Mössbauer spectra of the hyperfine structure of paramagnetic Fe^{3+} ions in weak magnetic fields

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Results are reported of an investigation of the hyperfine magnetic structure of the Mössbauer spectra of Fe^{57} nuclei in single-crystal $Al(NO_3)_3{\cdot}9H_2O{:}Fe^{3+}$. The orientation dependence of the spectra for Stark doublets of the Fe^{3+} ion in magnetic fields $H \leq 300$ Oe is analyzed in detail. Relations between the Hamiltonian parameters of the crystal field are found and the directions of the principal hyperfine interaction tensor (A_{jk}) axes are determined. Additional components of the Mössbauer spectrum outside the velocity range characteristic of the Fe^{57} nuclei in the Fe^{3+} ion in the high-spin state $^6S_{5/2}$ are observed by choosing the magnitude and direction of H in a specified manner. A theoretical analysis of the results shows that in this case Zeeman splitting of the Fe^{3+} ion electron levels is induced in the hyperfine structure spectra by a weak external magnetic field.

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1. INTRODUCTION

The number of papers devoted to the hyperfine structure (hfs) of Mössbauer spectra in paramagnetic substances is by now quite large. As a rule, the main purpose of these investigations is to study the influence of electron-spin relaxation processes on the hfs spectra, as well as the determination (or estimate) of the relaxation constants. So far, however, the structure of the hfs spectra has not yet been investigated in the limit of slow relaxation, i.e., under conditions when the relaxation processes can be neglected. This problem is the subject of only a relatively few studies.[1-11] Yet notwithstanding the apparent simplicity of the physical model, many questions remain unanswered. In addition, the experimental capabilities for these investigations have not yet been fully revealed.

The point is that hfs spectra in paramagnets, as predicted theoretically[1-3] and subsequently demonstrated experimentally,[4-7] are very sensitive to the action of very weak magnetic fields. The hfs spectra are influenced by fields such that the energy of the interaction of the magnetic field H with the electron shell ($\mu_{el}\cdot H$) turns out to be comparable with the hyperfine-interaction energy ($AI\cdot S$). Thus, for Fe^{3+} ions, these fields amount to only several dozen oersteds. Actually, however, the character and scale of the influence of the magnetic field on the hfs spectra are determined to a considerable degree by the interaction of the electron shell with the intracrystalline fields. This gives rise to a large number of qualitatively different types of hyperfine spectra.

Attempts to analyze different possible situations connected with the behavior of paramagnets in external magnetic fields were undertaken long ago by Wickman *et al.*[1,2] Until recently, however, the experimental investigations were confined only to the study of one quite distinctly realized phenomenon, the so-called "stabilization effect".[3,6,7] The gist of this method is that in almost all substances part of the hfs spectrum is sensitive to fields of only several oersteds, so that under ordinary conditions, in the absence of an external magnetic field, random fields from paramagnetic impurities or stray fields lead to a smearing of part of the hfs spectrum. When a magnetic field $H \gtrsim 100$ Oe is superimposed, however, the hfs spectra are completely restored.

It is natural to expect to observe in single-crystal samples, besides this effect, also a dependence of the hfs spectra on the direction of the magnetic field relative to the crystallographic axes of the sample. Investigations performed for this purpose on Fe^{57} nuclei in single-crystal $Al(NO_3)_3\cdot 9H_2O{:}\ Fe^{3+}$ have indeed revealed such an orientation dependence.[9] It was established there that the hfs spectra are sensitive to the direction of H only in a very narrow angle interval, on the order of several degrees. This circumstance has greatly hindered the experimental observation and investigation of the orientation dependence of the spectra. The strong sensitivity of the spectra to the H direction is due to the actual form of the interaction of the Fe^{3+} ion with the intracrystalline field. It has turned out that the hyperfine interaction tensor $A_{jk}^{(i)}$ is strongly anisotropic for the two Stark doublets. This fact explains the observed phenomenon fully. Moreover, the strong anisotropy of the tensor $A_{jk}^{(i)}$ has made it possible to observe one more effect, the manifestation of the Zeeman electron splitting in Mössbauer spectra.[10]

The present study was undertaken for the purpose of a more detailed investigation of the hfs spectra in single crystal $Al(NO_3)_3\cdot 9H_{20}{:}\ Fe^{3+}$ in the observed[9] region where the hfs spectra are sensitive to the direction of the external magnetic field. Whereas the change of the positions of the hfs lines was previously established for only one of the Stark doublets, in the present study we obtain the region of H directions in which the splitting of two doublets is determined simultaneously. This, naturally, manifests itself in a much stronger change of the shapes of the spectra and, furthermore, makes it possible to establish the direction of the principal axes of the hyperfine interaction tensor $A_{jk}^{(i)}$ in the crystal.

