# Nuclear relaxation caused in Van Vleck paramagnets by fluctuations of the hyperfine magnetic field

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A theory is derived for the relaxation of the nuclei of rare earth ions in Van Vleck paramagnets when there are rapid fluctuations in the hyperfine magnetic fields. The analysis is based on the principles of NMR theory in systems of moving spins. Bloch equations are derived. The rates of the longitudinal $(T_1^{-1})$ and transverse $(T_2^{-1})$ relaxation of the nuclear magnetization are derived for an axisymmetric crystal electric field. The theoretical conclusions are confirmed by experimental results on a thulium ethyl sulfate crystal. The dependence of $T_1^{-1}$ and $T_2^{-1}$ on the temperature (2.5–15 K) and the resonant frequency (5–150 MHz) has been found by steady-state and pulsed methods involving the NMR of $^{169}$Tm. The excitation lifetime of the 4f electron shell of the $Tm^{3+}$ ion is found to depend on the orientation of the crystal in an external magnetic field.

The nuclear magnetic resonance (NMR) of non-Kramers rare earth ions, which have a singlet ground state in the crystal electric field, has some interesting features because of the strong intraatomic electron-nucleus interaction: a huge and anisotropic paramagnetic shift of the NMR lines, a strong coupling of the nuclear moments with each other and with lattice vibrations, etc. Experimental and theoretical research, which has been particularly active over the past five years (see Refs. 1–5, for example), has led to a comprehensive interpretation of all the data available on the NMR spectra and nuclear relaxation at low temperatures, where the electrons of the unfilled 4f shell are in the ground state at all times and produce a "hyperfine" static magnetic field at the nucleus of the ion. It has been found that the characteristics of the resonance at low temperatures (the positions of the resonant lines, their widths, and the nuclear relaxation times) can be calculated quite simply if one knows the wave functions and energy levels of the host rare earth ions and the quantitative composition and relaxation times of the paramagnetic impurities. These calculations are based on a steady-state perturbation theory. Their basic results can be summarized by saying that the nuclear moments, surrounded by magnetic electrons, behave simply as anisotropic "intensified" dipole moments with components $\mu_i = \gamma_I \hbar (1 + \alpha_i^{(0)}) I_i$. The components $(\alpha_i^{(0)})$ of the paramagnetic NMR shift are proportional to the corresponding principal values of the Van Vleck tensor (which is independent of the temperature) of the paramagnetic susceptibility and can take on huge values. The paramagnetic NMR shift of $^{165}$Ho in the $Rb_2NaHoF_6$ crystal at temperatures below 2 K, for example, is 177, so that the effective magnetic moment of the holmium nucleus reaches[4] $0.4\mu_B$ ($\mu_B$ is the Bohr magneton). It has been found[3] that at low temperatures the spin-lattice relaxation of the nuclei of rare earth ions occurs through paramagnetic impurity ions (($Nd^{3+}$, $Er^{3+}$, etc.); i.e., this relaxation does not differ in principle from the relaxation of the nuclei of diamagnetic atoms. The role played by the 4f electron shell around the nucleus reduces in this case to one of simply strengthening the dipole-dipole interaction of the nucleus with impurity centers, with the result that the nuclear relaxation rate is usually increased by a factor of $(1 + \alpha)^2$. The natural abundances of impurities in rare earth compounds are generally quite high ($\gtrsim 10^{-4}$), so that the relaxation of the nuclei of the host rare earth ions involves a reservoir of dipole-dipole interactions of impurity centers, and the value of $T_1^{-1}$ measured in a strong magnetic field agrees with the rate at which energy is transferred from the nuclear Zeeman reservoir to the impurity dipole-dipole reservoir.

At elevated temperatures, in contrast, where the energy of the thermal lattice vibrations is high enough to excite 4f electrons, and the nuclear spins are subject to rapidly fluctuating hyperfine fields, the nuclear relaxation has received little attention, particularly theoretical. The gap was bridged in part in Ref. 5, where we described the results of a study of the transverse relaxation of $^{169}$Tm nuclei in thulium ethyl sulfate in a magnetic field directed parallel to the c axis of the crystal. The NMR line shape was analyzed theoretically in this particular case in a model of a random change in the resonant frequency caused by the thermal excitation of 4f electrons into a doublet state with an energy $\Delta = 32$ cm$^{-1}$. When the external magnetic field is oriented along the c axis of the crystal, the effective field at the nucleus during the excitation of the $Tm^{3+}$ ion changes only in magnitude; its direction remains the same. The splitting of the electron doublet exceeds the width of the energy levels. These conditions proved sufficient for use of the adiabatic theory for the disruption of the spectral fine structure due to the motion of spins (the Anderson-Weiss theory[6]). We found that the measured transverse relaxation rate $T_2^{-1}$ can be described well by this theory in the limit of short correlation times $(\tau_c)$ for the random hopping of an ion between the electronic ground and excited states, i.e., under the condition $\tau_c \Delta\omega \ll 1$, where $\Delta\omega$ is the frequency change upon fluctuations of the hyperfine magnetic field. The role of a correlation time is played in this case by the ion lifetime in the excited doublet. Simple

estimates of this time yielded $\tau_c \approx 3 \cdot 10^{-10}$ s.

