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Effect of Weak Magnetic Fields on the Paramagnetic Hyperfine Structure of the Mossbauer Line in $Fe(ClO_4)_3$

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An attempt is made to determine parameters of the crystal field Hamiltonian at the site of the Fe^{3+} ions in frozen aqueous iron perchlorate solutions. The analysis is based on data obtained by measuring the hyperfine structure spectra of the Mossbauer line. Underlying the method is the fact that weak magnetic fields strongly affect Mossbauer spectra in paramagnetic substances[1,2]. A large number of distinctly resolved lines appear in the hyperfine structure spectra on application of a weak external field. The positions of the lines and their intensities, which in turn depend on the direction of the magnetic field relative to the γ-quantum beam, yield sufficient experimental material for determination of the H_{CF} parameters, though subsequent calculations are quite formidable. In the analysis, advantage was taken of the fact that some of the spectral lines coincide. This immediately permits approximate determination of the H_{CF} parameters[4]. Further numerical calculations yielded more accurate values of the parameters.

1. INTRODUCTION

In connection with the previously observed influence of weak magnetic fields on the spectra of the Mossbauer-line hyperfine structure in paramagnets,[1,2] we carried out analogous investigations on samples of a frozen aqueous solution of iron perchlorate $Fe(ClO_4)_3$, containing Fe^{3+} ions in a state with $S = 5/2$. The behavior of the Mossbauer spectra in iron-perchlorate solutions as a function of the hydrogen-ion concentration in them was investigated by us earlier[3] for the purpose of ascertaining whether such solutions contain ion complexes with different structures in which Fe^{3+} ions take part. These measurements have shown that at small pH (~0.5) there predominate in the solution iron ions for which the hyperfine-structure spectra can be characterized by an effective magnetic field $H_{eff} = 575 \pm 10$ kOe and a near-zero electric-field gradient at the nucleus. It was suggested that such spectra can be due to ion complexes of the type $Fe(H_2O)_6^{3+}$. On the whole, the spectra for a solution with pH ~ 0.5 had a triangular form, thus indicating an intense spin-spin relaxation with participation of the iron ions.

In the present study, to increase the spin-spin relaxation time, the salt $Fe(ClO_4)_3$ was dissolved in a mixture of water (50%) with glycerine (50%), with addition of perchloric acid $HClO_4$, so that the solution had as a result $pH \cong 0$. We used two samples with different iron-ion concentrations. The first (which we shall arbitrarily call "concentrated") contained 3.5 mg iron enriched to 80% with Fe^{57} in 1 ml of the solution. In the second ("dilute" sample, the iron concentration was one-fifth as large. The measurements were performed at liquid-helium and liquid-nitrogen temperatures. The source was Co^{57} in chromium and was kept at room temperature.

The stabilized hyperfine-structure spectra observed by us differ strongly from the corresponding spectra for Fe^{3+} impurity ions in corundum.[2] It is clear that this is connected with the difference in the character of the crystal-field symmetry at the location of the Fe^{3+} ions in the two cases. In the case of the iron perchlorate, however, we had no information whatever on the crystalline surrounding of the Fe^{3+} ion. Nonetheless, it turned out that the measured Mossbauer spectra without an external field and in a stabilizing magnetic field contain very abundant information that makes it possible to reconstruct the form of the crystal-field Hamiltonian in which we are interested.

2. SPECTRA

An analysis of the hyperfine-structure spectra measured in a zero external magnetic field for the concentrated and dilute samples in a wide temperature range from 1.7 to 77°K has shown that in the case of the dilute sample, near liquid-helium temperature, the spin-spin and spin-lattice relaxations of the Fe^{3+} ions do not play a noticeable role in the formation of the Mossbauer spectrum. This has enabled us to focus our main attention on the study of the stabilization effect.[1,2]

When a weak external magnetic field is applied, the hyperfine-structure spectrum experiences significant changes. Figure 1 shows the spectra corresponding to the dilute sample at 4.2°K in a zero external magnetic field (Fig. 1a), in a 200-Oe magnetic field perpendicular to the wave vector **k** of the γ quanta (Fig. 1b), and in a 200-Oe magnetic field parallel to **k** (Fig. 1c). Attention must be called here to the following features of the spectra:

(1) In the spectrum of Fig. 1a, a group of six distinct lines, the positions of which remain practically unchanged when an external magnetic field is subsequently applied, dominates over a certain asymmetrical smeared "background." The shape of the lines, however, is noticeably altered by the magnetic field and becomes strongly asymmetrical. Were this group of six lines to form the spectrum for magnetically-ordered material, it would correspond to a field $H_{eff} = 578 \pm 5$ kOe at the nucleus.

