

In contrast to the pumping of vibrational levels of the molecules, we are dealing here with separation of definite aggregates of fast processes and acting on them during various stages of crystallization.

Besides gaseous media, great interest attaches to the action exerted on the degrees of freedom of a growing crystal by laser radiation at the frequencies of the atoms that make up the lattice. In this case the crystallization takes place in a state of an excited lattice that has properties (in particular stoichiometric) substantially different from those of the usual one. We note that in principle it is possible to use lasers to grow crystals in the liquid phase, by acting on definite chemical reactions that are connected with the crystallization process.<sup>16</sup>

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## Interactions of nuclear spins in strongly anisotropic van Vleck paramagnets

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Strong anisotropy of the second moment of the magnetic resonance line of <sup>169</sup>Tm nuclei in the dielectric van Vleck paramagnet LiTmF<sub>4</sub> (scheelite structure) has been theoretically observed and theoretically explained. The contributions made to the second moment of the absorption line by the interaction of the nuclear moments of the thulium with one another and with the nuclei of the diamagnetic ligands are calculated. It is shown that the dipole-dipole interaction of the nuclear magnetic moments of <sup>169</sup>Tm is effected via the 4f-electron shells of the Tm<sup>3+</sup> ions and is enhanced as a result by a factor  $(1 + \alpha_1)^2 \sim 5000$  times ( $\alpha_1$  is the paramagnetic shift of the NMR line of thulium).

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During the last ten years, owing to the progress made in the techniques of obtaining infralow temperatures, a new trend has developed in solid state physics, involving research on nuclear magnetic ordering. Chapelier *et al.*<sup>1</sup> have performed brilliant experiments with the diamagnetic crystal CaF<sub>2</sub>, in which they succeeded in attaining for the <sup>19</sup>F nuclei a spin temperature of the order of 10<sup>-7</sup> K and in observing the antiferromagnetic ordering of the nuclear moments of fluorine. Andres, Bucher, *et al.*<sup>4</sup> investigated the series of intermetallic

van Vleck paramagnets PrBi, PrCu<sub>2</sub>, PrCu<sub>5</sub>, in which the strong electron s-f exchange interaction shifted the temperatures of the magnetic ordering of the nuclear moments <sup>141</sup>Pr to the millidegree region. Finally, Bleaney and co-workers<sup>5</sup> were able to observe antiferromagnetic ordering of the nuclear spins of <sup>165</sup>Ho in the dielectric van Vleck paramagnet at a temperature 4.5 mK. In the planning of such experiments and in the development of methods for their realization one is inevitably faced with the question of preliminary esti-

mates of the energy of the internuclear interactions and of the ordering temperature. As for diamagnetic crystals of the  $\text{CaF}_2$  type, the interactions of the isotropic magnetic moments of the nuclei in them are simple to calculate and the ordering temperature can be easily estimated. At the same time, an estimate of the temperature of nuclear magnetic ordering in van Vleck paramagnets is made complicated by the fact that the magnitudes of the spin-spin interactions of the nuclei are not known beforehand.

We report here the results of a detailed investigation, by the nuclear magnetic resonance (NMR) method, of the nuclear spin-spin interactions in the dielectric van Vleck paramagnet  $\text{LiTmF}_4$ . By virtue of a number of considerations, this crystal, whose magnetic properties have strong anisotropy, is convenient for research. First, it has a rather high symmetry, ( $I4_1/a$ ) and its structure has been well studied.<sup>6,7</sup> Second, the intracrystalline electric field acting on the  $\text{Tm}^{3+}$  ions ( $4f^{12}$ ,  $^3H_6$ ,  $J=6$ ), also has sufficiently high symmetry ( $S_4$ ); its potential for the isostructural crystal  $\text{LiYF}_4$  was proposed in Ref. 8. Third, earlier investigations of the NMR spectra and of the spin-lattice relaxation of the nuclei  $^{169}\text{Tm}$  and  $^{19}\text{F}$  (Refs. 9–11) have established the parameters of the nuclear spin Hamiltonian of thulium ( $I=1/2$ )

$$\mathcal{H}_I = -\gamma\hbar(1+\alpha_{\parallel})H_xI_x - \gamma\hbar(1+\alpha_{\perp})(H_xI_x + H_yI_y) \quad (1)$$

