Relaxation of paramagnetic impurity centers via host lattice ions in Van Vleck paramagnets

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We investigate, theoretically and experimentally, the properties of spin-lattice relaxation of the paramagnetic impurity ions Nd^{3+}, Tb^{3+} and Er^{3+} in the Van Vleck paramagnet thulium ethyl sulfate. Relaxation of the first two ions in the liquid helium temperature range and higher is determined by magnetic interactions of the impurities with the paramagnetic host ions and the modulation of these interactions due to random thermal excitations of the thulium ions. A correct description of the influence of the host ions on impurity relaxation can be sustained only by taking into account the feedback fields of the impurities, i.e., the loss of symmetry of the crystal field at the thulium ions. Based on the picture derived above we can adequately interpret the temperature, frequency and orientational time dependence of the relaxation of Nd^{3+} and Tb^{3+} ions. As a consequence of the high relaxtion rate of Er^{3+}, there is no effect from the paramagnetic host ion; in this case, relaxation proceeds the same way as in the diamagnetic ethyl sulfates.

1. INTRODUCTION

Spin-lattice relaxation of paramagnetic impurity ions in dielectric diamagnetic crystals has been investigated in detail both experimentally and theoretically (see Ref. 1), a statement which cannot be made about the relaxation of impurity centers in paramagnetic hosts. The present work is devoted to investigating peculiarities of the spin-lattice relaxation of impurity ions in Van Vleck paramagnets, as compared to the relaxation of these same ions in analogous diamagnetic crystals, and elucidating the relaxation mechanism. The measurements we present of the relaxation times of the ions Nd^{3+} and Tb^{3+} in thulium ethyl sulfate point to an increase of the relaxation rate, and to temperature and field dependences of this rate which differ from those of lanthanum and yttrium ethyl sulfate. Obviously, this behavior is caused by the magnetic interactions of the impurity ions with the paramagnetic ions of the crystal host. Here we have to deal with a specific instance of the problem of mutual influence of the various paramagnetic ions in the crystal, when one species of ions forms a regular lattice. This significantly simplifies the theoretical interpretation of the experimental results, and sharpens the interpretation since it obviates the necessity for averaging over the various possible distributions of the ions relative to one another. Of the work employing this type of analysis, we can point only to Refs. 2–4. For example, a definitive observation of the effect of thulium ions on the spin-lattice relaxation of impurity ions (in this case, Fe^{3+} in thulium garnets) can be found only in Ref. 2. In Ref. 5 it was found that the relaxation of Cr^{3+} ions in Al_2O_3 takes place with the participation V^{3+} impurity ions; however, this result was not satisfactorily explained, apparently because the relative positions of the ions was not determined.

Our calculations show that thulium ions are able to affect the relaxation of impurity ions as a result of fluctuations in the magnetic field at a given impurity ion due to random thermal excitation of the thulium ions nearby. Thus, the relaxation mechanism turns out to be essentially a consequence of one of the mechanisms which mediates nuclear relaxation of Van Vleck paramagnets.[6] An analogous mechanism was investigated in Ref. 7 as a possible cause of EPR line broadening of impurity ions in Van Vleck intermetallics.[7] As is well known, at very low temperatures, the most important nuclear relaxation mechanism is interaction of the nuclei with impurity paramagnetic ions. In addition, the impurities lower the symmetry of the crystal field at the host ions, which in turn markedly affects the form of the NMR spectrum and relaxation as the temperature is lowered.[6,8] These circumstances have served as additional stimuli for direct investigations of the properties of the impurities. We have seen that the mutual influence of impurity and host ions is very important: the latter influence the impurity relaxation, but a correct picture of this influence can be established only by including the distortion of the crystal field at the host ions by the embedded impurities. Based on experimental data relating to relaxation of impurities, we can make preliminary inferences about the character of this distortion.

2. EXPERIMENT

Single-crystal TmES was obtained by evaporating a saturated solution of TmES in water at a temperature of 0° C. In order to prepare the aqueous solution of TmES, we used TuO-D grade thulium oxide and ethyl ether-sulphuric acid (diethylsulfate) as the original reagents. The crystals have hexagonal symmetry $C_{6h}^2 \equiv P6_3/m$, and the following unit cell parameters of the crystal at liquid helium temperature: $a = 13.59$ Å, $c = 6.86$ Å.[7] There are two molecules of TmES in a unit cell; the local symmetry of the Tm^{3+} ions is C_{3h}.

The single crystals we investigated were: 1—TmES + 0.5% Nd^{3+}, 2—TmES + 0.5% Nd^{3+} + 0.1%

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TABLE I. Low energy levels and wave functions for rare-earth elements in ethyl sulfates.

Ion	Energy, cm^{-1}	Wave function
Tm^{3+} (in TmES [7])	0	$0.119\|+6\rangle+0.986\|0\rangle+0.119\|-6\rangle$
	32.1	$0.305\|\pm5\rangle+0.953\|\mp1\rangle$
	110.9	$0.446\|\pm4\rangle+0.895\|\mp2\rangle$
Nd^{3+} (in YES [9])	0	$0.904\|\pm{}^7/_2\rangle+0.428\|\mp{}^5/_2\rangle$
	149	$0.752\|\pm{}^9/_2\rangle+0.659\|\mp{}^3/_2\rangle$
	154	$\|\pm{}^1/_2\rangle$
Tb^{3+} (in TbES [10])	0	$0.704(\|+6\rangle+\|-6\rangle)+0.087\|0\rangle$
	0.4	$0.707(\|+6\rangle-\|-6\rangle)$
	100.9	$0.910\|\pm5\rangle+0.416\|\mp1\rangle$
Er^{3+} (in ErES [10])	0	$0.713\|\pm{}^7/_2\rangle-0.701\|\mp{}^5/_2\rangle$
	44	$0.539\|\pm{}^{15}/_2\rangle+0.527\|\mp{}^9/_2\rangle-0.657\|\pm{}^3/_2\rangle$
	74.7	$0.837\|\pm{}^{15}/_2\rangle-0.420\|\mp{}^9/_2\rangle+0.350\|\pm{}^3/_2\rangle$

