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CONTRIBUTION TO THE THEORY OF "DEGENERATE" SPECTRA OF THE HYPERFINE STRUCTURE OF THE MOSSBAUER LINE IN PARAMAGNETS

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We obtain a class of Hamiltonians of the crystal field for the Mossbauer ion Fe^{3+} with $S = 5/2$, which yields for polycrystalline samples identical hyperfine structure spectra from two different Kramers doublets. The cases of greatest practical interest are analyzed.

1. INTRODUCTION

It is known that in the general case the hyperfine structure spectra of the Mossbauer lines have a much more complicated form in paramagnets than in magnetically-ordered substances[1]. The ground term of the Mossbauer ion in a paramagnet is split by the crystal field into a series of Stark sublevels, each characterized by its own hyperfine structure. The observed spectrum is a sum of the spectra of all the sublevels of the ion, with allowance for their populations at a given sample temperature.

The interpretation of the corresponding spectra is in the general case a very complicated problem even if the electron-spin relaxation time is infinitely long. This problem is relatively easy to solve if one knows the parameters of the Hamiltonian of the crystal field for the Mossbauer ions. Otherwise, the interpretation is by comparing the experimentally measured spectra with the spectra calculated under relatively simple assumptions with respect to the symmetry of the crystal field. Thus, in[2,3] they considered in detail the spectra for the Fe^{3+} ions in the case when the Hamiltonian $\mathscr{H}_{CF}$ of the crystal field is the sum of an axially-symmetrical term and a term of rhombic symmetry. The spectra for a purely cubic surrounding of the Fe^{3+} ions are also easy to calculate.

In an investigation of the Mossbauer effect in a frozen aqueous solution of the salt $Fe(ClO_4)_3$, containing Fe^{3+} ions in the state with $S = 5/2$, we encountered an interesting case when the hyperfine structures from two Stark levels of the Fe^{3+} ion apparently coincided. This raises the purely theoretical question of finding all the possible forms of the crystal-field Hamiltonian, which admits of such a coincidence. The solution of this problem, naturally, would greatly simplify the analysis in the reconstruction of the form of $\mathscr{H}_{CF}$ corresponding to the observed spectra. We present below this investigation, in which principal attention was paid to the important case of the Fe^{3+} ion ($S = 5/2$).

2. FORMULATION OF PROBLEM

We consider only ions with half-integer total angular momentum of the electron shell. The ground term of such ions is split by the crystal field in the general case into a series of Kramers doublets, and we are interested only in the case when the hyperfine structure of the Mossbauer spectra is the same for two of these doublets. We shall call such spectra "degenerate."

It is clear that such a degeneracy can take place only when the tensors of the hyperfine interaction for the two different Kramers doublets can be transformed into one another by rotating the coordinate frame. If the hyperfine interaction for the free ion is isotropic,

$$\mathscr{H}_{hf} = A\mathbf{IS}, \qquad (1)$$

then, on the other hand, for the spectra of the hyperfine structure from two different doublets to coincide it suffices that the wave functions of one doublet be transformable into the corresponding wave functions of the other doublet by a definite rotation of the coordinate axes. We see that in this case the degeneracy of the spectra of the hyperfine structure can be observed only in polycrystals or else in single crystals under certain strictly defined orientation of the latter.

We denote by z the axis rotation about which produces the indicated transformation of the wave functions of the two doublets. We write down in this coordinate system the wave functions corresponding to the i-th Kramers doublet in the form

$$|\Gamma_1^{(i)}\rangle = \sum_m c_m^{(i)}\,|m\rangle, \quad |\Gamma_2^{(i)}\rangle = \sum_m (-1)^{s-m} c_{-m}^{(i)*}\,|m\rangle, \qquad (2)$$

where $|m\rangle$ is the state of the electron shell with $S_z = m$. If the doublet $\Gamma^{(1)}$ goes over into the doublet $\Gamma^{(2)}$ by rotation of the coordinate system about the z axis through an angle φ, this means that

$$c_m^{(2)} = e^{i\varphi m} c_m^{(1)}. \qquad (3)$$

Using (3), and also the fact that the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are orthogonal to each other, we obtain a system of equations for the coefficients $c_m^{(1)}$ and the angle φ:

$$\sum_m e^{im\varphi} |c_m^{(1)}|^2 = 0,$$
$$\sum_m (-1)^{s-m} e^{im\varphi} c_m^{(1)} c_{-m}^{(1)} = 0. \qquad (4)$$

Naturally, conditions (3) and (4) limit the class of possible states of the considered ion in the crystal. On the other hand, if we know all the wave functions $|\Gamma^{(i)}\rangle$ and the corresponding eigenvalues λ_i, then we can reconstruct the Hamiltonian of the crystal field $\mathscr{H}_{CF}$:

$$\langle m|\mathscr{H}_{CF}|m'\rangle = \sum_i \lambda_i [c_m^{(i)} c_{m'}^{(i)*} + (-1)^{2s-m-m'} c_{-m}^{(i)*} c_{-m'}^{(i)}]. \qquad (5)$$

It is clear that the conditions (3) and (4) impose limitations on the class of the Hamiltonians $\mathscr{H}_{CF}$.

In concluding this section, we write out the formulas for the hyperfine interaction tensor characterizing each of the doublets $\Gamma^{(i)}$, which we shall need subsequently in the consideration of different concrete cases. We recall that usually the hyperfine interaction (1) is written for a Kramers doublet in the form of the spin Hamiltonian

$$\mathcal{H}_{hf}^{(i)}=\sum_{\alpha,\beta} A_{\alpha\beta}^{(i)} I_\alpha S_\beta', \tag{6}$$

where the effective spin $S' = 1/2$, and the indices α and β run through the values x, y, and z. The coefficients $A_{\alpha\beta}^{(i)}$ are then given by the expressions

$$\begin{aligned} A_{\alpha z}^{(i)} &= 2A\,\langle\Gamma_1^{(i)}|S_\alpha|\Gamma_1^{(i)}\rangle, \\ A_{\alpha x}^{(i)} &= 2A\,\mathrm{Re}\langle\Gamma_2^{(i)}|S_+|\Gamma_1^{(i)}\rangle, \\ A_{\alpha y}^{(i)} &= 2A\,\mathrm{Im}\,\langle\Gamma_2^{(i)}|S_\alpha|\Gamma_1^{(i)}\rangle, \end{aligned} \tag{7}$$

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

3. THE CASE OF SPIN $S = 3/2$

We start the consideration with the simplest case of the spin $S = 3/2$, corresponding to the behavior of the iron ions in a number of complex chemical compounds[4].

