

## A STUDY OF SPIN-LATTICE RELAXATION ON THE BASIS OF THE HYPERFINE

STRUCTURE OF  $\text{Fe}^{3+}$  MOSSBAUER SPECTRA

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The  $\text{Fe}^{3+}$  Mossbauer spectra are measured for a number of ion-exchange resins between 4.5°K and room temperature. A magnetic hyperfine structure (hfs) is detected in sulforesin ("zerolite") with adsorbed water. The hfs is a strong function of the temperature (above 27°K) and this indicates the importance of electron spin relaxation processes in the formation of the hfs spectra. Owing to the presence of well resolved lines in the spectra it has been possible to carry out a careful experimental study of the relaxation process itself and to determine the temperature dependence of the relaxation time in a broad temperature range between 4.5 and 250°K. A theoretical analysis is presented for those spin-lattice relaxation processes which are decisive for the samples with a small magnetic ion concentration. It is shown that for the  $\text{Fe}^{3+}$  ion in the S state only two-phonon processes can exert an appreciable effect on the shape of the hfs lines. A consequence of this is that a large number of elementary relaxation processes between various Kramers doublets can be described by a relatively small number of parameters. Thus for an axial symmetric surrounding of the  $\text{Fe}^{3+}$  ion only two parameters are required. On the basis of the analysis it is possible to relate the measured relaxation time to some definite processes, viz. to the total probability for transitions from the  $S_z = \pm 5/2$  state to the  $S_z = \pm 3/2, \pm 1/2$  states. The temperature dependence of the relaxation time corresponds to that for two-phonon spin-lattice relaxation. Owing to the absence of detailed information on the vibrational properties of the system the calculations were performed for two models, a Debye and an Einstein one. For the temperature range investigated by us the variation of the relaxation time can be satisfactorily described by either of the models. It furthermore has been possible for the first time to separate the relaxation times for  $S_z = \pm 5/2$  and  $S_z = \pm 3/2$ . Experimentally the value  $\tau_r(S_z = \pm 5/2)/\tau_r(S_z = \pm 3/2) = 1.5 \pm 0.3$  is obtained which is in satisfactory agreement with the theory proposed here.

## 1. INTRODUCTION

As was first shown theoretically<sup>[1]</sup> and then observed experimentally,<sup>[2]</sup> the hyperfine structure (hfs) of the Mossbauer spectrum in paramagnets is very sensitive to the relaxation time of the spin of the electron shell of the Mossbauer atom. A rather large number of papers devoted to this question have been published up to now (see, for example, [3]). However, it is quite difficult to extract from the experiments the concrete characteristics of the relaxation processes.

The presence of a complicated system of Stark levels of the Mossbauer atom leads, on the one hand, to a large number of hfs lines, since each Stark level contributes its own hfs system to the Mossbauer spectrum, and on the other hand, the relaxation process is described in the general case by a large number of parameters, namely the times of relaxation between different Stark levels. This question is analyzed in detail in [1], where a four-level system is used as an example to demonstrate the possible appearance of a large number of qualitatively different forms of the hfs of Mossbauer spectra in paramagnets.

So far, in all the experiments aimed at observing the hfs in paramagnets, the results were reduced with the aid of a rather crude model, in which one effective relaxation time was introduced. It is clear that such an

analysis can yield only a qualitative idea of the character of the relaxation.

In a number of cases, in spite of the large number of Stark levels, the relaxation process can be determined by a small number of parameters. Thus, for example, in the case of the  $\text{Fe}^{3+}$  ion, the fundamental term  ${}^6S$  of the ion is split by the crystal field into three Kramers doublets ( $S_z = 5/2, \pm 3/2, \pm 1/2$ ). However, the main relaxation process in the presence of a suitable symmetry of the crystal field is determined only by two parameters. This circumstance raises hope of obtaining, in a number of cases, complete information concerning the relaxation process.

We have investigated experimentally the magnetic hfs of the Mossbauer ion  $\text{Fe}^{3+}$  in a number of ion-exchange resins. These substances turn out to be very convenient for the study of the relaxation processes, since they have large spin-lattice relaxation times up to temperatures of 250°K, which furthermore turn out to be quite sensitive to the introduction of polar adsorbents. The results of the experiments are shown in section 2.

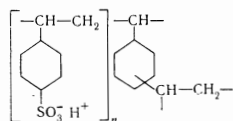
The obtained experimental data offer evidence that the spin-lattice relaxation plays a predominant role in the systems investigated by us. In Sec. 3 we present a detailed theoretical analysis of the spin-lattice relaxation processes, making it possible to reduce the exper-

imental data without using any crude models or assumptions.

In Sec. 4 we discuss the results. We succeed in determining exactly the spin-lattice relaxation time in sulforesin ("zerolite"), corresponding to the doublet  $S_z = \pm 5/2$ , in the temperature interval from 4.5 to 250°K. The obtained temperature dependence is well described by two-phonon spin-lattice relaxation processes, in full agreement with the theoretical notions of Sec. 3.