(at liquid helium temperatures  $\alpha_{\parallel}=1.75$ ,  $\alpha_{\perp}=67.9$ ), the energy interval between the ground singlet and the nearest excited doublet of the  $\text{Tm}^{3+}$  ion ( $\Delta=27\text{ cm}^{-1}$ ), and the character of the interaction of the nuclear magnetic moments of thulium and fluorine.

In experiments performed at frequencies from 3 to 150 MHz, we have investigated the width and the second moment of the NMR line of  $^{169}\text{Tm}$  at 4.2 K in magnetic fields from 0.15 to 11 kOe. The measurements have shown that the width of the NMR line depends strongly on the angle  $\theta$  between the direction of the external magnetic field and the  $c$  axis of the crystal (Fig. 1). This dependence does not differ in character from that observed by Stapleton and co-workers<sup>12</sup> in a study of the EPR line widths of rare-earth ions in lanthanum magnesium nitrate crystals. Stapleton *et al.*<sup>9</sup> found that the principal role in the broadening of the EPR lines is

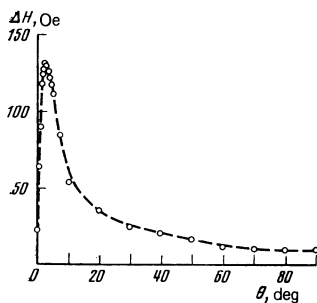


FIG. 1. Dependence of the width of the NMR line of  $^{169}\text{Tm}$  in  $\text{LiTmF}_4$ , defined as the interval between the maximum and minimum of the derivative of the absorption, on the orientation of the external magnetic field relative to the crystallographic  $c$  axis;  $\nu=3.9\text{ MHz}$ ,  $\varphi=60^\circ$ .

played by local stresses in the crystal, which lead to a scatter in the values of the  $g$  factors and to a "wandering" of the  $c$  axis of the crystal. Obviously, the contribution made by the crystal-lattice defects to the width of the resonance line can turn out to be substantial also in our case, since the paramagnetic shift  $\alpha$  of the NMR line of thulium depends on the crystal electric field. Following Ref. 12, we can write for the second moment of the NMR line of  $^{169}\text{Tm}$

$$M_2 = M_2^{ss} + \nu^2 [(1+\alpha_{\parallel})^2 \cos^2 \theta + (1+\alpha_{\perp})^2 \sin^2 \theta]^{-2} \times \{ (1+\alpha_{\parallel})^2 \cos^4 \theta \langle \delta\alpha_{\parallel}^2 \rangle + (1+\alpha_{\perp})^2 \sin^4 \theta \langle \delta\alpha_{\perp}^2 \rangle + [(1+\alpha_{\perp})^2 - (1+\alpha_{\parallel})^2] \sin^2 \theta \cos^2 \theta \langle \delta\theta^2 \rangle \}, \quad (2)$$

where  $M_2^{ss} = M_{2\text{Tm}} + M_{2\text{F}} + M_{2\text{Li}} + M_{2s}$  is the sum of the contributions due to the interaction of the nuclear moments of the thulium with one another, with the  $^{19}\text{F}$  and  $^7\text{Li}$  nuclei, and with the electronic moments of the paramagnetic impurities. In the right-hand side of (2) are contained the contributions made to the second moment by the scatter of the values of the paramagnetic shift ( $\langle \delta\alpha_{\parallel}^2 \rangle$  and  $\langle \delta\alpha_{\perp}^2 \rangle$ ) and by the "wandering" of the  $c$  axis of the crystal ( $\langle \delta\theta^2 \rangle$ ); a distinguishing feature of these contributions is their quadratic dependence on the frequency  $\nu$ .