The spin-lattice relaxation of the nuclei of rare earth ions in dielectric Van Vleck paramagnets has been under experimental study for 15 yr now (see Refs. 1, 3, and 7, for example), but we do not yet have a satisfactory theory for the relaxation processes at elevated temperatures. The exponential temperature dependence $T_1^{-1} \propto \exp(-\Delta/kT)$ which has been observed for the rate of the nuclear spin-lattice relaxation in all the experiments has heretofore been interpreted by the familiar approach in the field of electron spin resonance: It has been interpreted as a consequence of two-phonon relaxation through an excited state of the $4f$ shell. All attempts to explain the experimental data of Refs. 1, 3, 7, and 8 have been based on the assumption that the spin-lattice relaxation is definitely a "single-ion" process, and the investigators have ignored the important fact that in magnetically concentrated crystals (such as the crystals which have been studied experimentally) the Van Vleck ions are coupled very strongly by an interparticle interaction (a dipole-dipole interaction, for example), and it may be precisely this interaction which determines the lifetime of the electronic excitation and the width of the electronic energy levels.

In the present paper we derive a general theory for the relaxation of the nuclei of rare earth ions in dielectric Van Vleck paramagnets for the case of rapid fluctuations of the hyperfine magnetic field. We verify the theory with the results of special experiments carried out with the model crystal thulium ethyl sulfate.

## THEORY

We consider the general case of an arbitrary orientation of the magnetic field with respect to the crystal axes. For this particular problem we cannot use an adiabatic theory: When the external magnetic field does not lie along the $c$ axis of an axisymmetric crystal of the thulium ethyl sulfate type, the excitation of an electron shell is accompanied by a change in not only the magnitude but also the direction of the effective field of the nucleus, and the transverse component of the fluctuating field induces transitions between nuclear energy levels, i.e., a spin-lattice relaxation [we are including the electron subsystem in the concept of "lattice" here, since we are dealing with the short (electron-spin)-lattice relaxation times]. Since the correlation time is short, as noted in Ref. 5, we can analyze the behavior of the nuclear magnetization under these conditions by working from the Redfield and Bloch-Wangsness nonadiabatic theory.[6] The situation is reminiscent of the "scalar relaxation of the second kind" in liquids,[6] but the specific behavior of the electron angular momentum $\mathbf{J}$ of a rare earth ion in the crystal electric field and the external magnetic field requires some modification of the theory to deal with anisotropic systems.

We write the Hamiltonian for a nucleus with a spin $I = 1/2$:

$$\mathscr{H} = -\gamma_I \hbar \mathbf{IH} + A_J \mathbf{IJ}(t). \tag{1}$$

Here $\mathbf{H}$ is the external magnetic field, $A_J$ is the hyperfine interaction constant, and the electron angular momentum

$\mathbf{J}(t)$ is a random function of the time. We write (1) as

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}'(t), \tag{2}$$

$$\mathscr{H}_0 = -\gamma_I \hbar \mathbf{IH}_{eff}, \quad \mathbf{H}_{eff} = \mathbf{H} - \frac{A_J}{\gamma_I \hbar} \mathbf{J}_0 = (1+\tilde{\alpha})\mathbf{H},$$

$$\tilde{\alpha} = \frac{A_J}{g_J \mu_B \gamma_I \hbar} \tilde{\chi},$$

$$\mathscr{H}'(t) = A_J \mathbf{IF}(t), \quad \mathbf{F}(t) = \mathbf{J}(t) - \mathbf{J}_0, \tag{3}$$

where the subscript 0 means the expectation value with the equilibrium electron density matrix

$$\rho_0 = \{\mathrm{Sp}\exp(-\mathscr{H}_{el}/kT)\}^{-1}\exp(-\mathscr{H}_{el}/kT),$$

$g_J$ is the Landé factor; and $\tilde{\chi}$ is the temperature-dependent susceptibility tensor of the ion. In this formulation of the problem, the expectation value of $\mathscr{H}'(t)$ over the ensemble vanishes, and the effective Hamiltonian $\mathscr{H}_0$ turns out to be function of the temperature.

The method for analyzing systems subject to random perturbations which was worked by Redfield, Bloch, and Wangsness and which has been set forth in detail in the monograph by Abragam[6] allows us to write equations of motion for the nuclear magnetization:

$$d\langle I_p \rangle/dt = \gamma_I [\langle \mathbf{I} \rangle \mathbf{H}_{eff}]_p$$

$$- \sum_{qq'} j_{-q'q}(q\omega_0) \mathrm{Sp}\{(\sigma-\sigma_0)[[I_p, I_{-q}]I_{q'}]\}. \tag{4}$$

Here $\langle \mathbf{I} \rangle = \mathrm{Sp}(\sigma \mathbf{I})$, $\sigma$ is the density matrix of the nuclear system, $\sigma_0$ is the equilibrium value of this matrix, the subscripts $p$ and $q$ distinguish the cyclic components of the vectors, the $Z$ axis is directed along the effective field $\mathbf{H}_{eff}$, and $\omega_0 = \gamma_I H_{eff}$ is the resonant frequency. Here $j_{q'q}$ is the spectral density of the correlation function $k_{q'q}$,

$$j_{q'q}(\omega) = \frac{A_J^2}{\hbar^2} \int_0^\infty k_{q'q}(t) e^{i\omega t} dt, \tag{5}$$

and is assumed as usual to be real (the imaginary part reduces to an additional small level shift). Since the hyperfine field in excited electronic states is far stronger than in the ground state ($\omega_0 \ll \Delta\omega$), and since the condition $\Delta\omega\tau_c \ll 1$ holds, then the condition $\omega_0\tau_c \ll 1$ definitely holds; i.e., we have a "strong-contraction" condition, with $j(\omega_0) \approx j(0)$. The off-diagonal tensor components $j_{-q'q}$ in this case are small, so that Eqs. (4) assume the form of Bloch equations. We can thus write

$$\frac{1}{T_1} = j_{xx} + j_{yy}, \quad \frac{1}{T_2} = \frac{1}{2T_1} + j_{zz}. \tag{6}$$