The wave function $|\Gamma_1^{(i)}\rangle$ can be written without loss of generality in the form

$$|\Gamma_1^{(1)}\rangle = c_{3/2}^{(1)}\,|3/2\rangle + c_{1/2}^{(1)}\,|1/2\rangle + c_{-1/2}^{(1)}\,|-1/2\rangle, \tag{8}$$

where the coefficient $c_{3/2}$ is real. Then Eqs. (4) take the form

$$c_{1/2}^{(1)} c_{-1/2}^{(1)} \sin\frac{\varphi}{2} = 0, \tag{9a}$$

$$c_{3/2}^{(1)2}\cos\frac{3\varphi}{2} + (|c_{1/2}^{(1)}|^2 + |c_{-1/2}^{(1)}|^2)\cos\frac{\varphi}{2} = 0, \tag{9b}$$

$$c_{3/2}^{(1)2}\sin\frac{3\varphi}{2} + (|c_{1/2}^{(1)}|^2 - |c_{-1/2}^{(1)}|^2)\sin\frac{\varphi}{2} = 0, \tag{9c}$$

$$c_{3/2}^{(1)2} + |c_{1/2}^{(1)}|^2 + |c_{-1/2}^{(1)}|^2 = 1, \tag{9d}$$

to which we added the normalization condition for the coefficients $c_m^{(1)}$ of the function (8).

From (9a) we obtain two possible cases:

$$c_{1/2}^{(1)} = 0, \tag{10a}$$

$$c_{-1/2}^{(1)} = 0. \tag{10b}$$

The case $\sin(\varphi/2) = 0$ is of no interest, since it corresponds to rotations through the angles $\varphi = 0$ and 2π.

If we use (10) in the remaining equations of (9), we readily find that in the case (10a) there exists a nontrivial solution of the system (9) at a value of rotation angle $\varphi = \pi/2$, namely

$$c_{3/2}^{(1)} = \frac{1}{\sqrt{2}}, \quad c_{-1/2}^{(1)} = \frac{1}{\sqrt{2}}e^{i\alpha}, \tag{11}$$

and in the case (10b) such a solution corresponds to $\varphi = \pi$ and is given by

$$c_{3/2}^{(1)} = \frac{1}{\sqrt{2}}, \quad c_{1/2}^{(1)} = \frac{1}{\sqrt{2}}e^{i\alpha}, \tag{12}$$

where α is an arbitrary phase.

These relations together with Eq. (5) for the matrix elements of the Hamiltonian of the crystal field make it possible to reconstruct the form of $\mathcal{H}_{CF}$ of interest to us. In the case $S = 3/2$ under consideration, the Hamiltonian $\mathcal{H}_{CF}$ has only two eigenvalues, $\lambda_1 \equiv \lambda$ for the first doublet and $\lambda_2 = -\lambda$ for the second. The Hamiltonian $\mathcal{H}_{CF}$ for the case (11) has the following matrix form:

$$\begin{array}{c|cccc} m \backslash m' & 3/2 & -1/2 & 1/2 & -3/2 \\ \hline 3/2 & 0 & \lambda e^{-i\alpha} & 0 & 0 \\ -1/2 & \lambda e^{i\alpha} & 0 & 0 & 0 \\ 1/2 & 0 & 0 & 0 & \lambda e^{-i\alpha} \\ -3/2 & 0 & 0 & \lambda e^{i\alpha} & 0 \end{array} \tag{13}$$

and analogously for case (12):

$$\begin{array}{c|cccc} m \backslash m' & 3/2 & 1/2 & -1/2 & -3/2 \\ \hline 3/2 & 0 & \lambda e^{-i\alpha} & 0 & 0 \\ 1/2 & \lambda e^{i\alpha} & 0 & 0 & 0 \\ -1/2 & 0 & 0 & 0 & \lambda e^{-i\alpha} \\ -3/2 & 0 & 0 & \lambda e^{i\alpha} & 0 \end{array} \tag{14}$$

The phase α can be eliminated from the matrices (13) and (14) by rotating the coordinate axes, and it can be set equal to zero in (11) and (12).

The Hamiltonians $\mathcal{H}_{CF}$ corresponding to the matrices (13) and (14) are respectively

$$\mathcal{H}_{CF} = \frac{\lambda}{\sqrt{3}}(S_x^2 - S_y^2), \tag{15}$$

$$\mathcal{H}_{CF} = \frac{\lambda}{\sqrt{3}}(S_zS_x + S_xS_z). \tag{16}$$

It is easy to verify that the Hamiltonians (15) and (16) go over into each other as a result of rotation of the z axis through an angle $\pi/4$ with subsequent transformation of the coordinate axes, and are equivalent. Thus, in the case $S = 3/2$ only one Hamiltonian $\mathcal{H}_{CF}$ (for concreteness) of the type (15) has eigenstates that give an identical hyperfine structure.

The wave functions of the doublets corresponding to (15) are

$$|\Gamma_1^{(1)}\rangle = \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\right\rangle + \left|-\frac{1}{2}\right\rangle\right), \tag{17}$$

$$|\Gamma_1^{(2)}\rangle = \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\right\rangle - \left|-\frac{1}{2}\right\rangle\right) \tag{18}$$

Using (17) and (18), and also formula (7), we can easily show that for bolt doublets the nonzero components of the hyperfine-interaction tensor are

$$\begin{gathered} A_{xx}^{(1)} = A(\sqrt{3}+1), \quad A_{xx}^{(2)} = A(\sqrt{3}-1), \\ A_{yy}^{(1)} = A(\sqrt{3}-1), \quad A_{yy}^{(2)} = A(\sqrt{3}+1), \\ A_{zz}^{(1)} = A_{zz}^{(2)} = A. \end{gathered}$$

Thus, as expected, the spectra of the hyperfine structure of the Mossbauer line from both doublets coincide fully in the case of a polycrystalline sample.

