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Translated by J. G. Adashko

Nuclear magnetic relaxation and spin diffusion in the local fields of paramagnetic centers

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(Submitted 3 April 1980)
Zh. Eksp. Teor. Fiz. 79, 1438–1450 (October 1980)

It is shown that the current theory of nuclear relaxation in solid dielectrics should be modified to take into account the spatial distribution of the paramagnetic impurity spin-flip rates. This results in some new dependences of the nuclear relaxation time on the inhomogeneous EPR broadening, on the magnetic field strength, etc. These predictions are confirmed experimentally in the case of relaxation of ^{183}W nuclei in ZnWO$_4$:Cr^{+3} crystals. The existence of effective nuclear spin diffusion under the conditions of a strong "diffusion barrier" is confirmed here for the first time ever with the same crystals. The results are shown to agree quantitatively with the theory of spin diffusion induced by paramagnetic centers, with the multiexponential nature of the electronic correlation function for $S > 1/2$ playing the decisive role.

PACS numbers: 76.60.Es

INTRODUCTION

It is well known that, as a rule, nuclear magnetic relaxation in solid dielectrics is due to dipole coupling of nuclear spins in the matrix with electron spins of paramagnetic impurities, the nuclear spin diffusion playing a substantial role (see, for example Refs, 1 and 2). In the last decade significant progress has been achieved in the study of these phenomena, mainly as a result of a consistent allowance for the role of electronic spin-spin interactions regarded as a quasi-equilibrium "electronic spin-spin reservoir" (ESSR).[3-5] At the same time, a deeper understanding of the physical mechanism of nuclear relaxation has generated new problems, three of which are the subject of this paper. These are: first, the question of the rate of transfer of nuclear Zeeman energy of the ESSR; second, the question (closely connected with the first) of the characteristic times of the mutual electron spin flips ("flip-flops"), particularly under conditions of inhomogeneous broadening of the EPR line; third, the problem of induced nuclear spin diffusion in the strong local fields of paramagnetic centers. In the first section of this paper, we consider several aspects of the theory of these phenomena; in the second section we present results of experiments carried out on ZnWO$_4$ crystals doped with paramagnetic Cr^{+3} ions.

1. THEORETICAL BASIS

1.1 Transfer of nuclear Zeeman energy to the electronic spin–spin reservoir (ESSR)

As is well known, direct relaxation of the nuclear spin I_i falling within the "sphere of influence" of the nearest electron spin S_j occurs under the action of the fluctuating local magnetic field generated by the z-component S_{jz} of the electronic spin (the z axis is directed along the external magnetic field **H**). Averaged over all angles, the rate of this relaxation is

$$(\tau_{ij}^{dir})^{-1} = C_j r_{ij}^{-6}, \tag{1}$$

where r_{ij} is the separation between I_i and S_j and

$$C_j = \tfrac{3}{5}(\hbar \gamma_s \gamma_I)^2 J_j(\omega), \tag{2}$$

where γ_S, γ_I are the gyromagnetic ratios of the spins S and I, $\omega = \gamma_I H$, and

$$J_j(\omega) = (\langle S_z^2 \rangle - \langle S_z \rangle^2)\frac{2\tau_{cj}}{1+\omega^2\tau_{cj}^2} \tag{3}$$

is the Fourier transform of the correlation function

$$G_j(t) = \langle S_{jz}(0)S_{jz}(t)\rangle, \tag{4}$$

the variable part of which is assumed[1,2] to be exponential in the correlation time τ_{cj}.

If the function $G_j(t)$ is due to electronic spin-phonon interaction (as has usually been considered in earlier nuclear relaxation theories), then the Zeeman energy of the nucleus I_i is transferred directly to the lattice, and all τ_{cj} are the same and equal to the electronic spin-lattice relaxation time τ_{1e}. In this case, the subscript j in Eqs. (2)–(4) may be omitted and the parameter C, common to all the nuclei, is used in the calculation of the observable nuclear spin-lattice relaxation time τ_{1n}.

A more complicated situation arises when the correlator of Eq. (4) is due to electronic spin-spin interactions, leading to a flip-flop of the spins S. The first

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difficulty, which is experimental in nature, arises from the fact that now the Zeeman energy of the relaxing nuclei is not dumped directly into the lattice but via the ESSR, the heat capacity c_{SS} of which is usually much less than the heat capacity c_{IZ} of the nuclear Zeeman subsystem. Under these conditions, the ESSR-lattice portion is most often a bottleneck in the relaxation; thus the observable relaxation time τ_{1n} is not at all connected with the time τ_{ISS} characterizing the rate of transfer of nuclear Zeeman energy to the ESSR.[6] It is just for this reason that, until now, the contact between the nuclei and the ESSR has been studied very inadequately (we need point only to Refs. 7-9).