## 2. EXPERIMENTAL RESULTS

We have obtained the Mossbauer spectra of ion-exchange resins (anhydrous and with adsorbed water), containing trivalent iron ions and a certain admixture of divalent iron ions. The iron was enriched with  $Fe^{57}$  to 91%. All the ion-exchange resins were copolymers of styrene and divinylbenzene, and also methacrylic acid and divinylbenzene with groups of atoms capable of ion exchange. We investigated ion-exchange resins with functional groups of  $SO_3^-$  (sulforesins),  $PO_3^{2-}$  (KRF), and  $COO^-$  (KB-4). For sulforesin, the structure formula is



where the positive iron ion compensates for the charge of the  $SO_3^-$  group. For the remaining resins, the structure formulas are similar, but the group  $SO_3^-$  is replaced by  $PO_3^{2-}$  or  $COO^-$ . Thus, all these resins have a polymer structure joined together by bridges. Following sorption of polar adsorbents in the resin, such as water, the resin swells and its volume increases; the distance between the magnetic ions increases by several times. There are, however, also styrene-divinylbenzene resins which do not swell in water. Therefore, besides revealing the influence of the different functional groups, we investigated swelling and non-swelling resins with  $SO_3^-$  groups. To study the character of the relaxation of the electron spin of the iron in the resin, the Fe concentration was varied from 1.6 to 8 wt. %.

The  $Fe^{3+}$  ions were introduced by ion exchange of  $H^+$  from an acid aqueous solution of  $FeCl_3$ . The result was a system with  $Fe^{3+}$  that were separated from one another. (In the case of ion exchange in sulforesins, a certain amount of  $Fe^{2+}$  is produced as the result of the reducing centers in the resin, which are obtained after the synthesis of the resin.<sup>[41]</sup>)

The Mossbauer spectra were obtained with a setup of the electrodynamic type with a  $Co^{57}$  source in Cr. All the chemical shifts were reckoned from the sodium nitroprussite. Figure 1a shows the spectrum of the ion exchange sulforesin at a temperature 90°K. At this temperature, the spectrum consists of an  $Fe^{3+}$  doublet with an isomer shift  $\delta E_I = 0.64 \pm 0.10$  mm/sec and a quadrupole splitting  $\Delta E_Q = 0.56 \pm 0.10$  mm/sec, and  $Fe^{2+}$  doublet with  $\delta E_I = 1.3 \pm 0.1$  mm/sec and  $\Delta E_Q = 2.5 \pm 0.1$  mm/sec. The spectrum at 300°K differs little from the spectrum at  $T = 90^\circ K$ : for  $Fe^{3+}$  we have  $\delta E_I = 0.64 \pm 0.10$  mm/sec and  $\Delta E_Q = 0.56 \pm 0.10$  mm/sec; for  $Fe^{2+}$  we get  $\delta E_I = 1.3 \pm 0.1$  mm/sec and  $\Delta E_Q = 2.1 \pm 0.1$  mm/sec. The spectra of the resins KB-4

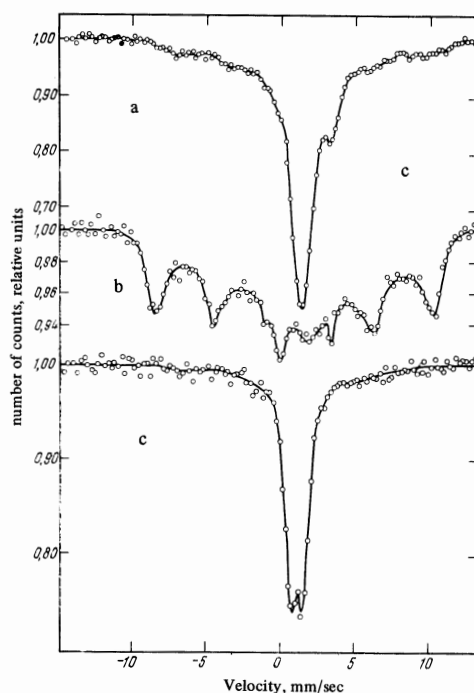


FIG. 1. Mossbauer spectra of ion-exchange resins containing iron at  $T = 90^\circ K$ : a – sulforesin before adsorption of water, b – sulforesin after adsorption of water, c – KB-4 after adsorption of water.

and KRF are similar to the sulforesin spectra. After adsorption of water in the sulforesin, the character of the spectra changes. An intense magnetic hyperfine structure appears (Fig. 1b) at  $T = 90^\circ K$ . The magnetic field at the  $Fe^{57}$  nuclei, determined from the extreme lines of the spectrum, is  $560 \pm 10$  kOe. The Mossbauer effect vanishes completely at 250°K.

We have also investigated the influence of the number of water molecules per iron ion on the form of the hfs. An intense magnetic hfs appears already in the presence of one water molecule per iron ion, although a fully formed hfs in final form occurs when there are 6 water molecules per iron ion.

No hfs occurs in the spectra of the resins KRF and KB-4 even after adsorption of water (Fig. 1c). The influence of swelling was investigated on both swelling and non-swelling sulforesins. It has turned out that the hfs are the same in both cases.

When the concentration increases from 1.6 to 3%, the character of the hfs for resin with water does not change, and with further increase of the concentration from 3 to 8%, the hfs collapses into one component.

Figure 2 shows the spectra of iron ( $Fe^{3+}$ ,  $Fe^{2+}$ ) in sulforesins with adsorbed water at temperatures from 4.5 to 237°K. It follows from the figure that the hfs lines broaden noticeably with temperature, without hardly changing their position, until a "triangle" spectrum is produced, which then narrows down and vanishes completely in the 250°K region.