4. CASE OF SPIN $S = 5/2$

In analogy with (8), we write the wave function $|\Gamma_1^{(1)}\rangle$ in the form

$$|\Gamma_1^{(1)}\rangle = c_{5/2}^{(1)}|5/2\rangle + c_{3/2}^{(1)}|3/2\rangle + c_{1/2}^{(1)}|1/2\rangle + c_{-1/2}^{(1)}|-1/2\rangle + c_{-3/2}^{(1)}|-3/2\rangle, \tag{19}$$

where the coefficient $c_{5/2}^{(1)}$ is real. Then Eqs. (4) take the following explicit form

$$\overset{(1)}{c}_{3/2}\overset{(1)}{c}_{-3/2}\sin\frac{3\varphi}{2}-\overset{(1)}{c}_{1/2}\overset{(1)}{c}_{-1/2}\sin\frac{\varphi}{2}=0, \tag{20a}$$

$$\overset{(1)2}{c}_{5/2}\cos\frac{5\varphi}{2}+\left(|\overset{(1)}{c}_{3/2}|^2+|\overset{(1)}{c}_{-3/2}|^2\right)\cos\frac{3\varphi}{2}+\left(|\overset{(1)}{c}_{1/2}|^2+|\overset{(1)}{c}_{-1/2}|^2\right)\cos\frac{\varphi}{2}=0, \tag{20b}$$

$$\overset{(1)2}{c}_{5/2}\sin\frac{5\varphi}{2}+\left(|\overset{(1)}{c}_{3/2}|^2-|\overset{(1)}{c}_{-3/2}|^2\right)\sin\frac{3\varphi}{2}+\left(|\overset{(1)}{c}_{1/2}|^2-|\overset{(1)}{c}_{-1/2}|^2\right)\sin\frac{\varphi}{2}=0, \tag{20c}$$

$$\overset{(1)2}{c}_{5/2}+|\overset{(1)}{c}_{3/2}|^2+|\overset{(1)}{c}_{-3/2}|^2+|\overset{(1)}{c}_{1/2}|^2+|\overset{(1)}{c}_{-1/2}|^2=1 \tag{20d}$$

We shall find it convenient to introduce the notation

$$\begin{gathered}\overset{(1)}{c}_{5/2}=r,\quad \overset{(1)}{c}_{3/2}=r_3\cos\gamma_3 e^{i\alpha_3},\quad \overset{(1)}{c}_{1/2}=r_1\cos\gamma_1 e^{i\alpha_1},\\ \overset{(1)}{c}_{-3/2}=r_3\sin\gamma_3 e^{i\alpha_{-3}},\quad \overset{(1)}{c}_{-1/2}=r_1\sin\gamma_1 e^{i\alpha_{-1}},\end{gathered} \tag{21}$$

where, without loss of generality, it can be assumed that r, r_1, and r_3 are positive and that the angles γ_1 and γ_3 are in the interval from zero to $\pi/2$.

If we use the orthonormality condition for the columns of the matrix made up of the coefficients d $c_m^{(1)}$ of the wave functions of all three doublets, then we can readily find a limitation to which the parameters r, r_1, and r_3 are subject:

$$0\leqslant r,\ r_1,\ r_3\leqslant 1/\sqrt{2}. \tag{22}$$

Equations (20) do not change when the angle φ is replaced by $-\varphi$, so that only the region $0 \leq \varphi \leq \pi$ need be considered. From (20b) and (20d) we can express r_1 and r_3 as functions of r and φ:

$$r_1^2=-\left[(1-r^2)\cos\frac{3\varphi}{2}+r^2\cos\frac{5\varphi}{2}\right]\Big/\left(\cos\frac{\varphi}{2}-\cos\frac{3\varphi}{2}\right), \tag{23a}$$

$$r_3^2=\left[(1-r^2)\cos\frac{\varphi}{2}+r^2\cos\frac{5\varphi}{2}\right]\Big/\left(\cos\frac{\varphi}{2}-\cos\frac{3\varphi}{2}\right), \tag{23b}$$

where $\varphi \neq 0$, π (the case $\varphi = \pi$ will be considered separately). The conditions (22) with allowance for (23) make it possible to impose additional limitations on the region of permissible values of r and φ.

It turns out, however, that even stronger limitations result from the obvious conditions

$$|\cos 2\gamma_1|\leqslant 1,\qquad |\cos 2\gamma_3|\leqslant 1. \tag{24}$$

The expressions for $\cos^2\gamma_1$ and $\cos^2\gamma_3$ are found from Eqs. (20a) and (20c) and are of the form

$$\cos 2\gamma_1=1+AB/2r^2r_1^2\sin\frac{\varphi}{2}\sin\frac{5\varphi}{2}, \tag{25a}$$

$$\cos 2\gamma_3=1-AC/2r^2r_3^2\sin\frac{3\varphi}{2}\sin\frac{5\varphi}{2}, \tag{25b}$$

where we introduce the notation

$$A=r_1^2\sin\frac{\varphi}{2}+r_3^2\sin\frac{3\varphi}{2}+r^2\sin\frac{5\varphi}{2}, \tag{26a}$$

$$B=-r_1^2\sin\frac{\varphi}{2}+r_3^2\sin\frac{3\varphi}{2}-r^2\sin\frac{5\varphi}{2}, \tag{26b}$$

$$C=-r_1^2\sin\frac{\varphi}{2}+r_3^2\sin\frac{3\varphi}{2}+r^2\sin\frac{5\varphi}{2} \tag{26c}$$

If we consider r and φ as polar coordinates on a plane, then, with account taken of (24), the region of permissible values of r and φ turns out to be sharply limited to sections of the plane lying between the curves A = 0, B = 0, C = 0, and D = 0, where

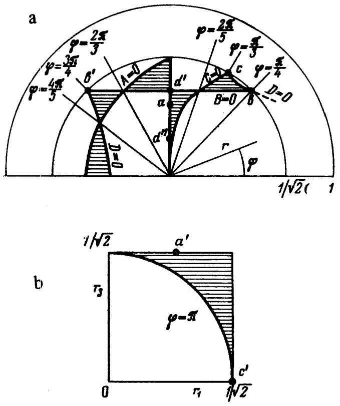

FIG. 1. Region of permissible values of r and φ, and also of r_1 and r_2 in the case $\varphi = \pi$.

$$D=r_1^2\sin\frac{\varphi}{2}+r_3^2\sin\frac{3\varphi}{2}-r^2\sin\frac{5\varphi}{2}, \tag{26d}$$

and also the axis $\varphi = \pi/2$. These regions are shown shaded in Fig. 1a. In particular, it is seen from Fig. 1a that the region of angles $\varphi < \pi/4$ drops out from consideration in general.