Nevertheless, assume that conditions have been successfully created under which the relaxation bottleneck is determined by contact between the nuclear spins and the ESSR, so that $\tau_{1n}=\tau_{ISS}$. Then a new problem appears (this time a theoretical one), which is connected with the use of Eq. (1) for the calculation of τ_{ISS}. The point is that, due to the random spatial distribution of the paramagnetic centers, each one exists in a different local environment of the remaining spins S; consequently their characteristic flipping times τ_{cj} also should be different. The inhomogeneous broadening of the resonance lines (i.e., a spread in the resonance frequencies of the spins S_j) which is usual for EPR also leads to the same result. From what has been said, it is clear that in each sphere of influence j, the nuclear relaxation should occur at a different rate, and the evolution of the integrated nuclear magnetization $M(t)$ observable in the experiment is determined by the summation over all j, taking into account the actual distribution of the correlation times τ_{cj}.

As the corresponding distribution function, we can use the expression obtained by Förster[10] and applied successfully by Salikhov and coworkers to the solution of an analogous problem in spin echo theory[11]:

$$\varphi(W)dW = \tfrac{1}{2}\pi^{-1/2}kW^{-3/2}\exp(-k^2/4W)dW, \qquad (5)$$

where $W \equiv 1/\tau_c$ is the rate of spin deexcitation with an isolated paramagnetic center, and $k^2 \equiv 1/\bar{\tau}_c$ is a parameter determining the spin-flip time averaged over the distribution in Eq. (5). We emphasize that the correlation function averaged over the distribution in Eq. (5) is no longer a simple exponential, but is proportional to[11]

$$\overline{G(t)} = \int_0^\infty G_j(t)\varphi(W)dW.$$

Although the considerations presented appear rather obvious, until now they have not been taken into account in descriptions of nuclear relaxation. Instead, τ_{ISS} has traditionally been calculated using a simple exponential correlation function, to which was added some j-independent time τ_c^0; this time, in turn, was computed[7,12] using the moments (averaged over j) of the function $G_j(t)$.

In order to illustrate the difference between results obtained by the two approaches described above, let us consider the limiting case of very fast spin diffusion, which ensures the establishment of a single nuclear Zeeman temperature over the entire volume of the sample. In this situation, the relaxation of $M(t)$ should be described by an exponential, the time constant τ_{1n}^{-1} of which is proportional to the value of the Fourier transform of the correlation function, averaged over all j:

$$\tau_{1n}^{-1} \propto \overline{J(\omega)} = \int_{-\infty}^{\infty} \overline{G(t)}\exp(-i\omega t)dt = \int_0^\infty J_j(\omega)\varphi(W)dW. \qquad (6)$$

In particular, in the high-frequency limit ($\omega\bar{\tau}_c \gg 1$) it follows from Eq. (6) that:

$$\overline{J(\omega)} = 3.07(\langle S_z^2\rangle - \langle S_z\rangle^2)\omega^{-3/2}\bar{\tau}_c^{-1/2}, \qquad (7)$$

whereas when we use an exponential correlation function with a single correlation time $\tau_c^0 \gg 1/\omega$ we have, as is well known[2]:

$$J(\omega) = 2(\langle S_z^2\rangle - \langle S_z\rangle^2)\omega^{-2}(\tau_c^0)^{-1}. \qquad (8)$$

Our Eq. (7) differs from the traditional one (8) in two respects. First, it predicts a different dependence of τ_{1n} on frequency (and consequently a different dependence on the field H); second, $\bar{\tau}_c$, rather than τ_c^0, enters into the equation as the characteristic correlation time. The latter circumstance is especially important; obviously, it is in force not only under conditions of fast spin diffusion, but also in the more general case for which the problem of calculating the function $M(t)$ averaged over j has not yet been solved.

The difference in the determination of the correlation times τ_c^0 and $\bar{\tau}_c$ is especially pronounced under conditions of inhomogeneous broadening of the EPR spectrum that belongs to the spin S. Indeed, the expression for τ_c^0 obtained for dipole interactions in Refs. 7 and 12 may be represented as

$$\tau_c^0 \approx 3\Delta_d^{-1}(1 + A\tilde{\Delta}^2/\Delta_0^2)^{1/2}, \qquad (9)$$

where Δ_d and $\tilde{\Delta}$ are the dipole halfwidth and the inhomogeneous width, respectively, of the EPR line; Δ_0^2 is the second dipole moment of the EPR line, which would be observed in the undiluted paramagnet (i.e., when the concentration of paramagnetic centers is $c = 100\%$); A is a coefficient approximately equal to 6. Since usually $\Delta_0/2\pi \approx 600-1000$ MHz, it follows from Eq. (9) that τ_c^0 is practically independent of the inhomogeneous width for the reasonable values $\tilde{\Delta}/2\pi < 200-300$ MHz.