The results of the experiments offer evidence that a convenient organic system was obtained for observing relaxation effects with large relaxation times at relatively high temperatures (up to  $\sim 250^\circ K$ ). Its distinguishing feature is also that adsorption of water influ-

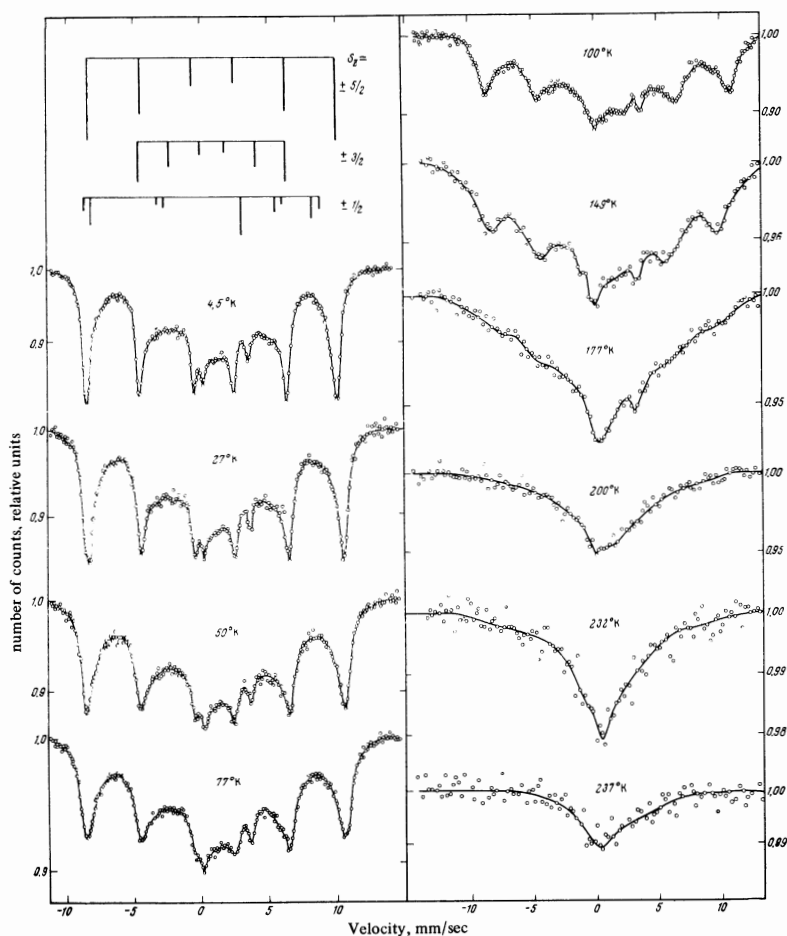


FIG. 2. Mossbauer spectra of sulforesins with iron concentration 1.6 wt% at different temperatures.

ences strongly the occurrence of the hfs and its character. The broadening of the hfs lines in a wide range of temperatures without a noticeable shift makes it possible to trace the temperature dependence of the relaxation time of the electron spin for the Stark level  $S_z = \pm 5/2$  and to relate it with a definite relaxation mechanism in the system.

### 3. THEORY

As shown by the experiments performed with samples having different iron-ion concentrations, the spin-spin relaxation processes can be neglected at low concentrations ( $\sim 1.6\%$ ). We shall therefore consider here only spin-lattice relaxation.

As a result of the fact that the  $\text{Fe}^{3+}$  ion is in the S state, the interaction of its electron shell with the intracrystalline electric field is realized indirectly via the spin-orbit coupling<sup>[5]</sup> and has a relatively simple form with Hamiltonian

$$\hat{H}_{\text{cr}} = \frac{1}{2} \sum_{ik} \varphi_{ik} \frac{3Q}{2S(2S-1)} \left( S_i S_k + S_h S_l - \frac{2}{3} \delta_{ih} S(S+1) \right), \quad (3.1)$$

where  $Q$  is the quadrupole moment,  $S_{i,k}$  is the projection of the ion spin,  $\varphi_{ik}$  is the tensor of the gradient of the electric field at the location of the ion. The components of the tensor  $\varphi_{ik}$  depend not only on the equilibrium positions of the atoms surrounding the iron ion, but also on the displacements of the atoms from the

equilibrium positions as the result of oscillations. Let us separate from  $\varphi_{ik}$ , as is customary, that part  $\varphi_{ik}^0$  which does not depend on displacements. By suitable choice of the coordinate system, we diagonalize the tensor  $\varphi_{ik}^0$ . Then the tensor  $\varphi_{ik}$ , and consequently also the tensor  $\varphi'_{ik} = \varphi_{ik} - \varphi_{ik}^0$ , will not be diagonal in this coordinate system. In accordance with the foregoing, we break down the Hamiltonian  $\hat{H}_{\text{cr}}$  into two parts

$$\hat{H}_{\text{cr}} = \hat{H}_{\text{cr}}^0 + \hat{H}_{\text{cr}}', \quad (3.2)$$

where

$$\hat{H}_{\text{cr}}^0 = D(S_z^2 - 1/3 S(S+1)) + E(S_x^2 - S_y^2), \quad (3.3)$$

$$\hat{H}_{\text{cr}}' = \hat{d}(S_z^2 - 1/3 S(S+1)) + \hat{e}(S_x^2 - S_y^2) + \hat{f}(S_x S_y + S_y S_x) + \hat{g}(S_x S_z + S_z S_x) + \hat{r}(S_y S_z + S_z S_y). \quad (3.4)$$

The Hamiltonian  $\hat{H}_{\text{cr}}^0$  is responsible for the Stark splitting of the main term of the  ${}^6\text{S}$  ion into three Kramers doublets; the Hamiltonian  $\hat{H}_{\text{cr}}'$  leads to the relaxation transitions between the different Stark sublevels. The coefficients  $\hat{d}$ ,  $\hat{e}$ ,  $\hat{f}$ ,  $\hat{g}$ , and  $\hat{r}$  in (3.4) are operators acting on the phonon subsystem. The interaction (3.4) leads to single-phonon, two-phonon, etc. processes of electron-spin relaxation. The single-phonon processes have practically no influence on the hfs in the case of the  $\text{Fe}^{3+}$  ion.