2. THEORY

We consider a paramagnet containing Fe^{3+} ions in the high-spin $^6S_{5/2}$ state with nuclei of the Mössbauer isotope Fe^{57}. At low temperatures and in sufficiently strongly diluted paramagnets, when the influence of the spin-lattice and spin-spin relaxations is negligibly small, the Mössbauer spectra have a magnetic hyperfine structure for which the hyperfine interaction of the nucleus with the electron shell of the paramagnetic ion ($\mathscr{H}_{\text{hf}}$) is responsible. However, even in the absence of relaxation processes the form of the hfs spectra depends to a substantial degree on the magnitude and character of the interaction of the ion with the intracrystalline fields ($\mathscr{H}_{\text{cf}}$), on the interaction of the ion with the external magnetic field ($\mathscr{H}_z$), and also on the relations between these interactions.

When the external field is varied, situations with $\mathscr{H}_z \gg \mathscr{H}_{\text{cf}}$ and $\mathscr{H}_z \ll \mathscr{H}_{\text{cf}}$ are possible. For the Fe^{3+} ions, the first case is realized in fields on the order of several dozen kOe. It was investigated theoretically and experimentally by Wickman and Wertheim,[2] and we shall not dwell on it. We are interested in situations in which $\mathscr{H}_z \ll \mathscr{H}_{\text{cf}}$.

The structure of the energy levels of the Fe^{3+} ions can be represented in the following manner. The crystal field splits the ground state of the Fe^{3+} ions into three doubly degenerate Stark levels. Each spectrum can be assigned an effective spin $S'=\frac{1}{2}$, and the Zeeman and hyperfine interactions are represented in terms of this effective spin as follows (see, e.g.,[7]):

$$\mathscr{H}^{(i)}=\mathscr{H}_z^{(i)}+\mathscr{H}_{hf}^{(i)}=\mu_B(g_{xx}^{(i)}S_x'H_x+g_{yy}^{(i)}S_y'H_y+g_{zz}^{(i)}S_z'H_z)$$
$$+A_{xx}^{(i)}I_xS_x'+A_{yy}^{(i)}I_yS_y'+A_{zz}^{(i)}I_zS_z'. \tag{1}$$

The index i numbers here the Stark doublets, and the remaining notation is standard; $g_{jj}^{(i)}$ and $A_{jj}^{(i)}$ are the principal values of the effective g-tensor and of the hyperfine interaction tensor, respectively. The tensors $g_{jk}^{(i)}$ and $A_{jk}^{(i)}$ are proportional, and the relations between the different components of these tensors depend on the form of the Hamiltonian $\mathscr{H}_{\text{cf}}$. Thus, in the case of a crystal field in the form

$$\mathscr{H}_{cf}=D[S_z^2-{}^1/_3S(S+1)]+E(S_x^2-S_y^2),$$
$$\lambda=E/D={}^1/_3 \tag{2}$$

we have two Stark doublets with the following principal values of the components of the tensor $A_{jk}^{(i)}$:

$$A_{xx}^{(1)}=4.8392A,\quad A_{yy}^{(1)}=0.3036A,\quad A_{zz}^{(1)}=0.4286A:$$
$$A_{xx}^{(2)}=0.3036A,\quad A_{yy}^{(2)}=4.8392A,\quad A_{zz}^{(2)}=0.4286A: \tag{3}$$
$$A_{xx}^{(3)}=A_{yy}^{(3)}=A_{zz}^{(3)}=2.1429A.$$

If the temperature is high enough, so that all three Stark doublets are populated, then the hfs spectra of the Mössbauer line constitutes a superposition of three individual spectra. The structure of each of these spectra, corresponding to different doublets, is determined by the forms of the tensors $g_{jk}^{(i)}$ and $A_{jk}^{(i)}$, and also by the relation between $\mathscr{H}_z^{(i)}$ and $\mathscr{H}_{\text{hf}}^{(i)}$. In weak magnetic fields at $\mathscr{H}_z \ll \mathscr{H}_{\text{hf}}$ the spectra are very sensitive to the field strength. This question has already been raised many times[3,6] and has been sufficiently well studied by now.