On the other hand, the estimate of the correlation time $\bar{\tau}_c$ given by Salikhov and coworkers[11] gives (for $S=\tfrac{1}{2}$)

$$\bar{\tau}_c^{-1} \approx 8.2\gamma_s^4\hbar^2 N_s^2(\Delta_d/\tilde{\Delta}^2)\left(\ln\frac{\tilde{\Delta}}{2\Delta_d}\right)^2, \qquad (10)$$

where N_S is the number of spins S in 1 cm³. From comparison of Eq. (9) and Eq. (10) it follows in particular, that under like conditions[11] $\bar{\tau}_c \gg \tau_c^0$. However, it is even more significant that Eq. (10) predicts a strong (not weaker than $\tilde{\Delta}^{-1}$) dependence of $\bar{\tau}_c^{-1}$ on the inhomogeneous width, even if $\tilde{\Delta} > \Delta_d$. Thus, the presence or absence of a dependence of the relaxation time τ_{ISS} on the parameter $\tilde{\Delta}$ may serve as a clear experimental criterion for choosing between the alternative approaches presented above.[1]

1.2 Induced nuclear spin diffusion

Theoretical papers[14-17] have recently appeared which predict the possibility of effective nuclear spin diffu-

sion inside the so-called diffusion barrier—i.e., at distances from the paramagnetic center for which the difference in resonant frequencies of two neighboring nuclear spins $\delta_{ik} \equiv \omega_i - \omega_k$ (due to the static component of the electronic local field) substantially increases the dipole width of the NMR line. It is assumed that under these conditions mutual spin flips of the nuclei I_i and I_k may occur under the action of the variable component of the local field of the spin S_j, and the energy deficit $\hbar\delta_{ik}$ will be made up by the lattice[14-16] or the ESSR[15], depending on which determines the correlation time τ_{cj}.

Taking into account such "induced" spin diffusion should substantially affect the results of traditional nuclear relaxation theory, in which for a long time the "rectangular" diffusion barrier model with radius d has been assumed.[2,18] We should also point out several experimental facts which are evidence for spin diffusion at $r_{ij} < d$.[19] Nevertheless, there is not yet a persuasive experimental test of the theory, which makes such special experiments a timely undertaking.

We now present the results of Refs. 15–17, reducing them to a form convenient for comparison with the experiment. Sabirov,[16,17] having applied probability theory to a three-spin system I_i, I_k, S_j with dipole coupling, obtained[2] for the induced diffusion coefficient D_1 (for $r_{ij} < d$ and $S, I = \frac{1}{2}$)[2]

$$D_1 = \frac{1}{60} \hbar^2 \gamma_I^4 \frac{\langle S_z^2 \rangle - \langle S_z \rangle^2}{\langle S_z \rangle^2} \tau_{cj} \sum_k r_{ik}^{-4} (1 + \delta_{ik}^2 \tau_{cj}^2)^{-1}, \tag{11}$$

where r_{ik} is the distance between I_i and I_k. On the other hand, Buishvili et al.,[15] using a many-body approach, obtained results from which it follows that:

$$D_1 = \frac{I(I+1)}{45} \hbar^2 \gamma_I^4 \frac{\langle S_z^2 \rangle - \langle S_z \rangle^2}{\langle S_z \rangle^2} \tau_{cj} \sum_k r_{ik}^{-4} \quad (\delta_{ik}\tau_{cj} \ll 1); \tag{12}$$

$$D_1 = \frac{1}{6\sqrt{2\pi}} \left(\frac{\langle S_z \rangle^2}{\langle S_z^2 \rangle - \langle S_z \rangle^2} \right)^{1/2} \exp\left(-\frac{1}{2} \frac{\langle S_z \rangle^2}{\langle S_z^2 \rangle - \langle S_z \rangle^2}\right) \sum_k \frac{r_{ik}^2}{\delta_{ik}} \quad (\delta_{ik}\tau_{cj} \gg 1). \tag{13}$$

It is evident that for $\delta_{ik}\tau_{cj} \ll 1$ the results of Refs. 16 and 17 and Ref. 15 agree; however, in the opposite limit they diverge substantially.

Taking into account the fact that

$$\delta_{ik} \approx 3\hbar\gamma_S\gamma_I r_{ij}^{-4} \langle S_z \rangle a,$$

where a is the distance between adjacent nuclei, we can introduce the characteristic distance from the paramagnetic center

$$d_1 = (3\hbar\gamma_S\gamma_I \langle S_z \rangle a\tau_{cj})^{1/4},$$

corresponding to the condition $\delta_{ik}\tau_{cj} = 1$. For $r_{ij}^4 \gg d_1^4$, i.e., outside the sphere with radius d_1, we have $\delta_{ik}\tau_{cj} \ll 1$ and in agreement with Eqs. (11) and (12) the parameter D_1 does not depend on r_{ij} (we designate this value of the diffusion coefficient as D_1^0). In the region $r_{ij} \gg d_1$ we may thus introduce according to the usual recipe[2] the "potential radius" of the paramagnetic center

$$b_1 = 0.68(C_j/D_1^0)^{1/4}. \tag{14}$$

It is different inside the sphere with radius d_1, i.e., in the region where $\delta_{ik} \gg \tau_{cj}^{-1}$. As is evident from Eq. (13), here $D_1 \propto r_{ij}^4$, and Eq. (11) predicts an even

stronger dependence: $D_1 \propto r_{ij}^8$.

Thus, for $r_{ij} < d_1$ the diffusion coefficient sharply drops compared with D_1^0, and the parameter d_1 in practice plays the role of the new radius of the diffusion barrier which, to be sure, by now is not rectangular.

