Spin-lattice relaxation of nuclei of paramagnetic ions in strongly anisotropic van Vleck paramagnets

L. K. Aminov, M. S. Tagirov, and M. A. Teplov

Kazan' State University

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We investigated experimentally the spin-lattice relaxation (SLR) of ^{169}Tm nuclei in LiTmF$_4$ in the temperature interval 1.6–15.5 K at various orientations of the magnetic field relative to the crystal axes. The strong anisotropy of the rate of two-phonon SLR of thulium nuclei, predicted by the theory for axial crystals, was not observed. The calculations show that the reason for the smoothing-out of the anisotropy are the local symmetry distortions due to defects of the crystal structure, as well as the strong dipole-dipole coupling of the neighboring Tm^{3+} ions.

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Spin-lattice relaxation (SLR) of the nuclei of paramagnetic ions in van Vleck paramagnets has been the subject of many theoretical and experimental studies. There is so far no answer, however, to the question of whether it is possible to observe in crystals with axial symmetry the theoretically predicted[3] extraordinarily strong anisotropy of the rate of the nuclear SLR via excited electronic states. This question, which at first glance is not of general character, actually touches upon the general problem of the agreement between the real crystals and the theoretical models, and is therefore worthy of a detailed study.

We shall explain the cause of the angular dependence of two-phonon nuclear SLR using as an example the tetragonal crystal LiTmF$_4$ with scheelite structure. In a crystal electric field of symmetry S_4 (Ref. 7), the lower multiplet level $^3H_6$ ($J=6$) of the Tm^{3+} ion splits into singlets and doublets (see the table). The structure of the wave functions of the $4f$ electrons is such that the operators J_x and J_y connect the ground singlet $|\psi_1\rangle$ only with the doublet $|\psi_{2,3}\rangle$, and J_z with the singlet $|\psi_5\rangle$. Since $E_{2,3} \ll E_5$, the paramagnetic shift α of the NMR line of thulium has a strong anisotropy. NMR measurements at 4.2 K yield for the parameters of the nuclear spin Hamiltonian ($I=\frac{1}{2}$)

$$\mathscr{H}_I=-\gamma\hbar(1+\alpha_\parallel)H_zI_z-\gamma\hbar(1+\alpha_\perp)(H_xI_x+H_yI_y) \tag{1}$$

the values $\alpha_\parallel=1.75$ (1), $\alpha_\perp=67.9$ (9). The gyromagnetic ratio for the free thulium nucleus is assumed here to be $\gamma=-2\pi\cdot 350$ sec^{-1}Oe^{-1}.

The rate of the two-phonon SLR of the thulium nuclei via an excited state with energy Δ can be expressed in standard form (see Fig. 1):

$$T_1^{-1}=\frac{2w_{CA}w_{CB}}{w_{CA}+w_{CB}}\exp(-\Delta/kT). \tag{2}$$

The probabilities of the transitions $C\to A$ and $C\to B$, which are induced by the electron spin-phonon interaction, depend on the makeup of the nuclear components of the wave functions. To illustrate this dependence, Fig. 1 shows the electron-hole functions of the lower states of the Tm^{3+} ion in the LiTmF$_4$ crystal at magnetic-field orientations parallel and perpendicular to the crystallographic axis c. We see that in a longitudinal magnetic field the relaxation (2) is forbidden (for each state $|C_i\rangle$, either w_{c_iA} or w_{c_iB} is equal to zero), whereas in a transverse field it can go through the states $|C_1\rangle$ and $|C_2\rangle$ at a rate close to the electronic rate.