Consider the case when

$$\mathscr{H}_z \gg \mathscr{H}_{hf}. \tag{4}$$

As a rule, this condition is satisfied by fields ~100 Oe, which lift the double degeneracy of the Stark levels. The hyperfine interaction can be taken into account by perturbation theory. The splitting of the nuclear levels by the hyperfine interaction is determined here by the effective magnetic field at the nucleus[7]

$$H_{\text{eff}}=\pm H_0\left[\frac{(A_{xx}^4\cos^2\varphi+A_{yy}^4\sin^2\varphi)\sin^2\theta+A_{zz}^4\cos^2\theta}{(A_{xx}^2\cos^2\varphi+A_{yy}^2\sin^2\varphi)\sin^2\theta+A_{zz}^2\cos^2\theta}\right]^{1/2}, \tag{5}$$

where the angles φ and θ determined the direction of the external field relative to the coordinate system in which the tensors $A_{jk}^{(i)}$ and $g_{jk}^{(i)}$ are diagonal.

It follows from this expression that in the presence of anisotropy of the tensor $A_{jk}^{(i)}$ the field H_{eff} should depend on the direction of the external magnetic field. For doublets with a sharply anisotropic tensor $A_{jk}^{(i)}$ (for example, the doublets 1 and 2 in the case described by formulas (2) and (3)), this dependence should manifest itself very strongly in a relatively small angle interval in a direction perpendicular to the principal axes of the tensor $A_{jk}^{(i)}$ with the maximum principal value.

In the case (4) considered above, the hyperfine spectra are described by the effective magnetic field, and when the nuclei go from the excited to the ground state (or conversely), the state of the electron shell of the ion remains unchanged. However, if the field is decreased (or else if its direction is specially chosen in strongly anisotropic cases), then the structure of the sublevels between which the Mössbauer transition takes place acquires already a mixed electron-nuclear character. In this situation, when a γ photon is emitted (or absorbed), the electronic state is also altered and as a result the structure of the Mössbauer line can also change greatly. This effect is easiest to observe in experiment, with the strongly anisotropic tensor $A_{jk}^{(i)}$ as an example.

We consider a tensor with components

$$A_{yy} \gg A_{xx}, A_{zz} \tag{6}$$

(see (2) and (3)). We can then neglect in the Hamiltonian the terms with A_{xx} and A_{zz} (but not the analogous terms in the Zeeman interaction). As a result we obtain at $\mathbf{H} \perp z$:

$$\mathscr{H}^{(2)}=\mu_B(g_{xx}^{(2)}S_x'H_x+g_{yy}^{(2)}S_y'H_y)+A_{yy}^{(2)}I_yS_y'. \tag{7}$$

Since the operator I_y is an integral of the motion, each of the levels of this Hamiltonian is described by the quantum numbers M and σ, where M is the projection of the nuclear spin on the y axis and $\sigma=\pm\frac{1}{2}$ is the projection of the electron spin on the y' axis. The angle

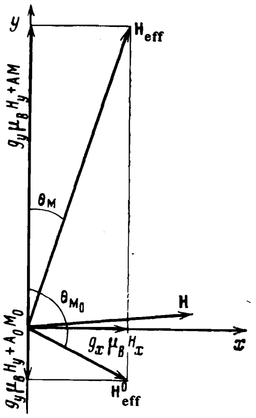

FIG. 1. Schematic representation of the quantization axes of the effective electron spin $S' = 1/2$ for the ground (H^0_{eff}) and excited (H_{eff}) states in a magnetic field H.

θ_M between the y and the y' axes (see Fig. 1) and the positions of the energy levels $E_{M,\sigma}$ as functions of the magnitude and direction of H are given by

$$\operatorname{tg}\theta_M = \frac{\mu_B g^{(2)}_{xx} H_x}{g^{(2)}_{yy}\,\mu_B H_y + A^{(2)}_{yy} M}, \tag{8}$$

$$E_{M,\sigma} = \sigma\left[(\mu_B g^{(2)}_{xx} H_x)^2 + (\mu_B g^{(2)}_{yy} H_y + A^{(2)}_{yy} M)^2\right]^{1/2}. \tag{9}$$