If $b_1 \gg d_1$, the new barrier does not play a role and for the calculation of τ_{1n} we may use the usual formulae of diffusion-limited nuclear relaxation theory[2] (with the obvious replacement of D and b by D_1^0 and b_1). If $d_1 > b_1$, we must solve the diffusion equation[2] taking into account the dependence of D_1 on r_{ij}. Using the method developed by Khutsishvili,[2] we obtained

$$\tau_{1n} = 0.602 R^3 (b_1 d_1)^{3/2} C^{-1}, \quad D_1 \propto r_{ij}^4, \tag{15}$$

$$\tau_{1n} = 0.574 R^3 b_1 d_1^2 C^{-1}, \quad D_1 \propto r_{ij}^8, \tag{16}$$

where $R = (\frac{3}{4}\pi N_s)^{1/3}$ is the radius of the sphere of influence; Eq. (15) is valid for $(b_1 d_1)^{3/2} \ll R^3$, while Eq. (16) is valid for $b_1 d_1^2 \ll R^3$. We note that Eq. (16) was obtained earlier by Skrebnev,[20] although the diffusion mechanism proposed there was entirely different.

From what has been said above, it follows in particular that for $d_1 \approx b_1$ the time τ_{1n} as a function of τ_{cj} has a minimum, which is reached for an "optimum" correlation time

$$\tau_{cj}^{opt} \approx 0.44 a\gamma_I^{-1} \left(\frac{\gamma_S \langle S_z \rangle}{\hbar\omega^2}\right)^{1/3},$$

and

$$(\tau_{1n}^{-1})_{max} \approx \frac{\langle S_z^2 \rangle - \langle S_z \rangle^2}{2\langle S_z \rangle^{3/2}} \frac{\hbar^2 \gamma_I^4}{a^3 R^3} \left(\frac{\gamma_S \tau_{cj}^{opt}}{\gamma_I \omega}\right)^{1/2}. \tag{17}$$

We note that the applicability of the induced diffusion formulae does not depend on the whether τ_{cj} is of a spin-lattice or of a spin–spin character[15,17]; but in the latter case the calculation of $M(t)$ should be performed, strictly speaking, by taking into account the average over j (see Sec. 1.1).

Finally, we point out that for $S > \frac{1}{2}$ the energy spectrum of the paramagnetic center in the crystal is multileveled and nonequidistant; therefore the correlation function $G_j(t)$ contains several $(2S > 1)$ exponentials with different time constants and amplitudes. As we see, this circumstance may prove to be quite important, leading in particular to lifting of the restriction in Eq. (17) on the maximum nuclear relaxation rate under induced diffusion conditions.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Experimental procedure

The experiments were carried out on the spin system of ^{183}W nuclei in ZnWO$_4$ crystals[3] doped with 0.08% and 0.01% Cr^{3+} ions, in a magnetic field $H = 12.4$ kOe at temperatures $T_0 = 4.2$°K and 1.8°K. This system was chosen for study due to the following characteristics of the given materials:

a) The magnetic moment of the only stable odd isotope of tungsten (^{183}W) is very small ($I = \frac{1}{2}$; $\gamma_I/2 = 175$ Hz/Oe), and the natural abundance of this isotope is only 14.4% (the role of the low-abundance odd isotopes

of oxygen and zinc may be neglected). Therefore even at low concentrations of the paramagnetic centers $(c \gtrsim 0.01\%)$ the relationship $c_{Iz} \lesssim c_{ss}$ is satisfied; if the time τ_{cj} is determined by spin-spin interactions, then the bottleneck in the nuclear relaxation occurs in the contact between the nuclei and the ESSR, so that $\tau_{In} = \tau_{ISS}$.

b) Inhomogeneous broadening of the EPR line in $ZnWO_4$:Cr^{3+} is determined by electrostatic interactions,[21] the symmetry of which does not coincide with the symmetry of the usual magnetic spin Hamiltonian.[22] In particular, when the field H lies in the ac crystallographic plane and makes an angle of $\theta = +4.5°$ with the magnetic z axis (i.e., is directed along the a axis), the width $\bar{\Delta}$ of the line corresponding to the $\pm\frac{1}{2}$ transition[4] is minimum; while for $\theta = -4.5°$ it increases about fourfold (see Table I), although the basic energy spectra are completely identical in both cases[21] (Fig. 1). This provides a unique opportunity for studying experimentally the dependence of τ_{In} on $\bar{\Delta}$ with other conditions unchanged.

c) The small magnetic moment of the ^{183}W nucleus sharply weakens the usual nuclear spin diffusion mechanism, leading to an increase in the radius of the diffusion barrier in our experiments to a value $d = 100$ Å. This means that for $c \gtrsim 0.01\%$, to which corresponds $R \lesssim 50$ Å, all the nuclei of the sample occur in relatively strong local fields of the paramagnetic centers, and if spin diffusion occurs at all it can be only induced.

Thus, the study of the spin-lattice relaxation of ^{183}W nuclei in $ZnWO_4$:Cr^{3+} allows us to expect a solution of all three problems formulated in the preceding section.