We see that estimating the line width and the spin-lattice relaxation time reduces to calculating the correlation functions $k_{q'q}(t)$.

A semiclassical calculation is the simplest. We assume that in the $i$-th electronic state the random vector function $\mathbf{F}$ takes on a value $\mathbf{F}_i$ with a probability which is obviously

equal to the Boltzmann factor of this state, $W_i$. We denote by $\pi_{mn}$ the probability for a transition per unit time from the state $m$ to the state $n$. The probabilities $p_n(t)$ for finding the system in the state $n$ at the time $t$ then obey the equations (which are similar to population equations)

$$dp_n/dt = \sum_{m \neq n} (-p_n \pi_{nm} + p_m \pi_{mn}). \tag{7}$$

For a three-level system, these equations can easily be solved for arbitrary initial conditions, so that we can find an explicit expression for the correlation function:

$$k_{q'q}^{cl}(t) = \sum_{mn} W_m p_{nm}(t) F_{mq'} F_{nq}, \tag{8}$$

where $p_{mn}(t)$ is the probability for finding the system in the state $n$ at the time $t$ if it was in the state $m$ at $t = 0$. Using the natural conditions (cf. Ref. 5)

$$W_1 \approx 1 \gg W_2 \approx W_3 \approx e^{-\Delta/kT}, \quad \pi_{31} \approx \pi_{21} \equiv \tau_c^{-1}, \quad \pi_{23} \approx \pi_{32} \approx 0, \tag{9}$$

which hold if the index 1 represents the electronic ground state and if the splitting of the doublet states 2 and 3 is small in comparison with $kT$, we find

$$k_{q'q}^{cl}(t) = k_{q'q}^{cl}(0) e^{-t/\tau_c}. \tag{10}$$

Again we see that the role of the correlation time is being played by the shortest of the lifetimes of the stationary states.

In weak magnetic fields (just how weak depends on the particular orientation) the splitting of the excited electronic doublet, $\hbar\Omega$, may turn out to be smaller than the width associated with the finite lifetime ($\sim \tau_c$). In this case a model of jumps among three electronic states is not sufficient—the excited states may be superpositions of the "stationary" doublet states—and we would instead use the quantum correlation functions

$$k_{q'q}^{qu}(t) = \mathrm{Sp}(\exp(-\mathscr{H}_{el}/kT) \hat{F}_{q'} \exp(i\mathscr{H}_{el}t/\hbar)$$
$$\times \hat{F}_q \exp(-i\mathscr{H}_{el}t/\hbar))$$
$$\times (\mathrm{Sp}\exp(-\mathscr{H}_{el}/kT))^{-1}, \tag{11}$$

where the operator $\hat{\mathbf{F}}$ replaces the classical random quantity F. In a systematic calculation of these functions, the Hamiltonian $\mathscr{H}_{el}$ would have to incorporate the lattice and the interaction of the electrons with the lattice, so that the levels of the reservoir would be quasicontinuous, and the correlation functions would therefore decay over time. Instead, we will again adopt as $\mathscr{H}_{el}$ the Hamiltonian of an individual ion, and we will take the decay into account in a semiphenomenological way, making use of the existence of a characteristic time $\tau_c$ and simply adding a factor $e^{-t/\tau_c}$ to the right side of (11). In the case of a large splitting ($\Omega\tau_c \gg 1$), the correlation functions calculated in this way agree with the classical functions (10).

We turn now to a specific example. We consider the $^{169}\mathrm{Tm}^{3+}$ ion in thulium ethyl sulfate, and we take into account three low-lying electronic states: a singlet ground state $g$ and a doublet of excitations $d, d'$, which are separated from

the singlet by an interval $\Delta$:

$$|g\rangle = 0.119|6\rangle + 0.986|0\rangle + 0.119|-6\rangle,$$
$$|d, d'\rangle = 0.305|\pm 5\rangle + 0.953|\mp 1\rangle. \tag{12}$$

