SOVIET PHYSICS JETP VOLUME 36, NUMBER 4 APRIL, 1973

ELECTRIC AND MAGNETIC HYPERFINE INTERACTIONS OF Fe^{57} *NUCLEI IN A* $Fe_3^{2+}Al_2Si_3O_{12}$ *CRYSTAL NEAR THE NEEL POINT*

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Submitted May 30, 1972

Zh. Eksp. Teor. Fiz. **63**, 1393–1400 (October, 1972)

Formulas for the line position and intensity are derived on the assumption of axial symmetry of the electric field gradient tensor. The formulas yield a description of the Mössbauer spectrum in the case when magnetic splitting of nuclear levels is small compared with electric quadrupole splitting. Mössbauer spectra of the almandine crystal $Fe_3^{2+}Al_2Si_3O_{12}$ are investigated at temperatures between 1.2 and 7°K. An analysis of the spectra near the Néel temperature ($T_N = 5.5$°K) yields the direction of the antiferromagnetic vector in the crystal and the direction of the symmetry axes of the electric field gradient tensor.

INTRODUCTION

CRYSTALS with garnet structure usually contain iron ions in tetrahedral d-sites and in octahedral a-sites. The dodecahedral c-sites are occupied as a rule by large rare-earth ions, of yttrium, calcium, etc. The only garnet containing iron ions Fe^{2+} in the dodecahedral c-sublattice is the natural mineral almandine $\{Fe_3^{2+}\}Al_2Si_3O_{12}$. An investigation of the Mössbauer spectra of Fe^{57} of this garnet in the paramagnetic temperature region has shown that the electric quadrupole interaction parameter Δ in this compound is quite large ($\Delta \approx 3.75$ mm/sec at T = 0°K)[1]. Such a large value of Δ affords the rare opportunity of experimentally investigating the singularities of the hyperfine splitting of nuclear levels near the magnetic phase-transition temperature under conditions when the magnetic hyperfine splitting is less than the electric quadrupole splitting.

We have investigated the Mössbauer spectra of Fe^{57} nuclei in the garnet $Fe_3^{2+}Al_2Si_3O_{12}$ in the temperature interval from 7°K to 1.2°K.

THEORY

In a certain temperature range below the magnetic phase-transition temperature it is apparently possible to regard the magnetic part of the Hamiltonian of the hyperfine interaction as a perturbation to the electric-quadrupole part. Since the eigenfunctions and eigenvalues of the Hamiltonian of the electric quadrupole splitting are known[2], it is possible to use standard perturbation theory to determine the perturbed eigenfunctions and eigenvalues, and use the latter to determine the positions and intensities of the lines in the Mössbauer spectrum.

A similar problem for a polycrystalline sample placed in an external magnetic field parallel to the γ-quantum direction was considered by Bykov et al.[3] and by Collins[4]. The electric field gradient (EFG) tensor was assumed in these papers to be axially symmetrical.

In our case, unlike these studies, the angle θ between the symmetry axis of the EFG tensor and the effective magnetic field is strictly fixed for each nucleus (there is no external magnetic field). In the case of a polycrystal, the angle ϑ between the direction of the magnetic field and the direction of the γ quanta is arbitrary and it is necessary to average over it.

Using Collins' results, we can write the formulas for the position of the line ξ in the Mössbauer spectrum

$$\begin{gathered}
\xi_\pm^{-3/2} = \varepsilon + {}^3/_2\alpha\cos\theta \mp \beta/2,\\
\xi_\pm^{+3/2} = \varepsilon - {}^3/_2\alpha\cos\theta \mp \beta/2,\\
\xi_\pm{}^{-} = -\varepsilon - (\alpha/2)(4-3\cos^2\theta)^{1/2} \mp \beta/2,\\
\xi_\pm{}^{+} = -\varepsilon + (\alpha/2)(4-3\cos^2\theta)^{1/2} \mp \beta/2,\\
\varepsilon = e^2qQ, \quad \alpha = g_0\mu H, \quad \beta = g_{\text{exc}}\mu H.
\end{gathered} \tag{1}$$

The upper and lower indices of ξ pertain respectively to the excited and ground state of the nucleus; e is the electron charge, $eq = V_{zz}$ is the second derivative of the potential of the electric field at the nucleus, Q is the nuclear quadrupole moment, g_0 and g_{exc} are the g-factors of the ground and excited states of the nucleus, μ is the nuclear magneton, and H is the magnetic field at the nucleus.