(2) The area of the "stable" group of six lines of the spectrum on Fig. 1a is approximately $2/3$ of the total area of the spectrum.

(3) Application of the field leads to the appearance

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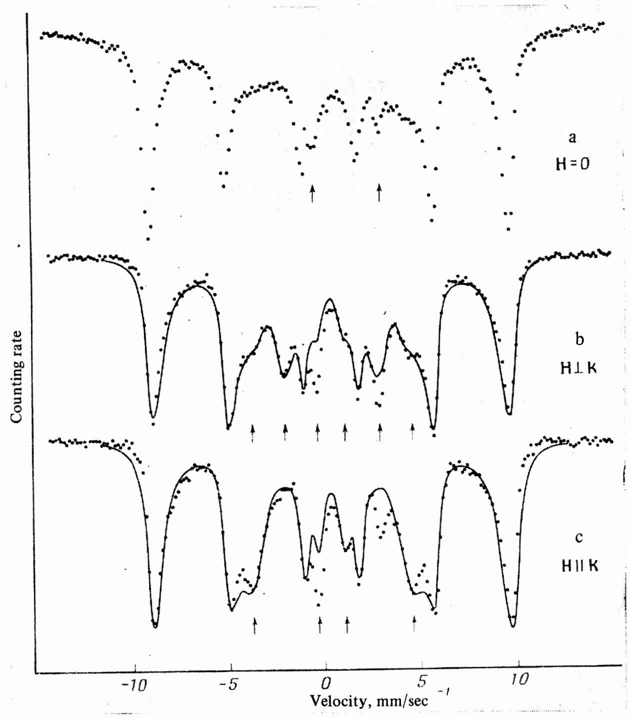

FIG. 1. Spectra for dilute sample at 4.2°K in a zero external magnetic field and in a stabilizing field H = 200 Oe.

of additional group of six lines in the case $H \perp k$, and a group of four lines in the case $H \parallel k$. These groups are almost completely missing from the spectrum obtained without the external magnetic field (they are designated by arrows in Figs. 1b and 1c). In addition, the spectra become symmetrical both with respect to the positions of their components relative to the center of gravity of the spectrum and with respect to the intensities of the corresponding components. A certain asymmetry in the central parts of the spectra on Fig. 1 is due to the additional contribution of the divalent iron which is present in small amounts in the sample. The quadrupole doublet characteristic of the Fe^{2+} ions can easily be traced in all the measured spectra, and is marked by the arrows in Fig. 1a.

(4) Attention is called to the absence of a noticeable contribution from the quadrupole interaction in the spectra for the Fe^{3+} ions.

Whereas the appearance of new distinct spectral components following application of a weak external field was not unexpected by us (this is connected with the stabilization effect predicted by Kagan and one of the authors[1]), all the other features listed above call for a special explanation.

3. REALIGNMENT OF HYPERFINE-STRUCTURE SPECTRA BY RANDOM MAGNETIC FIELDS. EFFECT OF CHANGE OF OBSERVED NUMBER OF COMPONENTS

To decipher the spectra, we started from the circumstance that the observed spectra, with and without an external field, should be superpositions of the hyperfine-structure spectra resulting from three Kramers doublets into which the ground term $(3d^5)^6S$ of the Fe^{3+} ion is split by the crystal field. The Hamiltonian of the crystal field was chosen in the form

$$H_{CF} = D[S_z^2 - {}^1/_3 S(S+1)] + E(S_x^2 - S_y^2) + {}^1/_6 a[S_\xi^4 + S_\eta^4 + S_\zeta^4 - {}^1/_5 S(S+1)(3S^2 + 3S - 1)], \qquad (1)$$

where the first term corresponds to the axially-symmetrical contribution, the second describes the deviation from the axial symmetry in the form of a rhombic increment, and the third term corresponds to a field of pure cubic symmetry. The z axis of the axially-symmetrical contribution may not coincide, in the general case, with either of the three mutually-perpendicular cubic axes ξ, η, and ζ. The energies of the Stark levels and the corresponding wave functions of the Fe^{3+} ions in the field (1) will be denoted by $\epsilon^{(i)}$ and $|\Gamma_j^{(i)}\rangle$, where $i = 1, 2$, and 3 and $j = 1, 2$.