Here $|M\rangle$ means the state with a projection $M$ of the total angular momentum $\mathbf{J}$ onto the $c\|z$ axis of the crystal; here $J = 6$. We can ignore excitation to the other states, which are separated from these by intervals much greater than $\Delta$. The Hamiltonian $\mathscr{H}_{el}$ is

$$\mathscr{H}_{el} = \mathscr{H}_{cryst} - g_J \mu_B \mathbf{HJ}, \tag{13}$$

and in a first approximation the doublet is split only by the parallel component of $\mathbf{H}$. If the field makes an angle $\theta$ with the $c$ axis of the crystal, the effective field is

$$\mathbf{H}_{eff} = H \cos\theta (1 + \alpha_\|)\mathbf{k} + H \sin\theta (1 + \alpha_\perp)\mathbf{i}, \tag{14}$$

where the unit vector $\mathbf{k}$ runs along the $c$ axis, and $\mathbf{i} \perp c$. Since[5] $\alpha_\perp \approx 73$ and $\alpha_\| \approx 0.36$, at $\theta \approx 5°$ the effective field at the nucleus becomes essentially perpendicular to the $c$ axis. For a given resonant frequency $\nu = (\gamma_I/2\pi)|H_{eff}|$ the magnetic field and the Zeeman splitting $\hbar\Omega$ of the doublet $d, d'$ depend strongly on the field orientation:

$$\hbar\Omega(\theta) = 4\pi g_J \mu_B \nu \left[ \left( \frac{a\cos\theta'}{\gamma_\|} \right)^2 + \left( \frac{b\nu \sin^2\theta'}{\gamma_\perp} \right)^2 \right]^{1/2}. \tag{15}$$

Here $\gamma_\| = \gamma_I(1 + \alpha_\|)$ and $\gamma_\perp = \gamma_I(1 + \alpha_\perp)$ are measurable parameters of the nuclear spin Hamiltonian, and

$$a = (d|J_z|d), \quad b = 4\pi g_J \mu_B (g|J_x|d)^2/\gamma_\perp \Delta, \tag{16}$$
$$\sin^2\theta' = \gamma_\perp^2 \sin^2\theta/(\gamma_\|^2 \cos^2\theta + \gamma_\perp^2 \sin^2\theta).$$

The degree of mixing of the doublet wave functions,

$$\psi_1 = p_1|d\rangle + q_1|d'\rangle, \quad \psi_2 = p_2|d\rangle + q_2|d'\rangle, \tag{17}$$

also depends strongly on the orientation of the external field:

$$\frac{p_1}{q_1} = \frac{b\nu \sin^2\theta'/\gamma_\perp}{[(a\cos\theta'/\gamma_\|)^2 + (b\nu\sin^2\theta'/\gamma_\perp)^2]^{1/2} + (a\cos\theta'/\gamma_\|)} \tag{18}$$

(the coefficients $p_2$ and $q_2$ are found from the orthogonality of $\psi_1$ and $\psi_2$).

We will not go through the detailed calculation of spectral functions (5); we simply note that this calculation is simplified substantially because of some particular characteristics of this system: The expressions

$$(1 - 4p_1^2 p_2^2) + 4p_1^2 p_2^2 (1 + \Omega^2 \tau_c^2)^{-1}$$

which arise in the calculations are very nearly equal to unity. In a field $\mathbf{H} \perp c$ the wave functions of the doublet are mixed ($p_1^2 p_2^2 \approx 1/4$), but the splitting (15) is small, so that we have $\Omega^2 \tau_c^2 \ll 1$. When the field is rotated toward the $c$ axis, the splitting of the doublet increases ($\Omega^2 \tau_c^2 \gtrsim 1$), but in this case we have $p_1^2 p_2^2 \approx 0$ according to (18). A calculation yields comparatively simple expressions for the relaxation rates:

$$T_1^{-1} = \frac{2A_J^2 \tau_c}{\hbar^2} \sin^2\theta' \left[ a^2 + b^2\nu^2 \left( 9\cos^2\theta' + \frac{1+\cos^2\theta'}{1+\Omega^2\tau_c^2} \right) \right]$$
$$\times \exp\left( -\frac{\Delta}{kT} \right), \tag{19}$$

$$T_2^{-1} = \frac{1}{2} T_1^{-1} + \frac{2A_J{}^2\tau_c}{\hbar^2} \Big[ a^2 \cos^2\theta'$$

$$+ b^2\nu^2 \sin^4\theta' \Big(9 + \frac{1}{1+\Omega^2\tau_c{}^2}\Big)\Big] \exp\Big(-\frac{\Delta}{kT}\Big). \qquad (20)$$

Looking at these relaxation characteristics, we first note that the relaxation rates $T_1^{-1}$ and $T_2^{-1}$ explicitly contain the hyperfine constant. This result is obviously due to our assumption of short correlation times $(A_J\tau_c \ll \hbar)$, and it reflects the fact that the electronic motion has less effect on the nuclear relaxation as the hyperfine coupling becomes weaker. Second, our calculations predict a pronounced anisotropy of the spin-lattice relaxation near the parallel orientation—the factor $\sin^2\theta'$ in (19) (the same result was predicted by earlier calculations[3,8] based on the assumption that the electronic energy levels are infinitesimally narrow). Third, the line width (or $T_2^{-1}$) does not depend on the resonant frequency in the parallel orientation. In the other orientations, the dependence is quite complicated, but in strong fields the width is proportional to the square of the frequency. For the fields ordinarily used we would have $\Omega\tau_c \lesssim 1$ and thus $T_2^{-1} = c' + c''\nu^2$, where the parameters $c'$ and $c''$ depend on $\theta$ and $T$. In contrast with $T_1^{-1}$, the orientational dependence of $T_2^{-1}$ is quite smooth over the entire range of $\theta$.

