ASYMMETRY OF QUADRUPOLE-SPLITTING COMPONENTS IN MÖSSBAUER SPECTRA OF SIDERITE SINGLE CRYSTALS AND POLYCRYSTALS

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Submitted August 8, 1967

Zh. Eksp. Teor. Fiz. 54, 78—83 (January, 1968)

Mössbauer absorption spectra of Fe^{57} in single crystals and polycrystals of siderite ($FeCO_3$) are investigated. The intensity ratio of the two quadrupole splitting components in the spectra of polycrystals and single crystals for different orientations of the single crystals with respect to the γ beam is consistent with the explanation of the line-area asymmetry of quadrupolar doublets for polycrystals as due to anisotropy of the Debye-Waller factor in the respective single crystals. The sign (+) of the electric field gradient on the iron nucleus in siderite at 300°K is determined, and also the mean square amplitude of iron atom vibrations along the threefold central axis of siderite (2.0×10^{-18} cm^2) and perpendicular to it (4.5×10^{-18} cm^2). It is shown that the absolute probability of the Mössbauer effect can be evaluated as a function of angle on the basis of the quadrupole splitting asymmetry exhibited by gamma resonance spectra of single crystals.

1. INTRODUCTION

IN our investigations[1,2] of the Mössbauer effect in organic tin compounds we have discovered area-integral asymmetry of the two quadrupole splitting components in the gamma resonance absorption spectra of isotropic polycrystals. In a discussion of these experimental results Karyagin[3] has suggested that the stated effect could be accounted for by anisotropy of the Debye-Waller factor in the corresponding single crystals (see also[1,2,4]). This origin of doublet asymmetry in the spectra of organic tin compounds was confirmed qualitatively in[5]. The same effect was subsequently observed most clearly in iron and tin surface atoms and was used to determine differences[6] and absolute values[7] for the mean square amplitudes of atomic thermal vibrations along and normal to the surfaces of adsorbents. The effect has recently been observed also in the Mössbauer scattering spectra of organic tin polycrystals.[8]

The probability of the Mössbauer effect and the character of doublet asymmetry for single crystals oriented at different angles with respect to the γ beam have not hitherto been compared quantitatively with the area asymmetry of the quadrupolar doublet components in the spectra of the corresponding isotropic polycrystals. We

are here reporting our experiment of this type performed on siderite ($FeCO_3$), which yielded the first quantitative demonstration of the aforementioned effect and also furnished information regarding the dynamics of iron atom motion in siderite crystals.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The siderite crystal possesses rhombohedral symmetry with a 46° rhombohedral angle. The iron ions are situated at the vertices and center of the unit cell and the planar CO_3^{-2} anions are situated on the threefold central axis (Fig. 1).[9] Because of the axial symmetry with respect to the threefold axis the gradient of the electric field acting on the iron nuclei is axially symmetrical (parallel to that axis).[10] Single crystals were cut along the {1010} cleavage plane and were ground to a thickness of 240 μ. X-ray studies revealed a mosaic misalignment of less than one degree, with the threefold axis oriented relative to the single crystal plane surface as shown in Fig. 2.

The specimens of polycrystalline siderite powder contained 30 mg/cm^2 of a natural iron isotope mixture, whose γ resonance absorption spectra were investigated at 77° and 300°K. A small difference was observed in the probability (f') of the Mössbauer effect, while the area asymmetry of the two quadrupolar doublet components remained practically identical. The latter result indicates that the asymmetry cannot be accounted for by
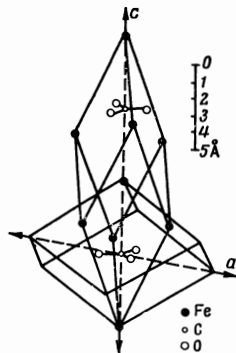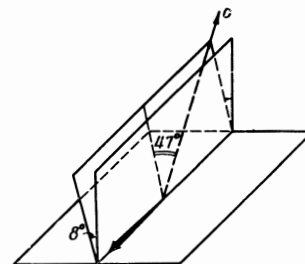
FIG. 1. The lattice of siderite. The threefold axis coincides with the c axis, to which the a axis is perpendicular. A unit cell of siderite (an elongated rhombohedron) is shown compared with a rhombohedron cut along the cleavage plane.

FIG. 2. Direction of axial symmetry relative to the surface of an investigated siderite single crystal.
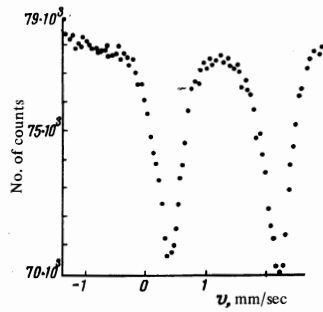
FIG. 3. Spectrum of a polycrystalline siderite sample.

relaxation processes.[11] Our main experimental work on both the siderite single crystals and isotropic polycrystalline samples was performed at 300°K. The radiation source was Co^{57} in chromium. In the case of a uniformly accelerated source the spectra were recorded using an electrodynamic γ resonance spectrometer. The γ beam was collimated to within $\pm 3°$; the crystal areas considerably exceeded the cross section of the beam.

