

*EFFECT OF A WEAK MAGNETIC FIELD ON THE HYPERFINE STRUCTURE
OF Fe³⁺ MOSSBAUER SPECTRA IN PARAMAGNETIC SUBSTANCES WITH
NONAXIAL SYMMETRY OF THE CRYSTAL FIELD*

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The nature of magnetic hyperfine structure (hfs) of Mossbauer spectra in paramagnets with a nonaxial symmetric crystal field is studied for the case of a weak magnetic field superimposed under conditions of the "stabilization" effect. An ion-exchange sulforesin with a Fe³⁺ ion is investigated. It is found that for $\lambda \neq 0$ the hfs lines are appreciably broadened and have an asymmetric shape. It is demonstrated that an analysis of the hfs Mossbauer spectra of paramagnets permits one to estimate the parameter of the deviation of the crystal field from axial symmetry. In the case of Fe³⁺ in a sulforesin, it was found to be $\lambda = 0.15 \pm 0.03$.

THE study of paramagnets with the aid of Mossbauer spectroscopy makes it possible to obtain rather detailed information on the electron-spin relaxation of a paramagnetic ion. It is possible in this case to study both the spin-lattice relaxation and its connection with the real phonon spectrum of a solid, and the spin-spin relaxation characterized by the interaction of the paramagnetic ions with one another.^[1] A no less interesting aspect of the application of Mossbauer spectroscopy to the investigation of paramagnets is also the investigation of the character of the crystal field. Great possibilities for the study of both the relaxation processes and the structure of the crystal field arise in connection with the effects of stabilization of the hyperfine structure (hfs) in weak magnetic fields. This effect was predicted recently by Afanas'ev and Kagan,^[2] and was discovered experimentally by Gorobchenko et al.^[3] According to the results of^[2], application of a weak magnetic field (several hundred Oe in the case of Fe³⁺) makes the spectrum more distinct, and in addition, it becomes possible to compare directly the experimental results with the theoretical calculations.

In our earlier paper^[1] we reported an investigation of the spin-lattice relaxation of the electron spin of Fe³⁺ in ion-exchange sulforesin. We determined experimentally and calculated theoretically the spin-lattice relaxation times for electron-spin projections $S_z = \pm 5/2$ and $S_z = \pm 3/2$ in an electric field of axial symmetry. However, although the theoretical calculations have shown that the spin-lattice relaxation times for $S_z = \pm 1/2$ and $S_z = \pm 5/2$ should be approximately equal, it was impossible to observe experimentally a distinct hfs from $S_z = \pm 1/2$. The reason for such a smearing of the hfs from $S_z = \pm 1/2$ lies in the influence exerted in these spectra by the weak magnetic fields of neighboring ions. The point is that even in an electric field of axial symmetry the resonant Mossbauer transitions corresponding to $S_z = \pm 1/2$ are not purely nuclear transitions, but are mixed with electronic transitions. As a result, a magnetic field of several Oe, acting on the nuclear levels via the electronic level, leads to a smear-

ing of the individual hfs lines. In the case of a Kramers doublet $S_z = \pm 3/2$, the magnetic hfs is also smeared out if the symmetry of the crystal field is not axial. The spectrum of $S_z = \pm 5/2$ is not very sensitive to deviation of the crystal field from axial symmetry. A similar picture is observed for a field $H < A/g_L \mu_B$, where A is the hyperfine interaction constant, g_L is the Lande factor, and μ_B is the atomic Bohr magneton. However, as proposed in^[2], there is a possibility of observing also the hfs from $S_z = \pm 1/2$. When a weak magnetic field $H > A/g_L \mu_B$ (but less than the distance between the Stark levels) is applied, unpairing of the electron and nuclear spins takes place, and the energy levels are determined by the projections of the electron and nuclear spins on the direction of the magnetic field, for example by the values of S_z and I_z . As a result, stabilization of the hfs from $S_z = \pm 1/2$ and $S_z = \pm 3/2$ should take place, and separate lines should appear, characterizing I_z and not the mixture of S_z and I_z .

