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POLARIZATION PHENOMENA, ABSOLUTE PROBABILITIES, AND ANISOTROPY OF THE MÖSSBAUER EFFECT IN SIDERITE

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Experiments similar to optical polarization investigations were carried out on Fe^{57} Mössbauer γ quanta. Uniaxial single crystals of siderite, $FeCO_3$, were used as the polarizer and analyzer. It was found that the asymmetry of the two peaks of quadrupole doublets depended on the azimuthal angle (α) of rotation of the crystal axis of the analyzer relative to the polarizer. This dependence was used to determine the absolute probability f′ of the Mössbauer effect in $FeCO_3$ at room temperature when the orientation of the crystal axis of siderite relative to the beam of γ quanta was $\theta = 90°$. The probabilities of the Mössbauer effect f′ for θ = 15, 30, 45, and 90° were determined also from the asymmetry of the doublets and from the total area under both peaks in the γ-resonance absorption spectra.

HOUSLEY, Gonser, and Grant[1] demonstrated that polarization phenomena must be taken into account in investigations of the resonance absorption of γ quanta by single crystals with non-zero values of the electric field gradient at the nuclei. We used the Mössbauer effect to observe the polarization of γ quanta by a uniaxial crystal of siderite ($FeCO_3$), i.e., a phenomenon similar to the polarization of visible light by crystals of quartz or Iceland spar. The polarization of γ quanta was manifested by a change in the ratio of the amplitudes of the quadrupole doublet lines ($A = I_\pi/I_\sigma$) caused by a change in the azimuthal angle α between the C axes of the electric field gradient in two single crystals of $FeCO_3$, one of which acted as the polarizer and the other as the analyzer of γ rays.

The polarization was observed using natural single crystals of siderite, 120 ± 10 μ thick, with the C axis lying in the plane of the crystal. The angle of incidence of γ quanta was $\theta = 90°$ with respect to the plane of the crystal. Figure 1 shows, by way of example, the $\theta = 90°$ absorption spectra of two $FeCO_3$ single crystals of the same thickness; these spectra were recorded using parallel ($\alpha = 0$) and perpendicular ($\alpha = 90°$) orientations of the C axes. Figure 2 shows the dependences of $A = I_\pi/I_\sigma$ on the azimuthal angle α.

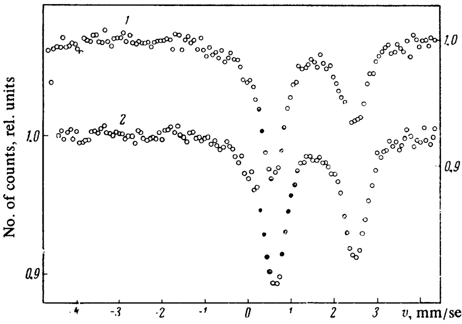

FIG. 1. Mössbauer spectra of two single crystals of siderite for azimuthal angles of $\alpha = 0$ (curve 1) and $\alpha = 90°$ (curve 2). The angle between the direction of the γ-ray beam (Co^{57} source in Cr) and the C axis of both single crystals was $\theta = 90°$ (T = 300°K). The thickness of each crystal was 120 ± 10 μ.

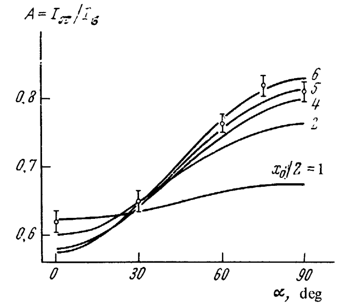

FIG. 2. Experimentally obtained and calculated dependences of the quantities $A = I_\pi/I_\sigma$ on the azimuthal angle α, obtained for single crystals of siderite for $\theta = 90°$ and different values of $x_0/2 = na\sigma_0f'$.