At small angles θ between the magnetic field and the c axis of the crystal, the wave functions $|C_i\rangle$ change insignificantly. As to the functions of the ground electron-nuclear doublet

$$\begin{aligned}|A\rangle&=\left(\frac{1-F}{2}\right)^{1/2}|\psi_1{}^+\rangle-\left(\frac{1+F}{2}\right)^{1/2}|\psi_1{}^-\rangle,\\ |B\rangle&=\left(\frac{1+F}{2}\right)^{1/2}|\psi_1{}^+\rangle+\left(\frac{1-F}{2}\right)^{1/2}|\psi_1{}^-\rangle,\\ F(\theta)&=\left[1+\left(\frac{1+\alpha_\perp}{1+\alpha_\parallel}\right)^2\operatorname{tg}^2\theta\right]^{-1/2},\end{aligned} \tag{3}$$

they are strongly altered; therefore the rate of the two-phonon relaxation

$$T_1^{-1}\sim(1-F^2) \tag{4}$$

should increase strongly with increasing angle, and, in particular, reach half its maximum value at

$$\theta_{1/2}=\operatorname{arctg}\frac{1+\alpha_\parallel}{1+\alpha_\perp} \tag{5}$$

($\theta_{1/2}=2.25°$ in the case of LiTmF$_4$).

Actually, owing to the magnetic hyperfine interaction $a_J\mathbf{J}\cdot\mathbf{I}$, the wave functions of the ground nuclear doublet in a longitudinal magnetic field are not "pure," but contain admixtures of states with opposite orientations of the nuclear spin:

TABLE I. Energies and wave functions of the lower states of the Tm^{3+} ion in the LiTmF$_4$ crystal.

Number of level i	Energy E_i, cm^{-1}	Wave function $\vert\psi_i\rangle$
1	0	$-0.120\vert 6\rangle+0.697\vert 2\rangle+0.697\vert -2\rangle-0.120\vert -6\rangle$
2	27^a, 31^b, 32^c	$-0.016\vert +5\rangle+0.848\vert +1\rangle+0.530\vert -3\rangle$
3		$-0.016\vert -5\rangle+0.848\vert -1\rangle+0.530\vert +3\rangle$
4	56^b, 57^c	$0.266\vert 4\rangle+0.926\vert 0\rangle+0.266\vert -4\rangle$
5	282^b, 287^c	$-0.638\vert 6\rangle+0.304\vert 2\rangle-0.304\vert -2\rangle+0.638\vert -6\rangle$

Note. a—Data on NMR of ^{169}Tm in LiTmF$_4$,[6] b—optical-spectroscopy data for Tm^{3+} in LiYF$_4$,[7] c—optical spectroscopy data for Tm^{3+} in LiTmF$_4$ (Ref. 8); the wave functions were calculated using the crystal potential of Ref. 7.

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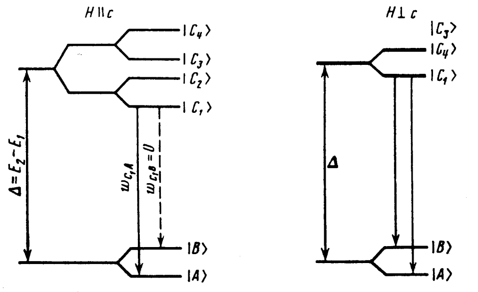

FIG. 1. Electron-nuclear functions of the lower states of the Tm^{3+} in the crystal $LiTmF_4$. $H \parallel c$: $|A\rangle = |\psi_1^-\rangle$, $|B\rangle = |\psi_1^+\rangle$, $|C_1\rangle = |\psi_2^-\rangle$, $|C_2\rangle = |\psi_2^+\rangle$, $|C_3\rangle = |\psi_3^+\rangle$, $|C_4\rangle = |\psi_3^-\rangle$; $H \perp c$: $|A\rangle = 2^{-1/2}(|\psi_1^+\rangle - |\psi_1^-\rangle)$, $|B\rangle = 2^{-1/2}(|\psi_1^+\rangle + |\psi_1^-\rangle)$, $|C_1\rangle = |\psi_2^-\rangle$, $|C_2\rangle = |\psi_3^+\rangle = 2^{-1/2}(|\psi_2^+\rangle - |\psi_3^-\rangle)$, $|C_4\rangle = 2^{-1/2}(|\psi_2^+\rangle - |\psi_3^-\rangle)$.

$$|A\rangle = (1-p^2)^{1/2}|\psi_1^-\rangle - p|\psi_2^+\rangle,\quad |B\rangle = (1-p^2)^{1/2}|\psi_1^+\rangle - p|\psi_3^-\rangle. \tag{6}$$

These admixtures, however, are very small $[p = (a_J/2\Delta)|\langle\psi_2|J_+|\psi_1\rangle| \sim 10^{-3}]$ and are incapable of ensuring an SLR rate larger than ~10^{-6} of the rate in a transverse field.

