MOSSBAUER SPECTRUM ASYMMETRY RESULTING FROM ANISOTROPIC DIFFUSION

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It is shown that anisotropy of the diffusion of Mossbauer atoms can lead under definite conditions to a new type of asymmetry of polycrystalline samples whose γ-resonant spectra have a hyperfine structure (hfs), namely, to different widths of the hfs components.

In experiments with polycrystalline samples whose γ-resonance spectra have quadrupole or magnetic splitting, one frequently observes asymmetry of the hfs line intensity. This asymmetry is either connected with the anisotropy of the Debye-Waller factor in the corresponding single crystals [1, 2], or is due to relaxation [3]. In this communication we wish to call attention to another type of asymmetry that can occur in the γ-resonance spectra of polycrystalline samples in many systems in which the Mossbauer atom executes anisotropic diffusion motion, namely, a difference in the broadening of the quadrupole doublet lines or of the magnetic hfs components.

The experimental shape of the γ-resonance line is described in the case of diffusion by the expression [4]

$$\sigma(S) = \frac{\sigma_0 \Gamma f f'}{2} \frac{\Gamma + \Delta E}{S^2 + (\Gamma + \Delta E)^2} = f'\sigma(E, \Delta E), \qquad (1)$$

where σ_0 is the cross section at resonance, f and f' are the recoilless emission and absorption probabilities for the source and absorber, $S = vE_0/c$, v is the velocity of the source relative to the absorber, c is the speed of light, Γ is the natural half-width of the line with energy E_0, and $2\Delta E$ is the line broadening due to the diffusion motion.

For continuous isotropic diffusion we have $\Delta E = \hbar k^2 D$ [4], where $\vec{k}$ is the wave vector of the γ quantum, D is the diffusion coefficient, and $\hbar$ is Planck's constant divided by 2π. For jumplike diffusion, the broadening depends on the orientation of the vector $\vec{k}$ relative to the crystallographic axes and on the mechanism of the diffusion motion [4, 5].

In the case of diffusion anisotropy of any type, the diffusion coefficients D(ρ) of Mossbauer atoms, at arbitrary angle ρ to the direction of the γ-quantum beam, turn out, for single crystals, to depend on the angles θ_i between the γ-quantum beam and the crystallographic axes. Thus, the orientation dependence of the line broadening enters in the resonant-absorption cross section via the parameter ΔE. For an individual single crystal, the absorption line shape should be described by expressions of the type

$$f'(\theta_i)\sigma[E, \Delta E(\theta_i)]I(\theta_i),\qquad(2)$$

where $f'(\theta_i)$ is the Debye-Waller factor, $\sigma[E, \Delta E(\theta_i)]$ is determined by an expression of the type (1), and $I(\theta_i)$ are the intensities of the individual components of the quadrupole doublet or of the magnetic hfs.

In practice, for many reasons, one deals mainly with polycrystalline samples, for which the absorption line contour is obtained after averaging expressions (2) over all the spatial positions of the individual single crystals. Such an averaging can lead to different shapes and widths of the spectral lines, owing to the difference between the angular dependences of $I(\theta_i)$ for different hfs components.

Let us explain this reasoning with a simple example. Assume we have a certain surface, and let the diffusion occur only over this surface. We consider the shape and intensity of the quadrupole-doublet lines for an individual plane, and then for a polycrystalline sample but with different orienting action of the surface on the electric field gradient (EFG) plane ($\vec{q}$). We assume that the z axis is perpendicular to the plane in question, and θ is the angle between the beam of the γ quanta and the z axis.

I. Fixed angle between the EFG axis and the surface.

a) For example, q is parallel to z (Fig. 1a). Then the shapes of the π and σ lines for the given surface are determined by the expressions

$$\sigma_\pi(E, \theta) \sim f'(\theta)\sigma[E, \Delta E(\theta)]I_\pi(\theta); \quad I_\pi = \frac{3}{2}(1 + \cos^2\theta)$$

$$\sigma_\sigma(E, \theta) \sim f'(\theta)\sigma[E, \Delta E(\theta)]I_\sigma(\theta); \quad I_\sigma = 1 + \frac{3}{2}\sin^2\theta.\qquad(3)$$

It is obvious that the broadenings of the π and σ lines are equal, but are functions of the angle θ, i.e., $\Delta E_\pi(\theta) = \Delta E_\sigma(\theta)$. We note that the ratio $A = f'I_\pi/fI_\sigma$ of the intensities of these lines is also independent of θ. For a polycrystalline sample, averaging of expressions (3) over θ leads in this case to unequal broadenings of the π and σ lines, owing to the different angular dependences of $I_\pi(\theta)$ and $I_\sigma(\theta)$, i.e., $\overline{\Delta E_\pi} \neq \overline{\Delta E_\sigma}$.
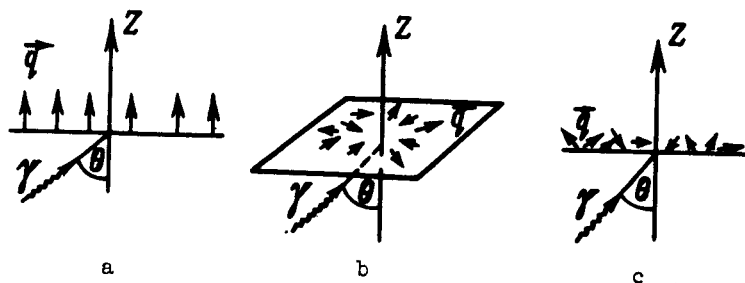

Fig. 1. Schematic representation of different orientations of the EFG axes ($\vec{q}$) on the surface element.

b) The axis $\vec{q}$ lies in the plane in question, but its direction relative to the x and y axes is arbitrary (Fig. 1b). It is easy to verify that in this case $\Delta E_\pi(\theta)$ and $\Delta E_\sigma(\theta)$, and the parameter A is also a function of the angle θ, but of different form than in the variant (a). Consequently, a polycrystalline sample is again characterized by unequal broadening of the π and σ lines, but different from the broadening in (a).