For an unpolarized primary beam of γ quanta the ratio of the amplitudes of the quadrupole doublet lines, due to π ($\pm 3/2 \rightarrow \pm 1/2$) and σ ($\pm 1/2 \rightarrow \pm 1/2$) transitions (for $\theta = 90°$), is given by

$$A = \frac{I_\pi}{I_\sigma} = \frac{a^\pi \cos^2\alpha + b^\pi \sin^2\alpha}{a^\sigma \cos^2\alpha + b^\sigma \sin^2\alpha}, \tag{1}$$

where $a^{\pi,\sigma}$ represents the contribution, to the amplitudes of the π and σ components, of the absorption (in the polarizer and analyzer) of the γ quanta polarized along the C axis; $b^{\pi,\sigma}$ is the corresponding contribution of the quanta polarized normally to the C axis. Moreover,

$$a^{\pi,\sigma} \backsim \Big[K\Big(\frac{C^{\pi,}_{A_{11}}}{2}\Big) + K(C_S) - K\Big(\frac{C^{\pi,\sigma}_{A_{11}}}{2} + C_S\Big) + K'\frac{C^{\pi,\sigma}_{A_{22}}}{2}\Big) + K(C_S) - K'\frac{C^{\pi.\sigma}_{A_{22}}}{2} + C_S\Big)\Big], \tag{2}$$

$$b^{\pi,\sigma} \backsim 2\Big[K\Big(\frac{C^{\pi,}_{A_{12}}}{2}\Big) + K(C_S) - K\Big(\frac{C^{\pi,}_{A_{12}}}{2} + C_S\Big), \tag{2'}$$

where $K(\kappa) = \kappa e^{-\kappa/2}[I_0(\kappa/2) + I_1(\kappa/2)]$; I_0, I_1 are the zeroth- and first-order Bessel functions of an imaginary argument; C_S is the effective dimensionless thickness of the radiation source, equal to $n_Saf\sigma_0$,

$$C^\pi_{A_{11}} = {}^3/_2\,x_0, \quad C^\pi_{A_{22}} = 0, \quad C^\pi_{A_{12}} = {}^3/_4\,x_0,$$

$$C_{A_{11}} = {}^1/_2\,x_0, \quad C^\sigma_{A_{22}} = 2x_0, \quad C^\sigma_{A_{12}} = {}^5/_4\,x_0,$$

and $x_0 = 2naf'\sigma_0$, where n is the number of iron nuclei per 1 cm² of one crystal.

An expression similar to Eq. (1) can be derived also for the ratio of the areas of the two peaks of a quadrupole doublet. However, in this case the expressions for $a^{\pi,\sigma}$ and $b^{\pi,\sigma}$ are different:

$$a^{\pi,\sigma} \infty [K(C_{A_{11}}^{\pi,\sigma}/2) + K(C_{A_{22}}^{\pi,\sigma}/2)], \tag{3}$$

$$b^{\pi,\sigma} \infty 2[K(C_{A_{12}}^{\pi,\sigma}/2)]. \tag{3'}$$

The expressions (2) and (2′), (3) and (3′) are derived on the basis of the results reported in[2] and they are valid, in the form given here, when the polarizer and analyzer have the same thickness. It follows from Eqs. (1), (3), and (3′) that a comparison of the experimental data with the theory can be used to determine directly the value of x_0, whereas in the case of Eqs. (1), (2), and (2′), we also have to know the value of C_S. However, an analysis of Eqs. (1), (2), and (2′) and of Eqs. (1), (3), and (3′) shows that the ratio of the amplitudes of the lines is a more sensitive function of the effective thickness of the crystals and of the angle α than the ratio of the areas of the two peaks of a quadrupole doublet. Moreover, an experimental determination of the ratio of the areas under the peaks is less accurate than a measurement of the ratio of the amplitudes because, in the former case, we have to make precise allowance for the profiles and widths of the lines in the spectrum and to resolve the spectrum into the π and σ components.

Therefore, we compared the theory with the experimental results on the polarization using the measured values of the ratio of the line amplitudes.