The Zeeman and hyperfine splittings for each isolated Kramers doublet $\Gamma^{(i)}$ can be described by a spin Hamiltonian of the form

$$\mathscr{H}^{(i)} = \mathscr{H}_{hf}^{(i)} + \mathscr{H}_z^{(i)} = A_x^{(i)} I_x S_x' + A_y^{(i)} I_y S_y' + A_z^{(i)} I_z S_z' + \mu_B (g_x^{(i)} H_x S_x' + g_y^{(i)} H_y S_y' + g_z^{(i)} H_z S_z'), \qquad (2)$$

where $S' = 1/2$ is the effective electron spin, I the spin of the nucleus, H the magnetic field, and μ_B the Bohr magneton. The parameters $A_\alpha^{(i)}$ (and also $g_\alpha^{(i)} = 2A_\alpha^{(i)}/A$, where A is the hyperfine-interaction constant for the isolated ion) depend on the character of the splitting of the ground term of the ion by the crystal field, and in general are functions of the parameters D, E, and a. Since the latter are unknown to us, we have chosen them in such a way that they describe the observed spectra as completely as possible. The main governing factor in such a choice was item (2) of Sec. 2, which indicates that two of the three Kramers doublets should give in our case almost identical hyperfine-structure spectra (and consequently have almost identical sets of constants A_α and g_α).

A special theoretical investigation, aimed at finding the classes of crystal-field Hamiltonians which yield, in the case of the Fe^{3+} ion, identical hyperfine structures for two of its Kramers doublets, was carried out in [4]. The cases obtained there were analyzed and it turned out that in first approximation the measured spectra are best described by a Hamiltonian H_{CF} of the type (1) at $a = 0$ and $\lambda \equiv E/D = 1/3$ (see [4], case $S = 5/2$, $\varphi = \pi/2$). The constants $A_\alpha^{(i)}$ for three doublets of such a Hamiltonian are respectively equal to

$$A_x^{(1)} = 4.8392A, \quad A_y^{(1)} = 0.3036A, \quad A_z^{(1)} = 0.4286A,$$
$$A_x^{(2)} = 0.3036A, \quad A_y^{(2)} = 4.8392A, \quad A_z^{(2)} = 0.4286A, \qquad (3)$$
$$A_x^{(3)} = A_y^{(3)} = A_z^{(3)} = 2.1429A.$$

As seen from (3), the sets of parameters $A_\alpha^{(i)}$ for the first two doublets coincide, apart from a redesignation of the coordinate axes, and therefore in a polycrystalline sample these doublets should correspond to identical hyperfine-structure spectra.

The use of the parameters (3) makes it possible to obtain the positions of all the observed spectrum components in the case when the sample is located in a stabilizing magnetic field. However, the spectra obtained in the absence of an external magnetic field differ noticeably from the theoretical spectra calculated with the aid of the parameters (3) at $H = 0$ (compare Fig. 1a with Fig. 2a).

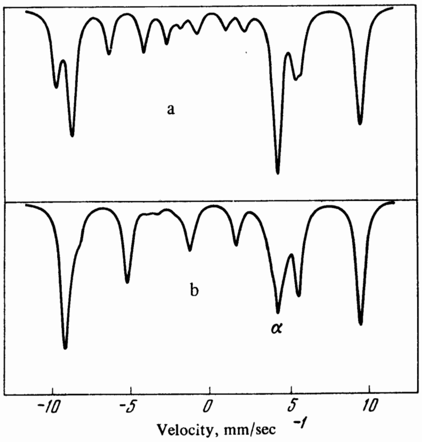

FIG. 2. Theoretical hyperfine-structure spectra for the case $\lambda = 1/3$ and a = 0 in a zero magnetic field (a) and in a field H = 3 Oe (b).

As to the doublet $\Gamma^{(3)}$, for which all the constants $A_{\alpha}^{(3)}$ are identical, its hyperfine structure, in accordance with the results of [1], should become smeared by weak random magnetic fields $H \sim \Gamma_0/\mu_B$, where Γ_0 is the natural line width (in the case of the Fe^{57} nucleus, these fields amount to only several Oe), and it is therefore not surprising that the contribution made to the observed spectra by the doublet $\Gamma^{(3)}$ differs from the theoretical one at H = 0. On the other hand, for the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$, one of the constants A_{α} is much larger than the two remaining ones, and in this case, in accordance with the theory,[1] in weak random fields these doublets should correspond to a distinct hyperfine structure. Nonetheless it turns out that, even for such doublets, weak random fields have a strong effect on the hyperfine-structure spectra, although they do not lead to a smearing. This influence becomes manifest primarily in a decrease of the number of observed spectral components.