As to the case $\varphi = \pi$, it calls for separate analysis, for at this value of the angle Eq. (20b) becomes an identity, and we lose one of the limitations on the coefficients $c_m^{(1)}$. To find the general class of the functions $|\Gamma_1^{(1)}\rangle$ needed by us, it is convenient here to regard the parameters r_1 and r_3 as independent. Then we get from the normalization condition (20d)

$$r=(1-r_1^2-r_3^2)^{1/2},$$

and the expressions for $\cos^2\gamma_1$ and $\cos^2\gamma_3$ are again given by (25) and (26), in which we must put $\varphi = \pi$. At the same time, as can be readily verified directly, the phases α_m satisfy the condition

$$\alpha_3+\alpha_{-3}=\alpha_1+\alpha_{-1}+\pi(2n+1).$$

The region of permissible values of the parameters r_1 and r_3 is bounded by the inequalities (22) and is shown in Fig. 1b.

In principle, if there are no limitations on the type of the crystal-field symmetry, then, as shown by Fig. 1, in the case of a spin $S = 5/2$ there exists an infinite number of Hamiltonians $\mathscr{H}_{\mathrm{Cf}}$, whose eigenstates have a degenerate hyperfine structure.

Let us show how to reconstruct effectively the form of the Hamiltonian $\mathscr{H}_{\mathrm{CF}}$ corresponding to an arbitrary point (r, φ) of the shaded region. In the general case we should have for $S = 5/2$

$$\mathscr{H}_{CF}=\sum_{k=-2}^{2}b_k^{(2)}\hat{O}_{-k}^{(2)}+\sum_{k=-4}^{4}b_k^{(4)}\hat{O}_{-k}^{(4)}, \tag{27}$$

where $b_k^{(n)}$ are numerical coefficients and $\hat{O}_k^{(n)}$ are irreducible tensor operators of rank n, constructed of components of the operator S, which transform when the coordinate system is rotated like the corresponding spherical harmonics $Y^{(n)}(\theta, \varphi)$. The explicit form of these operators can be found, for example, in[5].

The operators $\hat{O}_k^{(n)}$ possess the property

$$\mathrm{Sp}\,(\hat{O}_k^{(n)}\hat{O}_{-k'}^{(n')})=\delta_{nn'}\delta_{kk'}\,\mathrm{Sp}\,(\hat{O}_k^{(n)}\hat{O}_{-k}^{(n)}), \tag{28}$$

which makes it possible to obtain from (27) the following expression for the coefficients $b_k^{(n)}$:

$$b_k^{(n)} = \frac{\mathrm{Sp}\,(\hat{O}_k^{(n)}\mathcal{H}_{CF})}{\mathrm{Sp}\,(\hat{O}_k^{(n)}\hat{O}_{-k}^{(n)})} = \frac{\sum\limits_{m,\,m'} \langle m' | \hat{O}_k^{(n)} | m \rangle \langle m | \mathcal{H}_{CF} | m' \rangle}{\sum\limits_{m,\,m'} \langle m' | \hat{O}_k^{(n)} | m \rangle \langle m | \hat{O}_{-k}^{(n)} | m' \rangle}. \tag{29}$$

The matrix elements $\langle m | \mathcal{H}_{CF} | m' \rangle$ which enter here are determined by formula (5), which in the case $S = 5/2$ contains summation over three doublets. There is, however, the possibility of expressing these matrix elements only in terms of the coefficients $c_m^{(1)}$. To this end we introduce the quantities

$$\Lambda_1 = \lambda_1 - \lambda_3, \quad \Lambda_2 = \lambda_2 - \lambda_3. \tag{30}$$

Then, with allowance for (3) and (5), and also of the circumstance that $\lambda_1 + \lambda_2 + \lambda_3 = 0$, we obtain

$$\langle m | \mathcal{H}_{CF} | m' \rangle = \{c_m^{(1)} c_{m'}^{(1)*} + (-1)^{2S-m-m'} c_{-m}^{(1)*} c_{-m'}^{(1)}\} (\Lambda_1 + \Lambda_2 e^{i(m-m')\varphi}) - {}^1\!/_3 (\Lambda_1 + \Lambda_2)\,\delta_{mm'}. \tag{31}$$

Thus, the matrix elements $\mathcal{H}_{CF}$ can be easily calculated for the given point (r, φ) with the aid of formulas (21), (23), (25), (26), and (31). In the general case they will contain as parameters Λ_1 and Λ_2 and the phases $\alpha_{\pm 1}$ and $\alpha_{\pm 3}$. From (20a) we can easily deduce that the phase α_m are related by

$$\alpha_3 + \alpha_{-3} = \begin{cases} \alpha_1 + \alpha_{-1} + 2n\pi, & \pi/4 \leqslant \varphi < 2\pi/3, \\ \alpha_1 + \alpha_{-1} + (2n+1)\pi, & 2\pi/3 < \varphi \leqslant \pi, \end{cases}$$

where $n = 0, \pm 1, \pm 2, \ldots$ By virtue of this, only three phases α_m out of the four are independent, and consequently $\mathcal{H}_{CF}$ will contain five arbitrary parameters.

We shall need subsequently expressions for the coefficients $b_k^{(n)}$, which we present below:

$$\begin{aligned}
b_0^{(2)} &= \frac{1}{42}\left[5c_{5/2}^{(1)2} - (|c_{3/2}^{(1)}|^2 + |c_{-3/2}^{(1)}|^2) - 4(|c_{1/2}^{(1)}|^2 + |c_{-1/2}^{(1)}|^2)\right](\Lambda_1 + \Lambda_2), \\
b_1^{(2)} &= \frac{\sqrt{30}}{42}\left[c_{5/2}^{(1)} c_{3/2}^{(1)} + \frac{2}{\sqrt{10}}(c_{1/2}^{(1)} c_{3/2}^{(1)*} - c_{-1/2}^{(1)*} c_{-3/2}^{(1)})\right](\Lambda_1 + \Lambda_2 e^{-i\varphi}), \\
b_2^{(2)} &= \frac{\sqrt{15}}{42}\left[c_{5/2}^{(1)} c_{1/2}^{(1)} + \frac{3}{\sqrt{5}}(c_{1/2}^{(1)*} c_{-3/2}^{(1)} + c_{-1/2}^{(1)} c_{3/2}^{(1)*})\right](\Lambda_1 + \Lambda_2 e^{-2i\varphi}), \\
b_0^{(4)} &= \frac{1}{105}\left[c_{5/2}^{(1)2} - 3(|c_{3/2}^{(1)}|^2 + |c_{-3/2}^{(1)}|^2)\right. \\
&\qquad \left. + 2(|c_{1/2}^{(1)}|^2 + |c_{-1/2}^{(1)}|^2)\right](\Lambda_1 + \Lambda_2), \\
b_1^{(4)} &= \frac{2}{105}\left[c_{5/2}^{(1)} c_{3/2}^{(1)} - \frac{\sqrt{10}}{2}(c_{1/2}^{(1)} c_{3/2}^{(1)*} - c_{-1/2}^{(1)*} c_{-3/2}^{(1)})\right](\Lambda_1 + \Lambda_2 e^{-i\varphi}), \\
b_2^{(4)} &= \frac{3}{105}\left[c_{5/2}^{(1)} c_{1/2}^{(1)} - \frac{\sqrt{5}}{3}(c_{1/2}^{(1)*} c_{-3/2}^{(1)} + c_{-1/2}^{(1)} c_{3/2}^{(1)*})\right](\Lambda_1 + \Lambda_2 e^{-2i\varphi}), \\
b_3^{(4)} &= \frac{\sqrt{14}}{105} c_{5/2}^{(1)} c_{-1/2}^{(1)} (\Lambda_1 + \Lambda_2 e^{-3i\varphi}), \\
b_4^{(4)} &= \frac{\sqrt{14}}{105} c_{5/2}^{(1)} c_{-3/2}^{(1)} (\Lambda_1 + \Lambda_2 e^{-4i\varphi}).
\end{aligned} \tag{32}$$