Indeed, in order of magnitude, when  $T \gg \Delta$  the frequencies of the transitions between the different Stark levels are

$$P_{s,ph} \sim \frac{\Delta}{\hbar} \left( \frac{\Delta}{\Theta_D} \right)^4 \frac{T}{\Theta_D}, \quad (3.5)$$

where  $\Delta$  is the characteristic distance between the Stark levels,  $\Theta_D$  is the Debye temperature, and  $\hbar$  is Planck's constant

By virtue of the fact that  $\Delta$  for the case  $Fe^{3+}$  is of the order of several degrees and the ratio  $\Delta/\Theta_D \sim 10^{-2}$ , the single-phonon relaxation process is very slow and the corresponding relaxation times  $\tau = 1/P_{s,ph}$  are much larger than the lifetime  $\tau_0$  of the excited state of the nucleus.

The two-phonon relaxation processes are divided into two classes. The first includes processes resulting from second order of perturbation theory from the Hamiltonian (3.4) and connected with the linear terms of the expansions of the operators  $\hat{d}$ ,  $\hat{e}$ , etc. in powers of the displacements of the atoms from the equilibrium positions. But the relaxation frequencies  $P_{t,ph}^{(1)}$  connected with these processes are also negligibly small. Thus, when  $T \geq \Theta_D$  we have

$$P_{t,ph}^{(1)} \sim \frac{\Delta}{\hbar} \left( \frac{\Delta}{\Theta_D} \right)^3 \left( \frac{T}{\Theta_D} \right)^2, \quad (3.6)$$

i.e., in this temperature interval  $P_{t,ph}^{(1)} \ll P_{s,ph}$ .

Thus, as can be readily seen, this relaxation process also turns out to be insignificant for the hfs.

The second class includes processes that arise in first order of perturbation theory in the interaction (3.4). These, naturally, are already connected with the quadratic terms of the expansion of the operators  $\hat{d}$ ,  $\hat{e}$ , etc. in the displacements of the atoms. When  $T \gtrsim \Theta_D$  the corresponding relaxation frequencies  $P_{t,ph}^{(2)}$  turn out to be of the order of magnitude of

$$P_{t,ph}^{(2)} \sim \frac{\Delta}{\hbar} \frac{\Delta}{\Theta_D} \left( \frac{T}{\Theta_D} \right)^2. \quad (3.7)$$

Direct estimates show that when  $T \sim \Theta_D$  we have  $P_{t,ph}^{(2)} \gg 1/\tau_0$  and consequently these relaxation processes should exert a significant influence on the hfs. We shall henceforth be interested in just this process of two-phonon relaxation.

Before we proceed to analyze the relaxation processes, let us stop to discuss the static character of the hfs spectra in paramagnets in the presence of a crystal field. As a rule, in noncubic crystals the static interaction of the ion spin with the crystal field (3.3) is much larger than the hyperfine interaction, which for the free ion is given by

$$\hat{H}_{hf} = ASI, \quad (3.8)$$

where  $I$  is the nuclear spin and  $A$  the hyperfine interaction constant. Therefore the problem of finding the levels of the system made up of the electron spin and the nuclear spin can be solved in two stages.

In the first stage one determines the position of the levels of the atom spin in the crystal field, and then the splitting of the obtained levels as the result of the hyperfine interaction. The level structure of the electron spin of the atom depends on the form of the Hamiltonian (3.3), and more specifically on the parameter  $\lambda = E/D$ .

When  $\lambda = 0$ , corresponding to axial symmetry of the

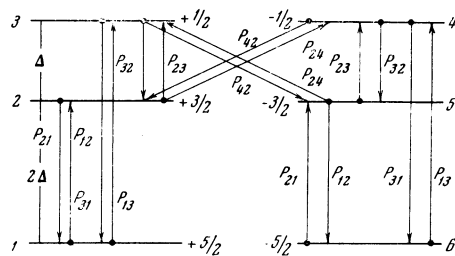


FIG. 3. Level scheme of the  $Fe^{3+}$  ion. The arrows indicate the possible transitions in two-phonon spin-lattice relaxation.

crystal field, the splitting has the simplest form. The main term  ${}^6S$  of the  $Fe^{3+}$  ion breaks up into three Kramers doublets with  $S_z = \pm 5/2$ ,  $\pm 3/2$ , and  $\pm 1/2$  respectively. The relative positions of the doublets and the distances between them are determined completely by the value of the parameter  $D$  (the corresponding level scheme is shown in Fig. 3 for  $D < 0$ ). Allowance for the hyperfine interaction is based on the method of the effective spin Hamiltonian, which is well known from EPR.<sup>[51]</sup> The gist of this method is that the initial hyperfine interaction is averaged over the wave functions of the corresponding Kramers doublet. Each doublet is assigned an effective spin  $S' = 1/2$ , and the average hyperfine interaction becomes anisotropic and takes the form

$$\hat{H}_{hf} = (A_z' S_z' I_z + A_y' S_y' I_y + A_x' S_x' I_x). \quad (3.9)$$

The interaction constants  $A_i$  already depend on the concrete structure of the Kramers doublet. In the case of axial symmetry, for the doublet  $S_z = \pm 5/2$  we have  $A_z = 5A$ ,  $A_x = A_y = 0$ , for  $S_z = \pm 3/2$  we get  $A_z = 3A$ ,  $A_x = A_y = 0$ , and for  $S_z = \pm 1/2$  we get  $A_z = A$ ,  $A_x = A_y = 3A$ .