Er^{3+}, 3—TmES + 0.5% Tb^{3+}, 4—YES + 0.5% Tb^{3+}. Judging from the intensity of the EPR signal, the actual concentration of Nd^{3+} ions in sample 1 was roughly one fourth that in sample 2. In addition, for all samples we detected an EPR spectrum of Gd^{3+} (concentration 0.05%) and Er^{3+} (concentration 0.001%, excluding, naturally, sample 2 in which the Er^{3+} was intentionally introduced).

In Table I we show the positions of the lowest energy levels and their wave functions for the Tm^{3+} host ions ($4f^{12}$, ${}^3H_6$), and also those of the impurity ions Nd^{3+} ($4f^3$, ${}^4I_{9/2}$), Tb^{3+} ($4f^8$, ${}^7F_6$) and Er^{3+} ($4f^{11}$, ${}^4I_{15/2}$) investigated in the present work. As is clear, EPR of the Tb^{3+} ion is observed close to the location of the singlet levels. The sizable separation of the excited levels for Nd^{3+} and Tb^{3+} ions allows us to suppose that for these ions the contribution to the spin-lattice relaxation rate due to two-step resonance fluorescence processes will be insigificant, which should favor detection of the influence of Van Vleck ions on the relaxation. At helium temperatures only the lowest levels of the ions under study are populated, and since all rare-earth ions in the crystal TmES are magnetically equivalent, the EPR spectrum is very simple—an intense line from the ions with zero nuclear spin, accompanied by weaker lines due to ions with nonzero nuclear spins. Measured values of the g-factors of rare-earth ions in TmES are as follows: Nd^{3+}—$g_{\parallel} = 3.69$, $g_{\perp} = 1.956$; Er^{3+}—$g_{\parallel} = 1.521$, $g_{\perp} = 8.732$. These quantities are close to the values in the diamagnetic crystals YES and LaES.[10,11]

Measurement of the spin-relaxation times T_1 were carried out in the temperature range 1.5–30 K at the frequencies 9.4, 24.0 and 36.0 GHz. Relaxation times $> 10^{-5}$ sec were measured by the method of pulse saturation of the EPR signal, while times in the range 10^{-8}–10^{-9} sec were extracted by spin-phonon broadening of the EPR line according to the formula[12]

$$T_1^{-1} = 1{,}4\pi g \cdot 10^6\, \Delta H_{\text{sp-ph}}\ [\mathrm{G}].$$

The results of measurements of the times T_1 are presented in Figs. 1–4. The temperature dependence of the time T_1 for the ion Nd^{3+} in TmES at the frequencies 9.4 and 24.0 GHz for the $H_0 \| c$ and $H_0 \perp c$ orientations is shown in Fig. 1. The results of these measurements are well described by the expres-

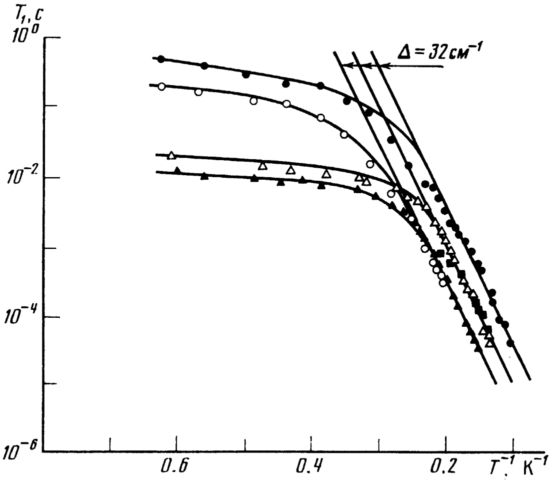

FIG. 1. Temperature dependence of the spin-lattice relaxation time for Nd^{3+} ions in single-crystal TmES: ●—$\nu = 9.4$ GHz, $H_0 \| c$; ○—$\nu = 9.4$ GHz, $H_0 \perp c$; △—$\nu = 24.0$ GHz, $H_0 \| c$; ▲—$\nu = 24.0$ GHz; $H_0 \perp c$; ■—$\nu = 36.0$ GHz, $H_0 \| c$. Smooth curves correspond to formula (10), the line—to the exponential part of these formulae, $T_1^{-1} \sim \exp(-32 \times 1.44/T)$.

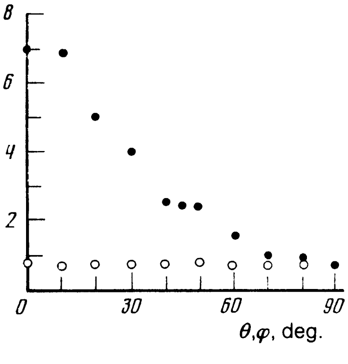

FIG. 2. Angular dependence of spin-lattice relaxation time for Nd^{3+} ions in single crystal TmES at the frequency 9.4 GHz for $T = 4.3$ K; ●—ca plane (θ), ●—ab plane (φ).