Let us examine this effect in greater detail. Assume, for concreteness, that $A_z \gg A_x, A_y$ and consequently $g_z \gg g_x, g_y$. This means that the magnetic-field components H_x and H_y are negligible when dealing with a weak random field. It is convenient to rewrite the Hamiltonian (2) in the form

$$\mathscr{H} = A_z S_z' I_z + g_z \mu_B H_z S_z' + {}^1/_4 (A_x + A_y)(S_+' I_- + S_-' I_+) + {}^1/_4 (A_x - A_y)(S_+' I_+ + S_-' I_-). \qquad (4)$$

The last two terms of the Hamiltonian (4) are responsible for the mixing of the nuclear and electronic wave functions when the states of the summary system (nucleus plus electron shell) are formed, as a result of which the Mossbauer spectrum for the considered doublet differs from the usual group of six lines in the magnetically-ordered material. However, the influence of these terms on the resultant spectrum becomes much weaker if they are smaller than the Zeeman term in the Hamiltonian (4), and becomes negligibly small when $H \gg (A_x + A_y)/4g_z\mu_B$ ($H \gg 0.4$ Oe in the case of the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$ of interest to us). Indeed, in magnetic fields satisfying such a condition, the state of the ion is determined in first approximation simply by the product of its nuclear and electronic wave functions, and in this case the Mossbauer spectrum of the corresponding doublet approaches the usual group of six absorption lines.

It should be noted that the change of the observed number of spectrum components can result from the influence of not only constant but also time-varying random magnetic fields. In the latter case, weak relaxation of the electronic state of the ion is possible, but in the presence of strong anisotropy in the coefficients $A_{\alpha}^{(i)}$, this relaxation becomes manifest primarily in a change of the number of components. This fact was encountered by Hirst[5] in the calculation of the concrete case of relaxation Mossbauer spectra for impurity Er^{166} ions in metallic zirconium. The unexpected appearance of new lines in the theoretical spectra induced him to call them "ghost" lines. The appearance of the new spectral components, however, is a consequence of the strong anisotropy of the tensor $A_{\alpha\beta}^{(i)}$, and not the result of some specific relaxation process, and it can be seen from the foregoing that such an effect takes place also in the absence of relaxation.

Comparison of Figs. 2b and 1a shows that allowance for the weak magnetic fields that are always present in a paramagnetic substance causes, in the case of the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$, a better agreement between theory and experiment. As to the doublet $\Gamma^{(3)}$, a certain disparity still remains here, in that the spectrum for this doublet cannot be as strongly smeared out by the random fields as obtained in the experiment. According to the calculations, the spectrum from $\Gamma^{(3)}$ in weak magnetic fields should contain an intense line (line α in Fig. 2b), in place of which experiment reveals a broad hump (see Fig. 1a). Moreover, further increase of the random field does not lead to a strong decrease of the central part of this line.

The second disparity concerns already the spectra obtained in stabilizing magnetic fields, and it becomes manifest in a noticeable difference between the calculated intensities of the individual components of the spectrum for all three doublets from the observed ones (whereas the theoretical and experimental positions of all the components are in sufficiently good agreement). The reason for such a discrepancy lies in the fact that the Hamiltonian (1) chosen by us, with a = 0 and $\lambda = 1/3$, is, naturally, not exact, since H_{CF} can also contain a small cubically-symmetrical increment, and the parameter λ can differ somewhat from $1/3$. This gives rise to the hope that by small variation of the parameters a and λ it will be possible to obtain better agreement between theory and experiment. In determining parameters a and λ, we shall turn primarily to the spectra in stabilizing magnetic fields, since they contain more information and are not subject to the influence of random fields that are difficult to take into account.