The coefficients $b_{-k}^{(n)}$ are obtained from the formula $b_{-k}^{(n)} = (-1)^k b_k^{(n)*}$.

In the next section we shall determine the form of $\mathcal{H}_{CF}$ for a number of characteristic points of the diagram of Fig. 1 which, as we shall see, correspond to a fully realistic type of crystal-field symmetry. We shall also present the spectra of the hyperfine structure of the Mossbauer line expected in this case for Fe^{3+} ions with the Fe^{57} nucleus.

5. DEGENERATE HYPERFINE STRUCTURE SPECTRA FOR A NUMBER OF CONCRETE CASES

We assume first that $\mathcal{H}_{CF}$ does not contain the operators $O_k^{(4)}$ and is expressed only in terms of the operators $O_k^{(2)}$, which are quadratic in the spin. This means that all the $b_k^{(4)} = 0$. From the expression for $b^{(4)}$ (see (32) it follows that there are two possibilities: a) $\Lambda_1 + \Lambda_2 = 0$ and b) $r^2 - 3r_3^2 + 2r_1^2 = 0$. An analysis shows that in the case (a) it is possible to cause all the parameters $b_k^{(4)}$ to vanish only at two values of the angle φ, namely $\varphi = \pi/2$ and $\varphi = \pi$, by specially choosing the coefficients $c_m^{(1)}$. In the case (b) the problem has no solution. Thus, let (a): $\varphi = \pi/2$, $\Lambda_1 + \Lambda_2 = 0$. From (32) we see that then $b_0^{(2)} = b_0^{(4)} = b_4^{(4)} = 0$. To cause $b_3^{(4)}$, $b_2^{(4)}$, and $b_1^{(4)}$ to vanish, it is necessary to stipulate, respectively, that

$$c_{-1/2}^{(1)} = 0, \quad c_{5/2}^{(1)} c_{1/2}^{(1)} - \frac{\sqrt{5}}{3} c_{1/2}^{(1)*} c_{-3/2}^{(1)} = 0, \quad c_{5/2}^{(1)} c_{3/2}^{(1)} - \frac{\sqrt{10}}{2} c_{1/2}^{(1)} c_{3/2}^{(1)*} = 0. \tag{33}$$

Solving the system (33) together with Eqs. (20), we readily find that the following coefficients $c_m^{(1)}$ differ from zero:

$$c_{5/2}^{(1)} = \frac{1}{2}\sqrt{\frac{5}{7}}, \quad c_{1/2}^{(1)} = \frac{1}{\sqrt{2}} e^{i\alpha} \quad c_{-3/2}^{(1)} = \frac{3}{2\sqrt{7}} e^{i2\alpha}$$

where α is an arbitrary phase, which can be set equal to zero. In accordance with (27) we have

$$\mathcal{H}_{CF} = \frac{1}{6}\sqrt{\frac{3}{14}}(\Lambda_1 - \Lambda_2)(\hat{O}_2^{(2)} + \hat{O}_{-2}^{(2)}) = \frac{\Lambda_1 - \Lambda_2}{4\sqrt{7}}(S_x^2 - S_y^2). \tag{34}$$

The components of the hyperfine-interaction tensor for the doublets $\Gamma^{(1)}$, $\Gamma^{(2)}$, and $\Gamma^{(3)}$ of the Hamiltonian (34) are equal to

$$\begin{aligned}
&A_x^{(1)} = {}^6\!/_7(3+\sqrt{7})A, \quad A_y^{(1)} = {}^6\!/_7(3-\sqrt{7})A, \quad A_z^{(1)} = {}^3\!/_7 A, \\
&A_x^{(2)} = {}^6\!/_7(3-\sqrt{7})A, \quad A_y^{(2)} = {}^6\!/_7(3+\sqrt{7})A, \quad A_z^{(2)} = {}^3\!/_7 A,
\end{aligned} \tag{35}$$

$$A_x^{(3)} = A_y^{(3)} = A_z^{(3)} = {}^{15}\!/_7 A.$$

We now consider another possibility:

(a′): $\varphi = \pi$, $\Lambda_1 + \Lambda_2 = 0$. In this case $b_0^{(2)} = b_2^{(2)} = b_0^{(4)} = b_2^{(4)} = b_4^{(4)} = 0$. In order for $b_3^{(4)}$ and $b_1^{(4)}$ also to vanish, we must have

$$c_{-1/2}^{(1)} = 0, \quad c_{5/2}^{(1)} c_{3/2}^{(1)} - \frac{\sqrt{10}}{2} c_{1/2}^{(1)} c_{3/2}^{(1)*} = 0,$$

whence, with allowance for (20), we obtain for the nonzero coefficients $c_m^{(1)}$

$$c_{5/2}^{(1)} = \frac{1}{2}\sqrt{\frac{10}{7}} \quad c_{3/2}^{(1)} = \frac{1}{\sqrt{2}} e^{i\alpha} \quad c_{1/2}^{(1)} = \frac{1}{\sqrt{7}} e^{i2\alpha}$$

Putting, as before, the arbitrary phase α equal to zero, we obtain from (27) with the aid of (32)

$$\mathcal{H}_{CF} = \frac{1}{6}\sqrt{\frac{3}{14}}(\Lambda_1 - \Lambda_2)(\hat{O}_{-1}^{(2)} - \hat{O}_1^{(2)}) = \frac{\Lambda_1 - \Lambda_2}{4\sqrt{7}}(S_z S_x + S_x S_z). \tag{36}$$

As already noted in Sec. 3, the Hamiltonian (36) is fully equivalent to (34). Thus, $\mathcal{H}_{CF}$ of the form (34) is the only crystal-field Hamiltonian containing no operators $O_k^{(4)}$ and having eigenstates with degenerate hyperfine structure.