As seen from (8), the direction of the quanitization axis of the electron spin depends on the projection M of the nuclear spin, and consequently is changed in the nuclear transition (see Fig. 1). If the electron-spin quantization axes corresponding to the nuclear transition $M \to M_0$ make an appreciable angle with each other, the hfs spectrum contains all the transitions with values $\sigma = \pm\frac{1}{2}$ and $\sigma_0 = \pm\frac{1}{2}$. The transition energies and the intensities of the corresponding lines are then determined by the formulas

$$\Delta E_{M,\sigma\to M_0,\sigma_0} = \pm(E_{M,\sigma} \mp E_{M_0,\sigma_0}), \tag{10}$$

$$P_{M,\sigma\to M_0,\sigma_0} = P_{M,M_0} P_{\sigma,\sigma_0}(M, M_0), \tag{11}$$

where P_{M,M_0} is the intensity and is determined by the nuclear interactions, while

$$P_{\sigma,\sigma_0}(M, M_0) = {}^1\!/_2\{1 + 4\sigma\sigma_0\cos(\theta_M - \theta_{M_0})\}. \tag{12}$$

If the angle between the quantization axes of the electron spin for the ground and excited states of the nucleus is close to $\pi/2$, then all the transitions with different electron-spin projections will be represented in the Mössbauer spectrum, and the positions of some of the transitions will lie outside the absorption spectrum usually observed for the Fe^{3+} ion (Fig. 2).

3. EXPERIMENT

Measurements of the Mössbauer absorption spectra of impurity Fe^{57} nuclei were made on single-crystal samples of $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} with monoclinic structure of the crystal lattice ($a = 10.86$ Å, $b = 9.59$ Å, $c = 13.83$ Å; $\alpha = \gamma = 90°$, $\beta = 96°10'$; space group $P_{2_1/a}$).[12] The samples were prepared by slow evaporation of aqueous solution of $Al(NO_3)_3$ containing 0.5 mol.% $Fe(NO_3)_3$ (the enrichment of the iron with the isotope Fe^{57} was 89%). Typical dimensions of the $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} crystals grown in this manner were ~15×15×5 mm. All the samples used in the experiment were identified by x-ray structure analysis, according to which the crystal-structure mosaic misorientation did not exceed 10'.

Since the predominant crystal growth was in the (bc) plane, the working samples were plates ~3 mm thick, ground in this plane. The samples were placed in an organic-glass container and were sealed for the purpose of preventing variations of the chemical composition of the compound.

In preliminary investigations[9] of the Mössbauer spectra of the Fe^{57} nuclei in $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+}, the external field was produced by a permanent magnet made up of ferrite rings. The direction of H was varied by rotating the magnet relative to the sample. The capabilities of such a system are limited when it comes to searching for all the interesting regions where the hfs spectra are sensitive to the direction of H, and the field was not sufficiently uniform over the sample. In the succeeding experiments, the field H was produced by three pairs of Helmholtz coils mounted in mutually perpendicular planes. This made it possible to vary the direction of H in any convenient region of angles relative to the sample placed in a helium cryostat at the center of the coils. The maximum value of H obtained in such a magnetic system was 300 Oe; the shield inhomogeneity over the sample did not exceed 0.01%. In all the experiments, the direction of the γ-ray beam from the source (Co^{57} in Cr; 50 μCi) was perpendicular to the sample plane (bc). The measurements were performed with a two-channel γ spectrometer operating in a semi-automatic regime with discrete variation of the source velocity.

As already noted[9] (see also[13]), the spin-lattice relaxation frequency of impurity Fe^{3+} ions in $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} at temperatures $T \leq 77$ °K is small in comparison with the frequency of the hyperfine structure of the Fe^{57} nuclei, and the line width of individual spectrum components is practically independent of the temperature in the interval 4.2–77 °K. This has made it possible to perform the majority of the measurements at liquid-nitrogen temperature. Thus, the compound $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} is a very convenient object for the investigation in those cases when the spin-lattice relaxation must be excluded.

The obtained hfs spectra were computer-reduced by a least-squares special program[14] with the spectral-

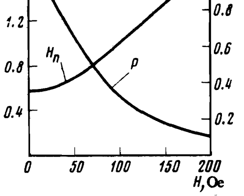

FIG. 2. Dependence of the splitting (H_n) and intensity (P) of the Mössbauer-spectrum line in the nuclear transition −3/2 → −1/2 on the value of H for the case when the direction of H is close to x axis (Fig. 1).