An unsuccessful attempt was made in Ref. 8 to observe the anisotropy of two-phonon nuclear SLR of ^{169}Tm in $LiTmF_4$; since the investigated sample was imperfect, the cause of the failure was assumed to be the variability of the crystallographic axes and the principal question remained in essence unanswered. In the present article we report the results of a detailed study of the nuclear relaxation of thulium in three samples of $LiTmF_4$ with different degrees of perfection and with different contents of the paramagnetic impurity Er^{3+} (I—0.01%, II—0.04%, III—0.3%). Preliminary quality control of the crystals with the aid of the ^{169}Tm NMR line width has shown[1)] sample II to be closest to perfect: no signs of a block structure was observed in it at all. At the same time, in samples I and III the crystallographic axes are subject to variation of the order of 11 and 8 minutes of angle. The crystallographic c axis was accurately aligned (±10′) with the external magnetic field H by maximizing the resonant value of the NMR line of thulium.

The nuclear SLR times T_1 were measured in the temperature interval from 1.6 to 5.5 K at a frequency 10.6 MHz using a pulsed NMR spectrometer. To estimate the times $T_{2\mathrm{sph}}$ of the transverse relaxation due to the spin-phonon interaction, we used the temperature dependence ($T = 5.5$–15.5 K) of the width and of the second moment of the absorption line of ^{169}Tm at the frequencies 4–7 MHz; thus, in the case of the $\mathbf{H} \parallel c$ orientation, when the line shape was close to Lorentzian, we assumed

$$T_{2\,\mathrm{sph}}^{-1} = \frac{3^{1/2}}{2}\gamma_\parallel(T)\,[\Delta H(T) - \Delta H(4.2\,\mathrm{K})], \tag{7}$$

where ΔH [Oe] is the interval between the maximum and the minimum of the absorption derivative; for angles $\theta \geqslant 0.5°$ the line shape was close to Gaussian; we used therefore in place of (7) the relation

$$T_{2\,\mathrm{sph}}^{-1} = \frac{3^{1/2}}{2}\gamma_\theta(T)\,[M_2(T) - M_2(4.2\,\mathrm{K})]^{1/2}, \tag{8}$$

where M_2 [Oe^2] is the second moment of the absorption line at the temperature T.

Temperatures higher than 4.2 K were obtained by heating the samples in a vacuum chamber immersed in liquid ^{4}He. The temperatures were measured with two temperature-sensitive resistors calibrated against a type-KG standard germanium resistance thermometer (produced by the Semiconductor Institute of the Ukrainian Academy of Sciences). The use of two thermometers mounted above and below the sample made it possible to take into account the temperature gradient in the vacuum chamber; under the worst conditions the difference between the thermometer readings reached 10%.

The measured temperature dependences of the rates of nuclear relaxation of ^{169}Tm are shown in Fig. 2. The figure shows for comparison the temperature dependence, borrowed from Ref. 6, of the rate of longitudinal relaxation of the ^{19}F nuclei in sample I. The greater part of the results obtained by the pulsed method pertain to the orientation $H \parallel c$; the strong spin-spin interactions and the resultant short times T_2 (6 μsec at $\theta = 0$ and 2.5 μsec at $\theta = 0.7°$) prevented us from observing the spin echo of the thulium nuclei at $\theta > 1°$. At the same time, we succeeded in measuring $T_{2\mathrm{sph}}$ by a stationary method in a wide range of θ. Analysis of the experimental data leads readily to the following conclusions.

