Investigation of the Anisotropy of Iron Atom Vibrations in Hematite and Ilmenite by Means of the Mössbauer Effect

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The anisotropy of iron-atomic vibrations in hematite and ilmenite single crystals is investigated. Absolute values of $f' = f(T)$ are calculated and it is found that $f'_{\parallel C}/f'_{\perp C} > 1$ for both crystals (C is the threefold symmetry axis), the vibration anisotropy decreasing when the temperature increases from 80 to 700°K.

THE study of the local dynamics of atom vibrations in crystals is of great interest for comparison with the dispersion relations of the frequencies and oscillations, and hence for a refinement of the real phonon spectrum of a solid. One of the highly interesting characteristics of atom vibrations is the anisotropy of their amplitudes with respect to different directions in the crystal. Such an anisotropy of the atom vibrations appears, as is well known, in the scattering of electrons, neutrons, and x-rays in crystals. We have investigated the anisotropy of atom vibrations with the aid of γ-resonance spectroscopy, and determined the probability of the Mossbauer effect at different angles of the crystal relative to the γ-quantum beam.

The objects of the investigation were single crystals of natural hematite αFe_2O_3 and ilmenite $FeTiO_3$, with area of several square centimeters. The single-crystal specimens were provided by the mineralogical museum of the USSR Academy of Sciences. As is well known, hematite has a rhombohedral lattice of the corundum type (Fig. 1) and has a magnetic ordering with a Neel temperature $T_N \sim 950$°K. Ilmenite also has a corundum structure, but some of the Fe^{3+} ions are replaced by Ti^{4+} ions, and the remaining iron ions are already in the divalent state. Ilmenite has $T_N \sim 60$°K. Thus, it is of interest to investigate these two substances, which have very similar crystal properties and axial symmetry, from the point of a comparison of their local vibration dynamics. The specimens were made by cutting the crystals at the required angles, after which the crystals were glued to beryllium plates and ground to a thickness 100–150 μ. The Laue patterns were used to determine the direction of the C axis. This resulted in hematite with a C axis inclined 45° to the substrate plate and ilmenite with a C axis inclined 90° to the substrate plate. An analysis of the Laue pattern has also shown that the two single crystals are of good quality, with mosaic disorientation not worse than 2–3°.

The investigations were made with a γ-resonance spectrometer with a Co^{57} source in Cr, the sample temperature varied from 90 to 700°K by means of cryostats and an oven. In both the cryostat and the oven, the crystal could be oriented at any desired angle α between the C axis and the direction of the γ quanta. The hematite was investigated at two angles α, equal to 0 and 90°, and the ilmenite at α equal to 0 and 45°. Figures 2 and 3 show, by way of an example, the spectra of αFe_2O_3 and $FeTiO_3$ measured at room temperature. The deviation of the observed ratio of the intensities of the components of the quadrupole splitting of the ilmenite spectrum, $A = I_\pi/I_\sigma = 1.5$, from the theoretically expected value is apparently due to the finite thickness of the crystal[1], to the poor resolution of the doublet, and also to the line broadening by the relaxation effects[2]. In the case of hematite at the angle $\alpha = 0$, the obtained ratio of the six lines of the magnetic hyperfine structure agrees qualitatively with this ratio for an infinitesimally thin specimen, for in this case the magnetic field is perpendicular to the

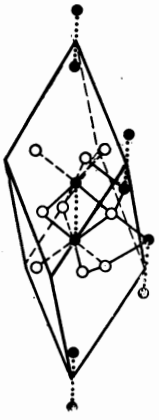

FIG. 1. Structure of hematite. ●–Fe, ○–O.

