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QUANTITATIVE TEST OF THE VIBRATIONAL ANISOTROPY ORIGIN OF THE ASYMMETRY OF QUADRUPOLE MÖSSBAUER DOUBLETS

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The comparison of quadrupole doublets of Mössbauer spectra for monocrystals of siderite at various orientation angles and those for polycrystalline siderite gives quantitative proof of the vibrational anisotropy origin of integral asymmetry of doublets in polycrystals. Such comparison has also been used for determination of the absolute probability of the Mössbauer effect and of the sign of the electric field gradient on iron nuclei in siderite (which was found to be positive).

The phenomenon of integral asymmetry of quadrupole doublets in Mössbauer spectra of isotropic polycrystals (i.e., the difference in two peak areas) was found in our previous studies of absorption spectra of organic tin compounds.[1,2] After we had investigated and rejected the trivial possible reasons for such asymmetry (e.g., partial orientation of the samples, presence of magnetic and other admixtures, etc.), Karyagin[3] proposed a possible explanation of our results based on anisotropy of the Debye-Waller factor in corresponding monocrystals (see also Refs. 1 and 2). The qualitative confirmation of this assumption was obtained by Goldanskii, Makarov, and Khrapov.[4] Later on the above-mentioned phenomenon was observed for surface atoms of iron and tin and used for the determination of differences[5] and absolute values[6] of the mean-square amplitudes of atomic thermal vibrations along the adsorbing surfaces and normal to them. It was found recently for organic tin polycrystals in Mössbauer scattering spectra as well.[7] However, up to now the Mössbauer-effect probabilities and the asymmetry of quadrupole doublets for monocrystals oriented at different angles to the γ-ray direction were not compared directly and quantitatively with the integral asymmetry of doublets for corresponding isotropic polycrystals. We have now made such comparison for siderite ($FeCO_3$) thus making the first quantitative test of the vibrational anisotropy origin of the discussed phenomenon and obtaining data on the dynamics of motion of Fe atoms in crystals of siderite.

The monocrystals of siderite are of a rhombohedral structure with axial symmetry relative to the triple axis. They were prepared by splitting along the cleavage plane (1010) and lapped to a thickness of 240 μm. X-ray studies gave us the angle between the triple axis and the surface of monocrystalline samples and have also shown that the mosaicity of samples was less than 1°. The polycrystalline siderite samples contained 30 mg cm^{-2} of naturally mixed iron isotopes and were studied at 77 and 300°K. The temperature dependence of the probability of Mössbauer effect (f') was found to be very weak and the integral asymmetry to be practically independent of

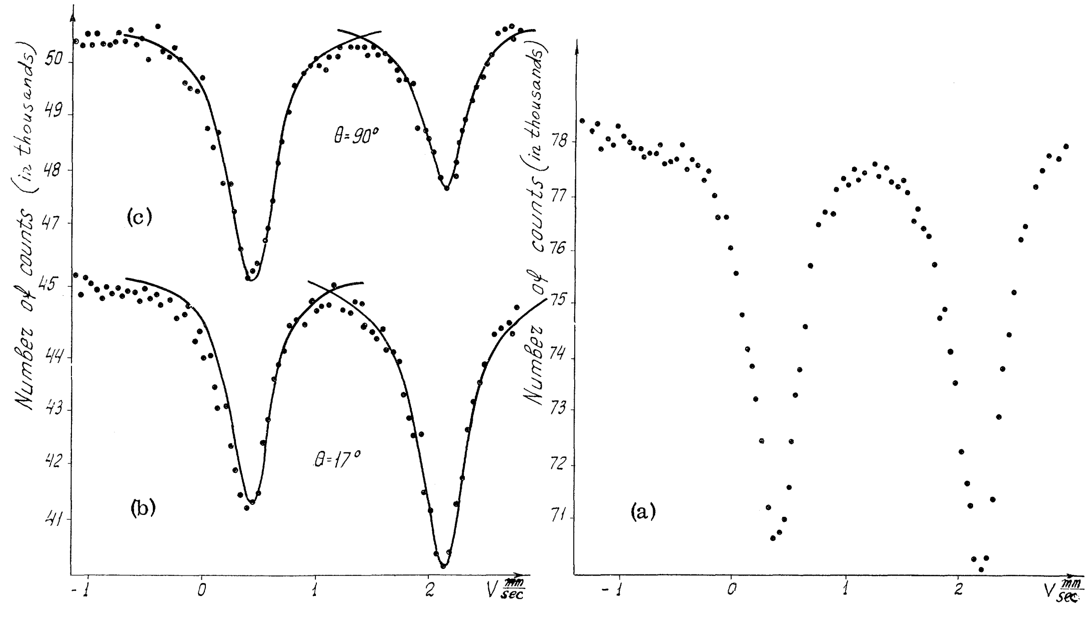

FIG. 1. Mössbauer spectra of siderite [300°K; Co^{57} (Cr) source]. (a) Polycrystalline sample. (b) Monocrystalline sample, $\theta = 17°$. (c) Monocrystalline sample, $\theta = 90°$.

temperature (contrary to the case of the paramagnetic relaxation mechanism[8] of asymmetry of quadrupole doublets which corresponds to the difference not in the areas but only in the shapes of the two peaks).