1. At low temperatures, the impurity paramagnetic Er^{3+} ions participate in the spin-lattice relaxation of the thulium nuclei and the SLR rate of ^{169}Tm is approximately quadratic in the concentration of the Er^{3+} impurity. It appears that in this case the nuclear relaxation is effected via the reservoir of dipole-dipole

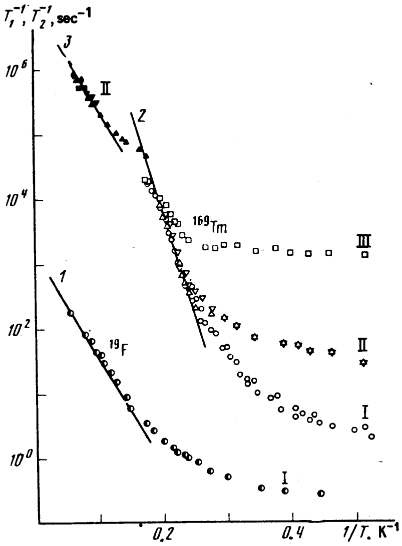

FIG. 2. Temperature dependences of the rates of relaxation of the ^{169}Tm and ^{19}F nuclei in single-crystal $LiTmF_4$. ^{19}F: ◐—T_1^{-1}, sample I, $\theta = 0$ (from Ref. 6); curve 1—$T_1^{-1} = 1.8 \cdot 10^3 \exp(-1.44 \cdot 27/T)$; ^{169}Tm: ○—T_1^{-1}, $\theta = 0$; △—T_1^{-1}, $\theta = 0$; ▽—T_1^{-1}, $\theta = 0.7°$; □—T_1^{-1}, $\theta = 0$; curve 2—$T_1^{-1} = 2.6 \cdot 10^{10} \exp(-1.44 \cdot 52/T)$; ▲—$T_2^{-1}$, $\theta = 0$; ▼—T_2^{-1}, $\theta = 0.5°$; ■—T_2^{-1}, $\theta = 1.5°$; ◆—T_2^{-1}, $\theta = 2.5°$; curve 3—$T_2^{-1} = 1.3 \cdot 10^7 \exp(-1.44 \cdot 27/T)$.

interaction of the impurity paramagnetic ions.[9] We estimate numerically the time of relaxation via this mechanism by using the formula [cf. Eq. (1.24) of Ref. 10]:

$$T_1^{-1}=\frac{3}{10}\gamma^2(1+\alpha_\perp)^2(g_\parallel\mu_B)^2N^2/\omega^2\tau_{2e}d^3R^3, \tag{9}$$

where $g_\parallel=2.96$ is the spectroscopic splitting factor of the Er^{3+} ions,[6] N is the relative concentration of the Er^{3+} ions, ω is the resonant frequency of the ^{169}Tm nuclei, τ_{2e} is the time of the spin-spin relaxation of the Er^{3+} ions in the concentrated paramagnet $LiErF_4$, d is the radius of the diffusion barrier, and $R=3.6$ Å is the distance between the neighboring Tm^{3+} ions. Assuming $\tau_{2e}\sim 10^{-10}$ sec and $d\sim 10$ Å we obtain $T_1^{-1}\sim 10^8N^2$, in satisfactory agreement with the experimental results.

2. At high temperatures, the SLR of the nuclear moments of thulium in all three samples goes through the excited states of the Tm^{3+} ions with energy of the order of[2)] 27 and 52 cm^{-1} (the process of the relaxation through the level with energy 27 cm^{-1} in samples II and III does not manifest itself because of the large content of the erbium impurity). There is no angular dependence $T_1^{-1}(\theta)$ in the range $0\leq\theta\leq 0.7°$ even in the high-grade sample (II), although according to (3) and (4) in an ideal crystal a tenfold change in the rate of the SLR should take place in this angle interval.