In fields of nonaxial symmetry for arbitrary values of the constant  $\lambda$ , Wickman, Klein, and Shirley<sup>[61]</sup> calculated the values of the constant  $A_i$  for all three Kramers doublets; these are shown in Fig. 4. The hyperfine splitting in the character of hfs depends to a considerable degree on the constant  $A_i$  (this problem was also analyzed in detail in <sup>[61]</sup>). In view of the fact that for different doublets these constants are different, the Mossbauer spectrum is a superposition of three hfs systems from different Kramers doublets. In the case

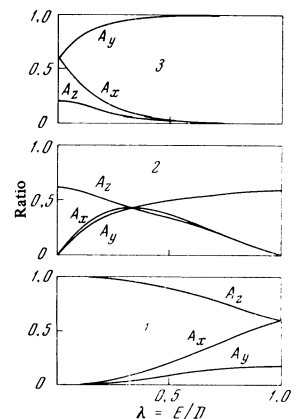


FIG. 4. Hyperfine interaction constants vs. the parameter  $\lambda = E/D$  for three Kramer doublets. The lower figure corresponds to  $S_z = \pm 5/2$ , the middle one to  $S_z = \pm 3/2$ , and the upper one to  $S_z = \pm 1/2$ .

of axial symmetry and in the absence of relaxation processes, the hfs from  $S_Z = \pm 5/2$  and  $S_Z = \pm 3/2$  consists of the group of six lines usually observed in ferromagnets, and the hfs from  $S_Z = \pm 1/2$  already consists of 11 lines. The positions of the most intense lines are shown in Fig. 2.

We now proceed to discuss relaxation processes.

The two-phonon relaxation causes transitions between the different Stark levels shown in Fig. 3. In designating the probabilities of the transitions between the different Stark sublevels on Fig. 3, account was taken of the symmetry of the levels relative to the reversal of the sign of the spin. As follows from the form of the Hamiltonian (3.4), relaxation processes are possible in which the projection of the electron spin changes by either unity or by 2. The probabilities (frequencies) of the transitions between different Stark sublevels are not all independent.

Some of the transition probabilities are connected with one another by the obvious thermodynamic relations

$$\begin{aligned} P_{12} &= P_{21}e^{-2\Delta/T}, & P_{23} &= P_{32}e^{-\Delta/T} \\ P_{13} &= P_{31}e^{-3\Delta/T}, & P_{42} &= P_{24}e^{-\Delta/T}. \end{aligned} \quad (3.10)$$

when  $T \gg \Delta$  we have  $P_{12} = P_{21}$ ,  $P_{23} = P_{32}$ , etc. As a result we are left with four transition probabilities

$$P_I = P_{12} = P_{21}, \quad P_I' = P_{23} = P_{32}. \quad (3.11)$$

$$P_{II} = P_{13} = P_{31}, \quad P_{II}' = P_{42} = P_{24}.$$

Let us proceed to calculate  $P_I$  and  $P_{II}$ .

According to the general formulas of quantum mechanics

$$\begin{aligned} P_I &= 2\pi \left\langle \sum_{\beta\beta'} |\langle n_\beta, n_{\beta'} + 1, 3/2 | H' | n_\beta + 1, n_{\beta'}, 5/2 \rangle|^2 \delta(\omega_\beta - \omega_{\beta'} - 2\Delta) \right\rangle_{av} \\ &= 2\pi \left\langle \left[ \sum_{\beta\beta'} \{ |\langle n_\beta, n_{\beta'} + 1 | \hat{g} | n_\beta + 1, n_{\beta'} \rangle|^2 + |\langle n_\beta, n_{\beta'} + 1 | \hat{r} | n_\beta + 1, n_{\beta'} \rangle|^2 \} \delta(\omega_\beta - \omega_{\beta'} - 2\Delta) \right] |\langle 3/2 | S_x S_z + S_z S_x | 5/2 \rangle|^2 \right\rangle_{av}. \end{aligned} \quad (3.12)$$

Here  $|n_\beta n_{\beta'} S_Z\rangle$  is the wave function of the system, characterized by the phonon occupation numbers  $n_\beta n_{\beta'}$  and by values of the electron spin projection  $S_Z$ . The symbol  $\langle \dots \rangle_{av}$  denotes temperature averaging over the initial phonon distribution.

Since  $\Delta$  is much smaller than the characteristic frequency of the phonon spectrum  $\omega_\beta$ , the term  $2\Delta$  in the  $\delta$  function can be neglected when  $T \gg \Delta$ . In addition, the matrix elements of the spin operators can be readily calculated and we obtain as a result

$$P_I = 80P_1, \quad (3.13)$$

where

$$\begin{aligned} P_1 &= 2\pi \left\langle \sum_{\beta\beta'} \{ |\langle n_\beta, n_{\beta'} + 1 | \hat{g} | n_\beta + 1, n_{\beta'} \rangle|^2 + |\langle n_\beta, n_{\beta'} + 1 | \hat{r} | n_\beta + 1, n_{\beta'} \rangle|^2 \} \delta(\omega_\beta - \omega_{\beta'}) \right\rangle_{av}. \end{aligned}$$

For  $P_I'$  we obtain analogously

$$P_I' = 32P_1. \quad (3.13')$$

Thus, the transition probabilities  $P_I$  and  $P_I'$  are not independent and are connected by a simple relation.

For the probabilities  $P_{II}$  and  $P_{II}'$  we obtain, making the same assumptions as in the calculation of  $P_I$  and  $P_I'$

$$P_{II} = 40P_2, \quad (3.14)$$

$$P_{II}' = 72P_2, \quad (3.14')$$

where

$$\begin{aligned} P_2 &= 2\pi \left\langle \sum_{\beta\beta'} \{ |\langle n_\beta, n_{\beta'} + 1 | \hat{e} | n_\beta + 1, n_{\beta'} \rangle|^2 + |\langle n_\beta, n_{\beta'} + 1 | \hat{r} | n_\beta + 1, n_{\beta'} \rangle|^2 \} \delta(\omega_\beta - \omega_{\beta'}) \right\rangle_{av}. \end{aligned}$$

Thus, in spite of the relatively large number of paths of relaxation between the different Stark sublevels, the relaxation process is determined by only two independent parameters,  $P_1$  and  $P_2$ .