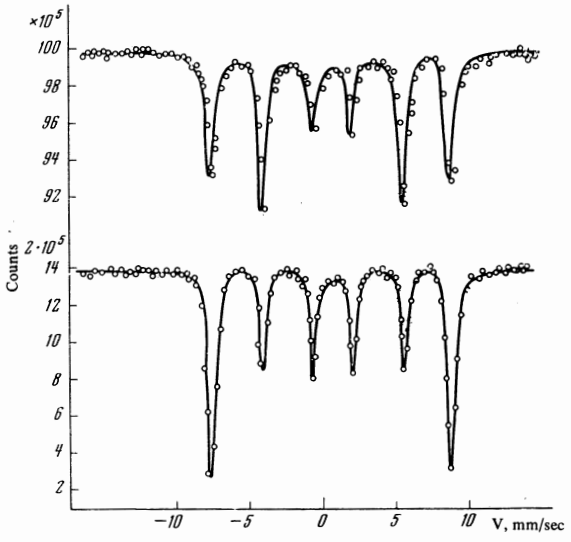

FIG. 2. γresonance spectra of hematite at T = 300°K for angles α = 0° (upper curve) and α = 90° (lower curve).

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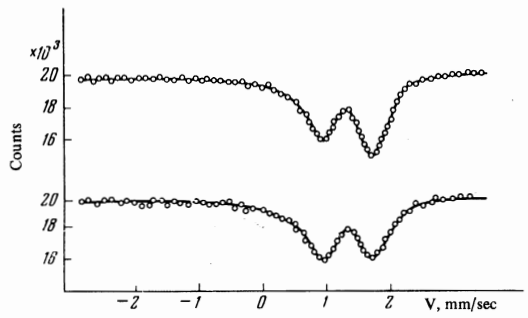

FIG. 3. γ-resonance spectra of ilmenite at T = 300°K for angles $\alpha = \theta$ equal to 0 (upper curve) and 45° (lower curve).

C axis at temperatures above the Morin point $T_M \sim 253$°K. At $\alpha = 90°$, the spectra obtained in our experiments did not contain lines characterizing the nuclear transitions $1/2 \rightarrow 1/2$, since the magnetic field direction, perpendicular to the C axis, was nonetheless parallel to the γ-quantum beam. We note that it would therefore have been most convenient to perform the measurements at $T < T_M$, in which case the magnetic field direction would have coincided with the C axis. Unfortunately, the Morin transition was not observed in the crystal studied by us. It should be noted however, that when the single crystal is broken up to form a polycrystalline specimen, the Morin transition begins to be observable and revealed by the change of the ratios of the hfs lines 1, 2, 5, 6. The reasons for the absence of a Morin transition in the single crystal are not clear.

The probability of the Mossbauer effect was determined by calculating the total area under the spectrum[1], taking the polarization of the γ quanta into account. In the case of a magnetic hyperfine splitting of the 3/2 and 1/2 of the Fe^{57} there is no analogous formula to take into account the polarization of γ rays with different γ-quantum transitions. The necessary theoretical expression that takes polarization into account can be obtained by using the general expression for the cross section for the absorption of γ quanta by Fe^{57} for the magnetic dipole transition $3/2 \rightarrow 1/2$:

$$\sigma(x_i, \mathbf{H}, \mathbf{k}, \pi) = A\sigma_0 \sum_{m_e m_g \lambda} \begin{pmatrix} 3/2 & 1/2 & 1 \\ -m_e & m_g & -\lambda \end{pmatrix} \frac{|(\pi, T_\lambda(\mathbf{H}, \mathbf{k}))|^2}{1 + x_i^2(\mathbf{H})} \quad (1)$$

In formula (1),*

$$T_{\lambda=\pm1}(\mathbf{H}, \mathbf{k}) = \pm \frac{[\mathbf{H}, \mathbf{k}] \mp i[\mathbf{H}[\mathbf{H}, \mathbf{k}]]}{\sqrt{2}\, k \sin\theta},$$

$\lambda = \pm 1$ is the index of the polarization, x_i (i is the set of indices m_e, m_g, and λ) is the energy difference between the resonant level and the γ quantum, **H** and **k** are the directions of the crystal quantization axis and of the γ quantum, π is the γ-quantum polarization, and σ_0 the γ-quantum absorption cross section at resonance. Normalization yields A = 3 for the $3/2 \rightarrow 1/2$ transition. According to (1), a beam of initially unpolarized γ quanta breaks up into two with polarizations parallel and perpendicular to the chosen direction.