3. The rate $T_{2\,\mathrm{sph}}^{-1}$ of the thulium transverse relaxation due to the spin-phonon interaction is insensitive to changes of the orientation of the crystal in a magnetic field; its temperature dependence (at $T>8$ K) is described by the expression

$$T_{2\,\mathrm{sph}}^{-1}=1.3\cdot 10^7\exp(-1.44\cdot 27/T). \tag{10}$$

The presence of the energy 27 cm^{-1} in the argument of the exponential seems natural, since the relaxation time of the transverse nuclear magnetization of thulium is in essence the lifetime of the electronic ground state of the Tm^{3+} ion, a time determined principally by the probability of the transition of the electron shell into an excited state with lowest energy.

4. The temperature dependences of T (^{169}Tm) and T_1^{-1} (^{19}F) are identical in character. This fact does not contradict the calculations of Ref. 13, according to which the rate of relaxation of the longitudinal magnetization of the ligand nuclei is also proportional to the probability of the transition of the paramagnetic ion into an excited state.

Thus, the experimental data offer incontrovertible evidence that the theoretically predicted strong anisotropy of the rate of the nuclear SLR via excited electronic states does not take place in real crystals, and that even in a longitudinal magnetic field the energy absorbed by the system of the nuclear spins is effectively transferred to the lattice.

Analyzing the causes of this contradiction, we should bear in mind two important circumstances. First, the crystal $LiTmF_4$ is a concentrated paramagnet, in which Tm^{3+} ions only 3.6 Å apart are coupled with one another by a strong magnetic dipole-dipole interaction[14] capable of ensuring rapid exchange of the energy of the electron excitation Δ in the system of paramagnetic ions. Second, all the investigated samples (including sample II) had an imperfect crystal structure. This is evidenced, in particular, by the appreciable inhomogeneous broadening of the NMR line of ^{169}Tm, due to the scatter of the values of the paramagnetic shift $\alpha_\perp$ or, in other words, due to the scatter of the energy of the excited doublet of the Tm^{3+} ion. Numerical estimates yielded[14]

$$\langle\delta E_{2,3}^2\rangle^{1/2}=0.2\ \mathrm{cm}^{-1}. \tag{11}$$

The causes of the distortions of the local symmetry can be impurity atoms, dislocations, and other lattice defects.

We consider now the influence of the distortions of the crystal structure on the nuclear SLR of paramagnetic ions. We represent the local distortion of the crystal symmetry by a small low-symmetry increment V to the ground Hamiltonian $\mathscr{H}_{\mathrm{ax}}$ of the axial crystalline field. Lowering the symmetry leads to a splitting of the doublet $E_{2,3}$, to a shift of all the energy levels, and to modification of the stationary states in such a way that the correct first-approximation wave functions become

$$|a_m\rangle=|a_m^0\rangle+\sum_n\frac{\langle a_n^0|V|a_m^0\rangle}{E_m^0-E_n^0}|a_n^0\rangle. \tag{12}$$

The superscript zero pertains here to the stationary states in the axial field, and the wave functions $|a_m^0\rangle$ are chosen such that the perturbation matrix V is diagonal.

Diagonalization of the matrix of the energy of the Zeeman and hyperfine interactions

$$\mathscr{H}_{Ze}+\mathscr{H}_{ZN}+\mathscr{H}_{\mathrm{ht}}=g_J\mu_B\mathbf{HJ}-\gamma\hbar\mathbf{HI}+a_J\mathbf{JI}, \tag{13}$$

calculated with the wave functions $|a_m^\pm\rangle$ (± corresponds to the different projections of their nuclear spin $I=\frac{1}{2}$) reduces to the following transformation of the functions:

$$\begin{gathered}|a_m'\rangle=(1-\hat{S})|a_m\rangle,\\ \langle a_n|\hat{S}|a_m\rangle=\frac{(g_J\mu_B\mathbf{H}+a_J\mathbf{I})\langle a_n|\mathbf{J}|a_m\rangle}{E_n-E_m}.\end{gathered} \tag{14}$$