In the case of weak fields (low frequencies), we find a slightly unusual relation from (19) and (20): When the field is oriented perpendicular to the $c$ axis we have $T_2 = 2T_1$. The reason for this result is the strong anisotropy of the hyperfine magnetic field. The hyperfine field of the excited $4f$ electrons has components only along the $c$ axis. Since in this case the $Z$ axis, which coincides with the effective field $\mathbf{H}_{\mathrm{eff}}$, is perpendicular to the $c$ axis, the spectral function $j_{zz}$ in (6) is zero.

## EXPERIMENTAL RESULTS AND DISCUSSION

We selected the thulium ethyl sulfate crystal for an experimental study because it is a simple system, for which we can exactly calculate the effects of the thermally excited $4f$ electrons and test the theory derived above. We used both steady-state and pulsed NMR methods in the experiments. We used the steady-state method[3,5] to measure the increment in the width of the NMR line of $^{169}$Tm with increasing temperature. We calculated the transverse relaxation rate from

$$(T_2^{-1})_\theta = (\sqrt{3}/2)\gamma_\theta{}^{(T)}[\delta H(T) - \delta H(4.2\ \mathrm{K})], \qquad (21)$$

where

$$\gamma_\theta{}^{(T)} = \gamma_I[(1+\alpha_\parallel{}^{(T)})^2\cos^2\theta + (1+\alpha_\perp{}^{(T)})^2\sin^2\theta]^{1/2}$$

is the effective gyromagnetic ratio of the thulium nuclei at the given temperature, and $\delta H$ is the interval between the extrema of the derivative of the resonant absorption. Measurements of $\alpha$ at temperatures from 4.2 to 15 K showed that the shift of the NMR line is strictly proportional to the paramagnetic susceptibility of the crystal in a field $\mathbf{H}\perp c$. This result is evidence in favor of our earlier assumption that the time for the correlation between two values of the fluctuating hyperfine field is short.[5]
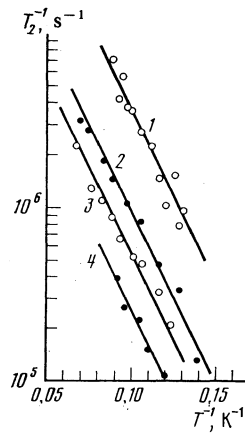
FIG. 1. Relaxation rate of the transverse nuclear magnetization of thulium in a thulium ethyl sulfate crystal as a function of the reciprocal temperature. The external magnetic field is directed perpendicular to the $c$ axis of the crystal. Here $T_2^{-1} = A\exp(-\Delta/kT)$, where $\Delta = 32\ \mathrm{cm}^{-1}$, and $A$ depends on the frequency. 1—152 MHz, $A = 3.53\cdot10^8\ \mathrm{s}^{-1}$; 2—42 MHz, $A = 0.92\cdot10^8\ \mathrm{s}^{-1}$; 3—18 MHz, $A = 0.53\cdot10^8\ \mathrm{s}^{-1}$; 4—5 MHz, $A = 0.25\cdot10^8\ \mathrm{s}$. The values of $A$ were found by the method of least squares.

Figure 1 shows some representative curves of the temperature dependence of the transverse relaxation rate, obtained at the frequencies 5, 18, 42, and 152 MHz. After determining that the relaxation rate depends on the temperature in accordance with

$$(T_2^{-1})_\theta = A_\theta \exp(-\Delta/kT) \qquad (22)$$

with a fixed parameter $\Delta = 32\ \mathrm{cm}^{-1}$, regardless of the orientation of the crystal in the magnetic field, we focused on the dependence of the coefficient of the exponential function on the resonant frequency and on the angle $(\theta)$ between the external field and the crystallographic $c$ axis. Our experiments with the parallel orientation $(\mathbf{H}\|c)$ were restricted by the low effective gyromagnetic ratio $(\gamma_\parallel/2\pi = -480\ \mathrm{Hz/Oe})$ and by the strongest field which our electromagnet was capable of producing (11 kOe). Measurements of the line width over the range 3.5–5 MHz revealed no frequency dependence of $T_2^{-1}$, yielding only the single result (cf. Ref. 5)

$$A_\parallel = 7,1\cdot10^8\ \mathrm{s}^{-1}. \qquad (23)$$

For the two other orientations of the crystal in the magnetic field $(\theta = 35°$ and $90°)$ we were able to carry out measurements over a broad frequency range (Fig. 2). Let us summa-
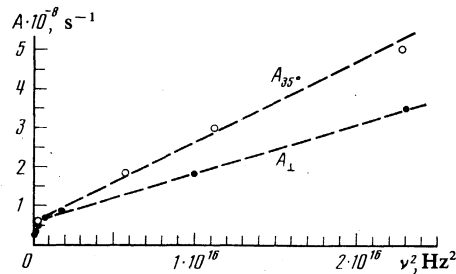
FIG. 2. Relaxation rate of the transverse nuclear magnetization of thulium in thulium ethyl sulfate as a function of the square of the resonant frequency. The dashed lines are plotted from expressions (24a) and (24b).

rize the experimental results: 1) The coefficient ($A_\theta$) of the exponential function, which determines the transverse relaxation rate at a given temperature, increases with increasing resonant frequency. Measurements at high frequencies ($\nu > 20$ MHz) yield a quadratic dependence $A_0 = c' + c''\nu^2$. 2) At fixed (and rather high) values of $T$ and $\nu$, the relaxation rate is minimized by directing the magnetic field perpendicular to the $c$ axis. 3) At low frequencies, $A_\perp$ deviates from a quadratic dependence.