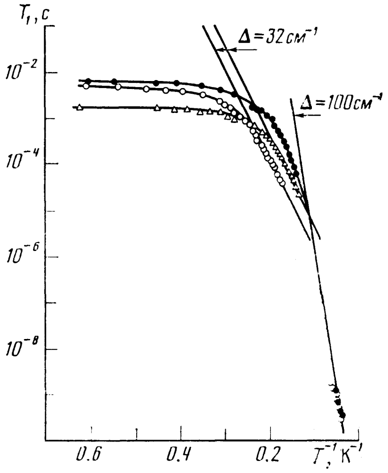

FIG. 3. Spin-lattice relaxation of Tb^{3+} ions in single-crystal TmES and YES for $H_0 \| c$; ●—$\nu = 24.0$ GHz, YES; ○—$\nu = 24.0$ GHz, TmES; △—$\nu = 36.0$ GHz, TmES. The continuous curves correspond to formulae (2). The straight line shows the exponentials $T_1^{-1} \propto \exp(-32 \cdot 1.44/T)$ and $T_1^{-1} \propto \exp(-100 \cdot 1.44/T)$.

sions

$$\mathbf{H}_0 \| c \begin{cases} 9.4\ \text{GHz} & T_1^{-1} = 0.8T^2 + 3.6 \cdot 10^6 \exp(-32 \cdot 1.44/T) \\ 24.0\ \text{GHz} & T_1^{-1} = 30T + 1.25 \cdot 10^7 \exp(-32 \cdot 1.44/T), \\ 36.0\ \text{GHz} & T_1^{-1} = 160T + 1.25 \cdot 10^7 \exp(-32 \cdot 1.44/T) \end{cases} \tag{1}$$

$$\mathbf{H}_0 \perp c \begin{cases} 9.4\ \text{GHz} & T_1^{-1} = 1.8T^2 + 5 \cdot 10^7 \exp(-32 \cdot 1.44/T) \\ 24.0\ \text{GHz} & T_1^{-1} = 50T + 5.0 \cdot 10^7 \exp(-32 \cdot 1.44/T). \end{cases}$$

The results of measuring the spin-lattice relaxation of Nd^{3+} in sample 2, which has a high content of Er^{3+} ions, coincide completely with the results for sample 1. In Fig. 2 we illustrate the detailed dependence of the relaxation time for Nd^{3+} ions in TmES on the orientation of the magnetic field both in the plane perpendicular to the optical axis of the crystal c and in a plane containing the c-axis. In Fig. 3 we present the temperature dependence of the time T_1 for Tb^{3+} ions in single crystals of TmES and YES. Measurement of T_1 for various components of the hyperfine structure of the Tb^{3+} ion gave identical results. The time T_1 also did not depend on the orientation of the external magnetic field relative to the crystal c-axis. The results of measuring T_1 for Tb^{3+} ions are well described by the expressions:

YES: $\nu = 24.0$ GHz

$$T_1^{-1} = 67T + 1.1 \cdot 10^{-2} T^7 + 7.5 \cdot 10^{11} \exp(-100 \cdot 1.44/T);$$

TmES: $\nu = 24.0$ GHz

$$T_1^{-1} = 100T + 7.7 \cdot 10^7 \exp(-32 \cdot 1.44/T) + 7.5 \cdot 10^{11} \exp(-100 \cdot 1.44/T); \tag{2}$$

TmES: $\nu = 36.0$ GHz

$$T_1^{-1} = 250T + 1.7 \cdot 10^7 \exp(-32 \cdot 1.44/T) + 7.5 \cdot 10^{11} \exp(-100 \cdot 1.44/T).$$

In Fig. 4 we present the results of measuring T_1 for Er^{3+} ions in single-crystal TmES. These results are well-described by the expressions:

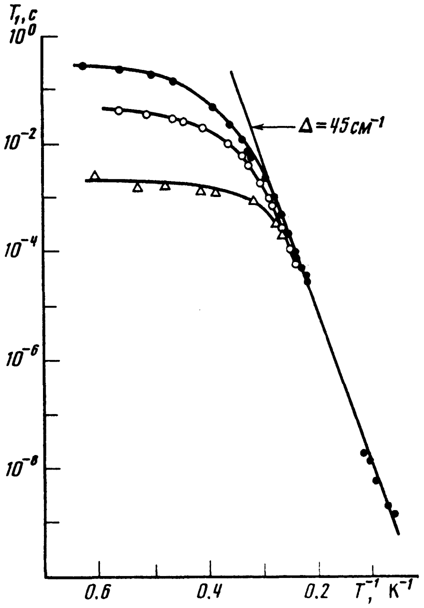

FIG. 4. Spin-lattice relaxation of Er^{3+} ions in single-crystal TmES: ●—$\nu = 9.4$ GHz, $H_0 \| c$; ○—$\nu = 9.4$ GHz, $H_0 \perp c$; △—$\nu = 24.0$ GHz, $H_0 \perp c$. The continuous curves correspond to formulae (3). The straight line corresponds to the function $T_1^{-1} \propto \exp(-45 \cdot 1.44/T)$.