The cases considered above are marked by points a and a′ in Fig. 1. The hyperfine-structure spectra corresponding to these points for a polycrystalline sample are shown in Fig. 2. Figure 2a shows the spectra for the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$, Fig. 2b the

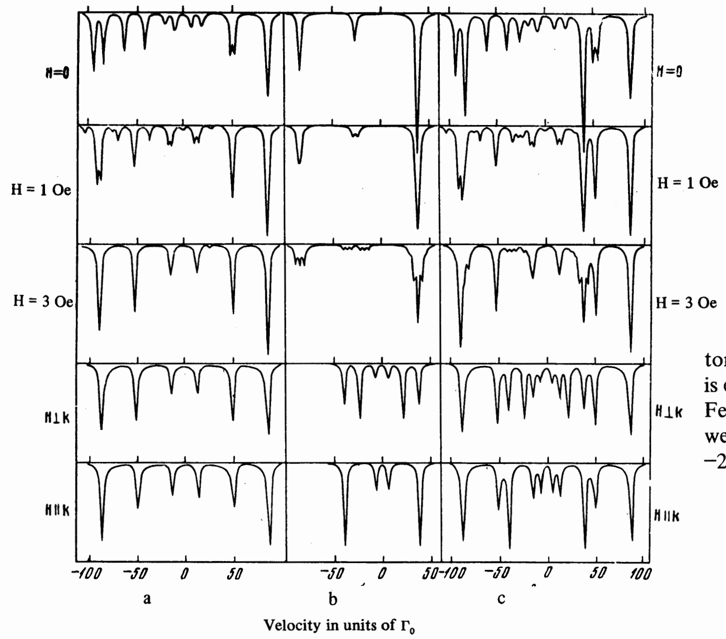

FIG. 2. Hyperfine-structure spectra for the doublets of the Hamiltonian (34) in the case of the ions Fe^{3+} ($S = 5/2$). The relative velocity is expressed in units of the natural width Γ_0 of the 14.4-keV line of the Fe^{57} nucleus. (In constructing all the spectra given in the present paper, we used the following values of their parameters: $\Gamma_a + \Gamma_s = 3\Gamma_0$, $A_0 = -26.62\Gamma_0$, $A = 0.571 A_0$.)

spectra for the doublet $\Gamma^{(3)}$, and Fig. 2c shows the summary spectra in magnetic fields corresponding to 0, 1, and 3 Oe, and also in stabilizing fields perpendicular and parallel to the direction of propagation of the gamma quanta.

As is well known[6,7], weak magnetic fields greatly influence the hyperfine structure of the Mossbauer line in paramagnets. According to the theory[6], the spectrum from the doublet $\Gamma^{(3)}$, for which the hyperfine-interaction tensor components are equal to one another (see (35)), should be strongly smeared out by weak magnetic fields, and in the stabilizing fields $H \gg A/2\mu_B$ it should reveal a distinct hyperfine structure (μ_B is the Bohr magneton). This is clearly seen from Fig. 2b. As shown in[6], the spectra of the hyperfine structure for the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$ should not be smeared out by weak magnetic fields, since for these doublets one of the parameters is much larger than the other two (see (35)). However, as seen from Fig. 2a, in this case small magnetic fields still noticeably influence the spectrum of the hyperfine structure, effectively reducing, as it were, the number of observed components of the spectrum. In essence, stabilizing fields are in this case on the order of only several Oe.

Figure 2 shows that the case considered by us, if encountered in experiment, is very difficult from the point of view of interpretation of the observed spectra, unless all the parameters of $\mathscr{H}_{CF}$ are known beforehand and the experiment is carried out without a magnetic field. Indeed, in this case the spectrum from the doublet $\Gamma^{(3)}$ turns out to be smeared out by the random magnetic fields, which are always present in a paramagnetic crystal, and the spectra from $\Gamma^{(1)}$ and $\Gamma^{(2)}$ differ noticeably from the theoretical spectra corresponding to the field $H = 0$, and are outwardly reminescent of the group of six lines characteristic of spectra in magnetically ordered substances (see Fig. 2 at $H = 3$ Oe).

We now lift the limitation $b_k^{(4)} = 0$. The most general crystal-field Hamiltonian customarily used for ions with $S = 5/2$ is[8]

$$\mathscr{H}_{CF} = D[S_z^2 - {}^1/_3 S(S+1)] + E(S_x^2 - S_y^2) + \frac{F}{180}\{35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2\} + \frac{a}{6}\left[S_\xi^4 + S_\eta^4 + S_\zeta^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)\right]. \quad (37a)$$

Here the terms with D and F correspond to axially-symmetrical fields of second and fourth orders, the term with E describes deviations from axial symmetry in the form of a rhombic increment, and the term with a corresponds to a field of cubic symmetry. The axis of the axially symmetrical contribution may not coincide in the general case with any of the three mutually perpendicular cubic axes ξ, η, and ζ.

In terms of the operators $\hat{O}_k^{(n)}$, expression (37a) takes the form

$$\mathscr{H}_{CF} = \frac{2}{3}D\hat{O}_0^{(2)} + \sqrt{\frac{2}{3}}E(\hat{O}_2^{(2)} + \hat{O}_{-2}^{(2)}) + \frac{2}{45}F\hat{O}_0^{(4)} + \mathscr{H}_{\text{cub}}. \quad (37b)$$

The cubically symmetrical term $\mathscr{H}_{\text{cub}}$ takes different forms for different orientations of the z axis relative to the coordinate system ξ, η, ζ. We present the form of $\mathscr{H}_{\text{cub}}$ which will be needed in what follows, for cases when the z axis coincides with one of the symmetrical directions of the cube:

the direction [1, 0, 0]

$$\mathscr{H}_{\text{cub}} = \frac{a}{15}\left[\hat{O}_0^{(4)} + \sqrt{\frac{5}{14}}(\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)})\right]; \quad (38a)$$

the direction [1, 1, 0]

$$\mathscr{H}_{\text{cub}} = -\frac{a}{60}\left[\hat{O}_0^{(14)} - \sqrt{10}(\hat{O}_2^{(4)} + \hat{O}_{-2}^{(4)}) - 3\sqrt{\frac{5}{14}}(\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)})\right]; \quad (38b)$$

the direction [1, 1, 1]

$$\mathscr{H}_{\text{cub}} = -\frac{2}{45}a\left[\hat{O}_0^{(4)} + \sqrt{\frac{10}{7}}(\hat{O}_3^{(4)} - \hat{O}_{-3}^{(4)})\right]. \quad (38c)$$