The last of these results seems to be due in large part to a somewhat flawed interpretation of the low-frequency measurements, so that we would hardly be justified in drawing any definite conclusions from it. When we work with Eq. (21) we can trust the estimates of the relaxation rate $T_2^{-1}$ only if the increment in the line width due to relaxation becomes much greater than the original width $\delta H$ (4.2 K) and if the shape of the original resonance curve (roughly Gaussian at low temperatures) ceases to be important. Measurements in a field $H \perp c$ show that when the sample is heated from 4.2 to 11 K the width of the NMR line of thulium at 5 MHz increases by a factor of only 1.5, while that at 100 MHz increases by a factor of 2.5. If we ignore the measurements at frequencies below 20 MHz, the other experimental points in Fig. 2 can be approximated by the two straight lines (the frequencies are expressed in hertz)

$$A_{35°} = 0.6 \cdot 10^8 + 2.1 \cdot 10^{-8} \nu^2, \tag{24a}$$

$$A_\perp = 0.6 \cdot 10^8 + 1.3 \cdot 10^{-8} \nu^2. \tag{24b}$$

Let us use Eqs. (19) and (20) to analyze these results. We first consider the case $H \perp c$. Extrapolation of the measured factor $A_\perp$ to a zero field yields $0.6 \cdot 10^8$ s$^{-1}$, so that the longitudinal relaxation rate in a weak field is

$$T_1^{-1} = 1.2 \cdot 10^8 \exp(-\Delta/kT). \tag{25}$$

Since the $d, d'$ doublet is almost unsplit in a weak field $H \perp c$, we can ignore $\Omega_\perp^2 \tau_c^2$ and assume that the measured relaxation rate in (25) is equal to

$$(2A_J^2/\hbar^2)\tau_c(d|J_z|d)^2 \exp(-\Delta/kT).$$

Substituting numerical values of the matrix element, $(d|\mathbf{J}_z|d)^2 = 0.196$, and of the hyperfine constant, $A_J/\hbar = -3.935 \cdot 10^8$ s$^{-1}$ (Ref. 9), into this last expression, we find the correlation time $\tau_c = 5 \cdot 10^{-11}$ s.

We have another way to find $\tau_c$. We can use the experimental value (Fig. 2) of the high-frequency slope of the line $A_\perp = f(\nu^2)$ [cf. (20)]:

$$\tau_c(80A_J^2/\hbar^2)(d|J_z|g)^4(2\pi g_J\mu_B/\gamma_\perp\Delta)^2 = 1.3 \cdot 10^{-8}. \tag{26}$$

Substituting the known values $|\gamma_\perp/2\pi| = 2.6 \cdot 10^4$ s$^{-1}$·Oe$^{-1}$ (Ref. 5), $(d|J_x|g)^4 = 93.3$, $\Delta = 32$ cm$^{-1}$, and $g_J = 1.1638$ (Ref. 10) into (26), we find the correlation time to be $\tau_c = 6.7 \cdot 10^{-11}$ s. We thus see that all the NMR data in a field $H \perp c$ show that the correlation time is close to $10^{-10}$ s in order of magnitude.

Measurements of the width of the NMR line in a field $H$ making an angle $\theta = 35°$ with the $c$ axis have yielded roughly the same result. In fields $H > 1$ kOe, which correspond to NMR frequencies above 15 MHz, the electron frequencies

$\Omega_{35°}$ are such that the condition $\Omega_{35°}^2 \tau_c^2 \gg 1$ holds at $\tau_c \sim 10^{-10}$ s, so that the functions $A_\theta(\nu)$ and $A_\perp(\nu)$ in Fig. 2 should be nearly identical. In fact, we have already seen that the result of an extrapolation to zero frequency, $0.6 \cdot 10^8$ s$^{-1}$, is approximately the same as in the case $H \perp c$ (so that the spin-lattice relaxation rates are the same for $\theta = 35°$ and $90°$). On the other hand, the slope of the line $A_{35°} = f(\nu^2)$ at high frequencies is larger than that of $A_\perp = f(\nu^2)$ by a significantly greater extent than would follow from (20). As a result we find $\tau_c = 1.1 \cdot 10^{-10}$ s; this value differs from those found above by a factor of 1.5 or 2.

Our estimates of the correlation time are smaller by a factor of 3–6 than the value $\tau_c \approx 3 \cdot 10^{-10}$ s which follows from studies for a parallel orientation of the magnetic field.[5] If the ion lifetime in the excited state is determined by an vibronic interaction, then since there is no reason to assume that this interaction depends on the orientation of the magnetic field we must attribute the observed discrepancies to the approximate nature of the determination of $T_2^{-1}$ from the broadening of the NMR lines. We note, however, that the differences in the values which we have found for $\tau_c$ do not reflect simply a scatter. Instead, there is a definite trend: The correlation time increases as the external field is rotated toward the crystal's $c$ axis. We observed the same tendency in experiments on the pulsed NMR of $^{169}$Tm.