$\mathbf{H}_0 \| c$: $\nu = 9.4$ GHz

$$T_1^{-1} = 2.2T + 10^{-3} T^9 + 5.5 \cdot 10^{10} \exp(-45 \cdot 1.44/T),$$

$\mathbf{H}_0 \perp c$: $\nu = 9.4$ GHz

$$T_1^{-1} = 14T + 10^{-3} T^9 + 8.5 \cdot 10^{10} \exp(-45 \cdot 1.44/T), \tag{3}$$

$\mathbf{H}_0 \perp c$: $\nu = 24.0$ GHz

$$T_1^{-1} = 270T + 10^{-3} T^9 + 8.5 \cdot 10^{10} \exp(-45 \cdot 1.44/T).$$

Let us compare the experimental results we have obtained in TmES with well-known results from the literature for the diamagnetic crystals YES and LaES. The spin-lattice relaxation of Nd^{3+} ions in YES and LaES was studied in Refs. 10, 11 and 13, and in more detail in Ref. 9. It was noted that the relaxation rate was determined by contributions from direct ($T_1^{-1} \sim T$) and Raman ($T_1^{-1} \sim T^9$) processes. In the region where Raman processes dominate, a weak anisotropy is observed in the relaxation time, which the authors of Ref. 9 attribute to a contribution from a process with the functional form $T_1^{-1} \propto H^2 T^7 \sin^2 \theta$. The spin-lattice relaxation of Tb^{3+} ions in YES was studied in Ref. 10 over the temperature range 1.5–5 K. The relaxation rate is this system is determined by direct and Raman processes ($T_1^{-1} \sim T^7$). The spin-lattice relaxation of Er^{3+} ions in LaES was studied earlier in Ref. 10. It was shown that a contribution to the relaxation was made by direct, Raman ($T_1^{-1} \sim T^9$) and two-step ($T_1^{-1} \sim \exp(-\Delta/T)$) processes; the latter corresponds to participation of a Stark level of the erbium ion with energy $\Delta = 44$ cm^{-1}.

Investigations carried out recently of the relaxation of Er^{3+} ions in TmES show that the relaxation of this ion in TmES and in LaES crystals has one and the same character (see Fig. 4 and formula 3). In Ref. 4, data was obtained for spin-lattice relaxation of Er^{3+} ions in TmES which differed from results obtained earlier. We claim that this difference is due to the presence in the samples used in Ref. 14 of very large quantities of other paramagnetic impurities, in particular Gd^{3+}. The Er^{3+} ions at helium temperatures relax significantly faster than Nd^{3+} and Tb^{3+} ions. It might be suggested that the Er^{3+} ions, being rapid-relaxation centers, could influence the spin-lattice relaxation of Nd^{3+} and Tb^{3+}. However, studies, of the relaxation of Nd^{3+} ions in TmES with various concentrations of Er^{3+} always give the same results.

We also note that by broadening the range of temperatures where T_1 was measured for Tb^{3+} ions in TmES and YES to ~ 30 K, we were able to separate out the contribution to the spin-lattice relaxation from the two-step processes which involve the intrinsic Stark levels of the Tb^{3+} ion with energies $\sim 100\ \mathrm{cm}^{-1}$ (see (21)).

Spin-lattice relaxation of impurity ions in the paramagnetic crystal TmES exhibits the following peculiarities, which we not describe:

1. The relaxation rates for Nd^{3+} and Tb^{3+} ions in thulium ethyl sulfate are significantly higher than in the diamagnetic ethyl sulfates.

2. The temperature dependence of T_1^{-1} for these ions in the high-temperature region ($T \gg 4$ K) has an exponential character; $T_1^{-1} \sim \exp(-\Delta/T)$, with $\Delta = 32\ \mathrm{cm}^{-1}$—the smallest excitation energy of the Tm^{3+} ion. Nevertheless, the the coefficient of the exponential is significantly smaller than values which are typical of intrinsic two-step processes (note that as a result of this Tm^{3+} has no influence on Er^{3+}).

3. A strong orientation dependence is observed in the relaxation times of Nd^{3+} ions.

4. For the $\mathbf{H}_0 \| c$ orientation, T_1^{-1} for Nd^{3+} grows with frequency, while for Tb^{3+} it decreases. For $\mathbf{H}_0 \perp c$, there is no frequency dependence for T_1^{-1}, while for Tb^{3+} it was not studied, since $g_\perp = 0$.

3. THEORY

The presence of the exponential factor $\exp(-\Delta/T)$ in the relaxation rates for Nd^{3+} and Tb^{3+} ions persuasively attests to the fact that over the corresponding temperature range the relaxation is due to interaction with Tm^{3+} ions. The spacings between rare-earth ions in ethyl sulfate is large ($\gtrsim 7$ Å); hence, we limit ourselves to magnetic dipole-dipole interactions between the Tm^{3+} ions and impurity ions, which are of the form

$$\mathscr{H}' = \mathbf{SF}, \quad F_\alpha = A g_{\alpha\alpha}\left(J_\alpha - \frac{3r_\alpha}{r^2}\mathbf{Jr}\right), \quad A = g_J\beta^2/r^3, \tag{4}$$

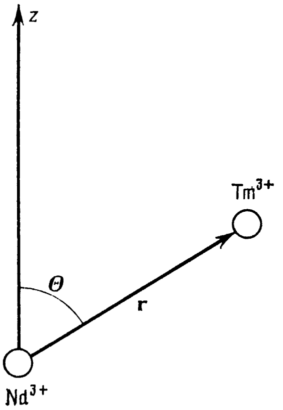

FIG. 5. Mutual positions of host and impurity paramagnetic ions.