The spin-lattice relaxation of ^{183}W nuclei was observed from the decay of the NMR signal after preliminary dynamic polarization of the nuclei by microwave pumping (polarization enhancement was 10^2-10^3). Since in this case the NMR line shape is determined by the local fields of the electron spins, in order to obtain information on the total nuclear magnetization, the integration was performed along the entire line contour (this was done using high modulation of the magnetic field with subsequent extraction of the first harmonic of the signal and corresponding scaling).

2.2 Results for $c = 0.08\%$

The relaxation curves obtained in a more concentrated sample are shown on Figs. 2 and 3. They are all composed of two sections: the initial (nonexponential) section and the final (exponential) section. In the initial sections, we observe the dependence $M(0) - M(t) \propto \sqrt{t}$ (as an example, one of them is shown on Fig. 2a as a function of $\sqrt{t}$). It is well known[2] that such kinetics are characteristic of direct relaxation of nuclei without
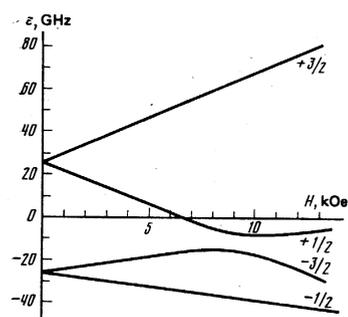

FIG. 1. Energy level diagram for the Cr^{3+} ion in a $ZnWO_4$ crystal for $\theta = \pm 4.5°$.

participation of spin diffusion. We note that the curves shown on Figs. 2 and 3 are obtained after rather prolonged preliminary microwave pumping, leading to the establishment of steady-state nuclear polarization in the entire sample. In the contrary case, the relative amplitude of the nonexponential parts and the decay rate increased, owing to the preferential polarization of nuclei nearest the Cr^{3+} ion.

Since the slope of the line in Fig. 2a is proportional[2] to $C^{1/2}$, we may directly determine this parameter from the initial sections of the relaxation curves. The values of C found in this way are presented in Table I; it is obvious that at both temperatures they clearly diminish with an increase in $\bar{\Delta}$. Thus, recognizing that the remaining parameters of the spin system are unchanged on going from $\theta = +4.5°$ to $\theta = -4.5°$, we may conclude that in this case the correlation time of the parameter S_{jz} has a spin-spin character and depends on the inhomogeneous broadening of the EPR line. This result, as indicated in Sec. 1.1, contradicts Eq. (9) of Refs. 7 and and 12 and unambiguously favors the theory which takes into account the distribution of the times τ_{cj} over the sample.

To compare theory with experiment in more detail, we take into account the fact that the energy spectrum of Cr^{+3} consists of four levels $(S = \frac{3}{2})$ and consequently
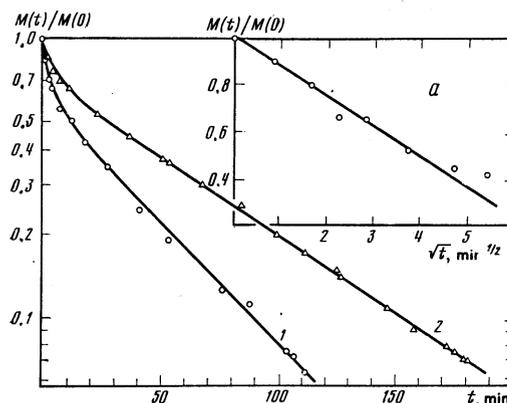

FIG. 2. Change in nuclear magnetization with time upon spin—lattice relaxation of the ^{183}W nuclei in a $ZnWO_4$ crystal for $c = 0.08\%$, $T_0 = 1.8$ °K. (1) $\theta = +4.5°$ (o) (2) $\theta = -4.5°$ (Δ); (a) the initial section of the change in nuclear magnetization for $\theta = +4.5°$.

TABLE I. Results for sample $c = 0.08\%$.

T_0, K	$\theta°$	$\bar{\Delta}/2\pi$, MHz	$C \cdot 10^{43}$, cm^6/s	$\tau_c^{(1)}$, μs	τ_{In}, min	$D_1 \cdot 10^{18}$, cm^2/s
4.2	+4.5	40.7	2.0±0.2	5.4	26±3	6.1
	−4.5	162	0.75±0.1	23	42±4	6.1
1.8	+4.5	40.7	2.0±0.2	5.2	50±5	1.7
	−4.5	162	0.80±0.1	20	78±8	1.7

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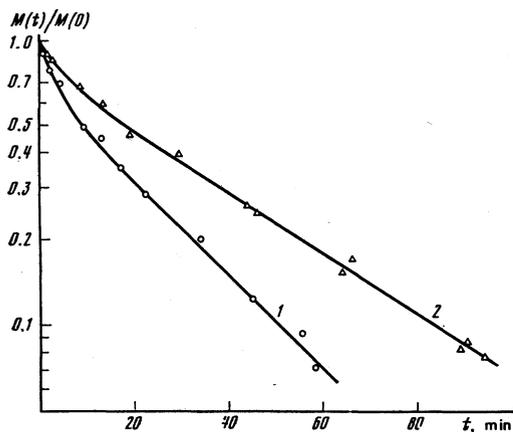
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FIG. 3. Change in nuclear magnetization with time upon spin–lattice relaxation of the ^{183}W nucleus in a ZnWO$_4$ crystal for $c = 0.08\%$, $T_0 = 4.2°$K. (1) $\theta = +4.5°$ (O); (2) $\theta = -4.5°$ ($\triangle$).