The main experiments were performed at 300°K using the Co^{57}(Cr) source. The γ-ray beam was collimated within ±3° and the area of the irradiated spot was found to be substantially less than the size of crystals. The absorption spectra obtained for polycrystals as well as for monocrystals oriented in two different ways are shown in Fig. 1 ($\theta = 17°$ and 90°, where θ is the angle between the γ beam and the triple axis of the monocrystal, which is the axis of electric field gradient). In the case of an axially symmetric gradient of the electric field the ratio of the areas of the two peaks corresponding to π ($\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$) and σ ($\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}$) transitions in monocrystals is given by

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

where S_π and S_σ are the areas of π and σ peaks, I_0, I_1 are Bessel functions of zero and first order, and $c_\pi(\theta)$ and $c_\sigma(\theta)$ are the angular dependences of the $\Delta m = 1$ and $\Delta m = 0$ transitions, respectively. Expression (1) is valid for any $n(\theta)$ [$n(\theta)$ is the effective thickness of the absorber in the direction θ] and is independent of the emission spectrum shape, provided it is symmetric, and the motion of the absorber proceeds at a constant velocity or with constant acceleration. The ratio S_π/S_σ also does not depend on the background. Figure 2 is a graphic representation of Eq. (1) as $S_\pi/S_\sigma = \varphi(c_\pi)$ for two different θ. It can be seen that for suf-

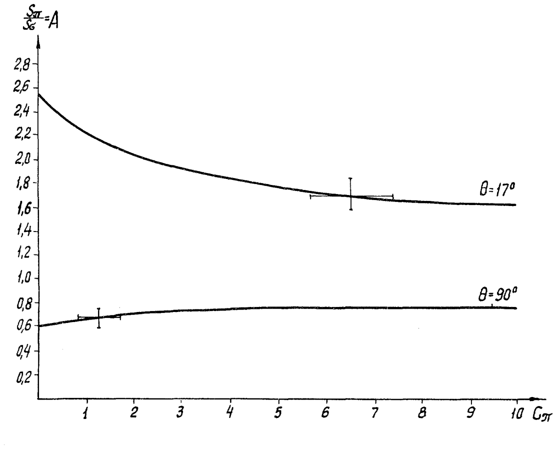

FIG. 2. The calculated asymmetry S_π/S_σ of quadrupole doublets of Mössbauer spectra for monocrystalline samples at various orientations as a function of parameter c_π (defined in the text), i.e., of the thickness of the sample. (a) $\theta = 17°$; (b) $\theta = 90°$. Crosses present experimental data.

ficiently small θ, S_π is always larger than S_σ.

Therefore it follows immediately from Fig. 2 that the electric field gradient on the iron nuclei in the siderite lattice at 300°K is positive. This conclusion was confirmed by measurements in external magnetic field ($H = 21$ kOe). It will be noted that the same sign of electric field gradient on Fe^{57} nuclei in siderite was obtained at 4.2°K by Ono and Ito.[9] Repeated measurements of asymmetry of quadrupole doublets gave us the data presented in Table I.

The Mössbauer-effect probability for an axial-symmetric monocrystal can be described[10] as

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

where K is the wave vector of γ quanta, $\langle z^2\rangle$ and $\langle x^2\rangle$ are the mean-square amplitudes of thermal vibrations of Fe^{57} nuclei along and normal to the triple axis z.

Using the above-mentioned f' values and Eq. (2), we find that

$$\langle z^2\rangle = (2.04 \pm 0.40)10^{-18}\ \mathrm{cm}^2;$$

$$\langle x^2\rangle = (4.54 \pm 0.33)10^{-18}\ \mathrm{cm}^2.$$

It will be seen that at 300°K $\langle z^2\rangle < \langle x^2\rangle$ and $\langle x^2\rangle/\langle z^2\rangle = 2.2^{+1.1}_{-0.7}$ for siderite. It will be noted here that the ratio of linear thermal expansion coefficients for siderite along a (α_x) and c (α_z) axes is $\alpha_x/\alpha_z = 3$ at 310°K,[11] and thus the correlation between these coefficients and mean-square thermal vibrational amplitudes is similar to that observed for Co^{57} in zinc monocrystals.[12]

Using the known constants and the above-mentioned analytical expressions for $f'(\theta)$ found from experiments using monocrystals, we obtain the expected asymmetry of quadrupole doublets for polycrystalline siderite by integration:

$$\frac{I_\pi}{I_\sigma} = \frac{\int_0^\pi S_\pi(\theta)\sin\theta d\theta}{\int_0^\pi S_\sigma(\theta)\sin\theta d\theta}, \qquad (3)$$

and we get in this way $(I_\pi/I_\sigma)_{\mathrm{calc}} = 1.08^{+0.02}_{-0.05}$. Repeated measurements of this asymmetry for polycrystalline samples gave $(I_\pi/I_\sigma)_{\mathrm{expt}} = 1.07 \pm 0.03$.