where **S** is the effective spin of the impurity ($S = 1/2$), **J** is the total angular momentum of the Tm^{3+} ion, the index α denotes the component of vectors in a crystallographic coordinate system (the z-axis is directed along the c-axis of the crystal), $g_{\alpha\alpha}$ is the g-factor of the impurity, g_J is the Lande factor of a Tm^{3+}, β is the Bohr magneton and **r** is a radius vector connecting the impurity ion with a Tm^{3+} ion (see Fig. 5). The quantities r, Θ for Tm^{3+} ions in several of the first coordination spheres are listed in Table II. Also listed are the numbers n_i of ions in the corresponding spheres. A schematic illustration of the states which participate in the relaxation transitions, and their energies, is presented in Fig. 6 (not to scale). By Ω_0 we denote the initial splitting of the excited doublet of thulium, which is primarily due to the axial crystal-field perturbation coming from the impurity ions. It is not difficult to calculate the wave function $|d_{1,2}\rangle$ for an arbitrary orientation of the external magnetic field:

$$|d_{1,2}\rangle = \frac{1}{(1+\alpha^2)^{1/2}}\left(|\pm 1\rangle \mp \alpha|\mp 1\rangle\right),$$

$$\alpha = \frac{2}{\Omega_0}\left(\frac{\Omega}{2} - g_J\beta a H_z\right), \quad \Omega = (4g_J^2\beta^2a^2H_z^2 + \Omega_0^2)^{1/2}, \tag{5}$$

$$a = \langle 1|J_z|1\rangle.$$

Here, the upper sign in the formula is related to $|d_1\rangle$, the lower to $|d_2\rangle$; **H** is the external magnetic field, and $|\pm 1\rangle$ is the conventional symbol for the doublet state of thulium (see Table I). We neglect mixing of the states $|d\rangle$ and $|g\rangle$ because of the small nonaxial crystal-field perturbation, and also the perpendicular component of the magnetic field (these are terms of order $|V|/\Delta$ in the wave function, where V is the perturbation).

TABLE II. Position of the host paramagnetic ions nearest to impurities in the TmEs lattice.

No. of Coordination Spheres	n_i	r_i, Å	Θ_i, Degrees
1	2	6.86	0
2	6	8.51	66.3
3	6	12.89	37.2
4	6	13.59	90
5	2	13.72	0

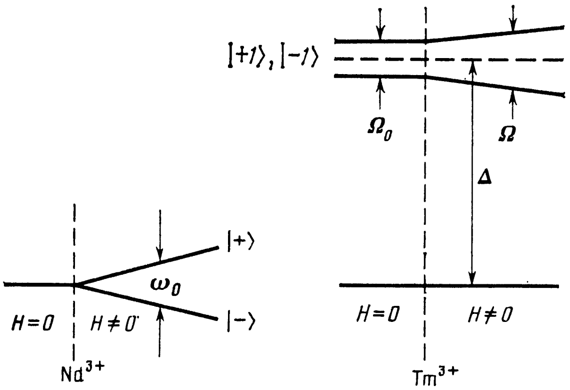

FIG. 6. Quantum state diagram for Tm–Nd pairs which participate in relaxation transitions.

Relaxation is caused by modulation of $\mathscr{H}'$ by lattice vibrations, transfer of thermal excitations between Tm^{3+} ions, etc. The modulation of the quantity $\mathbf{r}$ in (4) by lattice vibrations leads to a "Waller" mechanism for relaxation. The calculation is in some ways different from usual calculations using this mechanism; this is related to the fact that in this case we are investigating interactions between different paramagnetic ions. Expanding the operator F_α (4) in a power series in the displacements δr of the Tm^{3+} ions from their equilibrium positions, and expressing these displacements as a deformation tensor via the formula $\delta r_\alpha = \Sigma e_{\alpha\beta} r^0_\beta$, we can cast the perturbation Hamiltonian in the form

$$\mathscr{H}' = \sum_i V_i e_i, \qquad V_i = \sum_{\alpha,\beta} A g_{\alpha\alpha} S_\alpha J_\beta G_i^{\alpha\beta}, \tag{6}$$

where e_i are real spherical components of the deformation tensor: $e_1 = (e_{xx} + e_{yy} + e_{zz})/\sqrt{3}$ is the zero-order harmonic, e_2 to e_6 is the second-order harmonic and e_7 and e_9 is the first-order harmonic (see, e.g., Ref. 15); the structure factors $G_i^{\alpha\beta}$ have the form

$$G_1^{\alpha\beta} = -\sqrt{3}(\delta_{\alpha\beta} - 3n_\alpha n_\beta), \quad G_2^{\alpha\beta} = -\sqrt{3/2}\{(3n_z^2 - 1) \times (\delta_{\alpha\beta} - 3n_\alpha n_\beta) + 3n_\alpha n_\beta(\delta_{\alpha z} + \delta_{\beta z} - 2n_z^2)\} \text{ etc.}, \tag{7}$$

here, $\mathbf{n} = \mathbf{r}_0/r_0$, where the subscript 0 denotes the equilibrium value of the vector $\mathbf{r}$. Standard calculations, based on the Debye model of the lattice, of the transition probability between spin states n and k with absorption (or emission) of a phonon of frequency ω lead to the expression[15]

$$w_{nk} = \frac{1}{6}\frac{\omega^3}{\pi\hbar d v_m^5}\left[\frac{1}{\exp(\hbar\omega/kT) - 1}(+1)\right] \times \sum_i q_i |\langle k|V_i|n\rangle|^2, \tag{8}$$

where

$$v_m^{-5} = \frac{2}{5}\left(v_l^{-5} + \frac{3}{2}v_t^{-5}\right), \quad q_1 = \left(\frac{v_m}{v_l}\right)^5,$$

$$q_{2-6} = 1, \quad q_{7-9} = \left(\frac{v_m}{v_t}\right)^5,$$

v_l is the longitudinal sound velocity, v_T is the transverse velocity, d is the crystal density. Here, n, k are states of pairs of ions, e.g., Tm and Nd; thus, to obtain the spin-lattice relaxation time of an impurity ion we must carry out a summation of the transition probability (8) over final states and average over initial states of the Tm^{3+} ion:

$$T_1^{-1} = \sum_{\mathrm{Tm}} \sum_{p=1,2} (w_{+g,-d_p}\rho_g + w_{+d_p,-g}\rho_d + w_{-g,+d_p}\rho_g + w_{-d_p,+g}\rho_d), \tag{9}$$

where ρ_g, ρ_d are Boltzmann factors for the Tm ion, Σ_{Tm} denotes a sum over all the Tm ions which make up the environment of an impurity ion. The final formula is simplified as a consequence of the fact that in the temperature range of interest to us $\Delta \gg (kT, \Omega_0, \omega_0)$, so that $\rho_g \approx 1$, $\rho_d \approx \exp(-\Delta/kT)$. Introducing still another notation $\langle g|J_x|d\rangle = b/2$, we obtain

$$T_1^{-1} = \frac{1}{3}\frac{\Delta^3 b^2}{\pi\hbar d v_m^5} \times \exp(-\Delta/kT) \sum_{\mathrm{Tm}} \sum_i q_i A^2 \left(\left| \sum_\alpha g_{\alpha\alpha} G_i^{\alpha x} \langle + |S_\alpha| - \rangle \right|^2 + \left| \sum_\alpha g_{\alpha\alpha} G_i^{\alpha y} \langle + |S_\alpha| - \rangle \right|^2 \right). \tag{10}$$

For example, in the case of the Nd^{3+} ion and for parallel orientation of the magnetic field, this expression appears as follows:

$$\begin{aligned} T_1^{-1}(\mathbf{H}_0 \parallel z) = {} & \frac{1}{8}\frac{\Delta^3 b^2 g_\perp^2}{\pi\hbar d v_m^5} \\ & \times \exp(-\Delta/kT) \sum_{\mathrm{Tm}} \frac{g_J^2 \beta^4}{r^6} \{2q_1[1 + (1 - 3\sin^2\Theta)^2] \\ & + (1 - 3\cos^2\Theta)^2 + (2 - 15\sin^2\Theta\cos^2\Theta)^2 \\ & + 3\sin^4\Theta[3 + (3 - 5\sin^2\Theta)^2] \\ & + 6\sin^2\Theta\cos^2\Theta[3 + 2(2 - 5\sin^2\Theta)^2] \\ & + 6q_7\sin^2\Theta(1 + 2\cos^2\Theta)\}. \end{aligned} \tag{11}$$

All the parameters entering into (10), (11) are known well enough to obtain closely bounded estimates: setting $d = 2$ gm/cm, $v_m = 2 \times 10^5$ cm/sec, we obtain $T_1^{-1} \approx 10^3 \exp(-\Delta/kT)$. The same estimate is obtained also for the Tb^{3+} ion.

Although the results obtained correctly reflect the temperature dependence of the relaxation rate of the process, the coefficient of the exponential is too small compared to its experimental value. Moreover, according to theoretical estimates there is no frequency dependence in the relaxation rate, and the orientation dependence is the opposite to that observed experimentally. We therefore investigate a second relaxation mechanism which by convention we will refer to as the effect of "fluctuations in the moments of paramagnetic host ion."

Transitions between various states of the Tm^{3+} ion caused by their interactions with the lattice or with neighboring Tm^{3+} ions lead to random variation of the magnitude of the moment $\mathbf{J}$. As a consequence of this, the Hamiltonian $\mathscr{H}'$ (4) undergoes random fluctuations in time and causes

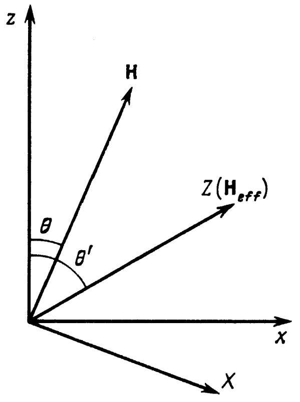

FIG. 7. Orientation of external magnetic field and effective field at an impurity ion.

relaxation transitions between the states $|+\rangle$ and $|-\rangle$ of the impurity ion (for definiteness we first investigate Nd^{3+}). The relaxation rate can be cast in the form (see Ref. 16):

$$T_1^{-1}=w_{+-}+w_{-+}=\sum_{\mathrm{Tm}}\frac{1}{2\hbar^2}\int_{-\infty}^{+\infty}\langle F_+F_-(t)\rangle_t\exp(-i\omega_0 t)\,dt, \tag{12}$$

where w_{+-} is the transition probability per unit time from the state $|+\rangle$ to the state $|-\rangle$, summed over all Tm^{3+} ions which are neighbors of the neodymium. The brackets $\langle\ldots\rangle_t$ denote the correlation function; the quantum statistical average involved in calculating this function must be taken with the full Hamiltonian, including the interactions of a Tm^{3+} ion with neighbors and with the lattice; these interactions cause the correlation function to decay. From here on, in place of this complicated procedure we will make use of the assumption that there exists a unique correlation time τ_c (see Ref. 6) and correspondingly write

$$\langle\ldots\rangle_t=\langle\ldots\rangle\exp(-|t|/\tau_c), \tag{13}$$

where the angle brackets without the subscript t denote an average of the single-particle Hamiltonian for the Tm^{3+} ion. In our calculations we take into account only three states of the Tm^{3+}, those shown in Fig. 6, since the population of higher-lying levels in the temperature interval of interest to us can be neglected. We remark, however, that relaxation transitions are caused by the component of the random field perpendicular to the Z direction of the effective field $\mathbf{H}_{\mathrm{eff}}$ at the Nd^{3+} ion (Fig. 7); therefore, the subscript $\pm$ for the operator F in (12) distinguishes circular coordinates in the plane perpendicular to the Z axis. Obviously,

$$\operatorname{tg}\theta'=(g_\perp/g_\parallel)\operatorname{tg}\theta. \tag{14}$$