Figure 3 shows a spectrum obtained for polycrystalline siderite, and Fig. 4 shows spectra for a single crystal at two orientations of its c axis with respect to the γ beam ($\theta = 17°$ and $90°$).

3. TREATMENT OF EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

In the case of an axially symmetric tensor of the electric field gradient the area asymmetry of the quadrupolar doublet peaks corresponding to the transitions $\pi(\pm 3/2 \rightarrow \pm 1/2)$ and $\sigma(\pm 1/2 \rightarrow \pm 1/2)$ is given, for a single crystal, by

$$\frac{S_\pi}{S_\sigma} = \frac{c_\pi(\theta)\exp\{-c_\pi(\theta)/2\}\{I_0[c_\pi(\theta)/2]+I_1[c_\pi(\theta)/2]\}}{c_\pi(\theta)\exp\{-c_\sigma(\theta)/2\}\{I_0[c_\sigma(\theta)/2]+I_1[c_\sigma(\theta)/2]\}} \quad (1)$$

where $S_\pi(\theta)$ and $S_\sigma(\theta)$ are the areas of the peaks for the π and σ transitions, while

$$c_\pi = {}^3/_8(1 + \cos^2\theta)f'(\theta)n(\theta)\sigma_0,$$
$$c_\sigma = {}^1/_8(5 - 3\cos^2\theta)f'(\theta)n(\theta)\sigma_0,$$

I_0 and I_1 are the zeroth and first order Bessel functions for an imaginary argument, $f'(\theta)$ is the probability of the Mössbauer effect in the absorber, $n(\theta)$ is the effective thickness of the absorber, and θ is the angle between the γ beam and the direction of the electric field gradient.

Equation (1) does not depend on the intensity of the background γ rays, but is valid for any symmetrical shape of the emission line from a source that is moving at a constant velocity or with uniform acceleration relative to the absorber. Equation (1) can be written as

$$S_\pi / S_\sigma = K(c_\pi) / K(ac_\pi), \quad (2)$$

where

$$K(c_\pi) = c_\pi \exp\left\{-\frac{c_\pi}{2}\right\}\left\{I_0\left(\frac{c_\pi}{2}\right) + I_1\left(\frac{c_\pi}{2}\right)\right\},$$
$$a = \frac{5 - 3\cos^2\theta}{3(1 + \cos^2\theta)}.$$

In the limiting cases of an infinitesimally thin and infinitely thick absorber Eq. (2) ceases to depend on $f'(\theta)$ and becomes

$$\frac{S_\pi(\theta)}{S_\sigma(\theta)}\bigg|_{c_\pi \to 0} \to \frac{3(1 + \cos^2\theta)}{5 - 3\cos^2\theta}; \quad \frac{S_\pi(\theta)}{S_\sigma(\theta)}\bigg|_{c_\pi \to \infty} \to \sqrt{\frac{3(1 + \cos^2\theta)}{5 - 3\cos^2\theta}}. \quad (2b)$$

In Fig. 5, Eq. (2) is represented graphically as a function of c_π for $\theta = 17°$ and $90°$. We note that for small values of θ the emission line area for the π transition always exceeds that for the σ transition, in accordance with (2). It follows directly from the $\theta = 17°$ case in Fig. 4 that a positive gradient of the electric field acting on iron nuclei exists in the siderite lattice at $300°K$; we obtained additional confirmation with the aid of an external transverse 21-kOe magnetic field. In[12] the same sign of the electric field gradient was obtained for Fe^{57} in siderite at $4.2°K$.

In treating the experimental spectra recorded using an electrodynamic gamma resonance spectrometer with a uniformly accelerated source special attention must be devoted to the line shape in the near-zero region of velocities of the source, where an appreciable error in the law of motion can be anticipated. The solid curves in Fig. 4 are Lorentzian approximations of our experimental spectral lines based on their right-hand slopes. It is clearly observable how one line contour is distorted in the region where the radiation-source velocity is extremely small.