The value $\xi = 0$ corresponds to the center of gravity of the spectrum. We note that in our case there are produced nuclear states that are mixed with respect to the spin projection, so that all eight transitions between the sublevels of the hyperfine structure (hfs) of the Fe^{57} nuclei are possible; the spectrum should therefore consist of eight lines. The formulas for the intensities of these lines can be obtained by multiplying the squares of the wave vectors of the ground and excited states by the corresponding angle factors[2]. This operation was indeed performed by us. The formulas presented here pertain to a polycrystalline sample, i.e., they are the result of averaging with respect to the angle (the formulas for a single crystal are given in the Appendix):

$$\begin{gathered}
I_+^{-3/2} = I_-^{+3/2} = {}^1/_4\sin^2(\theta/2),\\
I_+^{+3/2} = I_-^{-3/2} = {}^1/_4\cos^2(\theta/2),\\
I_+{}^{-} = I_-{}^{+} = \frac{1}{12}\left(1+\sin^2\frac{\theta}{2}\sin^2\delta + \cos^2\frac{\theta}{2}\cos^2\delta\right),\\
I_+{}^{+} = I_-{}^{-} = \frac{1}{12}\left(1+\cos^2\frac{\theta}{2}\sin^2\delta + \sin^2\frac{\theta}{2}\cos^2\delta\right),\\
\operatorname{tg}\delta = \left(\frac{(4-3\cos^2\theta)^{1/2}-\cos\theta}{(4-3\cos^2\theta)^{1/2}+\cos\theta}\right)^{1/2}.
\end{gathered} \tag{2}$$

The indices in formulas (1) and (2) correspond to the level scheme given by Collins. Formulas (1) and (2) were obtained under the assumption of axial symmetry of the EFG tensor, which is quite probable for the c-sites of the garnet structure by virtue of the high symmetry of the dodecahedron.

It should be noted that relations (1) and (2) can be useful for the interpretation of the spectra of a magnetic material near the magnetic-ordering point. Agreement between the experimental and theoretical spectra should mean that the fluctuation effects connected with the singularities of the phase transition are small, since formulas (1) and (2) were derived under the condition that the magnetic field at the nucleus is constant in time. The absence of such agreement should apparently denote that fluctuations do take place.

EXPERIMENTAL PROCEDURE

The Mössbauer spectra were obtained with a setup operating at constant acceleration, using a multichannel AI-256 analyzer[5]. The sample was in the vacuum jacket of a cryostat and contact with the helium bath was through a cold finger. The temperature of the sample was measured with a resistance thermometer of pure indium. The lowest sample temperature obtained by us with this setup was 4.85° K. The spectra at 1.2 and 4.2°K were obtained with a constant-velocity setup, in which the sample was immersed in a bath with liquid helium. A polycrystalline sample of natural $Fe^3Al_2Si_3O_{12}$ garnet was prepared from ground minute single crystals.

The investigation of the Mössbauer spectra in the paramagnetic temperature region (from 80 to 850° K) has shown that all the iron in our samples is in the divalent state and occupies the c-sublattice. The spectrum is a symmetrical doublet with large quadrupole splitting.

EXPERIMENTAL RESULTS AND DISCUSSION

When the temperature drops below 5.5° K, an effective magnetic field appears at the nuclei of the Fe^{2+} ions, and the lines of the quadrupole doublet begin to broaden (Fig. 1). This is due to the magnetic phase transition. According to measurements of the magnetic susceptibility of almandine[6], this transformation is a transition into the antiferromagnetic state.

In the interval from 5.5 to 5°K, one of the doublet lines splits into a "doublet" and the other into a "triplet" (Fig. 1). In this temperature region, the magnetic splitting is less than the quadrupole splitting, and we can interpret the spectra by using perturbation theory results (formula (1) and (2)).