From here on the calculation reduces to a transformation to the crystallographic coordinate system; as a result, the correlation function in (12) including (4) is expressed through the function $\langle J_\alpha J_\beta(t)\rangle$. If we remain within the approximation of using (5) as a description of the thulium wave function, we note that only one of the correlation functions $\langle J_\alpha J_\beta(t)\rangle$ is different from zero:

$$\begin{aligned}\langle J_zJ_z(t)\rangle&=[\mathrm{Sp}\exp(-\mathscr{H}/kT)]^{-1}\\&\times\mathrm{Sp}[\exp(-\mathscr{H}/kT)J_z\exp(i\mathscr{H}t)J_z\exp(-i\mathscr{H}t)]\\&\approx\exp(-\Delta/kT)\{\langle d_1|J_z|d_1\rangle^2+\langle d_2|J_z|d_2\rangle^2\\&+\langle d_1|J_z|d_2\rangle^2[\exp(i\Omega t)+\exp(-i\Omega t)]\},\end{aligned} \tag{15}$$

where $\mathscr{H}$ is the Tm^{3+} ion Hamiltonian and we have used the approximation $\Delta\gg kT$. Finally, we obtain the following expression for the relaxation time:

$$\begin{aligned}T_1^{-1}=\frac{2}{\hbar^2}a^2\exp(-\Delta/kT)\sum_i A_i^2n_i\Big[&(1-3\cos^2\Theta_i)^2g_\parallel^2\sin^2\theta'\\&+\frac{9}{2}g_\perp^2\sin^2\Theta_i\cos^2\Theta_i(1+\cos^2\theta')\Big]\Big\{\Big(\frac{1-\alpha_i^2}{1+\alpha_i^2}\Big)^2\frac{\tau_c}{1+\omega_0^2\tau_c^2}\\&+\frac{2\alpha_i^2}{(1+\alpha_i^2)^2}\Big[\frac{\tau_c}{1+(\Omega_i-\omega_0)^2\tau_c^2}+\frac{\tau_c}{1+(\Omega_i+\omega_0)^2\tau_c^2}\Big]\Big\},\end{aligned} \tag{16}$$

where the subscript i enumerates the coordination spheres; n_i is the number of Tm^{3+} ions in the ith sphere. For the relaxation rate of Tb^{3+} we obtain the analogous formula by replacing the first square brackets under the summation sign by the factor $g_\parallel^2(1-3\cos^2\Theta)^2$, i.e., in this case, in agreement with experiment, there is no dependence of the relaxation rate on orientation of the magnetic field.

4. DISCUSSION OF RESULTS

As is clear, formula (16) predicts a rather complicated dependence for the relaxation time on the magnitude and orientation of the external magnetic field; the character of this dependence is essentially determined by the values of the parameters τ_c and Ω_{0i}. In a perfect crystal with impurities, all the Ω_{0i} are zero; in the absence of an initial splitting according to formula (5), $\alpha=0$; then from formula (16) there follows a dependence of the relaxation rate of the Nd^{3+} ion on the frequency ω_0 which is reversed compared with experiment. In fact, of course, the impurity ion Nd^{3+} deforms the axial crystal field of the host Tm^{3+} ions next to it, giving rise to the splitting of their doublet states. The quantities Ω_{0i} must depend significantly on the geometry of the coordination sphere. For Tm^{3+} ions located along the same c-axis which contains the Nd^{3+} ion, the latter is an axial perturbation, and in this case $\Omega_{0i}=0$. The axial symmetry of the crystal field must be broken most strongly for Tm^{3+} ions in the second sphere, so that $\Omega_{02}>\Omega_{03}$. It must be surmised also that $\Omega_{02}\lesssim 1$–$2\ \mathrm{cm}^{-1}$; otherwise, an isovalent substitution at the rather large spacing (8.5 Å) would imply a small probability for any strong reconstruction of the crystal field for Tm^{3+} ions in the second sphere. Thus, in the spectrum of Ω_{0i} we encounter values close to the EPR frequency, and the corresponding Tm^{3+} ions will be most active in sampling the energy of the impurity ions. As regards the correlation time τ_c, its magnitude can hardly be chosen to be much different from $\sim10^{-10}$ sec (see Ref. 6). The shortest time is related to the resonant transfer of the excitation energy Δ between neighboring Tm^{3+} ions. The spread in these energies due to the variation in the initial splittings Ω_{0i} of the doublet impairs the resonance condition, but in any case τ_c cannot be longer than 10^{-9} sec, due to interactions of thulium ions with lattice vibrations.