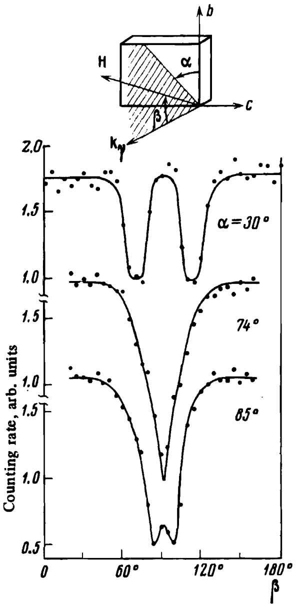

FIG. 3. Dependence of the counting rate of γ rays of energy 14.4 keV passing through an $Al(NO_3)_3 \cdot 9H_2O:Fe^{3+}$ absorber on the direction of the magnetic field $H = 200$ Oe at a fixed velocity ($v = +9.8$ mm/sec) of the source (Co^{57} in Cr). Temperature of absorber $T = 77$ °K, of source 300 °K.

component line shape approximated by a Lorentzian. The program made it possible to vary the position, amplitude, and width of each of the 18 (in the most typical case) components, and also carry out the reduction under different additional conditions imposed on the relations between the intensities of the individual lines.

The complete series of investigated spectra was obtained with different samples, each of which was identified by x-ray structure analysis. The agreement between the crystallographic characteristics of the different samples, and also the reproducibility of the Mössbauer spectra obtained under the same conditions (T, H) allow us to conclude that the distribution of the impurity Fe^{3+} ions in $Al(NO_3)_3 \cdot 9H_2O$ is quite stable and unambiguous when this particular method is used to grow the single crystals.

To find angle regions in which the hfs spectra are most sensitive to the direction of H, we used a "scanning" method. It consisted of comparing the counting rate of the γ photons in both analyzed channels (for two source velocities "$+v$" and "$-v$") at a fixed velocity corresponding to the top of one of the outermost lines of the spectrum. The current in the coils was varied in such a way that the field H, remaining constant in magnitude, was rotated in some particular plane relative to the sample. On approaching the angle region of interest, where the hfs of the spectrum turned out to be sensitive to small changes of the H direction, the difference between the counting rates in the analyzer channels began to vary. Further rotation of H established a difference between the counts in the channels (Fig. 3). It was thus possible to determine with sufficient degree of accuracy the boundaries of the region where the hfs spectra are sensitive to the direction of H, a region measuring, as already noted, only several degrees. The described procedure made it possible to eliminate the insignificant instability of the spectrometer gain, which could nevertheless turn out to be essential because of the small value of the effect, at the start of the sought region of angles and the very narrowness of the region of the strongest angular dependence. Once the regions of interest were found, the subsequent study of the angular dependence required that the complete hfs spectra be obtained.

4. DISCUSSION OF RESULTS

The interpretation of the absorption spectra of Fe^{57} nuclei in single-crystal $Al(NO_3)_3 \cdot 9H_2O:Fe^{3+}$, obtained in the absence of an external magnetic field, is quite difficult even when the Hamiltonian of the crystal field in the given substance is known. As already noted, the main reason is the influence of the weak magnetic field produced by the paramagnetic ions in the crystal itself. In an external "stabilizing" field H it is possible to expect a clearer picture corresponding to the hfs spectra from three Stark doublets into which the ${}^6S_{5/2}$ term of the Fe^{3+} ion is split by the crystal field.

It is seen from Fig. 4 that in this case there is indeed an appreciable change in the shape of the Mössbauer spectrum, manifesting itself primarily in the fact that the spectrum becomes symmetrical, and additional distinct lines appear in its central part. However, instead of the expected 18 components (6 each for each of the three Stark doublets), only 12 lines are observed in the spectrum. Such a spectrum can be interpreted as a sum of two hfs spectra corresponding to hyperfine fields $H_{eff} = 574 \pm 5$ kOe and $H_{eff} = 255 \pm 5$ kOe. The total ratio of the intensities of the components of these spectra is 2:1.

It is known (see, e.g., [15]) that the splitting of energy levels of S-state ions in a crystal field is small ($\Delta \approx 0.1$ °K). Since in our case $T \gg \Delta$ and consequently all the Stark levels of the Fe^{3+} are equally populated, the Mössbauer spectrum must contain hfs of all three doublets. In this case the shape of the observed Mössbauer spectrum corresponds to the fact that the hfs from the two doublets coincide fully at arbitrary orientation of the external magnetic field.