On the wave functions (14), the matrix elements of the operator (13) between the different electronic singlets vanish in first order, and energy of the individual singlet is written in the form of the effective Hamiltonian

$$\mathscr{H}_m'=E_m+\delta E_m-\gamma\hbar\sigma_{jk}^{(m)}H_jI_k, \tag{15}$$

where δE_m is the total shift of both nuclear sublevels on account of the perturbation V,

$$\begin{gathered}\sigma_{jk}^{(m)}=\delta_{jk}+\alpha_{jk}^{(m)},\\ \alpha_{jk}^{(m)}=\frac{2a_Jg_J\mu_B}{\gamma\hbar}\sum_n{}'\frac{\langle a_m|J_j|a_n\rangle\langle a_n|J_k|a_m\rangle}{E_n-E_m}.\end{gathered} \tag{16}$$

We have obtained the stationary states of the system in the magnetic field by diagonalizing the effective Hamiltonians (15). At an arbitrary direction of the magnetic field, the nuclear splitting of the m-th level is equal to

$$\begin{aligned}\varepsilon_m&=\gamma\hbar(\sigma_{jk}^{(m)}\sigma_{jl}^{(m)}H_kH_l)^{1/2}\\ &=\gamma\hbar(H_j'H_j')^{1/2}=\gamma\hbar H',\quad (H_j'=\sigma_{jk}H_k),\end{aligned} \tag{17}$$

and the electron-nuclear wave functions can be written in the form

$$|m^+\rangle=N^+\left(|a_m{}'+\rangle+\frac{H_x{}'+iH_y{}'}{H_z{}'+H'}|a_m{}'-\rangle\right),$$
$$|m^-\rangle=N^-\left(|a_m{}'-\rangle+\frac{H_z{}'-H'}{H_x{}'+iH_y{}'}|a_m{}'+\rangle\right), \tag{18}$$

where N^+ and N^- are normalization coefficients.

Let now $H\parallel z$; if we put σ_{xz}, $\sigma_{yz}\ll\sigma_{zz}$, then the stationary states of (18) take the form

$$|m^+\rangle=|a_m{}'+\rangle+\frac{\sigma_{xz}^{(m)}+i\sigma_{yz}^{(m)}}{2\sigma_{zz}^{(m)}}|a_m{}'-\rangle,$$
$$|m^-\rangle=|a_m{}'-\rangle-\frac{\sigma_{xz}^{(m)}-i\sigma_{yz}^{(m)}}{2\sigma_{zz}^{(m)}}|a_m{}'+\rangle. \tag{19}$$

We see that the distortion of the local symmetry results in the sought mixing of the nuclear states in the longitudinal magnetic field. To estimate its magnitude, we use the energy level scheme of the Tm^{3+} ion in a distorted crystalline field (Fig. 3) and write out, e.g., some of the components $\sigma_{jk}^{(2)}$ accurate to first order in V:

$$\sigma_{zz}^{(2)}=1+\frac{2a_Jg_J\mu_B}{\gamma\hbar}\frac{|\langle a_2{}^0|J_z|a_3{}^0\rangle|^2}{\mathscr{E}}+\ldots,$$
$$\sigma_{xx}^{(2)}=1-\frac{2a_Jg_J\mu_B}{\gamma\hbar}\left[\frac{|\langle a_1{}^0|J_x|a_2{}^0\rangle|^2}{E_2-E_1}+\frac{|\langle a_2{}^0|J_x|a_4{}^0\rangle|^2}{E_2-E_4}+\ldots\right],$$
$$\sigma_{xz}^{(2)}=\frac{2a_Jg_J\mu_B}{\gamma\hbar}\left[\frac{\langle a_2{}^0|J_z|a_3{}^0\rangle\langle a_3{}^0|V|a_1{}^0\rangle\langle a_1{}^0|J_x|a_2{}^0\rangle}{\mathscr{E}(E_3{}^0-E_1{}^0)}\right.$$
$$\left.+\frac{\langle a_2{}^0|J_z|a_3{}^0\rangle\langle a_3{}^0|J_x|a_1{}^0\rangle\langle a_1{}^0|V|a_2{}^0\rangle}{\mathscr{E}(E_2{}^0-E_1{}^0)}+\ldots\right]. \tag{20}$$