4. HYPERFINE-STRUCTURE SPECTRA IN THE CASE OF A STABILIZING FIELD

By "stabilizing magnetic field" is meant a field that causes a much larger splitting of the Kramers doublet than the hyperfine splitting, and at the same time is not sufficiently strong to cause mixing of ion states belonging to different doublets. The assumptions made with respect to the magnitude of the magnetic field mean that to find the hyperfine-structure spectrum of the i-th doublet we can use the Hamiltonian (2), in which the principal term is the Zeeman term $\mathscr{H}^{(i)}$, and the hyperfine interaction $\mathscr{H}_{hf}^{(i)}$ is a small perturbation. The eigenvalues and eigenfunctions of $\mathscr{H}_Z^{(i)}$ can be obtained easily and are given by

$$\begin{gathered}\varepsilon_1 = {}^1/_2 G\mu_B H,\\ \psi_1 = [2G(G+G_z)]^{-1/2}\{(G+G_z)|{}^1/_2\rangle + G_+|-{}^1/_2\rangle\}.\\ \times\,\varepsilon_2 = -{}^1/_2 G\mu_B H,\\ \psi_2 = [2G(G+G_z)]^{-1/2}\{G_-|{}^1/_2\rangle - (G+G_z)|-{}^1/_2\rangle\},\end{gathered} \tag{5}$$

where

$$\begin{gathered}G_z = g_z\cos\theta,\quad G_x = g_x\sin\theta\cos\varphi,\quad G_y = g_y\sin\theta\sin\varphi;\\ G_\pm = G_x \pm iG_y,\quad G = (G_x^2+G_y^2+G_z^2)^{1/2}.\end{gathered} \tag{6}$$

The angles θ and φ in (6) determine the direction of the stabilizing field relative to the coordinate system in which the tensors A and g are diagonal. We note that the wave functions (5) do not depend on the intensity of the stabilizing field, although they do depend strongly on its spatial orientation.

If $\epsilon_1 - \epsilon_2 = G\mu_B H \gg A$, then we can find the effective Hamiltonians of the hyperfine interaction for the Zeeman sublevels ϵ_1 and ϵ_2 by averaging $\mathscr{H}_{hf}$ over the wave functions of the corresponding sublevels. Such an averaging yields

$$\overline{\mathscr{H}}_{hf}^{(1,2)} = \langle\psi_{1,2}|\mathscr{H}_{hf}|\psi_{1,2}\rangle = \pm{}^1/_2 G^{-1}(G_xA_xI_x + G_yA_yI_y + G_zA_zI_z), \tag{7}$$

where the plus sign pertains to the state ψ_1 and the minus sign to the state ψ_2. Formula (7) can be rewritten in the form

$$\overline{\mathscr{H}}_{hf} = -g_n\mu_n\mathbf{H}_{\text{eff}}\mathbf{I}, \tag{8}$$

where g_n is the g-factor of the nucleus and μ_n is the nuclear magneton. The effective field H_{eff} has the same absolute value for both Zeeman sublevels ψ_1 and ψ_2 (although the directions are opposite) and is determined by the formula

$$H_{\text{eff}} = \frac{A}{2g_n\mu_n}\Omega(\theta,\varphi), \tag{9}$$

where

$$\Omega(\theta,\varphi) = \left\{\frac{(A_x^4\cos^2\varphi + A_y^4\sin^2\varphi)\sin^2\theta + A_z^4\cos^2\theta}{(A_x^2\cos^2\varphi + A_y^2\sin^2\varphi)\sin^2\theta + A_z^2\cos^2\theta}\right\}^{1/2}. \tag{10}$$

The parameters A_α in (10) are expressed in units of the hyperfine constant of the interaction A. (Formulas (9) and (10) are used in the study of the hyperfine structure of the EPR spectra for ions in which the electronic energy levels consist of doublets ($S' = 1/2$)[6].) It is important that H_{eff} does not depend on the external magnetic field, as a result of which the Mossbauer spectrum corresponding to (8) is stable with respect to small fluctuating magnetic fields.

It is clear that the states ψ_1 and ψ_2 should correspond to identical Mossbauer spectra. For the isotope Fe^{57}, such spectra will consist in the general case of six absorption lines, the positions of which are given by the formulas

$$\begin{gathered}\omega_{1,6} = \pm{}^1/_4(3A - A_0)\Omega(\theta,\varphi),\quad \omega_{2,5} = \pm{}^1/_4(A - A_0)\Omega(\theta,\varphi),\\ \omega_{3,4} = \mp{}^1/_4(A + A_0)\Omega(\theta,\varphi),\end{gathered} \tag{11}$$