In the case of non-axial symmetry of the crystal field, when  $\lambda \neq 0$ , the relaxation process is already described by four independent parameters. At small  $\lambda$ , however, relations (3.13), (3.13'), (3.14), and (3.14') remain in force. At arbitrary relations between the parameters  $P_I$  and  $P_{II}$  and the hyperfine interaction constants, the picture of the relaxation spectrum turns out to be quite complicated. However, when the relaxation frequencies are small compared with the hfs frequencies, the influence of the relaxation processes, as shown in  $^{11}$ , reduces to a broadening and shift of the hfs components. For the line broadening (the notation is that of  $^{11}$ ) and for the shift we get respectively

$$\Delta\Gamma_i = \sum_h P_{ih}, \quad (3.15)$$

$$\delta E = - \sum_h \frac{(P_{ih})^2}{\omega_i - \omega_h}. \quad (3.16)$$

The shift turns out to be much smaller than the broadening, and this can serve as a criterion of the correctness of the applicability of formula (3.15). Using (3.15), and also (3.13) and (3.14), we obtain for the change of the widths of the hfs lines corresponding to the different Kramers doublets the following expression:

$$\begin{aligned} S_z = \pm 5/2, & \quad \Delta\Gamma_{5/2} = 40P_2 + 80P_1, \\ S_z = \pm 3/2, & \quad \Delta\Gamma_{3/2} = 72P_2 + 112P_1, \\ S_z = \pm 1/2, & \quad \Delta\Gamma_{1/2} = 132P_2 + 32P_1. \end{aligned} \quad (3.17)$$

It follows therefore that the hfs lines from  $S_Z = \pm 3/2$  broaden more strongly than the hfs lines from  $S_Z = 5/2$ . A direct calculation of the coefficients  $P_1$  and  $P_2$  is a rather complicated problem, since a detailed knowledge of the characteristics of the phonon spectrum of the system is required. If we use the Einstein approximation and the Debye approximation, then we obtain for the temperature dependences of  $P_1$  and  $P_2$  the following formulas:

Einstein model

$$P_{1,2} = c_{1,2} \frac{e^{\omega_E/T}}{(e^{\omega_E/T} - 1)^2}; \quad (3.18)$$

here  $\omega_E$  is the Einstein frequency.

Debye model

$$P_{1,2} = d_{1,2} \int_0^{\infty} \frac{x^7 e^{-x} dx}{(e^x - 1)^2}; \quad (3.19)$$

where  $x = \omega_D/T$ ,  $\omega_D$  is the Debye frequency, and  $c_{1,2}$  and  $d_{1,2}$  are certain numerical constants.

#### 4. DISCUSSION OF RESULTS

Observation of a distinct and strongly temperature-dependent magnetic hfs in sulforesin following adsorption of water molecule makes it possible to trace the character of the variation of the relaxation of the electron spin with temperature, and on the other hand to clarify the influence of the polar molecules on the state of  $\text{Fe}^{3+}$  in such resins.

The insensitivity of the spectrum to changes of the iron-ion concentration from 1.6 to 3% offers evidence of the smallness of the role of the spin-spin relaxation in our case. The same is evidenced also by the fact that the hfs in swelling and non-swelling sulforesins do not differ from each other, although in the case of a swelling resin the distance between the magnetic  $\text{Fe}^{3+}$  ions increases, and in a non-swelling resin these distances remain the same as before.

Thus, the relaxation process is determined to an overwhelming degree by the spin-lattice relaxation, as is also evidenced by the strong dependence on the temperature of the hfs spectrum in sulforesin with adsorbed water.

The absence of magnetic hfs from the spectra of ion-exchange resins with  $\text{Fe}^{3+}$  points unambiguously to the presence of small spin-lattice relaxation times, which in this case are much shorter than the period of the Larmor precession of the nuclear spin in an effective magnetic field  $\sim 500$  kOe ( $\tau_L \sim 10^{-8}$  sec). The appearance of a distinct hfs following the adsorption of the water in the sulforesins with  $\text{Fe}^{3+}$  is evidence of the increase of the spin-lattice relaxation time.

Such an increase of the relaxation time is apparently connected with the fact that the water weakens the coupling between the  $\text{Fe}^{3+}$  and the  $\text{SO}_3^-$  in the sulforesins, as is also evidenced by the decrease of the Mossbauer-effect probability following sorption of water (at room temperature, the Mossbauer effect vanishes completely). On the other hand, in the case of KRF and KB-4 resins with the functional groups  $\text{PO}_3^{2-}$  and  $\text{COO}^-$ , the  $\text{Fe}^{3+}$  ion is bound more strongly with the resin lattice, and no sufficient weakening of this bond takes place after the adsorption of the water. This is evidenced, on the one hand, by the absence of hfs following the adsorption of the water, and on the other hand by the much weaker change in the probability of the Mossbauer effect, which is conserved also at room temperature.

Let us proceed to analyze the hfs spectra with an Fe concentration of 1.6 wt.%, obtained with sulforesin with sorbed water.

