by SMIRNOV et al. [2.24] for an antiferromagnetic haematite crystal - α -⁵⁷Fe₂O₃ during investigations of diffraction in the [111] direction. Although the unit cells of the magnetic and crystallographic structure coincide for this case, the symmetry of the unit cell is such that the total Rayleigh scattering amplitude for the ((2n + 1)(2n + 1)(2n + 1)) reflections becomes zero. Magnetic fields at the iron atoms are not parallel. Only one of the spin subsystems participates in the coherent scattering of the quantum and there is no cancellation of the scattering amplitudes. This leads to the observation of pure nuclear diffraction maxima. Some works have reported a purely nuclear diffraction in scatterers when only guadrupole splitting is present. For example [2.25] studies of the diffraction of the ¹²⁵Te Mössbauer radiation by a Te single crystal have enabled the observation of pure nuclear reflections (001) and (002) which are caused by electric quadrupole interactions in the scatterer.

The Mössbauer lines are fairly symmetric when pure nuclear diffraction due to the absence of interference with Rayleigh scattering occurs. Nevertheless, thorough analysis of Mössbauer lines at the ((2n + 1)(2n + 1)(2n + 1)) reflections from an α -Fe₂O₃ single-crystal (a = 85 %, mosaicity ~ 30") has shown that a dispersion term caused by interference of scattering from various components of the hyperfine structure can be separated [2.26]. For the (999) reflection,the line asymmetry of the central lines of the spectra (i.e. the ratio of the dispersion curve amplitude to the line amplitude) is approximately 5 %. The value of the interference term decreases rapidly with the distance between the resonances, which is about $30\Gamma_{nat}$ even for the central lines of haematite. However, the high sensitivity of the resonance line shape, measured under pure nuclear diffraction conditions, allows the detection of such a small interference effect.

The nuclear transition energies in spin sublattices of a crystal may happen to be close. This leads to a complex interference pattern. Thus, for example, in Fe₃BO₆ the γ -transition energies in ferric ions in 4c and 8d positions are close and, as a result, the first line of the spectrum obtained at the (1100) reflection is split [2.27].

The most complex spectral shapes are observed when the interference occurs between Rayleigh and nuclear scattering from single crystals at Bragg angles. The coherent elastic scattering amplitude from all atoms and resonant nuclei may be considered as a sum of the amplitudes of elastic scattering from each of them if the corresponding phase shifts are taken into account. An idea of the Mössbauer spectrum from a monatomic substance in the absence of both the hyperfine splitting and resonant absorption is given by the following expression which is obtained from Born's approximation [2.15]

$$I(S) \sim \left\{ \frac{2 N^2 a^2 f_1 f_2}{S^2 + 4} + A^2 f_R + \frac{2 a N C A S \sqrt{f_1 f_2 f_R}}{S^2 + 4} \right\}$$
$$\sum_{n m} \sum_{m} \exp \left\{ i (\underline{k}_0 - \underline{k}_f) (\underline{r}_n - \underline{r}_m) \right\} , \qquad (2.48)$$

where \underline{r}_n , \underline{r}_m are the atom positions in the lattice. The second factor of the right-hand part (cf.(2.44)) shows that the scatterer is a crystal. Bragg peaks are observed in the directions for which the condition $\underline{k}_0 - \underline{k}_f = \underline{\tau}$ holds (τ , the reciprocal lattice vector). In an idealized case of diffraction of Mössbauer radiation from a perfect crystal, the γ -quanta should be elastically scattered only in those directions; in all other directions the intensities will be quenched due to coherence of the processes involved. A change of the incident and scattering angles by several minutes may lead to a sharp change in intensity of the scattered radiation. Under these conditions the angular dependence of the first factor in (2.48) may be neglected.

The experimental investigation of the shape of Mössbauer spectra on diffraction requires that the F_r values be changed, as well as ratios of the elastic nuclear scattering amplitude to the elastic Rayleigh scattering amplitude $\xi = F_r / F_R$; and the resonant absorption cross section. The F_r value can be increased by lowering the temperature, but under such conditions the resonant absorption is also significantly changed. The elastic Rayleigh scattering amplitude can be decreased (and thereby the ξ parameter value increased), by using higher-order reflections. Thus, for example, the reflection of the 23.8 keV Mössbauer radiation from a source of ^{119m}SnO₂ from the (020) plane of a tin single-crystal film (a = 88 %) gives rise to a typical diffraction peak (see Fig.2.12) [2.28], $F_R = 1.15 \ 10^{-11}$ cm. At room temperature $\xi = 0.45$, and the Mössbauer

spectrum obtained on diffraction at an angle of 5°7' is given in Fig.2.13. Lowering the temperature to 110 K results in the increase of the ξ value by a factor of ~ 7 due to the sharp increase of the f' factor. Further lowering of the temperature leads to an insignificant increase of the ξ parameter, but causes the resonant absorption to play a greater role. An increase in the contribution of the resonant channel without changing the resonant absorption cross section was achieved by using higher-order reflections from the (020) plane (see Fig.2.13).