the function $G_j(t)$ has the form

$$G_j(t) = \langle S_z \rangle^2 + (\langle S_z^2 \rangle - \langle S_z \rangle^2) \sum_{n=1}^{3} A_n \exp[-t/\tau_{cj}^{(n)}].\tag{18}$$

The time constants $\tau_{cj}^{(n)}$ are the roots of the cubic secular equation and are expressed in terms of the partial transition probabilities W_{lm} between different pairs of energy levels l, m; the coefficients A_n are determined from the initial conditions averaged with the thermal equilibrium density matrix (we note that $\Sigma_n A_n = 1$).

It is reasonable to assume that in our case one of the times $\tau_{cj}^{(n)}$ (e.g., $\tau_{cj}^{(1)}$) is much shorter than the rest and is determined by spin flips within the $\pm\frac{1}{2}$ doublet (see Fig. 1). The basis for this is, first, the large value of the matrix element of the $S_j{}^{+}S_{j'}$ operator which corresponds to this transition, and second, the fact that close to $\theta = 0$ the $\pm\frac{1}{2}$ line undergoes the least additional inhomogeneous broadening (compared with the other transitions) by the various crystal defects.

Making this assumption and recognizing that $\omega\tau_{cj}^{(n)} \gg 1$, we may restrict ourselves in the calculation of C_j and $J_j(\omega)$ from Eqs. (2) and (3) to the first terms of the sum in Eq. (18). Furthermore, since the measurable parameter is $C^{1/2}$ (see Fig. 2a), in order to compare theory with experiment we must average the expression found for $C_j{}^{1/2}$ over the distribution in Eq. (5). For $\omega\tau_{cj}^{(1)} \gg 1$ this gives

$$\overline{(C^{1/2})}^2 = \frac{3}{10\pi} A_1 (\hbar\gamma_I\gamma_S)^2 (\langle S_z^2 \rangle - \langle S_z \rangle^2) \frac{[\ln(4\omega\tau_c^{(1)})]^2}{\omega^2\tau_c^{(1)}}.\tag{19}$$

Having computed $\langle S_z^2 \rangle$, $\langle S_z \rangle^2$, and A_1, and having compared Eq. (19) with the values of C presented in Table I, we determined the time $\overline{\tau}_c^{(1)}$ (see Table I); it is evident that it is practically proportional to Δ, in good agreement with Eq. (10) (we note that in this case $\Delta_d/2\pi \approx 3$ MHz, Ref. 23).

The absolute values of $\overline{\tau}_c^{(1)}$ also agree satisfactorily with Eq. (10), corrected by taking it into account that $S = \frac{3}{2}$. We note that Eq. (19) predicts a very weak temperature dependence of the parameter $\overline{C}^{1/2}$, in complete agreement with experiment. This is explained by the fact that the increase in $\langle S_z \rangle^2$ accompanying the reduc-

tion in T_0 from $4.2°$K to $1.8°$K is compensated for by the increase in the coefficient A_1 due to the increase in the population of the $\pm\frac{1}{2}$ doublet.

Let us now go the exponential sections of the relaxation curves. Above all we emphasize that the very presence of such sections is evidence for the essential role of spin diffusion (in the contrary case the law $M(t) \propto \exp(-k\sqrt{t})$ would have been observed[24] for all t), which, as has already been noted, can only be induced spin diffusion. Simple estimates show that in this sample the condition $\delta_{ik}\tau_{cj} \ll 1$ is satisfied for the overwhelming majority of nuclei, so that we may expect that the condition $b_1 \gg d_1$ is satisfied. Considering further that the time t (corresponding to the instant of transition to the exponential relaxation law) is on the order of b_1^6/C (Ref. 2), we obtain the estimate $b_1 \approx (0.7-1.0)R = 19-27$ Å, from which, using Eq. (14), we find $D_1 \sim 10^{-17}-10^{-18}$ cm^2/s. This parameter is substantially smaller than the usual free spin diffusion coefficient D, which for this material is about $5.3 \cdot 10^{-15}$ cm^2/s.

We may obtain a somewhat more accurate estimate of the parameter D_1 using the time constants τ_{1n} of the exponential sections. As is evident from Table I, at both temperatures $\tau_{1n} \propto C^{1/2}$; this agrees well with the theoretical expression

$$\tau_{1n}^{-1} = LC^{1/4}D^{1/4}N_s^{4/3},$$

obtained[25] for the case $b \gtrsim R$. Choosing the reasonable value[25] 20 for the coefficient L, we arrive at the values of D_1 presented in Table I.