In accordance with the results of[8], where a theo-

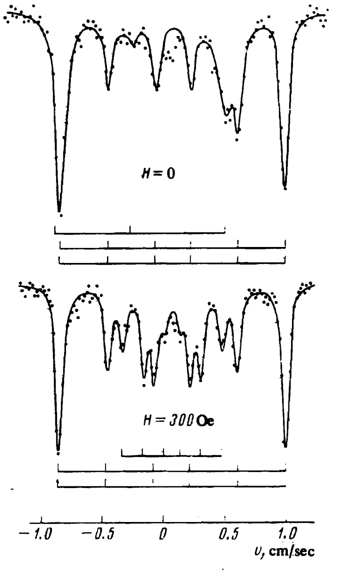

FIG. 4. Mössbauer absorption spectar of Fe^{57} nuclei in the investigated single crystal in the absence of an external field and in a stabilizing field $H = 300$ Oe ($H \perp k_\gamma$); $T = 77$ K.

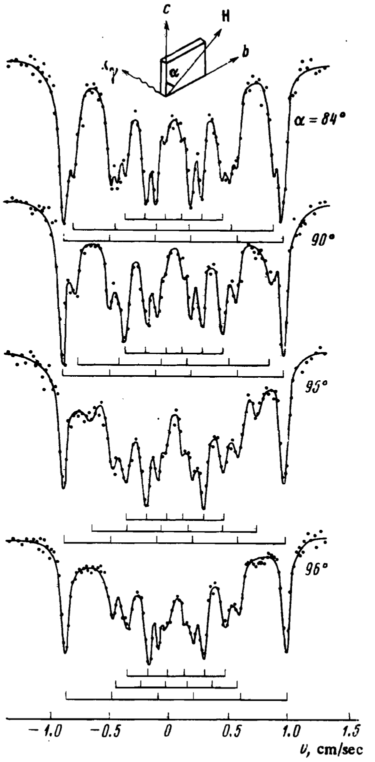

FIG. 5. Absorption spectra at the different orientations of the sample in a magnetic field $H = 300$ Oe ($H \perp k_\gamma$); $T = 77$ K.

retical analysis of similar "degenerate" hfs spectra was carried out, this makes it possible to reconstruct the Hamiltonian $\mathscr{H}_{\mathrm{cf}}$ of the crystal field at the location of the Fe^{3+} ion in the $Al(NO_3)_3 \cdot 9H_2O$ spectrum. In particular, the ratio of the constants $E/D \equiv \lambda$ for $\mathscr{H}_{\mathrm{cf}}$ (see (2)) turns out to be $\frac{1}{3}$ (we note that ESR data for $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} yield $\lambda = \frac{1}{6}$).[13] It follows therefore that the hyperfine-interaction tensors for the two "coinciding" Stark doublets should be strongly anisotropic, $A_{xx}^{(1)} \gg A_{yy}^{(1)}$, $A_{zz}^{(1)}$ and $A_{yy}^{(2)} \gg A_{xx}^{(2)}$, $A_{zz}^{(2)}$, and the components $A_{jk}^{(i)}$ from the third doublet are exactly equal to each other: $A_{xx}^{(3)} = A_{yy}^{(3)} = A_{zz}^{(3)}$ (see Sec. 2). This conclusion is confirmed by the change in the shape of the spectrum when an external magnetic field is applied. Indeed, the influence of H manifested itself in a change of the hfs for one of the doublets, for which the tensor $A_{jk}^{(i)}$ is isotropic, whereas the hfs of two other doublets with sharply anisotropic tensors remained pratically unchanged.

However, the anisotropy of $A_{jk}^{(i)}$ should cause the hfs of these doublets to be more sensitive to changes of the direction of H relative to the crystallographic axes of the sample. From (5), and also if the conditions (3) are taken into account, it follows that the effective field at the Fe^{3+} ion, at arbitrary values of the angles φ and θ, is determined by the largest of the principal values of the tensor $A_{jk}^{(i)}$ (the doublets (1) and (2)). At the same time, when the angle φ is close to zero or $\pi/2$, or when the angle θ tends to zero, the value of H_{eff} is determined, by virtue of the anisotropy of $A_{jk}^{(i)}$, by the smallest component of hyperfine interaction constant. As a consequence, the positions of the individual components of hfs spectrum begins to depend on the direction of the external field H. The range of sensitivity of the hfs spectrum subtends in this case over the angle region $(A_{yy}/A_{xx})^2 \leqslant \alpha \leqslant (A_{yy}/A_{xx})$, i.e., at $A_{yy} \approx 0.1 A_{xx}$ we have $0.5° \leqslant \alpha \leqslant 5°$. In other words, in order to observe a noticeable ($\sim A_{yy}/A_{xx}$) change of the splitting of hfs spectrum, it is necessary to direct the field H practically perpendicular to the principal axis x or y of the tensor A_{jk}. This should be accompanied by a splitting of the outermost components of the resultant spectrum. Since the direction of the axes of A_{jk} in the given crystal is not known, a series of special experiments was performed (see Sec. 3) to find the angle regions with the largest sensitivity of the hfs spectra to changes of the direction of the field H.