Table I. The measured integral asymmetry of quadrupole doublets $S_\pi(\theta)/S_\sigma(\theta)$ and the calculated probability of Mössbauer effect (f') for various orientations of monocrystals of siderite.

θ (deg)	$S_\pi(\theta)/S_\sigma(\theta)$	$f'(\theta)$
17	1.70 ± 0.05	0.31 ± 0.05
21	1.55 ± 0.05	0.26 ± 0.05
47	1.12 ± 0.03	0.19 ± 0.03
77	0.72 ± 0.04	0.08 ± 0.04
90	0.68 ± 0.03	0.09 ± 0.04

Thus quantitative proof for the vibrational anisotropy origin of the integral asymmetry of quadrupole doublets in Mössbauer absorption spectra of siderite has been obtained. The results described also show the possibility of determination of the absolute probability of Mössbauer effect in monocrystals and of the absolute values of mean-square amplitudes of atomic thermal vibrations from the asymmetry of quadrupole doublets rather than from the areas of the peaks (without the necessity of taking the background into account).

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OBSERVATION OF SPATIAL ION-WAVE ECHOES

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This is a report on some preliminary experimental results of the spatial ion-wave echo, predicted by Gould, O'Neil, and Malmberg.[1] According to their theory, if an ion wave of frequency f_1 is continuously excited at one point in a collision-free plasma and if an ion wave of frequency $f_2(>f_1)$ is continuously excited at a distance l from this point, then a spatial echo of frequency f_2-f_1 appears at a distance $lf_1/(f_2-f_1)$ from the point where the second wave is excited.

A schematic diagram of the experimental arrangement is shown in Fig. 1. The plasma is produced by surface ionization of a beam of cesium atoms on a hot tantalum plate[2] (~2200°K), and is confined radially by a uniform and constant magnetic field of intensity up to 2500 G. The plasma column, about 1 m long and 2 cm in diameter, is terminated at the opposite end from the generating plate by a stainless-steel wall which is left at room temperature. Two grids, separated by 9.5 cm from each other, are inserted in the plasma column as exciters of ion waves. The surface of the grid is normal to the magnetic lines of force. The grids consist of molybdenum wires 0.1 mm in diameter, spaced 2 mm apart. They are biased at −10 V with respect to the generating hot tantalum plate, and each grid absorbs about 50% of the streaming ions from the plate. By applying alternating voltage of 10 V peak-to-peak to the exciting grids continuously, the transmission rate of the ions through the grid is modulated[3] by about 30%. The plasma density is uniform within a variation of 15% along the column, where the experiment is performed. The ion waves are received by the third grid, movable along the axis of the machine and biased at −20 V relative to the hot plate for detecting the density fluctuation of the ions. A signal from the receiving grid is fed to a synchronous detector with a reference signal of the frequency f_2-f_1. The reference signal is generated from a ring modulator and a filter, suppressing the f_1+f_2 signal, by feeding f_1 and f_2 from the excitation sources. Here, f_1 and f_2 are the exciting frequencies of the first grid (hot-plate side) and of the second grid (receiver side), respectively.

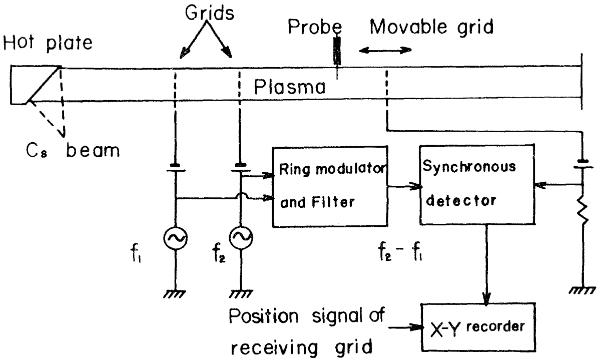

FIG. 1. Schematic diagram of the experimental arrangement.

The plasma density N and the electron temperature T_e measured by a Langmuir probe are 2×10^9/cc and 0.7 eV, respectively. The electron temperature depends on the bias of the exciting grids.[4] The ion temperature as determined by the ion sensitive probe[5] is 0.25 eV. The background neutral pressure is 5×10^{-6} Torr. From these parameters the mean free paths between particles are calculated as follows: $\lambda_{i\text{-}n}\simeq7\times10^2$ cm, $\lambda_{i\text{-}i}\simeq70$ cm, $\lambda_{ee}\simeq4\times10^2$ cm, and $\lambda_{e\text{-}n}\simeq2\times10^2$ cm, where the suffixes i, e, and n refer to ions, electrons, and neutral atoms, respectively. For the present ion-wave experiments, extending over a length of about 30 cm, the plasma is collision free in the sense of the theory.

The ion waves excited by the grids propagate in both directions along the plasma column. While the wavelength is comparable with, or longer than, the plasma diameter, no dispersion of the wave is observed at the ion cyclotron frequency (~20 kc/sec). This fact suggests