where A and A_0 are the respective hyperfine-interaction constants for the excited and ground states of the nucleus. The intensities of the lines (11) depend not only on the angles θ and φ, but also on the angles θ_k and φ_k, which characterize the direction of the γ-quantum beam incident on the absorber relative to the chosen coordinate system. If the γ-quantum beam is not polarized, then the expressions for the intensities of the Mossbauer transitions (11) can be represented in the form

$$\begin{gathered}I_{1,6} = {}^1/_8(1+\cos^2\alpha),\quad I_{2,5} = {}^1/_6\sin^2\alpha,\\ I_{3,4} = {}^1/_{24}(1+\cos^2\alpha),\end{gathered} \tag{12}$$

where α is the angle between the effective magnetic field H_{eff} and the wave vector k of the γ quanta. Here

$$\begin{gathered}\cos^2\alpha = [(A_x^2\cos\varphi\cos\varphi_k + A_y^2\sin\varphi\sin\varphi_k)\sin\theta\sin\theta_k\\ + A_z^2\cos\theta\cos\theta_k]^2[(A_x^4\cos^2\varphi + A_y^4\sin^2\varphi)\sin^2\theta + A_z^4\cos^2\theta]^{-1}.\end{gathered} \tag{13}$$

As seen from formulas (11)–(13), in the case of a single-crystal sample, the positions and intensities of the lines of the stabilized Mossbauer spectrum should vary in a distinct fashion when the angles θ, φ and θ_k, φ_k are changed, and this makes it possible in the general case to determine exactly the sets of the constants A_α of the hyperfine interaction for all the Kramers doublets. This information may turn out to be perfectly sufficient for the reconstruction of the form of the crystal-field Hamiltonian at the location of the Mossbauer ions.

In the case of a polycrystalline sample, it is necessary to carry out an averaging that takes into account the different orientations of the individual crystallites relative to the fixed directions of the stabilizing magnetic field H and the wave vector k of the γ quanta. We confine ourselves below to the two most important cases, when **H** ⊥ **k** and **H** ∥ **k**. In both cases, at each value of ω, the absorption is determined by a double integral of the type

$$I(\omega) = \sum_{i=1}^{6}\frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\frac{I_i(\theta,\varphi)\sin\theta}{[\omega - \omega_i(\theta,\varphi)]^2/\Gamma^2 + 1}, \tag{14}$$

where $\Gamma = (\Gamma_a + \Gamma_s)/2$ and the positions ω_i and the intensities I_i of the individual components are given by expressions (11) and (12). Here $\cos^2\alpha$ is the following function of the angles θ and φ:

1) In the case **H** ⊥ **k**

$$\begin{gathered}\cos^2\alpha = {}^1/_2\sin^2\theta[(A_x^2\cos^2\varphi + A_y^2\sin^2\varphi - A_z^2)^2\cos^2\theta\\ + (A_x^2 - A_y^2)^2\sin^2\varphi\cos^2\varphi][(A_x^4\cos^2\varphi\\ + A_y^4\sin^2\varphi)\sin^2\theta + A_z^4\cos^2\theta]^{-1};\end{gathered} \tag{15}$$

2) In the case **H** ∥ **k**, formula (13) holds true if we put in it $\theta_k = \theta$ and $\varphi_k = \varphi$. Depending on the concrete values of the set $A_x^{(i)}$, $A_y^{(i)}$, and $A_z^{(i)}$ of the hyperfine-interaction parameters for the i-th doublet, the form of the Mossbauer spectrum for a polycrystalline absorber can be qualitatively quite different and range from a completely smeared-out picture to a group of six distinct lines. This is exemplified by the stabilized spectra calculated for a number of particular cases in [4].

We now proceed to find the connection between the components of the hyperfine-interaction tensor and the parameters of the crystal-field Hamiltonian. In the general case, the spin Hamiltonian of the magnetic hyperfine interaction for the i-th doublet is

$$\mathscr{H}_{hf}^{(i)} = \sum_{\alpha,\beta}A_{\alpha\beta}^{(i)}I_\alpha S_\beta', \tag{16}$$

where

$$\begin{gathered}A_{\alpha x}^{(i)} = 2A\,\mathrm{Re}\langle\Gamma_2^{(i)}|S_\alpha|\Gamma_1^{(i)}\rangle,\\ A_{\alpha y}^{(i)} = 2A\,\mathrm{Im}\langle\Gamma_2^{(i)}|S_\alpha|\Gamma_1^{(i)}\rangle,\\ A_{\alpha z}^{(i)} = 2A\langle\Gamma_1^{(i)}|S_\alpha|\Gamma_1^{(i)}\rangle;\end{gathered} \tag{17}$$

Here S_α is the α-th component of the true spin of the ion.