According to (19), the mixing of the nuclear states of the excited doublet is determined by the relation

$$\frac{\sigma_{+z}^{(2)}}{\sigma_{zz}^{(2)}}\approx\frac{\langle a_2{}^0|J_z|a_3{}^0\rangle[\langle a_3{}^0|V|a_1{}^0\rangle\langle a_1{}^0|J_+|a_2{}^0\rangle+\langle a_3{}^0|J_+|a_1{}^0\rangle\langle a_1{}^0|V|a_2{}^0\rangle]}{\Delta_{12}|\langle a_2{}^0|J_z|a_3{}^0\rangle|^2} \tag{21}$$

Substituting the angular-momentum matrix elements, we obtain

$$\sigma_{+z}^{(2)}/\sigma_{zz}^{(2)}\approx50\langle|V|\rangle/\Delta_{12}.$$

We see that practically complete mixing of the nuclear states of the excited doublet is reached even for rather small low-symmetry components of the crystal field, such that $\langle|V|\rangle\sim0.5$ cm^{-1}. As a measure of $\langle|V|\rangle$ it is reasonable to use the deviation of the doublet energy from its mean value (11). If we assume that these deviations have a Gaussian distribution, then we can easily calculate that approximately one out of every hundred Tm^{3+} ions will be in a sufficiently strong low-symmetry field and will consequently relax rapidly independently of the orientation of the crystal in the constant magnetic field.

As to the bulk of the ("defect-free") Tm^{3+} ions, which are less subject to the influence of the distortions of the crystal structure, the nuclear states of the doublet are more weakly mixed in them and an anisotropy of the rate of the nuclear SLR should make its appearance, although not in the form that follows from (3) and (4). However, in a concentrated paramagnet of the type $LiTmF_4$ the angular dependence of the SLR is practically unobservable, inasmuch as the dipole-dipole interaction transfers the energy of the nuclear spins rapidly to the "defect" Tm^{3+} centers, and the latter are in good contact with the lattice at any orientation of the external magnetic field. In view of the high concentration of the rapidly relaxing ions, the time of energy transfer to them is of the order of the time of the spin-spin relaxation $T_2\sim10^{-5}$ sec. Anisotropy of the nuclear SLR can be expected only in the case of high-grade magnetically-diluted crystals such as $LiYF_4:Tm^{3+}$.

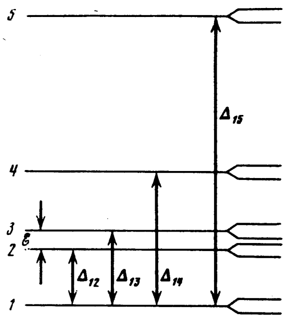

FIG. 3. Electron-nuclear energy levels of Tm^{3+} ion occupying in the $LiTmF_4$ crystal a position with distorted symmetry.

In conclusion, returning to the question posed at the start of the article, we can state the following. Local distortions of the symmetry in real crystals can smooth out to a considerable degree the anisotropy of the rate of diffusion SLR of nuclei of paramagnetic ions via excited electronic states. In concentrated van Vleck paramagnets, where the paramagnetic ions are coupled by a strong dipole-dipole interaction, the angular dependence of the two-phonon nuclei SLR can be completely suppressed.

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[1] Owing to the strong anisotropy of the effective gyro-magnetic ratio of the ^{169}Tm nuclei in $LiTmF_4$, it is possible to identify by the stationary NMR method the block structure of crystals even in those cases when the deviations of the c axis of the different blocks do not exceed 3 minutes of angle.

[2] Compare with the data in the table. The causes of the frequently observed difference between the excited-state energies obtained from the optical spectra and from the temperature dependence of the rate of the spin-lattice relaxation were discussed in Refs. 11 and 12.