We note three features of the experimental spectra near the Néel temperature, which greatly facilitate the interpretation of the spectra: a) the distance between the outer lines of the "triplet" is 2.1 times larger than the distance between the "doublet" lines; b) the intensity of the central line of the "triplet" is double the intensity of its outer lines; c) the spectral lines are quite strongly broadened in the antiferromagnetic temperature region, thus indicating the presence of several Zeeman components.

The feature (a) can be expressed analytically with the aid of formulas (1) for the line position:

$$2{,}1[\alpha(4-3\cos^2\theta)^{1/2}+\beta] = 3\alpha\cos\theta+\beta \quad \text{if} \quad \varepsilon > 0,$$
$$\alpha(4-3\cos^2\theta)^{1/2}+\beta = 2{,}1(3\alpha\cos\theta+\beta) \quad \text{if} \quad \varepsilon < 0.$$

The first of these equations has no solution in the region $0 \le 0 \le \pi/2$. The solution of the second equation is $\theta \approx \pi/2$. This means that the symmetry axis of the EFG tensor is perpendicular to the magnetic field direction. In this case $\epsilon < 0$, i.e., $V_{zz} < 0$ and the quadrupole interaction has a negative sign.

According to neutron diffraction data[6], the cubic unit cell of almandine coincides with the magnetic cell in the antiferromagnetic phase. If we assume that the almandine has a simple magnetic structure and consists of two antiparallel magnetic sublattices, then the most probable directions of the antiferromagnetism vector **l** should be of the type [111] or [100] (if the relation between the anisotropy constants is $|K_1| \gg |K_2|$[7]). In a garnet structure, the local axes in the dodecahedral c-sites (the principal axes of the EFG tensor) have directions of the type [100], [011], and [01$\bar{1}$]. Taking the foregoing into account, we can determine the direction of the antiferromagnetism vector in almandine. The best agreement between the experimental and theoretical spectra is obtained by choosing for the vector **l** the direction [100]; the symmetry axis of the EFG tensor should then have the directions [100], [010], and [001].

It follows from the foregoing that there should exist in almandine two types of iron ions in the c-sublattice, the difference between which appears in the magnetically-ordered phase: 1) for 2/3 of all the Fe^{2+} c-ions, the direction of the antiferromagnetism vector makes an angle $\theta = \pi/2$ with the symmetry axis of the EFG tensor; such ions will be designated Fe(c′); 2) for 1/3 of

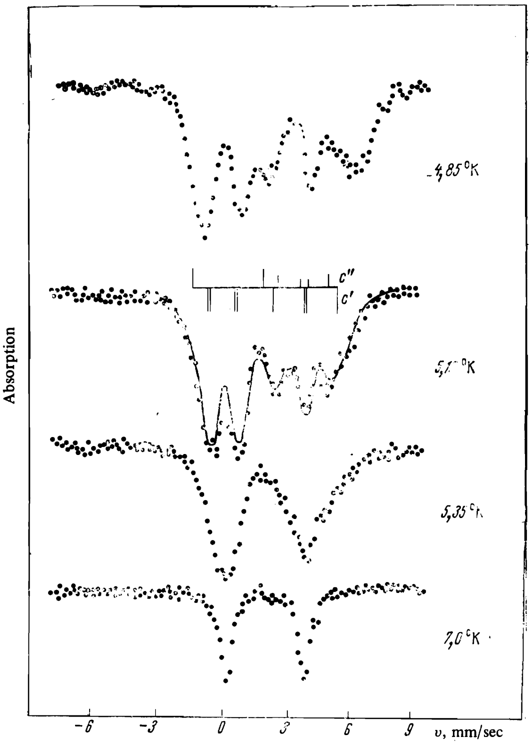

FIG. 1. Mössbauer spectra of Fe^{57} nuclei in almandine crystal in the para- and antiferromagnetic temperature regions. The theoretical position of the lines and the calculated spectrum (solid line) are shown for T = 5.15°K.

all of the iron ions, this angle θ is equal to zero, and these ions will be designated Fe(c″).