The value of C_S was determined as follows. We investigated the dependence of the total area under the two peaks in the spectrum of polycrystalline iron oxalate (FeC_2O_4) on the thickness of the sample. It can be shown that the relationship between the total area under the peaks (S_{exp}) and the probability of resonance absorption (f′) is given by the following expression (in the case of quadrupole splitting and identical peaks):

$$S_{\text{exp}} = \frac{\pi\Gamma f}{1+\beta\mathscr{E}} K\left(\frac{C_A}{2}\right)\left\{1 - \frac{2K(C_A/2) - K(C_A)}{2K(C_A/2)} \frac{1}{1+(\Delta/\varkappa)^2}\right\}, \tag{4}$$

where $\varkappa$ is the experimental value of the line width; Γ is the natural line width; f is the probability of resonance emission of a γ quantum without recoil; β is the ratio of the background intensity of γ radiation to the intensity of the resonance (14.4 keV) radiation in the primary beam $\mathscr{E} = \exp\sum_i \sigma_{ph}^i n_i$; σ_{ph}^i is the photoeffect cross section of nuclei of an i-th type; n_i is the number of nuclei of the i-th type per 1 cm² of a sample; Δ is the quadrupole splitting; C_A is the effective thickness of the absorber (in units of x_0).

In the case of iron oxalate we can ignore the second term in Eq. (4) since $\Delta/\varkappa$ is very large. The value of f′ for FeC_2O_4 is known[1][3] and is equal to 0.275.

A comparison of the obtained experimental data with Eq. (4) allows us to find the values of f and β. Figure 3 shows the experimentally obtained and the calculated dependences of the ratio $S_{exp}/\pi\Gamma$ on the thickness of polycrystalline samples of iron oxalate. Curve 5 in Fig. 3 (for FeC_2O_4) yields the values f = 0.62 ± 0.02 and β = 0.10 ± 0.005. A comparison of the experimental and calculated dependences of the amplitude of a quadrupole doublet peak on the thickness of a sample of polycrystalline iron oxalates gives C_S = 6.3 ± 0.5 for the cited values of f and β. The amplitude of the peak is then calculated from the formula

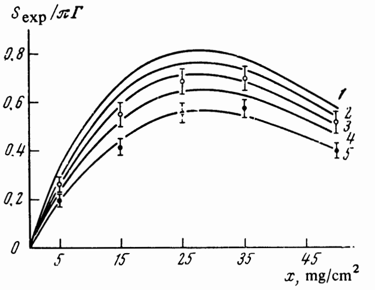

FIG. 3. Experimental data and calculated dependences of the total area under both peaks in Mössbauer spectra $S_{exp}/\pi\Gamma$ on the thickness of polycrystalline samples of FeC_2O_4 (5) and $FeCO_3$ (1–4). The curves for $FeCO_3$ are plotted for f′ = 0.5, 0.45, 0.4, and 0.35 (curves 1, 2, 3, and 4, respectively).

$$I = \frac{f}{1+\beta\mathscr{E}} \frac{K(C_A/2) + K(C_S) - K(C_A/2 + C_S)}{K(C_S)}. \tag{5}$$

Using the obtained value of C_S, we can estimate the expected width of the absorption line using the empirical expression given in[2]. The expected value is $\varkappa$ = 0.36 mm/sec and the experimental value is $\varkappa_{exp}$ = 0.33 ± 0.04 mm/sec. The values of f, β, and C_S just obtained can be used to determine the value of f′ for siderite on the basis of polarization experiments on single crystals. The value of f′ found in this way is 0.44 ± 0.05 for θ = 90° (cf. Fig. 2).

It is interesting to compare the value of f′ found from the polarization experiments with the probability of the effect deduced from the total area under the spectrum and from the value of $A = I_\pi/I_\sigma = \varphi(C_A)$ for various angles θ (as has been done by us in[4]). Figure 3 shows the experimental values of S_{exp} and the calculated curves S for various thicknesses of a polycrystalline sample of siderite $FeCO_3$, deduced from Eq. (4). This comparison of the calculated and experimental data gave f′ = 0.40 ± 0.04 and, moreover, it provided an additional independent confirmation of the values of β (0.1) and f (0.62) deduced from experiments on iron oxalate.[2] Moreover, the values of f′ for single crystals were determined for θ = 90° and θ = 15° from the total area under both absorption peaks. The value of f′ (in terms of C_A) was calculated from the formula

$$\frac{2S_{\text{exp}}}{\pi\Gamma} = \frac{f}{1+\beta\mathscr{E}} \frac{1}{2} \sum_i [K(C_{A_i}^{\pi}) + K(C_{A_i}^{\sigma})]. \tag{6}$$