In order to compare these results with the theoretical Eqs. (11) and (12), we must recognize that in this case $\delta_{ik}\tau_{cj} \ll 1$; therefore $D_1 \propto \tau_{cj}$, so that the largest contribution to the parameter D_1 is made by the slowest components of the function $G_j(t)$ [see Eq. (18)]. According to the assumptions made above, these components are due to spin-spin relaxation in the $+\frac{1}{2} \rightarrow \pm\frac{3}{2}$ transitions that undergo additional inhomogeneous broadening even at $\theta = +4.5°$; therefore the corresponding correlation times $(\tau_{cj}^{(2)}$ and $\tau_{cj}^{(3)}$ should not change appreciably as functions of θ. This conclusion is in excellent agreement with the absence of an angular dependence for D_1 (see Table I).

Within the framework of the same assumption, the temperature dependence of the relaxation time τ_{1n} is completely explained: calculation of the coefficients A_2 and A_3 in Eq. (18), taking into account Eq. (12), gives the value $D_1(4.2°$K$)/D_1(1.8°$K$) \approx 4$ [compare with the experimental ratio 3.6 (Table I)]. Finally, comparison of the obtained absolute values of D_1 with Eq. (12) leads to a correlation time on the order of 10^{-4} sec, which agrees well with the expected rate of change of the slow part of $G_j(t)$.

Of course, the given estimates of D_1, made without systematic consideration of the distribution in Eq. (5), are only qualitative in nature. For a more detailed test of the theory of induced diffusion, it is desirable to deal with a spin-lattice correlation function, that does not require averaging over j. To this end, we set up ex-

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periments in samples with lower concentrations of Cr^{+3} ions.

2.3 Results for $c = 0.01\%$

All the relaxation curves for this sample were strictly exponential; the corresponding time constants τ_{1n} are presented in Table II ("experiment" column). The absence of nonexponential sections is obviously explained by the sharp decrease in the ratio b_1/R (in the given case, $R = 53$ Å), which in turn suggests effective induced spin diffusion.

Also noteworthy is the pronounced weakening (and at 4.2°K, practical disappearance) of the dependence of τ_{1n} on Δ, which undoubtedly indicates the predominately spin-lattice character of the function $G_j(t)$. Nevertheless, the calculation according to the equations in Sec. 1.2, assuming that $\tau_c = \tau_{1e}$ (the time τ_{1e} measured in the $\pm\frac{1}{2}$ transition at 4.2°K is equal to 1.0 ms), leads to values of τ_{1n} which are more than an order of magnitude greater than the experimental values. Furthermore, the measured times τ_{1n} are significantly shorter than the minimum relaxation times determined from Eq. (17) and admitted by the theory for a single-exponential correlation function. We emphasize that the latter statement refers equally to any parasitic paramagnetic impurity whose presence might affect the relaxation of the tungsten nucleus.

The resolution of this paradox is possible only by taking into account the multiexponential character of the function $G(t)$, which can be now calculated much more definitively than for spin-spin interactions. Taking into account the measured value of τ_{1e} and the known relationship for the probabilities of single-phonon spin-lattice transitions,[26] we calculated the time constants $\tau_c^{(n)}$ of all three exponentials in Eq. (18) (see Table II), and also their amplitudes A_n (which were of comparable magnitude). It is seen that the values of $\tau_c^{(1)}$, $\tau_c^{(2)}$, and $\tau_c^{(3)}$ span two orders of magnitude. Bearing in mind that the parameter C is determined by the fastest, and the coefficient D_1 by the slowest, component of the correlation function, it is not difficult to understand that the multiexponential character of the latter ensures simultaneously both fast direct relaxation and effective induced diffusion; as a result, a drastic shortening of the time τ_{1n} occurs.

The estimates show that in this case the inequality $d_1 \gg b_1$ is realized (the values of d_1 reach 27 Å at 4.2°K and 37 Å at 1.8°K); therefore we must choose between Eqs. (13), (15), and Eqs. (11), (16). The calculation showed that Eqs. (13), (15) provide much better agreement with experiment; the theoretical values of D_1^0, C, and τ_{1n}^{theor} are obtained using these equations.

As is evident from Table II, at 4.2°K there is fairly good agreement between calculated (column a) and measured values of τ_{1n}; however, at 1.8°K there is no such agreement. Obviously, this is explained by the fact that when the temperature is lowered, the spin-spin flip-flop rates becomes comparable with the times $\tau_c^{(n)}$; the appearance of an angular dependence of τ_{1n} also indicates this. Assuming that the resulting additional correlation rate is $1.7 \cdot 10^3$ s^{-1} in the $\pm\frac{1}{2}$ transition [estimated using Eq. (10)], we have introduced into $G_j(t)$ a correlation that manifested itself a shortening of the time $\tau_c^{(2)}$ to $2.6 \cdot 10^{-5}$ s and $1.7 \cdot 10^{-5}$ s at 4.2°K and 1.8°K respectively. As a result, the parameter C increased appreciably and the values of τ_{1n}^{theor} obtained in this way (Table II, column b) were markedly closer to the experimental values.