As shown in[9], with changing direction of the field H relative to the crystallographic axes of the sample, the components of one of the coinciding hfs spectra shift, in a definite region of the angles α ($\alpha = 84°$), to the center of gravity of the resultant spectrum. It turns out that a change of only one degree in the direction of H decreases strongly the splitting of the hfs spectrum for the given doublet (Fig. 5).

The character of the change of the hfs corresponds to the condition that the field H can be located near one of the planes (xz) or (yz), with the hfs corresponding to the two other doublets remaining unchanged. This behavior is determined by the fact that $A_{jk}^{(i)}$ of one of the doublets is fully isotropic and its hfs is entirely independent of the direction of H, while for the other doublet the direction of H is far from the plane containing the small components of the corresponding tensor $A_{jk}^{(i)}$. It is obvious that when H lands in this plane the splitting of the spectrum of the hfs of the second doublet should in turn decrease appreciably. On the other hand if the direction of H coincides with the z axis, an overall narrowing of the spectrum should be observed.

Further more detailed investigations of the anisotropy of the hyperfine interaction in the $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} crystal have made it possible not only to find both planes (xz) and (yz), but also to establish the direction of the z axis. The corresponding Mössbauer spectra are shown in Fig. 6. With changing angle β between the vectors H and k_γ, the magnetic field lands in the indicated planes $\alpha = 74°$, $\beta = 84°$; $\alpha = 74°$, $\beta = 100°$; here $\alpha = 74°$ is the angle between the b axis and the plane in which the direction of H varies). This is accompanied by a successive "collapse" of the hfs for both isotropic doublets. At an angle $\beta = 92°$, when the vector H is close enough to the z axis, a shift of the components of the hfs to the center of gravity of the spectrum (with simultaneous broadening) is observed for both doublets. The observed broadening is obviously connected with the fact that the Fe^{3+} ions are acted upon, besides the field H, also by random fields produced by the nearest environment. For this reason the resultant field changes from ion to ion, and this causes the broadening of the spectral line in the region of the strongest angular dependence. On the basis of the results we have determined the directions of the principal axes of the tensor A_{jk} relative to the crystallographic axes of the sample (Fig. 7, table).

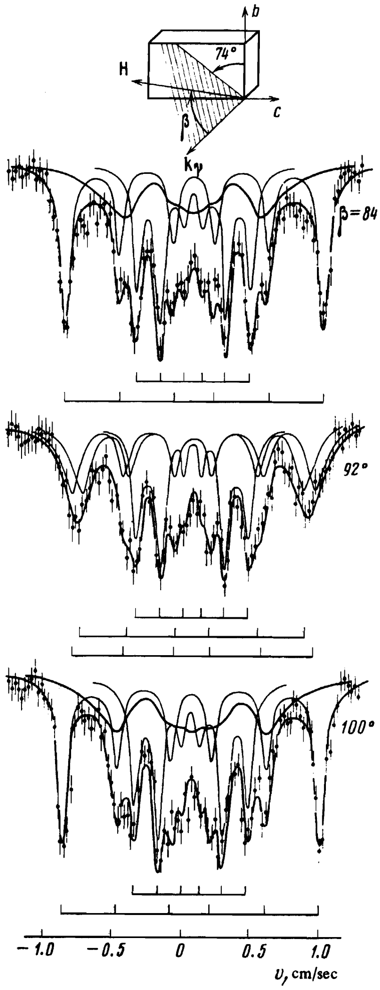

FIG. 6. Absorption spectra of Fe^{57} nuclei for three fixed directions of $H = 200$ Oe relative to the sample. The solid line show the calculated hfs spectra for individual Stark doublets of the Fe^{3+} ion.

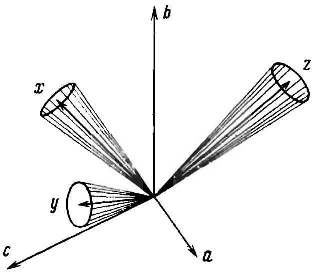

FIG. 7. Schematic representation of the directions of the principal axes $\{x, y, z\}$ of the hyperfine interaction tensor A_{jk} of the Fe^{57} nuclei in the investigated crystal.