We now turn to Fig. 1 and see what information is contained in some of its characteristic points. We consider the following case:

(b): $\varphi = \pi/4$. At this value of the angle there is only one allowed point, at which $r = r_3 = 1/\sqrt{2}$, $r_1 = 0$, $\gamma_3 = \pi/2$. Accordingly, the following coefficients $c_m^{(1)}$

differ from zero:

$$c_{5/2} = \frac{1}{\sqrt{2}}, \quad c_{-3/2} = \frac{1}{\sqrt{2}} e^{i\alpha}, \tag{39}$$

where α is an arbitrary phase, which we set equal to zero. Using these values of $c_m^{(1)}$, and also (32), we get in accordance with (27)

$$\mathscr{H}_{CF} = \frac{\Lambda_1 + \Lambda_2}{21} \hat{O}_0^{(2)} - \frac{\Lambda_1 + \Lambda_2}{105} \hat{O}_0^{(4)} + \frac{\sqrt{14}}{210} (\Lambda_1 - \Lambda_2) (\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)}). \tag{40}$$

Thus, in the case considered here $\mathscr{H}_{CF}$ is a sum of terms with D, F. and a and should correspond to cubic symmetry with tetragonal distortion. Assume, for example, that F = 0. Comparing (40) with (37) and (38a), we easily find that a = − 2D, $\Lambda_1 + \Lambda_2 = -7a$ and $\Lambda_1 - \Lambda_2 = \sqrt{5a}$, whence we obtain for the energies of the three respective Kramers doublets

$$\lambda_{1,2} = -\frac{a}{6}(7 \mp 3\sqrt{5}), \quad \lambda_3 = \frac{7}{3} a.$$

Naturally, these λ_i would be different fro $F \neq 0$, but this does not matter to us in the sense that the coefficients (39) would then become invariant and the hyperfine structure of the doublets would remain unchanged. A change of λ_i changes only the populations of the different doublets at a specified sufficiently low temperature T, and this is suitably reflected only in the intensity of the lines of the summary Mossbauer spectrum.

We present the values of the components of the hyperfine-interaction tensor for the three doublets of the Hamiltonian (40):

$$\begin{gathered} A_x^{(1)} = A_y^{(1)} = A_x^{(2)} = A_y^{(2)} = \sqrt{5} A, \; A_x^{(3)} = A_y^{(3)} = 3A, \\ A_z^{(1)} = A_z^{(2)} = A_z^{(3)} = A. \end{gathered} \tag{41}$$

In this case the small random fields will smear out the spectra from all three doublets, and therefore Fig. 3 shows directly the summary spectrum in a stabilizing field perpendicular to the wave vector **k** of the gamma quanta. (We shall henceforth show in the figures only the spectra in stabilizing magnetic fields **H ⊥ k**.)

Case (b′): $\varphi = 3\pi/4$, $r = 1/\sqrt{2}$ (point b′ in Fig. 1). It is easy to verify that this case is exactly equivalent to the just-analyzed case (b).

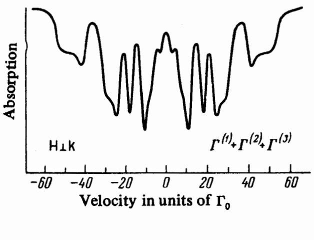

FIG. 3. Mossbauer spectrum corresponding to the Hamiltonian of crystal field (40), in a stabilizing magnetic field **H ⊥ k**.

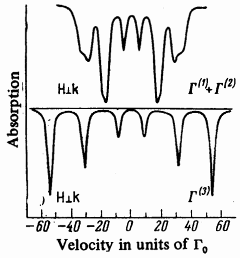

FIG. 4. Mossbauer spectra for the doublets $\Gamma^{(1)}$ and $\Gamma^{(2)}$ of the Hamiltonian (42) in a stabilizing magnetic field **H ⊥ k**.

Let us consider the following case of interest: c): $\varphi = \pi/3$, $r = 1/\sqrt{2}$ (see Fig. 1). It is easy to verify that in this case only the coefficients $c_{5/2}^{(1)} = 1/\sqrt{2}$ and $c_{-1/2} = (1/\sqrt{2})e^{i\alpha}$ differ from zero, and the Hamiltonian $\mathscr{H}_{CF}$ is given by

$$\mathscr{H}_{CF} = \frac{\Lambda_1 + \Lambda_2}{84} \hat{O}_0^{(2)} + \frac{\Lambda_1 + \Lambda_2}{70} \hat{O}_0^{(4)} - \frac{\sqrt{14}}{210} (\Lambda_1 - \Lambda_2) (\hat{O}_3^{(4)} - \hat{O}_{-3}^{(4)}). \tag{42}$$

A comparison with (38c) shows that (42) corresponds to a surrounding of cubic symmetry with axially-symmetrical distortion along the trigonal axis of the cube. Neglecting F, we find that a = − 18 D, $\lambda_{1,2} = -14a/27 \pm (2/3)a\sqrt{5}$, $\lambda_3 = 28a/27$. The components of the hyperfine-interaction tensor for the three doublets of the Hamiltonian (42) are

$$A_x^{(1)} = A_x^{(2)} = 3A/2, \quad A_y^{(1)} = A_y^{(2)} = 3A/2, \quad A_z^{(1)} = A_z^{(2)} = 2A,$$

$$A_x^{(3)} = A_y^{(3)} = 0, \quad A_z^{(3)} = 3A.$$

The Hamiltonian (42) corresponds also to the point c′ in Fig. 1b. The Mossbauer spectra for the doublets $\Gamma^{(1)}$ and $\Gamma^{(3)}$ are shown in Fig. 4.