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Density of electron levels in ferromagnetic semiconductors

A. P. Grigin

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The electron level density in a randomly oriented magnetic-moment field is considered. The optimal-fluctuation method is used to obtain an expression for the tail of the level density in wide-band ferromagnetic semiconductors at temperatures above the Curie point.

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1. INTRODUCTION

A characteristic feature of ferromagnetic semiconductors is the strong interaction of the conduction electrons with localized moments of the lattice magnetic atoms. Below the Curie point, the interaction of the electrons with the magnetic subsystem is described within the framework of the spin-wave approximation.[1] The long-range ferromagnetic order leads then simply to a shift of the bottom of the conduction band, without disturbing the translationally invariant system. In the paramagnetic region of temperatures, on the other hand, the magnetic order is disturbed, and the conduction electrons interact with the random field of the magnetic moments. This produces in the forbidden band a level-density tail due to exchange interaction of the electrons with the random vector field. The notion of a magnetic level-density tail has already been used a number of times to explain the optical and electrical properties of magnetic semiconductors at temperatures above the Curie point.[2]

In the present paper, using the optimal-fluctuation method, an expression is obtained within the framework of the single-electron approximation for the tail of the level density both for paramagnetic temperatures and for temperatures where the Ornstein-Zernike-Ginzburg-Landau expansion is valid.

2. PARAMAGNETIC TEMPERATURE REGION

In a ferromagnetic semiconductor, each crystal cell contains a rare-earth or transition element atom whose inner electron shell is only partly filled. The interaction of the conduction electron with the magnetic atoms is described by the *s-d* exchange Hamiltonian[1]

$$H_{s-d}=\frac{A}{2N}\sum_g (\mathbf{S}_g\mathbf{s})_{\sigma\sigma'}\Psi_\sigma^+(\mathbf{r})\Psi_{\sigma'}(\mathbf{r}), \qquad (1)$$

where A is the *s-d* exchange constant, N is the number of atoms per unit volume, $\mathbf{S}_g$ is the spin of the magnetic atom, $\mathbf{s}$ is the spin of the conduction electron, $\Psi_\sigma^+(\mathbf{r})$ ($\Psi_{\sigma'}(\mathbf{r})$) is the operator of creation (annihilation) of an electron with spin $\sigma(\sigma')$ at the point $\mathbf{r}$. It is assumed that the width W of the conduction band is much larger than the *s-d* exchange energy AS, and furthermore $2S+1\gg 1$.

It is possible to separate in the Hamiltonian (1) components with diagonal ($\sigma=\sigma'$) and off-diagonal ($\sigma\neq\sigma'$) terms. The ratio of the contributions of the off-diagonal and diagonal terms is AS/W and will not be taken into account.

The starting point of the optimal-fluctuation method is a calculation of the probability of the fluctuation of a random quantity in a given spherical volume of radius R.[3] There are no known combinatorial formulas for the probability of the fluctuation of the magnetic moment produced in the region R by a random orientation of noninteracting spins. All that are available are some recurrence relations,[4] but their use calls for numerical methods.

In wide-band ferromagnetic semiconductors, where the parameter AS/W is small, a localized energy level is formed only by fluctuations whose radius is much larger than the lattice constant. To find the probability of their formation we can use the thermodynamic theory of fluctuations.[5] The probability P of the fluctuation of the moment M in a volume V and in the paramagnetic region of temperatures is given by

$$P\sim\exp[-M^2/2V\chi T]; \qquad (2)$$

here χ is the magnetic susceptibility and T is the temperature. Reckoning the energy of the localized state down from the bottom of the conduction band, we express it in the form

$$-E=\frac{\hbar^2}{2mR^2}-\frac{AS}{2N_R}\frac{M}{\mu}, \qquad (3)$$

where $N_R=V/a^3$ is the number of atoms in the volume, while a^3 and μ are the volume and the magnetic moment