The nuclear spin-lattice relaxation of thulium in thulium ethyl sulfate crystals was measured with a broad-band coherent pulsed NMR relaxometer. The times $T_1$ were measured by a four-pulse method, from the restoration of the spin-echo amplitude upon an increase in the interval between pairs of probing pulses. The $^{169}$Tm NMR line in a field $H$ not parallel to the $c$ axis is broadened primarily by the dipole–dipole interaction[2] of the nuclear moments of thulium and the protons of the water of crystallization. The scatter in the local magnetic fields from the protons is sufficient for a rapid dephasing of the nuclear spins of thulium, so that the spin echo can be observed in a uniform magnetic field with $5° \lesssim \theta \lesssim 90°$. At $\theta \approx 0$, the NMR line of thulium in thulium ethyl sulfate is homogeneously broadened (the width is due to the nuclear spin-spin relaxation of the thulium), as it is in LiTmF$_4$ (Ref. 3), and the spin echo is formed only in a nonuniform external field.

Figure 3 shows the experimental results on the rate of the nuclear spin-lattice relaxation of $^{169}$Tm at liquid-helium temperatures. For all three orientations of the magnetic field ($\theta = 0$, 7.5°, and 90°), the relaxation rate is seen to have an exponential temperature dependence:

$$T_1^{-1} = B_\theta \exp(-\Delta'/kT). \tag{27}$$

The energy found for the $d, d'$ doublet in this manner is $\Delta' = 28.1$ cm$^{-1}$, i.e., 12% lower than the true value. We will not go into the reasons for the low values found for the energies of excited electronic states from relaxation measurements,[3,7,11,12] but we do wish to call attention to the angular dependence of the coefficient of the exponential function, $B_\theta$. According to (19), this coefficient contains the product $\tau_c\sin\theta'$. Because of the extreme anisotropy of the tensor $\tilde{\alpha}$, the quantity $\sin\theta'$ is approximately one in the angular inter-

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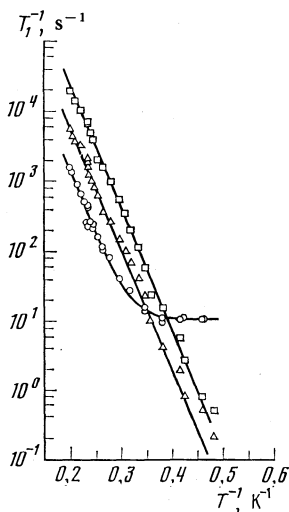
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FIG. 3. Spin-lattice relaxation rate of thulium nuclei in thulium ethyl sulfate as a function of the reciprocal temperature. Here $T_1^{-1} = C + B \exp(-\Delta'/kT)$, where $\Delta' = 28.1\,\text{cm}^{-1}$. $\bigcirc$—$\theta = 0$, $B = 4.6\cdot10^6\,\text{s}^{-1}$; $\square$—$\theta = 7.5°$, $B = 7.2\cdot10^7\,\text{s}^{-1}$; $\triangle$—$\theta = 90°$, $B = 2\cdot10^7\,\text{s}^{-1}$, Here $\theta$ is the angle between the $c$ axis of the crystal and the external magnetic field.

val $4° \lesssim \theta \lesssim 90°$; thus the observed increase in the rate of the nuclear spin-lattice relaxation as $\theta$ is reduced from 90° to 7.5° would naturally be attributed to an increase in the correlation time $\tau_c$. This conclusion confirms our earlier estimates of $\tau_c$ from the line width measured by the steady-state NMR method. When the external magnetic field is oriented along the $c$ axis, the rate of the nuclear spin-lattice relaxation of thulium in an ideal crystal should have been zero [see (19)]. In a real crystal, on the other hand, $T_1^{-1}$ will be nonzero although small because of the local distortions of the symmetry of the crystal field due to structural defects.[3] The correlation time cannot be calculated for this situation.

Figure 4 gives a clear picture of the angular variations of the rate of the nuclear spin-lattice relaxation of thulium in thulium ethyl sulfate. These measurements were carried out at 4.25 K; the frequency 7.5 MHz (corresponding to resonant fields H = 15.6–12.3 kOe) was used for the angular interval $\theta = 0$–50′, while 13 MHz (5.6–0.5 kOe) was used for
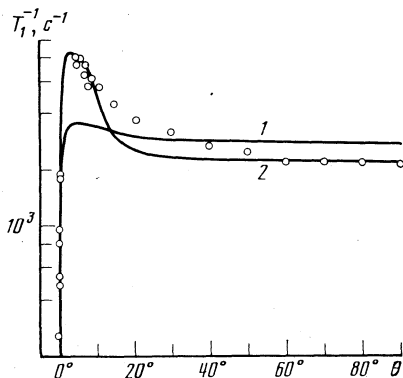


FIG. 4. Angular dependence of the spin-lattice relaxation rate of thulium nuclei in thulium ethyl sulfate. The curves are calculated from Eqs. (19) and (31) with the following parameter values: 1—$\tau_0 = 8\cdot10^{-11}$ s, $\sigma = 1$; 2—$\tau_0 = 2\cdot10^{-10}$ s, $\sigma = 19$.

$\theta = 5$–90°. Ignoring the data for the narrow angular interval $\theta = 0$–50′ (which yields little information, despite the extremely complicated experiments required), we see only a monotonic increase in $T_1^{-1}$ as the external field is rotated away from the $c$ axis. The rate of the nuclear spin-lattice relaxation of thulium behaves as if the correlation time $\tau_c$ increased by a factor of four as $\theta$ is reduced from 90° to 5°.