Fairly good agreement with experiment for Nd^{3+} is obtained when we take into account the contribution to T_1^{-1} of the first five coordination spheres for the following values of the initial splitting:

$$\Omega_{01}=\Omega_{05}=0,\quad \Omega_{02}=1.17\ \text{см}^{-1},$$
$$\Omega_{03}=0.85\ \text{см}^{-1},\quad \Omega_{04}=0.74\ \text{см}^{-1}. \tag{17}$$

Assuming still that $\tau_c = 10^{-10}$ sec, we find in agreement with (16) that $T_1^{-1} = A(\nu)\exp(-\Delta/kT)$; the values of A (ν in GHz) for the $\mathbf{H}_0 \perp c$ orientation are

$$A(9.4)=1.07\cdot10^7,\quad A(24.0)=0.51\cdot10^7,\quad A(36.0)=1.31\cdot10^7. \tag{18}$$

For the parallel orientation they are as follows:

$$A(9.4)=1.7\cdot10^5,\quad A(24.0)=0.94\cdot10^6,\quad A(36{,}0)=1.12\cdot10^7. \tag{19}$$

These numbers reflect approximately the qualitative dependences on frequency and orientation of an external field seen in experiments, and in order of magnitude coincide with measured relaxation rates. Still better agreement with experiment is obtained for the results of calculated estimates of the relaxation rates for the Tb^{3+} ion. Assuming $\tau_c = 10^{-10}$ sec and

$$\Omega_{01}=\Omega_{05}=0,\ \Omega_{02}=0.64\ \text{см}^{-1},\ \Omega_{03}=0.42\ \text{см}^{-1},\ \Omega_{04}=0.32\ \text{см}^{-1}, \tag{20}$$

we obtain

$$A(24)=6.4\cdot10^7,\quad A(36)=2.02\cdot10^7. \tag{21}$$

We remark that in a real TmES crystal, in addition to distortion of the symmetry of the Tm^{3+} centers due to their close proximity to Nd^{3+} ions we must point out that there is distortion due to other crystal lattice defects. The latter distortions have a random character and by themselves lead to splitting of the excited doublet of the thulium ion; the root-mean-square value of this splitting amounts to $\sim 0.1\ \text{cm}^{-1}$.[6] In fact, in real crystals the splittings Ω_{0i} have no fixed values, but are distributed in a spectrum of width $\sim 0.1\ \text{cm}^{-1}$. However, taking this distribution into account did not lead to a noticeable change in calculated estimates.

5. CONCLUSION

The important mechanism for spin-lattice relaxation of impurity paramagnetic ions in Van Vleck paramagnets is relaxation via the paramagnetic ions of the host crystal—a mechanism which up to now has been considered more typical of nuclear relaxation. The coupling between various ions is mediated by magnetic dipole-dipole interactions, although in dense crystals with small spacings between paramagnetic ions (for example $LiTmF_4$) one cannot exclude exchange interactions. These interactions are modulated as a consequence of variations in the relative positions of the ions as the lattice vibrates; however, more important is the modulation caused by intrinsic relaxation processes of the host ions. A realistic model of the relaxation of impurity ions via the host paramagnetic ions can be assembled only by including the distortion of the crystal field of the ideal lattice by the incorporation of impurities. Based on these assumptions it is possible to interpret satisfactorily the extensive complex of experimental data on impurity ion relaxation in thulium ethyl sulfate.

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[1] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyi Paramagnitnyi Resonans Soedinenii Elementov Promezhutochnykh Grupp (Electron Paramagnetic Resonance of Compounds from the Intermediate Groups), Nauka, Moscow (1972).
[2] L. Rimai and R. W. Bierig, Phys. Rev. Lett. **12**, 284 (1964).
[3] F. J. Rachford and C. Y. Huang, Phys. Rev. **B3**, 2121 (1971).
[4] A. A. Antipin, I. S. Konov, S. L. Korableva *et al.*, Fiz. Tverd. Tela (Leningrad) **21**, 111 (1979) [Sov. Phys. Solid State **21**, 65 (1979)].
[5] G. M. Zverev, A. M. Prokhorov and A. K. Shevchenko, Fiz. Tverd. Tela (Leningrad) **4**, 3136 (1963) [Sov. Phys. Solid State **4**, 2297 (1963)].
[6] L. K. Aminov, A. A. Kudryakov, M. S. Tagirov and M. A. Teplov, Zh. Eksp. Teor. Fiz. **86**, 1791 (1984) [Sov. Phys. JETP **59**, 1042 (1984)]; L. K. Aminov and M. S. Teplov, Usp. Fiz. Nauk **147**, 49 (1985) [Sov. Phys. Usp. **28**, 762 (1985)].
[7] D. Davidov, V. Zevin, R. Levin *et al.*, Phys. Rev. **B15**, 2771 (1977).
[8] L. K. Aminov, M. S. Tagirov and M. A. Teplov, Zh. Eksp. Teor. Fiz. **79**, 1322 (1980) [Sov. Phys. JETP **52**, 669 (1980)].
[9] R. L. Marchand and H. J. Stapleton, Phys. Rev. **139**, 14 (1974).
[10] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966).
[11] P. L. Scott and C. D. Jeffries, Phys. Rev. 1962, **127**, 32 (1962).
[12] A. A. Antipin, A. N. Katyshev, I. N. Kurkin and L. Ya. Shekun, Fiz. Tverd. Tela (Leningrad) **10**, 595 (1968) [Sov. Phys. Solid State **10**, 468 (1968)].
[13] G. H. Larson and C. D. Jeffries, Phys. Rev. **145**, 311 (1966).
[14] S. A. Al'tshuler, F. L. Aukhadeev and M. A. Teplov, Pis'ma Zh. Eksp. Teor. Fiz. **9**, 46 (1968) [JETP Lett. **9**, 26 (1968)].
[15] L. K. Aminov, in the collection "Spektroskopiya Kristallov" (Spectroscopy of Crystals), Nauka, Leningrad (1978), p. 116.
[16] A. Abragam, Yadernyi Magnetizm (Nuclear Magnetism), IL, Moscow (1963).

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