For γ quanta polarized parallel to the direction of the magnetic field we have

$$\sigma(x, \mathbf{H}, \mathbf{k}, \pi_\parallel) = \frac{\sigma_0}{8}\left(\frac{3}{1+x^2_{3/2\,1/2}} + \frac{3}{1+x^2_{-3/2\,-1/2}} + \frac{1}{1+x^2_{1/2\,-1/2}} + \frac{1}{1+x^2_{-1/2\,1/2}}\right).$$

For γ quanta polarized perpendicular to the magnetic field direction we have

$$\sigma(x, \mathbf{H}, \mathbf{k}, \pi_\perp) = \frac{\sigma_0}{8}\cos^2\theta\left(\frac{3}{1+x^2_{3/2\,1/2}} + \frac{3}{1+x^2_{-3/2\,-1/2}} + \frac{1}{1+x^2_{1/2\,-1/2}} + \frac{1}{1+x^2_{-1/2\,1/2}}\right) + \frac{\sigma_0}{4}\sin^2\theta\left(\frac{2}{1+x^2_{1/2\,1/2}} + \frac{2}{1+x^2_{-1/2\,-1/2}}\right).$$

Here θ is the angle between the direction of the γ quanta and the magnetic field **H** in the crystal.

Taking into account the separation of the lines and the symmetry of the intensities, we can take the cross section only for the lines $3/2 \rightarrow 1/2$, $1/2 \rightarrow 1/2$, and $-1/2 \rightarrow 1/2$, and then double the result to obtain the total area:

$$\sigma(x, \mathbf{H}, \mathbf{k}, \pi_\parallel) = {}^3/_8\sigma_0 \frac{1}{1+x^2_{3/2\,1/2}} + {}^1/_8\sigma_0 \frac{1}{1+x^2_{1/2\,-1/2}},$$

$$\sigma(x, \mathbf{H}, \mathbf{k}, \pi_\perp) = {}^3/_8\sigma_0\cos^2\theta \frac{1}{1+x^2_{3/2\,1/2}} + {}^1/_8\sigma_0\cos^2\theta \frac{1}{1+x^2_{1/2\,-1/2}} + {}^1/_2\sigma_0\sin^2\theta \frac{1}{1+x^2_{1/2\,1/2}}.$$

As a result, the total area under the spectrum takes the form

$$S = {}^1/_2 a\pi f\Gamma \sum_i K(c_i). \quad (2)$$

Here a is the fraction of the resonant γ quanta in the amplitude spectrum past the absorber, f is the probability of the Mossbauer effect in the source, Γ is the line width,

$$K(c) = ce^{-c/2}[I_0(c/2) + I_1(c/2)];$$

and I_0 and I_1 are Bessel functions of imaginary argument. The summation over i in (2) is summation over m_e, m_g and the polarization state λ, so that i = 1 corresponds to $3/2\ 1/2_\parallel$, i = 2 to $1/2 - 1/2_\parallel$, i = 3 to $3/2\ 1/2_\perp$, i = 4 to $1/2\ 1/2_\perp$, i = 5 to $1/2 - 1/2_\perp$.

Furthermore,

$$c_1 = {}^3/_8\sigma_0 n,\ c_2 = {}^1/_8\sigma_0 n,\ c_3 = {}^3/_8\sigma_0 n\cos^2\theta,\ c_4 = {}^1/_2\sigma_0 n\sin^2\theta,\ c_5 = {}^1/_8\sigma_0 n\cos^2\theta,$$

n = Nf′, N is the number of Fe^{57} nuclei per cm^2, and f′ is the probability of the Mossbauer effect in the investigated specimen. Figure 4 shows the plots of $\Sigma K(c_i)$ calculated from formula (2) for the angles $\theta = 0$ and 90°. It is clear from their form that the polarization must be taken into account in the calculations of f′ if the spectra have magnetic hfs.