We have investigated the influence of a weak magnetic field on the hfs of Fe³⁺ in an ion-exchange resin with adsorbed water. The concentration of the iron ions was 1.6 wt.%, so that the main relaxation process in the system was spin-lattice relaxation. The spectrum were

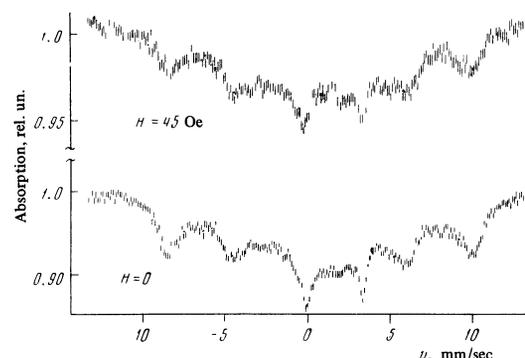


FIG. 1. Mossbauer spectra of ion-exchange resin with adsorbed water in an external magnetic field and without a field, at 90°K. The magnetic field is perpendicular to the direction of γ -quantum emission.

obtained with an electrodynamic setup with a Co^{57} source in Cr. The isomer shifts were reckoned relative to sodium nitroprussite. Figure 1 shows two spectra obtained at 90°K in the absence of a magnetic field and in a magnetic field of 450 Oe, applied perpendicular to the direction of the γ -quantum beam. After application of the magnetic field, the character of the spectrum changed: the central lines became much more intense than the outer lines, and in addition, they broadened greatly. Such a change in the spectrum is connected with the possibility, discussed by Afanas'ev and Kagan,^[21] of the appearance of hfs from $S_Z = \pm 1/2$ in a weak magnetic field.

The positions of the hfs lines were determined by the effective spin Hamiltonian, since the distance between the Stark levels was much larger than the energy of the hyperfine interaction:

$$\hat{H}_{\text{eff}} = \mu_B (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) + (A_x S_x I_x + A_y S_y I_y + A_z S_z I_z).$$

For an axially symmetrical field, the hyperfine interaction constants are given by

$$\begin{array}{lll} \text{for } S_z = \pm 5/2, & A_z = 5A, & A_x = A_y = 0 \\ \text{for } S_z = \pm 3/2, & A_z = 3A, & A_x = A_y = 0 \\ \text{for } S_z = \pm 1/2, & A_z = A, & A_x = A_y = 3A \end{array}$$

The magnetic field influences only the position of the hfs lines from $S_Z = \pm 1/2$. Thus, for example, when a magnetic field is applied along the x axis of a single crystal, only the term with $3A_x S_x I_x$ remains in the Hamiltonian of the hyperfine interaction for $S_Z = 1/2$,^[22] and gives for the hfs lines positions that coincide with the positions of the $S_Z = \pm 3/2$ lines. As a result, the intensity of the central lines should increase, as is indeed observed in the experiment.^[23]

In our sample, the crystal field was not axially symmetrical. This means that in the Hamiltonian

$$\hat{H}_{\text{cr}} = D[S_z^2 - 1/3 S(S+1)] + E(S_x^2 - S_y^2),$$

which is responsible for the interaction between the Fe^{3+} ion and the crystal field, the parameter $\lambda = E/D \neq 0$. In the earlier paper^[11] we obtained an approximate estimate of the parameter λ . In principle, we estimated the upperbound, i.e., a value of λ for which there is still no smearing of the hfs lines from $S_Z = \pm 5/2$ ($\lambda \leq 0.2$). The present investigation has shown that the effect of hfs stabilization makes it possible to determine λ more accurately.

The variation of the hyperfine interaction constants with change of the parameter λ is given in^[1,4]. The limits of variation of the constants in our case fit within the framework indicated in^[22], which limits the possibility of observing the stabilization effect in polycrystalline samples. In our case, when a weak magnetic field is applied, the hfs becomes stabilized not only for $S_Z = \pm 1/2$ but also for $S_Z = \pm 3/2$, for all three constants of the hyperfine interaction for $S_Z = \pm 3/2$ differ from zero when $\lambda \neq 0$. It is obvious that the positions of the hfs from these Kramers doublets will no longer coincide, as in the case of an axially symmetrical field, but will depend on λ . The behavior of these hfs lines as functions of λ will be determined by the behavior of the largest of the hyperfine interaction constants for the corresponding Kramers doublets. In our case, this causes the hfs lines from $S_Z = \pm 3/2$ to shift inward, and

the hfs lines from $S_Z = \pm 1/2$ to shift outward relative to the lines of the same Kramers doublets in the case $\lambda = 0$. The line shifts occur in proportion to the changes in the largest of the hyperfine interaction constants for the corresponding Kramers doublets.