We note first that the tensor $A^{(i)}_{\alpha\beta}$ is in the general case not diagonal, and in order to be able to use formulas (10)–(15), in which the diagonal elements $A^{(i)}_{\alpha}$ enter, the tensor must be diagonalized. However, an even more inconvenient fact is that, with the exception of a few simple cases, the tensor $A^{(i)}_{\alpha\beta}$ is not even symmetrical. This is why the magnetic hyperfine interaction for Kramers doublets is sometimes written in the form[7]

$$\mathscr{H}_{hf} = A_x I_x S_x' + A_y I_y S_y' + A_z I_z S_z' + C_{xy}(S_x' I_y - S_y' I_x). \qquad (18)$$

By means of a separate unitary transformation of the wave functions for each doublet, the tensor $A^{(i)}_{\alpha\beta}$ can be reduced to a symmetrical form, and only then can it be diagonalized. It is obvious that such a procedure is quite cumbersome, and we present here other formulas for the calculation of a hyperfine-structure spectra for polycrystalline samples.

We make use of the fact that our final formulas (11)–(13) contain only the squares of the diagonal components of the tensor $A^{(i)}_{\alpha\beta}$. On the other hand, it can be shown that these quantities are diagonal elements of the tensor

$$B^{(i)}_{\alpha\beta} = \sum_{\gamma} A^{(i)}_{\alpha\gamma} A^{(i)}_{\beta\gamma}. \qquad (19)$$

The tensor $B^{(i)}_{\alpha\beta}$, unlike $A^{(i)}_{\alpha\beta}$, is already symmetrical, so that we are left only with the problem of its diagonalization. Starting from (17) and (19), we readily find that

$$B^{(i)}_{\alpha\beta} = 8A^2 \operatorname{Sp}(\hat{\rho}^{(i)} S_\alpha \hat{\rho}^{(i)} S_\beta), \qquad (20)$$

where the "local density matrix" $\hat{\rho}^{(i)}$ for each Kramers doublet is determined by the formula

$$\hat{\rho}^{(i)} = \frac{1}{2} \sum_{k=1,2} |\Gamma_k^{(i)}\rangle\langle\Gamma_k^{(i)}|. \qquad (21)$$

The matrix $\hat{\rho}^{(i)}$ has the following properties:

$$\operatorname{Sp}(\rho^{(i)}) = 1, \qquad (22a)$$

$$[H_{CF}, \hat{\rho}^{(i)}] = 0, \qquad (22b)$$

$$H_{CF}\hat{\rho}^{(i)} = \varepsilon^{(i)}\hat{\rho}^{(i)}, \qquad (22c)$$

$$(\hat{\rho}^{(i)})^2 = \hat{\rho}^{(i)}, \qquad (22d)$$

where the symbol [a, b] denotes a commutator. The properties (22a)–(22c) are obvious, and the property (22d) is the consequence of the fact that the density matrix is made up of purely quantum-mechanical states.

Starting from (22), we easily obtain an explicit expression for the matrix $\hat{\rho}^{(i)}$:

$$\hat{\rho}^{(i)} = c_0^{(i)} + c_1^{(i)} H_{CF} + c_2^{(i)} H_{CF}^2 + \ldots, \qquad (23)$$

where $c^{(i)}_k$ are numerical coefficients. In the case $S = 5/2$ the series (23) ends with the first three terms that have been written out (in the general case the number of terms in the series (23) is equal to $S + 1/2$). The coefficients $c^{(i)}_k$ are determined here by the formulas

$$c_0^{(i)} = \frac{h_3}{6h_3 + \varepsilon^{(i)} h_2}, \quad c_1^{(i)} = \frac{(\varepsilon^{(i)})^2}{6h_3 + \varepsilon^{(i)} h_2}$$
$$c_2^{(i)} = \frac{\varepsilon^{(i)}}{6h_3 + \varepsilon^{(i)} h_2}, \qquad (24)$$

where

$$h_2 = \operatorname{Sp}(H_{CF}^2), \quad h_3 = \operatorname{Sp}(H_{CF}^3), \qquad (25)$$

and $\epsilon^{(i)}$ is the energy of the i-th doublet, which is obtained by solving the cubic equation

$$\varepsilon^3 - {}^1/_4 h_2 \varepsilon - h_3 = 0. \qquad (26)$$

Formulas (20), (23), and (24)–(26) make it possible to write a simple and universal computer program with which to determine the necessary parameters A^2_α.