Asymmetry of quadrupole doublets and probability of the Mössbauer effect for siderite single crystals oriented at different angles with respect to a γ-ray beam

θ, deg	17	21	45	77	90
S_π/S_σ	1.70 ± 0.05	1.55 ± 0.05	1.12 ± 0.03	0.72 ± 0.04	0.68 ± 0.03
$f'(\theta)$	0.31 ± 0.05	0.26 ± 0.05	0.19 ± 0.03	0.08 ± 0.04	0.09 ± 0.04
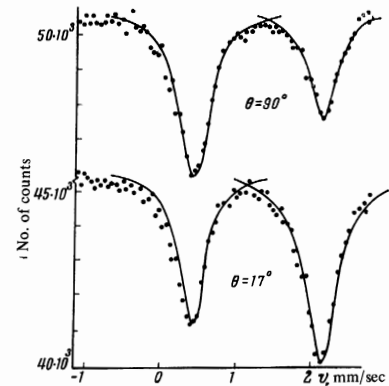
FIG. 4. Spectra of siderite single crystal at $\theta = 90°$ and $17°$.
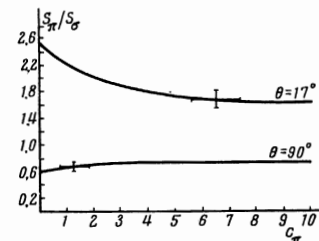
FIG. 5. Calculated curves of $S_\pi/S_\sigma = f(c_\pi)$ for the angles $\theta = 90°$ and $17°$.

Our numerous measurements of the asymmetry in the areas of the peaks at different single-crystal orientations yielded the results given in the accompanying table. Here the S_π/S_σ ratios are experimental; values of $c_\pi(\theta)$ were calculated from the curves in Fig. 5 as a basis for obtaining $f'(\theta)$ using known constants in the expression for $c_\pi(\theta)$.

The known formula for the probability of the Mössbauer effect in an axisymmetric crystal is[13]

$$f'(\theta) = \exp\{-k^2[\langle z^2\rangle - \langle x^2\rangle]\cos^2\theta - k^2\langle x^2\rangle\}, \quad (3)$$

where k is the wave vector of the γ quantum, while $\langle z^2\rangle$ and $\langle x^2\rangle$ are the mean square amplitudes of Fe^{57} vibrations parallel and perpendicular, respectively, to the crystal symmetry c axis (the z axis). Using the values of $f'(\theta)$ for two angles, we obtain from Eq. (3):

$$\langle z^2\rangle = (2.04 \pm 0.40)\cdot 10^{-18}\ cm^2,$$
$$\langle x^2\rangle = (4.54 \pm 0.83)\cdot 10^{-18}\ cm^2.$$

The angular dependence $f'(\theta)$ in siderite at 300°K can then be written as

$$f'(\theta) = \exp(1.3\cos^2\theta - 2.4) \quad (4)$$

with $\langle z^2\rangle$ smaller than $\langle x^2\rangle$ at 300°K.

We note that at 310°K, $\alpha_a/\alpha_c = 3$ is obtained for the ratio of the linear expansion coefficients of siderite along the a and c axes,[14] while in the present work (at 300°K) the ratio of the corresponding mean square displacements is

$$\frac{\langle x^2\rangle}{\langle z^2\rangle} = 2.2 \pm \frac{1.1}{0.7}.$$

For Co^{57} in a zinc single crystal,[15] which, unlike siderite, is symmetric about the a axis, a correspondence between the two ratios (of linear expansion coefficients and mean square amplitudes along the a and c axes) has also been observed. For isotropic polycrystalline siderite powder the area ratio of the quadrupolar doublet components becomes, using Eq. (1),

$$\frac{I_\pi}{I_\sigma} = \left\{\int_0^\pi c_\pi(\theta)\exp\left\{-\frac{c_\pi(\theta)}{2}\right\}\left\{I_0\left[\frac{c_\pi(\theta)}{2}\right] + I_1\left[\frac{c_\pi(\theta)}{2}\right]\right\}\sin\theta\, d\theta\right\}$$

$$\times\left\{\int_0^\pi c_\sigma(\theta)\exp\left\{-\frac{c_\sigma(\theta)}{2}\right\}\left\{I_0\left[\frac{c_\sigma(\theta)}{2}\right] + I_1\left[\frac{c_\sigma(\theta)}{2}\right]\right\}\sin\theta\, d\theta\right\}^{-1}. \quad (5)$$

Using known constants and the foregoing expression (4) derived for $f'(\theta)$, the integrals yield the value of I_π/I_σ for isotropic polycrystalline siderite powder at 300°K:

$$\left(\frac{I_\pi}{I_\sigma}\right)_{exp} = 1.08 \pm \frac{0.02}{0.05}.$$

From the numerous measurements of areas under the peaks in the experimental spectra of the polycrystals we obtain

$$(I_\pi/I_\sigma)_{calc} = 1.07 \pm 0.03.$$

We thus have quantitative evidence that the asymmetry of the quadrupolar doublet components in γ-resonance spectra of polycrystalline siderite samples can be attributed to anisotropy of the Debye-Waller factor in the corresponding single crystals.

The foregoing discussion shows that it is possible to calculate the absolute probability of the Mössbauer effect in single crystals, not from the areas of the peaks, but from the asymmetry of the quadrupolar doublet components, and also to calculate the mean square displacements of atoms along different directions in single crystals. It becomes unnecessary to take the background into account.

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Translated by I. Emin
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