Let us consider the following case:

(d): $\varphi = \pi/2$. For this angle φ we can readily find that $r_1 = 1/\sqrt{2}$, $\gamma_1 = 0$, $r_3^2 = (1 - 2r^2)/2$, $\gamma_3 = \pi/2$, from which we obtain the following non-zero coefficients $c_m^{(1)}$ and $b_k^{(n)}$:

$$c_{5/2} = r, \quad c_{1/2} = \frac{1}{\sqrt{2}} e^{i\alpha}, \quad c_{-3/2} = r_3 e^{i\beta}; \tag{43}$$

$$\begin{gathered} b_0^{(2)} = \frac{1}{84}(12r^2 - 5)(\Lambda_1 + \Lambda_2), \\ b_2^{(2)} = \frac{\sqrt{30}}{84}\left(re^{i\alpha} + \frac{3}{\sqrt{5}} r_3 e^{i(\beta-\alpha)}\right)(\Lambda_1 - \Lambda_2), \\ b_0^{(4)} = \frac{1}{210}(8r^2 - 1)(\Lambda_1 + \Lambda_2), \\ b_2^{(4)} = \frac{3\sqrt{2}}{210}\left(re^{i\alpha} - \frac{\sqrt{5}}{3} r_3 e^{i(\beta-\alpha)}\right)(\Lambda_1 - \Lambda_2), \\ b_4^{(4)} = \frac{\sqrt{14}}{105} r r_3 e^{i\beta} (\Lambda_1 + \Lambda_2). \end{gathered} \tag{44}$$

Let at first $\Lambda_1 - \Lambda_2 = 0$. It is clear that then $\mathscr{H}_{CF}$ should be a sum of terms with D, F, and a. We put, as before, F = 0 and stipulate in accordance with (38a) that $b_4^{(4)}/b_0^{(4)} = \sqrt{5/14}$. This gives rise to two possibilities: 1) $r^2 = 5/12$, $\beta = 0$ and 2) $r^2 = 1/92$, $\beta = \pi$. We easily see from the expression for $b_0^{(2)}$ that case (1) corresponds to the Hamiltonian of the crystal field of pure cubic symmetry. In case (2) we have

$$\mathscr{H}_{CF} = -\frac{4}{69}(\Lambda_1 + \Lambda_2)\hat{O}_0^{(2)} - \frac{\Lambda_1 + \Lambda_2}{230}\left[\hat{O}_0^{(4)} + \sqrt{\frac{5}{14}}(\hat{O}_4^{(4)} + \hat{O}_{-4}^{(4)})\right] \tag{45}$$

which corresponds to cubic symmetry with axially-symmetrical distortion along the [1, 0, 0] axis of the cube. Then a = (3/4)D. The condition $\Lambda_1 - \Lambda_2 = 0$ denotes that $\lambda_1 = \lambda_2$, and thus, the eigenstates of the Hamiltonian (45), as well as the Hamiltonian for the purely cubic field, are a quartet and a doublet. We shall not consider this case in greater detail, since the presence of the quartet calls for a special approach. In particular, for the quartet we cannot use formulas (7) for the component of the hyperfine-interaction tensor.

Let now $\Lambda_1 - \Lambda_2 \neq 0$. Then, obviously, we should stipulate that $\mathscr{H}_{CF}$ correspond to a field of cubic symmetry with distortion along the [1, 1, 0] direction of

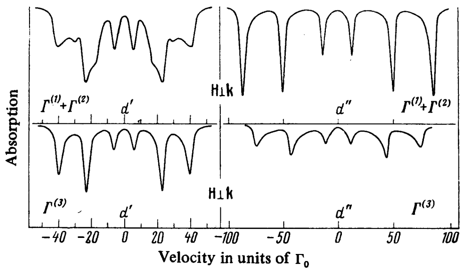

FIG. 5. Hyperfine-structure spectra in the cases (d') and (d'') in a stabilizing magnetic field **H** ⊥ **k**.

the cube, or in other words, satisfaction of the relation (see, (38b))

$$b_2^{(4)}/b_0^{(4)} = -\sqrt{10}, \quad b_4^{(4)}/b_0^{(4)} = -3\sqrt{5/14}. \tag{46}$$

An analysis of the second equation of (46) shows that two situations are possible: (d') $r^2 = (139 + 14\sqrt{46})/916$, $\beta = \pi$ and (d'')$r^2 = (139 - 14\sqrt{46})/916$, $\beta = 0$ (see the corresponding points in Fig. 1). In both cases the Hamiltonian of the crystal field has the form (37b) with F = 0 and $\mathscr{H}_{\text{cub}}$ described by relation (38b). The parameters of the Hamiltonian $\mathscr{H}_{\text{CF}}$ and the components of the hyperfine-interaction tensor are then equal to:

in case (d')

$$a = -0{,}1118(\Lambda_1 + \Lambda_2), \quad a = 3{,}2347D, \quad D = -3{,}0753E,$$

$$A_x^{(1)} = A_y^{(2)} = 1{,}5960A, \quad A_x^{(3)} = A_y^{(3)} = 2{,}2355A,$$

$$A_y^{(1)} = A_x^{(2)} = 2{,}3605A, \quad A_z^{(1)} = A_z^{(2)} = 1{,}0433A, \quad A_z^{(3)} = 0{,}9135A;$$

in case (d'')

$$a = 0{,}0659(\Lambda_1 + \Lambda_2), \quad a = -0{,}8347D, \quad D = 0{,}5420E,$$

$$A_x^{(1)} = A_y^{(2)} = 4{,}8482A, \quad A_x^{(3)} = A_y^{(3)} = 1{,}3185A,$$

$$A_y^{(1)} = A_x^{(2)} = 0{,}5297A, \quad A_z^{(1)} = A_z^{(2)} = 0.6153A, \quad A_z^{(3)} = 4{,}2306A.$$

The Mossbauer spectra corresponding to cases (d') and (d'') are shown in Fig. 5, see the points d' and d''.

6. CONCLUSION

As seen from the preceding section, the general method developed in this paper makes it possible to find relatively simply a number of concrete crystal-field Hamiltonians that give a "degenerate" hyperfine structure. On the other hand, it was shown in Sec. 4 that in the case $S = 5/2$ there exist an infinite number of Hamiltonians of general form admitting of such degeneracy. However, if the Mossbauer ion is in the S-state, then the class of the Hamiltonians $\mathscr{H}_{\text{CF}}$ is already limited per se. Thus, for the trivalent ion Fe^{3+} ($S = 5/2$) the most general Hamiltonian used for the interpretation of the Mossbauer spectra and the EPR spectra is the Hamiltonian of the type (37). In this case, as can be readily shown, the degenerate spectra of the hyperfine structure will correspond on the (r, φ) diagrams not to regions but to individual lines. If furthermore we recognize that the term with F in (37) is as a rule much smaller than the remaining terms and can be neglected in the first approximation, then only individual points will correspond in this case to "degenerate" spectra.

This circumstance gives reasons for hoping that there exists for the Fe^{3+} ion only a finite number of cases with "degenerate" hyperfine structure. However, the general analysis in this case is quite complicated.

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34