Thus, the Mössbauer spectrum of almandine should consist of two Zeeman components, and the experimental lines should be broadened at $T < T_N$. This explains the spectrum features noted in item (c). The ratio of the line intensities in the Zeeman components c′ and c″ confirms the correctness of our model and explains item (b) (see also Fig. 1).

We note that for the ions Fe(c′) and Fe(c″) the magnetic field is directed along one of the principal axes of the EFG tensor. In this case the problem of finding the eigenvalues of the Hamiltonian of the hyperfine interaction can be solved exactly[8]. Using Wertheim's results, we obtained an analytic relation for the line positions ξ in the spectrum for all values of the magnetic field at the nuclei of the ions Fe(c′) and Fe(c″):

$$\xi_i = \beta/2 + E_i,\ \xi_{i+4} = -\beta/2 + E_i\ (i = 1, 2, 3, 4);$$

$$E_{1,3} = \alpha/2 \pm (\varepsilon/2)[(1 + 2\alpha/\varepsilon)^2 + 3]^{1/2} \text{ for } (c'),$$

$$E_{2,4} = -\alpha/2 \pm (\varepsilon/2)[(1 - 2\alpha/\varepsilon)^2 + 3]^{1/2} \text{ for } (c');$$

$$E_{1,3} = \alpha/2 \pm (\varepsilon + \alpha),$$

$$E_{2,4} = -\alpha/2 \pm (\varepsilon - \alpha) \quad \text{for } (c''). \tag{3}$$

Figure 2 shows a nomogram illustrating the changes of the line positions in the Mössbauer spectrum of almandine for different values of the effective magnetic field, calculated from formulas (3). It follows from it that a noticeable deviation from the linear relations, obtained by perturbation theory (formulas (1)), appears only in fields stronger than 100 kOe.

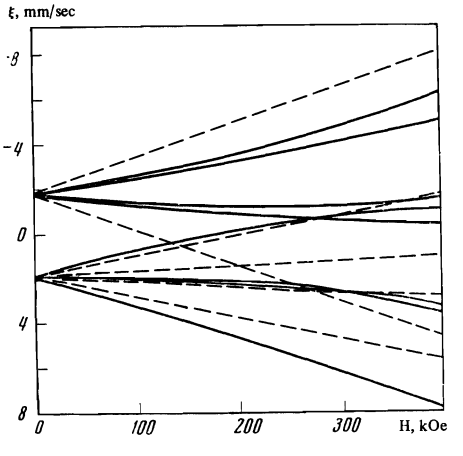

FIG. 2. Nomogram showing the positions of the lines in the Mössbauer spectrum of an almandine crystal for different values of the effective magnetic field. Dashed–c″($\theta = 0$), solid–c′($\theta = \pi/2$); $\epsilon < 0$.

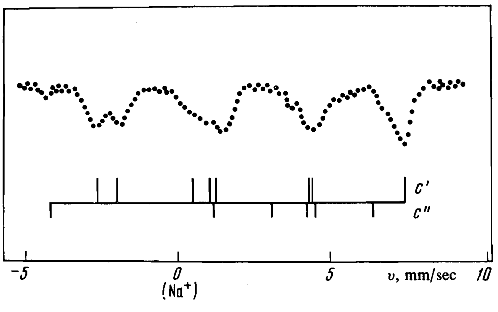

FIG. 3. Mössbauer spectrum of almandine at T = 1.2°K. The calculated positions of the spectral lines are shown.

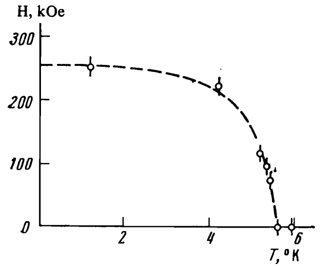

FIG. 4. Temperature dependence of the effective magnetic field at the nuclei of the Fe^{2+} ions in an almandine crystal.

Using relation (3), we can compare the experimental spectra in the low-temperature region with the theoretical ones, and thus verify the validity of our model, see Fig. 3; we see that the agreement between theory and experiment is good. This has enabled us to plot the effective magnetic field against the temperature in the entire temperature range (Fig. 4) and determine the Néel point: $T_N = 5.5 \pm 0.1$°K.