CONCLUSIONS

The results obtained in this work allow us to draw the following conclusions.

a) The rate of transfer of nuclear Zeeman energy to the ESSR (electron spin-spin reservoir) strongly depends on the inhomogeneous width of the EPR line; this contradicts the predictions of the current theory[7,12] and points to the necessity for a consistent allowance for the distribution of electron spin-spin correlation times τ_{cj}. The use of the Förster distribution[10] [Eq. (5)] to this end provides good agreement with experiment; the average correlation time $\bar{\tau}_c$ found by this means agrees with theoretical estimates by Salikhov and coworkers.[11]

b) Nuclear spin diffusion may be effective enough even in strong local fields of the paramagnetic centers, i.e., inside a sphere with the traditional diffusion barrier radius d. The observable relaxation rate agrees well with the theory of induced spin diffusion[15-17] when the electronic correlation function has either a spin-spin or a spin-lattice character.

c) When paramagnetic centers have a multilevel nonequidistant spectrum ($S > \frac{1}{2}$) the multiexponential character of the function $G_j(t)$ plays an essential role. In this case the induced spin diffusion is stimulated primarily by the slow components of the correlation function, while the direct nuclear relaxation is stimulated by the fast components.

Considering all that has been said, we may conclude that the picture of nuclear relaxation and spin diffusion in paramagnetic crystals has proven to be tremendously more complicated than was considered even a few years ago. Obviously, for complete resolution of the raised problems, additional investigations are necessary—both theoretical and experimental. We hope that this research is a step in this direction.

TABLE II. Results for sample $c = 0.01\%$.

T_0, K	θ^*	$\Delta/2\pi$, MHz	τ_{1n}, min (experiment)	$\tau_c^{(1)}$, ms	$\tau_c^{(2)}$, ms	$\tau_c^{(3)}$, ms	$C \cdot 10^{48}$, cm^6/s	$D_1^0 \cdot 10^{14}$, cm^2/s	τ_{1n}^{theor}, min	
									a	b
4.2	+4.5	40	100±10	0.08	1.0	4.8	9.7	2.8	230	140
	−4.5	122	110±10							190
1.8	+4.5	40	135±15	0.12	4.7	13.2	1.9	1.9	1300	180
	−4.5	122	170±20							360

[1] Another approach, based on the calculation of the rate of three-spin electron-nuclear cross relaxation, also leads to a strong dependence of τ_{1ss} on $\bar{\Delta}$.[13]

[2])We note that "induced diffusion of the second kind," due to indirect nuclear-nuclear interaction,[16][17] will be a fortiori weaker than the direct relaxation for any r_{ij}; therefore its role may be neglected.

[3])The crystals were obtained from the Institute of Semiconductors of the Ukrainian Academy of Sciences.

[4])Here and later on, the magnetic quantum numbers correspond to the states that are significantly predominant in the given energy level (no pure states are realized in the spectrum of the given material).

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Translated by Cathy Flick

Nature of the spontaneous and field-induced low-temperature orientational transitions in erbium orthoferrite

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(Submitted 3 April 1980)
Zh. Eksp. Teor. Fiz. 79, 1451–1460 (October 1980)

A theory is constructed and an experimental investigation is carried out on the field-induced spin-flip transitions in $ErFeO_3$ at low temperatures, for two orientations of the external magnetic field: $H\|a$ and $H\|c$, where a and c are the crystal axes. The threshold fields of the phase transitions are determined from the isotherms of the magnetostriction $\lambda(H)$ along the c axis. The dependence of the threshold fields on the ratio of the Er-Er and Er-Fe interactions is explained; from a comparison of the theoretical and experimental results, estimates are obtained for the values of these interactions in $ErFeO_3$. It is shown that interaction between rare-earth ions plays a dominant role in low-temperature spin-flip phenomena in erbium orthoferrite.

PACS numbers: 75.50.Gg, 75.30.Kz

$ErFeO_3$ is the only orthoferrite in which ordering of the rare-earth ions at low temperatures is accompanied by a simultaneous spin-flip (SF) transition in the subsystem Fe^{3+} ions, such that the rare-earth and iron spin configurations resulting from the phase transition belong to a single representation of the symmetry group of the orthoferrites, i.e., are compatible spin configurations. It has been established experimentally[1,2] that the low-temperature SF transition in the subsystem of Fe^{3+} spins at $T = T_R \approx 4$ K is a second-order phase transition $\Gamma_2 - \Gamma_{12}$.[1]) We recall that in the configuration

Γ_2, the antiferromagnetism vector $G\|c$, while in the configuration Γ_1, $G\|b$; here c and b are the crystal axes, and Γ_i denotes the appropriate irreducible representation of the symmetry group of orthoferrites. Γ_{12} is a reducible representation, consisting of Γ_1 and Γ_2; in the configuration Γ_{12}, the vector G lies in the plane bc. On lowering of temperature, the angle of deviation of the iron spins from the c axis increases continuously; extrapolation to $T = 0$ K gives $\varphi_0 = 49°$. The Er^{3+} ions are, for $T < T_R$, ordered antiferromagnetically along the c axis (according to the mode C_z

0038-5646/80/100732-06$02.40