The angular dependence $\tau_c(\theta)$ suggests that the lifetime of the $\text{Tm}^{3+}$ ion in the excited state is determined by an interparticle interaction (a dipole-dipole interaction, a quadrupole-quadrupole interaction, or an interaction through the phonon field) rather than by an electronic-vibrational interaction: If the lifetime of the electronic excitation, $\Delta$, were due to a transfer of excitation to neighboring ions, then in the field orientation $\text{H}\perp c$ the splitting of the doublet would be small, and the excitation could be transferred to any of the states $\psi_1$, $\psi_2$ of a neighboring ion, while in the orientation $\text{H}\|c$ the splitting would be large, and the excitation could be transferred to only one of these states (with energy conservation). The nature of the behavior $\tau_c(\theta)$ can be found approximately in the following way. We denote by $\mathcal{H}_{1i}$ the Hamiltonian of the dipole-dipole interaction of an ion with its $i$-th neighbor, and we denote by $\alpha$ and $\beta$ the excited states (17) of the ion and its neighbor, respectively. The rate at which excitation leaves the ion can then be written

$$\frac{1}{\tau_c} = \frac{2\pi}{\hbar^2}\sum_{i,\beta} |(\mathcal{H}_{1i})_{\alpha\beta}|^2 g(\omega_{\alpha\beta}). \tag{28}$$

We choose the form factor $g(\omega)$ to be a Lorentzian curve,

$$g(\omega) = \frac{1}{\pi}\frac{\tau_c}{1+\tau_c^2\omega^2}, \tag{29}$$

in accordance with our assumption that the correlation functions decay. Here $\omega_{\alpha\beta}$ is the frequency difference between the excited states $\alpha$ and $\beta$, which is equal to 0 and $\Omega$ for the two possible values of $\beta$. We introduce

$$\frac{2}{\hbar^2}\sum_i |(\mathcal{H}_{1i})_{\alpha\beta}|^2 = \frac{1}{\tau_0^2} \tag{30}$$

and rewrite (28) as

$$\frac{1}{\tau_c^2} = \frac{1}{\tau_0^2}\left[1 + \frac{\sigma}{1+\Omega^2\tau_c^2}\right]; \tag{31}$$

then

$$\tau_c^2 = 2\tau_0^2\{1+\sigma-\Omega^2\tau_0^2+[(1+\sigma-\Omega^2\tau_0^2)^2+4\Omega^2\tau_0^2]^{1/2}\}^{-1}. \tag{32}$$

The first term in square brackets in (31) corresponds to transitions of the types $\psi_1^{(1)}\to\psi_1^{(i)}$ and $\psi_2^{(1)}\to\psi_2^{(i)}$, which are caused by the interaction

$$\hat{B} = -\tfrac{1}{4}(g_J^2\mu_B^2/r_i^3)(1-3\cos^2\theta_i)(J_+^{(1)}J_-^{(i)}+J_-^{(1)}J_+^{(i)}). \tag{33}$$

Since the excitation energy ($\Delta + \hbar\Omega/2$ or $\Delta - \hbar\Omega/2$) is conserved in this process, the frequency difference $\omega$ in (29) is zero. The second term in (31) stems from transitions $\psi_1^{(1)}\to\psi_2^{(i)}$ and $\psi_2^{(1)}\to\psi_1^{(i)}$, which are accompanied by a change $\pm\hbar\Omega$ in the excitation energy. The matrix elements of the corresponding operator,

$$\hat{E}+\hat{P}=-{}^3/_4(g_J{}^2\mu_B{}^2/r_i{}^3)\sin^2\theta_i(e^{-2i\varphi_i}J_+^{(1)}J_+^{(i)}+e^{2i\varphi_i}J_-^{(1)}J_-^{(i)}) \quad (34)$$

are generally different from the matrix elements in (33), so that we have $\sigma\neq1$ in (31). In the thulium ethyl sulfate crystals, the transitions of the first type occur primarily because of the two nearest neighbors of the $Tm^{3+}$ ion $(r_i = 7$ Å; $\theta_i = 0, \pi)$, while the transitions of the second type result from the six neighbors of the next coordination sphere $r_i = 8.7$ Å, $\theta_i = 66°$; 114°), so that we have $\sigma\approx1$ and $\tau_0 = 8\cdot10^{-11}$ s. Curve 1 in Fig. 4 shows results calculated from (19) and (32) with the parameter values given above. We see that even a simplified calculation incorporating only the dipole-dipole interaction in an ideal crystal gives a qualitatively correct, and to some extent a quantitatively correct, description of the experimental data. Similar calculations for the rate of the nuclear spin-lattice relaxation rate of $^{169}Tm$ in $TmPO_4$, with the wave functions of Ref. 13 for the $Tm^{3+}$ ion, yield results in good agreement with experiment.[7]

These calculations of the correlation times have of course been oversimplified. We should actually have taken into account all the interparticle interactions and the scatter in the energy levels of neighboring ions caused by the structural defects which exist in a real crystal. As a result, we might have found a different value for $\tau_0$ and a different relation between the form factors and the probabilities for the transitions of the various types. For example, our experimental results can be described better by using $\tau_0$ and $\sigma$ as adjustable parameters and setting $\tau_0 = 2\cdot10^{-10}$ s and $\sigma = 19$ (curve 2 in Fig. 4).

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