Notice should be taken of the rather low limiting value of the effective magnetic field at 0°K, namely 250 kOe. This is apparently an indication of a large positive contribution made to this field by the orbital angular momentum, which is probably not fully "quenched" in the Fe^{2+} ions of almandine.

CONCLUSIONS

Formulas (1) and (2), obtained for the line positions and intensities assuming actual symmetry of the EFG, enable us to describe the Mössbauer spectrum in the case when the magnetic splitting of the nuclear levels is small in comparison with the electric quadrupole splitting.

An analysis of the Mössbauer spectra of the crystal $Fe_3^{2+}Al_2Si_3O_{12}$ near the Néel temperature shows that for most Fe^{2+} ions, the effective magnetic field at the nucleus is perpendicular to the symmetry axis of the EFG tensor. This makes it possible to determine, within the framework of the simple model of two sublattice antiferromagnetism, the direction of the antiferromagnetism vector and the directions and signs of the symmetry axis of the EFG tensor. Investigations at temperatures much lower than T_N have confirmed the correctness of the conclusions. It must be emphasized that this entire information can be obtained even if polycrystalline samples are used in the investigation.

We note that to explain the experimental spectra there is no need to involve arguments connected with fluctuations near the Néel point.

The authors are grateful to Academician P. L. Kapitza for the opportunity of performing the experiments at helium temperatures. We are also grateful to M. V. Zverkov and A. Ya. Parshin for help with the experiments.

APPENDIX

The line intensity in the Mössbauer spectrum in the case of a single crystal is given by:

$$I_{+-}^{-3/2} = I_{-+}^{+3/2} = \sin^2\frac{\theta}{2}\,(1 + \cos^2\vartheta),$$

$$I_{--}^{-3/2} = I_{++}^{+3/2} = \cos^2\frac{\theta}{2}\,(1 + \cos^2\vartheta)$$

$$I_{+}{}^{+} = I_{++}^{++} + I_{++}^{+-} + I_{+-}^{++} + I_{+-}^{+-},$$

$$I_{+}{}^{-} = I_{++}^{--} + I_{++}^{-+} + I_{+-}^{--} + I_{+-}^{-+},$$

$$I_{-}{}^{+} = I_{-+}^{++} + I_{--}^{+-} + I_{--}^{++} + I_{-+}^{+-},$$

$$I_{-}{}^{-} = I_{-+}^{--} + I_{-+}^{-+} + I_{--}^{--} + I_{--}^{-+},$$

$$I_{++}^{--} = I_{--}^{++} = \frac{1}{3}\cos^2\frac{\theta}{2}(1 + \cos^2\vartheta)\sin^2\delta,$$

$$I_{+-}^{--} = I_{-+}^{++} = \frac{4}{3}\sin^2\frac{\theta}{2}\sin^2\vartheta\sin^2\delta,$$

$$I_{+-}^{--} = I_{+-}^{++} = \frac{1}{3}\sin^2\frac{\theta}{2}(1 + \cos^2\vartheta)\sin^2\delta,$$

$$I_{--}^{--} = I_{++}^{++} = \frac{4}{3}\cos^2\frac{\theta}{2}\sin^2\vartheta\sin^2\delta,$$

$$I_{++}^{-} = I_{--}^{+-} = \frac{4}{3}\cos^2\frac{\theta}{2}\sin^2\vartheta\cos^2\delta,$$

$$I_{+-}^{-+} = I_{-+}^{+-} = \frac{1}{3}\sin^2\frac{\theta}{2}(1 + \cos^2\vartheta)\cos^2\delta,$$

$$I_{-+}^{-+} = I_{+-}^{+-} = \frac{4}{3}\sin^2\frac{\theta}{2}\sin^2\vartheta\cos^2\delta,$$

$$I_{--}^{-+} = I_{++}^{+-} = \frac{1}{3}\cos^2\frac{\theta}{2}(1 + \cos^2\vartheta)\cos^2\delta.$$

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Translated by J. G. Adashko
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