5. RESULTS OF REDUCTION OF THE EXPERIMENTAL SPECTRA

The spectra measured in a stabilizing magnetic field (see Figs. 1b and Fig. 1c) were reduced on the basis of the foregoing formulas by least squares with a computer. Two parameters determining H_{CF} were varied, namely $\lambda = E/D$ and $\mu = a/D$, at three mutual orientations of the coordinate frames x, y, z and ξ, η, ζ. The latter were chosen such that in the x, y, z frame the cubically-symmetrical contribution to H_{CF} was reduced to one of the following forms:

$$H_{\text{cub}} = {}^1/_{15} a \{\hat{O}_0^{(4)} + \sqrt{{}^5/_{14}}(\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)})\}, \qquad (27)$$

$$H_{\text{cub}} = -{}^1/_{60} a \{\hat{O}_0^{(4)} - \sqrt{10}(\hat{O}_2^{(4)} + \hat{O}_{-2}^{(4)}) - 3\sqrt{{}^5/_{14}}(\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)})\}, \qquad (28)$$

$$H_{\text{cub}} = -{}^2/_{45} a \{\hat{O}_4^{(4)} + \sqrt{{}^{10}/_7}(\hat{O}_3^{(4)} - \hat{O}_{-3}^{(4)})\}. \qquad (29)$$

Here $\hat{O}^{(n)}_k$ are irreducible tensor operators of rank n, constructed out of the components of the operator **S**.[8] At such a choice of H_{CF}, the z axis is, respectively, a fourfold, twofold, and threefold symmetry axis of the cubic potential.

The parameters λ and μ were varied in all three cases in a rather wide range. The corresponding analysis has shown that the Hamiltonians of the crystal field with cubic terms of the type (27) and (28) cannot describe the experimental spectra satisfactorily. In the case of the H_{cub} given by (29), such a description is possible, and the best agreement is obtained for values $\lambda = 1/3$ (this is precisely the value of λ predicted on the basis of the "degeneracy" of the hyperfine structure[4]) and $\mu = 0.53$. It is important that the parameters λ and μ were determined independently from a reduction of stabilized spectra at $H \perp k$ and $H \parallel k$, and it turned out that the minimum χ^2 in both cases was obtained with high accuracy at the same values $\lambda = 1/3$ and $\mu = 0.53$. These values correspond to the following parameters $A^{(i)}_\alpha$:

$$A_x^{(1)} = 4.7580A, \quad A_y^{(1)} = 0{,}3334A, \quad A_z^{(1)} = 0{,}3668A,$$
$$A_x^{(2)} = 0{,}5284A, \quad A_y^{(2)} = 4{,}5926A \quad A_z^{(2)} = 0.9327A, \qquad (30)$$
$$A_x^{(3)} = 2.4965A, \quad A_y^{(3)} = 1.9266A, \quad A_z^{(3)} = 1{,}5373A$$

(Compare (30) with (3)).

The continuous curves on Figs. 1b and 1c show the theoretically-calculated spectra at $\lambda = 1/3$ and $\mu = 0.53$. It is seen from these figures that in the case $H \perp k$ it is possible to obtain sufficiently good agreement between the theoretical and experimental results, whereas for $H \parallel k$ the theoretically calculated spectrum turns out to be less resolved than the spectrum observed experimentally in the region of the extreme lines of the doublet $\Gamma^{(2)}$ (the lines corresponding to the external arrows on Fig. 1c). It is possible that this disparity can be eliminated by not limiting oneself, for further refinement of H_{CF}, to cubic contributions of the type (27)–(29), and by permitting an arbitrary mutual orientation of the coordinate systems x, y, z and ξ, η, ζ. Realization of such a program would consume a rather long time and, on the other hand, it seems to us that to refine the parameters H_{CF} it is necessary to perform additional experimental investigations. In particular, it would be of great interest to measure the stabilized spectra at infralow temperatures, when the Stark levels of the Fe^{3+} ions can be successively populated. However, even the present analysis shows that the stabilizing-field method is effective for the investigation of the crystalline surroundings of Mossbauer ions in paramagnets.

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