The spectra on Fig. 2 are superpositions of hfs of the three Kramers doublets of the main term  ${}^6S_{5/2}$  of the  $\text{Fe}^{3+}$  ion. The positions of the lines in these spectra depend in the general case on the structure of the doublets themselves which in turn are determined by the symmetry of the surrounding of the ion, and particular-

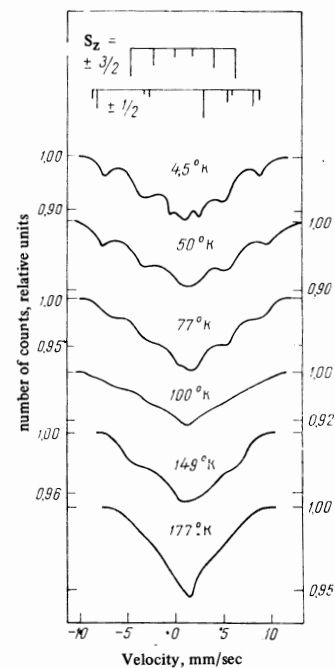


FIG. 5. Mossbauer spectra of sulforesin with iron concentration 1.6 wt.% from two Kramers doublets  $S_Z = \pm 3/2$  and  $S_Z = \pm 1/2$  at different temperatures, obtained after subtracting the hfs from  $S_Z = \pm 5/2$  from the spectra of Fig. 2.

ly by the parameter  $\lambda$ , which characterizes the deviation from axial symmetry. In our case, the spectra corresponding to  $T = 4.5$ – $100^\circ\text{K}$  reveal a distinct system of lines, which correspond in its position<sup>[2]</sup> to the Kramers doublet with  $S_Z = \pm 5/2$ . Such a doublet is realized in an axial-symmetry field. However, the structure of this doublet, and also the corresponding hfs, change little when  $\lambda$  deviates from 0 to 0.2 (see Fig. 4).

Thus, in our case, the surrounding of the  $\text{Fe}^{3+}$  ion has a symmetry which is close to axial with the indicated region of the variation of the parameter  $\lambda$ . The presence of a resolved hfs from  $S_Z = \pm 5/2$  makes it possible to separate the corresponding part of the spectrum. Such a subtraction was made, and the widths of the hfs lines corresponding to  $S_Z = \pm 5/2$  were assumed to be the same and were determined from the width of the outermost lines. The intensities of the outermost hfs lines from  $S_Z = \pm 5/2$  were chosen such that the area of the hfs spectrum from  $S_Z = \pm 5/2$  was  $1/3$  of the total area after subtracting the two lines from  $\text{Fe}^{2+}$ . It has turned out here that the main part of the intensity of the outermost lines of the total spectrum is due to the hfs from  $S_Z = \pm 5/2$ . The spectra remaining after the subtraction are connected with the hfs due to the two other Kramers doublets.

Figure 5 shows the spectra of the Kramers doublets  $S_Z = \pm 3/2$  and  $\pm 1/2$ , at different temperatures. The spectrum from these doublets is strongly smeared out and has no distinct lines, although the presence of lines from the doublet  $S_Z = \pm 5/2$  might be expected. The position of the lines of this doublet for  $\lambda = 0$  is shown in Fig. 5. Such a smearing may be due to the following



causes. The crystal field in the resin, acting on the iron ion, may differ somewhat from the axial symmetry field, i.e.,  $\lambda \neq 0$ , and in addition the values of  $\lambda$  can change somewhat in the resin from ion to ion. This scatter in  $\lambda$  is connected, on the one hand, with the amorphous structure of the polymer, and on the other hand is due to the stresses in the resin, which arise after the swelling of the resin at low temperatures, as the result of compression of the ice in the pores of the resin.

The scatter in  $\lambda$  should affect the hfs from the doublet  $S_Z = \pm 5/2$  relatively little. Indeed, as seen from Fig. 4, the hyperfine interaction constants  $A_i$  depend little on the values of  $\lambda$  in the region of small  $\lambda$ . However, the hfs lines from the two other doublets are very sensitive to small changes of  $\lambda$ , since the constants  $A_i$  depend strongly on  $\lambda$  (Fig. 4). This should lead to an appreciable broadening of the corresponding hfs line; part of the spectrum can then go beyond the position of the outermost lines from the doublet  $S_Z = \pm 5/2$  for the axially-symmetrical case. In addition, at  $\lambda \neq 0$ , owing to the fact that all the constants  $A_i$  for the doublets  $S_Z = \pm 3/2$  and  $\pm 1/2$  differ from 0, the corresponding hfs spectra should broaden strongly as the result of the presence of weak magnetic fields, which in particular arise as the result of the presence of the magnetic ions  $Fe^{3+}$ . [7]

Another cause of broadening of the hfs lines is the smaller spin-lattice relaxation time from the level  $S = \pm 3/2$ . The temperature dependence of the spectra of  $S_Z = \pm 3/2$  and  $\pm 1/2$  when  $T > 27^\circ K$  offers evidence that an appreciable contribution is made to the hfs line broadening by spin-lattice relaxation processes.

We have attempted to separate experimentally the relaxation times of  $S_Z = \pm 5/2$  and  $S_Z = \pm 3/2$ . To this end, we have compared the line widths of the hfs from  $S_Z = \pm 5/2$  and  $S_Z = \pm 3/2$ .

Attention is called to the fact that the lines of the magnetic hfs from  $S_Z = \pm 5/2$  and from  $S_Z = \pm 3/2$  are broadened even at  $4.5^\circ K$ . In addition, a comparison of the line widths of the hfs for  $S_Z = \pm 5/2$  at  $T = 4.5, 27,$  and  $50^\circ K$  and  $S_Z = \pm 3/2$  at  $T = 4.5$  and  $27^\circ K$  shows that in this temperature range there is no additional broadening. All this indicates that the broadening of the hfs lines at these temperatures is not of the relaxation type. Part of the line width is connected with the double natural width and the finite thickness of the sample ( $\Gamma \sim 0.4$  mm/sec) and a part is apparently connected with the action of the weak magnetic fields. As a result, these low-temperature experimental data can be used as a unique background, which must be subtracted from the spectra at higher temperatures in order to observe the relaxation effects in pure form.