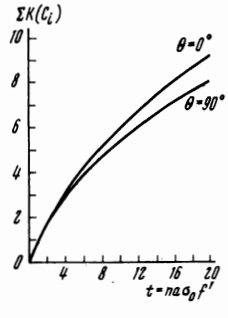

FIG. 4. Calculated plot of $\Sigma K(c_i)$ for the hyperfine magnetic splitting of the levels 3/2 and 1/2 of the Fe^{57} nucleus at θ equal to 0 and 90°.

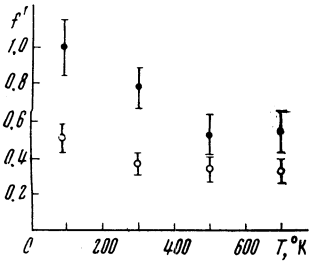

FIG. 5. Experimental plot of f' = f(T) for hematite, ●–$\alpha = 0°$ (for $f_{\parallel C}$), ○–$\alpha = 90°$ (for $f_{\perp C}$).

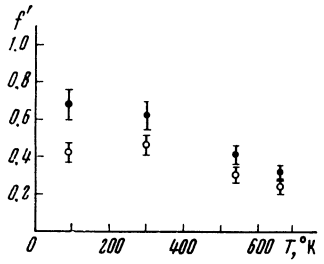

FIG. 6. Experimental plot of f' = f(T) for ilmenite: ●–$f_{\parallel C}$, ○–$f_{\perp C}$.

Formula (2) allows us to calculate f' in the hematite crystal. Using the values f = 0.62, a = 0.4, Γ = 0.09 mm/sec, and a crystal thickness 130 μ, we obtained the values of f' = f(T) for θ equal to 0 and 90° (α equal to 90° and 0°). The result of the calculations are shown in Fig. 5. It should be noted that the calculations were made under the following assumption. For the angle $\alpha = 90°$ between the C axis in the crystal and the γ-quantum beam, we do not know the exact direction of the magnetic field in the crystal. However, by using the intensity ratio of the hfs of the crystal spectrum (Fig. 2) for $\alpha = 90°$ (1.9 : 0.9 : 1), we can conclude that the angle between the magnetic field in the crystal and the γ-quantum beam is approximately 45°. The calculated $\Sigma K(c_i)$ curve passes in this case near and slightly above the plot for $\theta = 0$ ($\Sigma k(c_i)$ as a function of the angle θ at a constant crystal thickness has a maximum in the region of $\alpha = 35°$). However, the accuracy with which the value of θ itself is determined is such that it makes sense to use the $\Sigma k(c_i)$ curve for $\theta = 0°$. For the angle $\alpha = 0$, any direction of the magnetic field in the crystal is perpendicular to the γ-quantum beam, so that we always have here $\theta = 90°$.

We calculated f' for ilmenite by using a formula similar to that previously employed for the quadrupole splitting of the $^3/_2$ level of Fe^{57}, with allowance for polarization. However, in the case of ilmenite, which has a poorly resolved doublet spectrum, we took into account the interference of the overlapping components of the quadrupole spectrum. The resultant values of f' = f(T) for two angles θ, equal to 0 and 90°, between the direction of the field and the γ-quantum beam, are shown in Fig. 6. The valculations were made with allowance for the crystal thickness (100 μ). For both the hematite and the ilmenite (Figs. 5 and 6) there is anisotropy of the vibrations of the Fe atoms. This anisotropy decreases with increasing temperature. The probability f' of the Mossbauer effect along the C axis is larger than in the perpendicular direction. Unlike in hematite, however, the anisotropy of the Fe atom vibrations is smaller in ilmenite. The values of f' are also lower, probably as a result of the more friable structure obtained when the Fe atoms are replaced by Ti. Thus, the rms amplitudes of the iron atoms in hematite and the ilmenite along the layers of the cations and of the oxygen atoms (perpendicular to the C axis) are larger than along the C axis, and this difference decreases with increasing temperature. A similar temperature dependence of the vibration-amplitude anisotropy was observed for siderite[4], although in that case there was a temperature inversion point above which the vibration anisotropy again started to increase. These data indicate that in crystals with uniaxial symmetry the anisotropy of the vibrations is a rare phenomenon, and a temperature rise smooths out the difference between the vibration amplitudes in different directions.

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