The appearance in the Mössbauer spectrum of a dip instead of a peak may in the first instance be associated with resonant absorption which leads to a sharp reduction of the penetration depth where Rayleigh scattering occurs. A smaller value of ξ also favours the appearance of dips in the Mössbauer spectrum. To observe peaks, the ξ parameter should be sufficiently large (i.e. more than 6, see [2.28]).

Mössbauer spectra, corresponding to Bragg reflections, are significantly complicated if the hyperfine splitting is present. The interference of differently polarized waves may be weakened by polarization factors and this depends on the additional polarization phase shift [2.11]. These features of Mössbauer spectra were demonstrated by observation of the (2n 2n 2n) reflections from a haematite single crystal [2.29], but not the ((2n + 1)(2n + 1)(2n + 1)) reflections, where coherent Rayleigh scattering is absent [2.24]. The Mössbauer spectra were classified into three groups: asymmetric peaks at the (101010) and (888) reflections; asymmetric dips at the (444) reflection, and dispersion-like curves at the (666) and (222) reflections.



Fig.2.12 Angular dependence of the 23.8 keV γ -radiation intensity scattered by a single crystal tin film 5 μ m thick.

Dips were observed when Rayleigh scattering was dominant, peaks when the Mössbauer scattering dominated, and dispersion-like



Fig.2.13 Mössbauer diffraction spectrum from a mosaic single crystal of tin (a = 88 %, d = 5 μ m) [2.28] : solid circles - T = 293 K, the (020) reflection; open circles - T = 110 K, the (020) reflection; crosses - T = 110 K, the (040) reflection; triangles - T = 110 K, the (060) reflection. The curves have been calculated assuming a mosaic structure of the crystal and are normalized at v = - 6.7 mm/s.

curves were associated with interference when $F_r \approx F_R$. At certain scattering angles the phase relationships on scattering from the unit cell may be such that, unlike scattering by a single atom or by a polycrystalline foil [2.19], the interference between Rayleigh and nuclear resonant scattering is constructive for incident energies below resonance and destructive above resonance.

The interference of the elastically scattered radiation gives rise to a mirror reflected wave. The mirror scattered wave intensity becomes significant when the angle of incidence is less than the angle of total reflection - γ_{cr} . This is discussed later in Sec.2.5 where the total reflection of Mössbauer radiation applied for thin surface layer studies is considered.

The diffraction effects are observed when the incident beam of γ -quanta is strongly collimated such that the divergence angle is usually not more than 20". This considerably lowers the radiation intensity and requires long exposures to record statistically reliable spectra. No considerable decrease in the intensities of the scattered radiation is usually observed on departure from Bragg angles. There are many reasons

for that. Not all resonantly scattered radiation is coherent, even for scattering by a single atom. Indeed, if the ground-state spin is not zero the nucleus may, after scattering, be in some other spin state and coherence is lost despite there being no energy loss due to recoil (see Table 2.4). If it is also assumed that a magnetic field H_{eff} causes the levels with spins I_e, I_g to split, then the recoilless resonant scattering of γ -quanta, which is followed by a change of the spin state, is an inelastic (or energy-shifted) and an uncoherent process. The nuclear transition of multipolarity M1 from the ground state with m_g = +1/2, into an excited state with m_g = +1/2, may be followed by the elastic transition into the initial state with m_g = +1/2, or by the inelastic one into the state with m_g = - 1/2 (see Fig.1.3).

The diffraction peaks are significantly influenced by the isotopic abundance and for scatterers with a low enrichment of the resonant isotope an isotopic incoherence results since $\sigma_{coh} \sim a^2$. For ordinary iron $a^2 \approx 5 \ 10^{-4}$. Spin incoherency also reduces the effects related to nuclear diffraction.

Each resonantly scattered γ -quanta may have a coherent counterpart in Rayleigh inelastic scattering which occurs with a probability $f(1 - f_R)$. For this coherence to be realized it is initially necessary that the lattice be in the same state after each of the processes. The total contribution of coherent inelastic scattering also depends on temperature. The contribution is small and may be considered as a second-order process relative to elastic scattering. A contribution to the intensity registered at a Bragg angle by the source recoil radiation arises if elastical scattering resulting from Rayleigh scattering occurs. Incoherent scattering (elastic and inelastic) does not cause any interference effects since it only appears in the background.