II. The EFG axes are not fixed in any way relative to the surface (Fig. 1c), i.e., their directions have a spherically symmetrical distribution. Although in this case we have as before $\Delta E_\pi(\theta) = \Delta E_\sigma(\theta)$, now the ratio of the intensities of the π and σ lines does not depend on θ. An obvious consequence of this is the equal broadening of the π and σ lines in polycrystalline samples, i.e., $\overline{\Delta E_\pi} = \overline{\Delta E_\sigma}$. Thus, in spite of the fact that in our cases we deal with the same type of anisotropic diffusion motion (surface diffusion), the character of the orientation of the molecules on the surface leads to an essential difference in the shapes of the γ-resonance spectra. A similar analysis is possible, of course, also for anisotropic three-dimensional diffusion, both continuous and jumplike. An analysis of the different variants leads to the following general conclusion: If the anisotropy of the diffusion of the Mossbauer atoms and the anisotropy of the distribution of the axes of the EFG or H acting on these atoms are combined in the structural units of the investigated system (e.g., inside single crystals or on some plane surfaces), then different broadenings of the components of the quadrupole doublets or of the magnetic hfs will occur in an isotropic set of such structural units (e.g., in polycrystalline powders or in absorbents with extensively developed surfaces). An important particular cause of the different broadenings of the hfs components of the Mossbauer spectra is the occurrence of a definite orientation of the EFG or of H in the field of external forces causing the anisotropic diffusion. Thus, the anisotropy of the diffusion can become manifest in different broadenings of the components of the quadrupole or magnetic hfs of the spectra, just as anisotropy of the Debye-Waller factor leads to asymmetry in the intensities of these components.

In conclusion, let us consider the case Ia in greater detail. If the diffusion is continuous, the absorption line shape of an individual plane is described by expression (1) with $\Delta E = \hbar k^2 \sin^2\theta$. The contours of the π and σ lines for polycrystalline samples can then be written in the form

$$\overline{\sigma}_{\pi,\sigma}(S) = \int \sigma(S,\theta) I_{\pi,\sigma}(\theta)\, d\Omega = \sigma_0 \Gamma f_\pi \exp\left(-\frac{\overline{x_\perp^2}}{\overline{\lambda^2}}\right)$$

$$\times \int_0^\pi \exp\left(-\frac{\overline{x_\parallel^2} - \overline{x_\perp^2}}{\overline{\lambda^2}}\cos^2\theta\right)$$

$$\times \frac{\Gamma + \hbar k^2 D \sin^2\theta}{s^2 + (\Gamma + \hbar k^2 D \sin^2\theta)^2} I_{\pi,\sigma}(\theta)\sin\theta\, d\theta, \qquad (4)$$

where $\overline{x_\parallel^2}$ and $\overline{x_\perp^2}$ are the rms displacements of the atoms along and across the axes of the electric-field gradients, and λ is the γ-quantum wavelength divided by 2π. By way of example, the line shapes at $\hbar k^2 D = 4\Gamma$ and at different values of the parameter $(\overline{x_\parallel^2} - \overline{x_\perp^2})/\overline{\lambda^2}$ were calculated from the presented formulas. The results are shown in Fig. 2, from which we see that there exists a region where the difference between
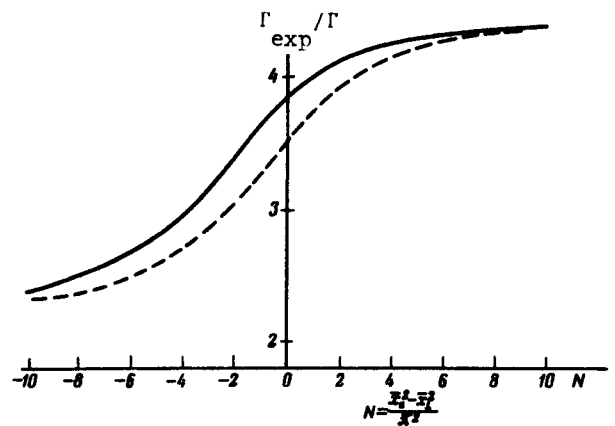

Fig. 2. Dependence of the widths of the quadrupole doublet lines π and σ (in relative units) on the parameter $N = (\overline{x_\parallel^2} - \overline{x_\perp^2})/\overline{\lambda^2}$: solid – for the π line, dashed – for σ line.

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the broadening of the π and σ lines is large.

The phenomenon considered here may be useful for a number of applications of γ-resonance spectroscopy: in the study of the diffusion of surface atoms, motion in zeolite channels, Brownian motion of nonspherical particles in liquids, diffusion of protein globules, and in a number of other cases. In addition, it should be taken into consideration in the calculation of the diffusion coefficients in such systems from the experimental spectra.

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