If all the $A_i \neq 0$, $H_z > A_x$ and $A_z > A_y$, then the line shape can be estimated by means of the following formula (private communication from A. M. Afanas'ev):

$$I(\omega) = \sum_i \frac{1}{4\pi} \int_{-\pi}^{\pi} \int_0^{2\pi} \frac{\Gamma \Phi(\theta, \varphi) dt d\varphi}{[\omega - \omega_i(t, \varphi)]^2 + \Gamma^2}$$

where $\Phi(\theta, \varphi)$ is a certain function of the order of unity for all values of the angles; Γ is the natural line width; $t = \cos \theta$;

$$\omega_i(t, \varphi) = \omega_0^i \frac{1}{A_z} \left[\frac{A_x^4 \sin^2 \theta \cos^2 \varphi + A_y^4 \sin^2 \theta \sin^2 \varphi + A_z^4 \cos^2 \theta}{A_x^2 \sin^2 \theta \cos^2 \varphi + A_y^2 \sin^2 \theta \sin^2 \varphi + A_z^2 \cos^2 \theta} \right]^{1/2};$$

$i = 1, 2, \dots, 6$; ω_0^i is the position of the hfs lines in a stabilizing magnetic field directed along the z axis. For $S_Z = \pm 3/2$, where $A_z > A_x = A_y$, the calculated line shapes become simpler. In this case the dependence on φ disappears. The calculation of the theoretical spectra for both the Kramers doublet $S_Z = \pm 3/2$ and for $S_Z = \pm 1/2$ was carried out with an electronic computer, with variation of the parameters λ and Γ .

Figure 2 shows the spectrum of a sulforesin in a 450-Oe magnetic field after subtracting the hfs corresponding to the Kramers doublet $S_Z = \pm 5/2$ and the doublet of Fe^{2+} (thick line). The same figure shows the line positions for $S_Z = \pm 3/2$ and $S_Z = \pm 1/2$ at $\lambda = 0$, and also for $S_Z = \pm 3/2$ and $S_Z = \pm 1/2$ at $\lambda = 0.15$ and $\Gamma = 2.2$ mm/sec, at which the best agreement between the theoretically calculated spectrum and the experimental one is observed. If the line shape were symmetrical, then the total intensity of the central line at the same $\lambda = 0.15$ and $\Gamma = 2.2$ mm/sec would not ensure complete filling of the central part of our spectrum (Fig. 2b). This discrepancy disappears completely when the lines have the shape that follows from our calculations, i.e., strongly broadened inside and cut off on the outside.

The calculations explain the appearance of the hfs spectra with broadened lines. Even at an insignificant

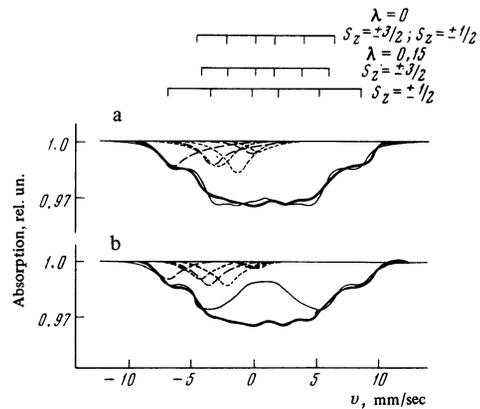


FIG. 2. Mossbauer spectrum of ion-exchange resin in an external magnetic field of 450 Oe, for two Kramers doublets, $S_Z = \pm 3/2$ (dotted curves) and $S_Z = \pm 1/2$ (dashed curves), obtained after subtracting from the spectrum of Fig. 1 the hfs for $S_Z = \pm 5/2$ (thick line). Thin lines — theoretically-calculated spectra at $\lambda = 0.15$ and $\Gamma = 2.2$ mm/sec with symmetrical (b) and asymmetrical (a) line shapes.

deviation of λ from zero, the line becomes strongly broadened, and a characteristic feature is the asymmetry of this broadening. On the other hand, in the case described in [31], the lines turned out to be narrow and the hfs from $S_z = \pm 1/2$ was quite distinctly pronounced since the Fe^{3+} in the corundum was situated in a crystal field of axial symmetry and $\lambda = 0$. In spite of the fact that the spectra with $\lambda \neq 0$ are strongly smeared out, it has turned out that by varying λ and Γ it is possible to determine quite accurately from the Mossbauer spectra the parameter λ , which turned out in our case to equal 0.15 ± 0.03 .

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