To summarize, two physical problems which have been studied in detail due to the progress in nuclear diffraction of Mössbauer radiation must be considered. Firstly, it is dynamical diffraction of Mössbauer radiation. The dynamical theory of Bragg reflection predicts that the reflectivity of a perfect crystal reaches nearly unity within a small angular region around the exact Bragg angle. The width and absolute position of this region is determined primarily by the real part of the scattering amplitude . The existence of the total reflection region near exact Bragg angle results in a broadeing of the effective energy width of the resonance. This occurs because, for a plane wave at the Bragg angle, the reflectivity is always high, even if the range of reflection is small. The energy broadening is significant and of the same order as the splitting of the multiplet [2.30].

At first dynamical diffraction of resonant radiation has been only studied in forward directions. Backward reflections are much weaker than forward reflections in the case of

electronic scattering, because the spatial extension of the atomic shell causes a loss of coherency at large scattering angles. Nuclear resonant scattering, by contrast, is not affected by such a spatial incoherence, and strong reflections are also expected here in backward scattering. Back-reflections in Bragg geometry offer in addition an essential practical advantage: the cross section off the beam accepted by the crystals is usually much larger in the back-reflection geometry than for the forward reflections. Characteristic features of resonant dynamical diffraction appeared in the Mössbauer spectrum of the reflection (3311) from ⁵⁷FeBO₃ measured with a high angular resolution [2.31]. A considerable broadening of the resonance peaks and interference between the hyperfine transitions were observed.

Secondly, the suppression of inelastic scattering channels requires attention. The effect is the nuclear resonant analogue of the Borman effect and is realized when a thick perfect crystal containing Mössbauer nuclei is set up at a diffraction angle and the transmittance of the crystal increases when the source velocity is such that the system is brought into resonance. The problem is reviewed in [2.22, 23].

Considerable interest in pure nuclear back-reflections arises also from possible applications in γ -optical devices, such as the filtering of Mössbauer radiation from the white spectrum of synchrotron radiation [2.31 - 35]. The observation of nuclear resonant diffraction of synchrotron radiation has opened a new field of experiments with sub-ieV beams of high brilliance. The use of pure nuclear back-reflections (with almost total reflectivity in an angular region of 10" - 20") as a pre-monochromator allows more Mössbauer radiation to be extracted from the synchrotron beam. Filtered X-ray beams with extremely narrow band width ($10^{-6} - 10^{-8}$ eV) and small angular width (0.4 arc sec) have been obtained from the synchrotron radiation continuum. Progress in this technique has made it feasible to produce diffracted γ -quanta with intensities unattainable from conventional Mössbauer sources [2.32], thereby increasing interest in hyperfine spectroscopy.

Previously, the nuclear resonance of ⁵⁷Fe at 14.4 keV was used for pure nuclear Bragg reflection from highly enriched single crystals. Yttrium iron garnet and iron borate are well known examples. In 1990, it was shown that enriched epitaxial crystals provided an alternative to the use of large amounts of expensive bulk isotope for monochromating synchrotron X-ray beams to sub-µeV bandwidths. Later the measurement of coherent nuclear diffraction of synchrotron radiation from grazing- incidence antireflection films (GIAR films) containing ⁵⁷Fe showed that nuclear resonant filtering by the films was possible.

At present, resonant beams of a few hundreds of photon/sec have been obtained using synchrotron radiation. By optimizing the diffraction techniques and using more intense primary beams expected from undulators in future synchrotron light sources, it is anticipated that beams about 10⁵ photons/sec will be obtained [2.33].

This new technique promises to become a powerful tool not only for hyperfine spectroscopy but also for γ -optical experiments. The standard experiment in the future will be the time-resolved observation of forward scattering from a polycrystalline target instead of the pure nuclear reflection from a single crystal which has been used to date. Using the time of excitation, which is known precisely and the spectrum of the delayed resonant quanta from the sample, the hyperfine interaction parameters may be determined within a few hours, even with resonant counting rates of only 1 Hz [2.34].

The use of synchrotron radiation may allow the Mössbauer effect to be observed in new isotopes. Such isotopes would need low-energy excited nuclear levels but need not have appropriate parent nuclei and hence they are not given in Table 1.1.

Additionally, this technique may be especially promising for magnetic field and EFG structure studies in crystals [2.35], and the measurement of the total external reflection of sub- μ eV beams of high brilliance may be useful in the analysis of near surface layers (see subcec. 2.5 and 3.8).