Subtracting subsequently the widths of the outermost lines of  $S_Z = \pm 3/2$  at  $T = 4.5^\circ K$  from the widths of the outermost lines of the total hfs spectra of  $S_Z = \pm 3/2$  and  $\pm 1/2$  (Fig. 5) at  $T > 27^\circ K$ , and subtracting from the hfs for  $S_Z = \pm 5/2$  at  $T > 50^\circ K$  the width of the line  $\Gamma = 0.8$  mm/sec corresponding to  $T = 4.5^\circ K$ , we can quantitatively compare the relaxation times  $\tau_R$  for  $S_Z = \pm 5/2$  and  $S_Z = \pm 3/2$ .

Comparison of the hfs line widths for  $S_Z = \pm 5/2$  and  $S_Z = \pm 3/2$  at  $77^\circ \leq T \leq 100^\circ K$  yields the following rela-

tion between the relaxation times for  $S_Z = \pm 5/2$  and  $\pm 3/2$ :

$$\tau_r(S_Z = \pm 5/2) / \tau_r(S_Z = \pm 3/2) = 1.5 \pm 0.3.$$

This result agrees well with the theoretical calculations based on (3.17), thus emphasizing the two-phonon character of the relaxation. Separation of the individual relaxation time of  $S_Z = \pm 1/2$  from the total spectrum for  $S_Z = \pm 5/2, \pm 3/2,$  and  $\pm 1/2$  is so far difficult.

Let us analyze now in greater detail the hfs corresponding to the doublet with  $S_Z = \pm 5/2$ . The strong change of the hfs line width with temperature at a relatively weak change of the positions of the lines makes it possible to relate directly this broadening with the processes of spin-lattice relaxation (in this case with processes of two-phonon spin-lattice relaxation). The relaxation time determined by us is a definite transition time from the level  $S_Z = +5/2$  or  $-5/2$  to the levels  $S_Z = +3/2, +1/2$  ( $-3/2, -1/2$ ). Figure 6 shows the temperature dependence of the line width  $\Delta\Gamma = \Gamma_{sl}$  and of the relaxation time  $\Delta\tau = \tau_{sl}$  (the value  $\Gamma_0 = 0.8$  mm/sec, corresponding to  $T = 4.5^\circ K$ , was subtracted from the experimentally determined width).

The obtained experimental  $\tau(T)$  dependence is well described by the expressions

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{sl}}, \quad \frac{1}{\tau_{sl}} = 40P_2 + 80P_1, \quad (4.1)$$

where  $\tau_0$  has no relation to the spin-lattice relaxation, and can be connected, on the one hand, with the spin-spin relaxation, and on the other with the line broadening due to the scatter of the values of the parameter  $\lambda$ ;  $\tau_{sl}$  is the spin-lattice relaxation time. The temperature dependence of  $\tau_{sl}$  depends on the concrete oscillatory properties of the system and cannot be calculated without model approximations. We have used two models for the calculations: the Einstein model and the Debye model (see formulas (3.18), (3.19), and (4.1)). The best agreement with experiment is obtained with the following parameters: in the Einstein model  $\omega_E \approx 325^\circ K$ ,  $c = 3.56$  and in the Debye model  $\omega_D \approx 400^\circ K$  and  $d = 0.65$ ; for  $\tau_0$ , a value on the order of  $3 \times 10^{-8}$  sec is obtained.

Thus, the broadening not connected with the spin-lattice relaxation equals 0.4 mm/sec and constitutes a

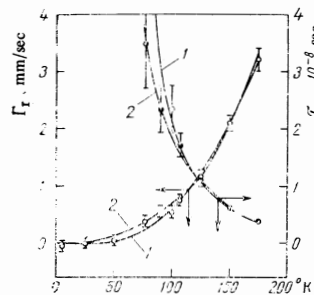


FIG. 6. Temperature dependence of the broadening of the Mossbauer lines and of the relaxation time for  $S_Z = \pm 5/2$ . The points denote the experimental values:  $\circ$  — for  $\Gamma_{sl}$ ,  $\bullet$  — for  $\tau_{sl}$ . The solid lines show the calculated values of  $\Gamma_{sl}$  and  $\tau_{sl}$  at the different temperatures in the Einstein (1) and Debye (2) approximations.

small fraction of the total broadening. The appearance of such relatively high frequencies may be connected only with the strong influence exerted on the relaxation process by the optical oscillations, which are apparently connected with the oscillations of the  $\text{SO}_3^-$  group. Therefore, at high temperatures the Einstein model is preferable, although it gives poorer agreement at the lower temperatures. (An estimate of the Debye temperature from the temperature dependence of the Mossbauer-effect probability in the temperature range from 80 to 180° gives a close value.) The role of the water in the pores of the resin reduces probably to a drawing of the iron ion away from the  $\text{SO}_3^-$  group, which, without changing significantly the frequency of the oscillations of this group, reduces the gradient on the crystal field acting on the  $\text{Fe}^{3+}$  ion, as a result of which the distance between the Kramers doublets decreases and the spin-lattice relaxation time increases. (The relaxation probability is proportional to the square of the distance between the doublets.)

As a result, to observe the spin-lattice relaxation in a wide temperature range, two conditions must be satis-

fied: a high oscillation frequency of the ions or of groups of ions ensuring the relaxation, and a small gradient of the crystal field.

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