Here, the summation was carried out over two mutually perpendicular polarizations of γ quanta (parallel and perpendicular to the C axis):

$$C_{A_1}^{\pi} = x_0(1 + a^{\pi})C^{\pi}, \qquad C_{A_2}^{\pi} = x_0(1 - a^{\pi})C^{\pi},$$
$$C_{A_1}^{\sigma} = x_0(1 + a^{\sigma})C^{\sigma}, \qquad C_{A_2}^{\sigma} = x_0(1 - a^{\sigma})C^{\sigma},$$
$$C^{\pi} = [{}^1/_2 + {}^1/_8(3\cos^2\theta - 1)], \qquad C^{\sigma} = [{}^1/_2 - {}^1/_8(3\cos^2\theta - 1)],$$
$$a^{\pi} = \frac{\sin^2\theta}{1 + \cos^2\theta}, \qquad a^{\sigma} = \frac{3\sin^2\theta}{5 - 3\cos^2\theta}.$$

A comparison of the values of S_{exp} calculated using Eq.

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[1] It is reported in [3] that f′ = 0.44. However, when later data on the conversion coefficient of Fe^{57} are used, it is found that the resonance cross section is $\sigma_0 = 2.38 \times 10^{-18}$ cm² and therefore f′ = 0.275.

[2] Integration over the angles taking into account all six values of f′(θ), obtained in the present investigation by three different methods, gave f′ = 0.47 ± 0.05 for a polycrystalline sample.

(6) with those obtained experimentally yielded the values f′ = 0.55 ± 0.05 ($\theta = 15°$) and f′ = 0.47 ± 0.04 ($\theta = 90°$) in good agreement with the polarization data (f′ = 0.44 ± 0.05, $\theta = 90°$).

The values of f′ for θ = 15, 30, and 45° were determined by a method similar to that described in[4], i.e., using the data on the asymmetry of the quadrupole doublets of single crystals for different angles θ and taking into account the polarization.[1] The values of C_A necessary in the determination of f′ were found by comparison of the experimental values of $A = I_\pi/I_\sigma$ with the formula

$$A = \frac{I_\pi}{I_\sigma} = \frac{\sum\limits_i [K(C^\pi_{A_i}) + K(C_S) - K(C^\pi_{A_i} + C_S)]}{\sum\limits_i [K(C^\sigma_{A_i}) + K(C_S) - K(C^\sigma_{A_i} + C_S)]} \qquad (7)$$

assuming that $C_S = 6.3$.

The values found in this way were:

$$f' = 0.64 \pm 0.08 \ (\theta = 15°),$$
$$f' = 0.65 \pm 0.08 \ (\theta = 30°),$$
$$f' = 0.33 \pm 0.25 \ (\theta = 45°).$$

An analysis of the angular dependence of f′ showed that the anisotropy of iron atom vibrations in a crystal of siderite was very weak at room temperature. Our experiments on polycrystalline samples of siderite gave A > 1. In the early series of experiments the values of A exhibited a fairly large scatter and when the siderite powder was carefully dispersed the values of A increased to 1.10–1.15. However, experiments involving variation of the angle θ indicated a dependence A(θ) which showed that these samples had some texture. Therefore, we had to disperse again the paraffin matrix (shavings) containing siderite and then we found that the dependence A(θ) of polycrystalline samples of siderite disappeared but the value of A(90°) decreased to 1.02 ± 0.03.

Preliminary experiments on siderite crystals carried out using various angles and temperatures (T = 90 and 490°K) showed that the anisotropy of the thermal vibrations of iron atoms increased and that $\langle z^2 \rangle < \langle x^2 \rangle$ at T = 90°K and $\langle z^2 \rangle > \langle x^2 \rangle$ at T = 490°K, i.e., an inversion of the anisotropy of vibrations occurred between these temperatures.

These results explain why the room-temperature anisotropy of the thermal vibrations of iron atoms is fairly weak in strongly anisotropic crystals of $FeCO_3$.

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