Principal axes of tensor A_{jk}	Angles with the crystallographic axes, deg.		
	a	b	c
x	136±2	48±2	79±6
y	47±2	48±2	79±6
z	85±2	74±8	164±8

We note that the accuracy with which the directions of the principal axes were determined in this experiment amounts to several degrees, and our "scanning" procedure is no longer very effective for a further refinement of these parameters. For an exact solution of the problem it is necessary to carry out a detailed experimental investigation of a large number of complete Mössbauer spectra in a chosen "cone" of the z-axis directions. At the same time the very use of nuclear γ-resonance spectroscopy methods not only for the calculation of the parameters of the crystal-field Hamiltonian but also for the establishment of the orientation of the principal axes of the hyperfine interaction tensor in a crystal is quite promising.

As already noted in the theoretical discussion (Sec. 2), the presence of anisotropy of the tensor makes it possible to observe experimentally one more effect, the manifestation of the electron Zeeman splitting in Mössbauer spectra. Indeed (see, (9)), the position of the energy levels of the ion is determined both by the electronic and by the nuclear variables. The direction of quantization of the electron spin turns out to be significantly different for the ground and the excited state of the nucleus if the Zeeman splitting is comparable with the hyperfine interaction ($\mu_B gH \sim AIS$). In this case the transition of the nucleus from the excited state to the ground state (or conversely) changes the state of the electron shell of the ion, and consequently causes an abrupt change in the hfs spectrum of the Mössbauer line.

To observe experimentally this phenomenon, we have undertaken detailed investigations of the hfs spectra as functions of the applied field in the regions sensitive to the direction of H. Thus, in a field H equal to 35 Oe (Fig. 8), there appear in the hfs spectrum components the distance between which greatly exceeds the usually observed splitting for the Fe^{57} nuclei of the Fe^{3+} ion. This splitting is equivalent to an effective magnetic field ~ 700 kOe acting on the Fe^{57} nuclei. Actually we are dealing here with a manifestation of the electronic Zeeman splitting in the Mössbauer spectrum. It is easy to establish that the additional components of the spectra correspond to a nuclear transition $-\frac{3}{2} \to -\frac{1}{2}$ with energy determined from formulas (9) and (10). The intensities

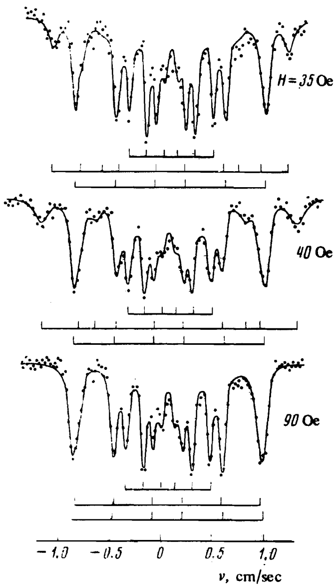

FIG. 8. Mössbauer absorption spectra of Fe^{57} nuclei in the investigated crystal at a fixed direction of H ($\alpha = 74°$, $\beta = 75°$—Fig. 6) relative to the crystallographic axes of the sample.

of these lines for the indicated transition decrease with the field less than the remaining ones and their experimental observation is easiest.

The increase of H when its direction is fixed relative to the sample leads, in accordance with the calculation, to an increase of the distance between the outermost components of the spectrum and simultaneously to a decrease of their intensities (Fig. 2). The maximum splitting observed by us experimentally corresponds to an effective field $H_{eff} = 850$ kOe. On the other hand, the magnitude of the observed effect on these components is only 0.14%, so that further increase of H (90 kOe) leads ultimately to a complete reconstruction of the initial structure of the spectrum.

CONCLUSION

The results of our investigations show that application of weak magnetic fields makes it possible to simplify considerably the interpretation of very complicated Mössbauer spectra of ferromagnetic crystals. This in turn makes it possible to obtain extensive information on the structure of the crystal field. Thus, an investigation of single-crystal $Al(NO_3)_3 \cdot 9H_2O$: Fe^{3+} yielded the relations between the parameters of the crystal-field Hamiltonian and the directions of the principal axes of the hyperfine interaction tensor of the Fe^{57} nuclei. In addition, by specially choosing the magnitude and the direction of H, we observed additional components in the Mössbauer spectrum, outside the limits of the hfs spectrum characteristic of the Fe^{57} nuclei of the Fe^{3+} ion. The reason for this effect is the Zeeman splitting of the electron levels of the Fe^{3+} ion by the weak magnetic field.

It is natural to expect the phenomena investigated in the present paper to be of effective use in the study of relaxation effects in paramagnets.

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