An investigation of the frequency dependence of  $M_2$  (Fig. 2) has shown that the main cause of the inhomogeneous broadening of the NMR line of  $^{169}\text{Tm}$  is the scatter of the values of the "perpendicular" paramagnetic shift  $\alpha_{\perp}$  or, in other words, the spatial distribution of the energy  $E_d$  of the nearest excited doublet of the  $\text{Tm}^{3+}$  ion over the crystal. According to our measurements, the value of  $\langle \delta E_d^2 \rangle^{1/2}$  is approximately  $0.2\text{ cm}^{-1}$ . The most surprising result of these experiments, which have prompted us to undertake more detailed investigations, was the exceedingly strong angular dependence<sup>11</sup> of  $M_2^{ss}(\theta)$ . As seen from Fig. 2, lowering the frequency of the oscillating magnetic field makes it possible to eliminate the manifestations of the defects in the crystal and to determine the second moment  $M_2^{ss}$  of the absorption line broadened only by the spin-spin interactions. To eliminate completely the influence of the lattice defects, the frequency of the oscillating mag-

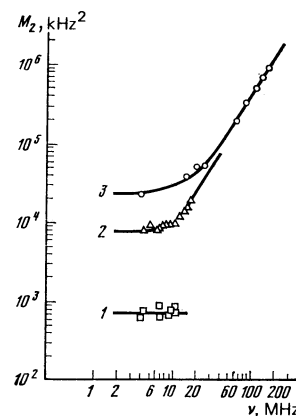


FIG. 2. Second moment of the absorption line of thulium as a function of the frequency of the oscillating magnetic field (the value  $fM_2$  was obtained by numerically integrating the experimental resonant-absorption curves): 1—for  $\theta=0$ , 2—for  $\theta=2.5^\circ$ , 3—for  $\theta=90^\circ$ .

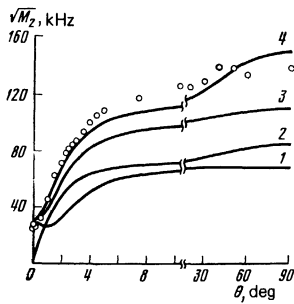


FIG. 3. Angular dependence of the square root of the second moment of the NMR line of  $^{169}\text{Tm}$  at  $\varphi = 60^\circ$ . The circles represent the experimental data, and the solid curves describe the following contributions: 1—of the dipole-dipole interaction of the thulium nuclei with one another, 2—of the dipole-dipole interaction of the thulium nuclei with the fluorine nuclei; 3—of the combined (1+2) dipole-dipole interaction; 4—of the combined interaction with account taken of the overlap of the electron orbits of the thulium and fluorine ions.

netic field was chosen in the succeeding experiments to be 4 MHz. Figure 3 shows the results of detailed measurements of  $(M_2^{ss})^{1/2}$  as a function of the angle  $\theta$ . We see that the main changes of the second moment occur in the region of small  $\theta$ : a deviation of  $10^\circ$  from parallel orientation causes  $M_2^{ss}$  to increase by 25(1) times, but the change is insignificant with further increase of  $\theta$  to  $90^\circ$ .

The tetragonal symmetry of the  $\text{LiTmF}_4$  crystal manifests itself in a dependence of the second moment of the NMR line of  $^{169}\text{Tm}$  on the angle between the magnetic field and the crystallographic axes  $a$  and  $b$ . Figure 4 illustrates the change of  $(M_2^{ss})^{1/2}$  following rotations of the crystal in the magnetic field such that the vector of the field moves over the surface of a cone about the  $c$  axis with an apex angle  $2\theta = 15^\circ$ ; a polar angle  $\varphi = 0$  corresponds to orientation of the magnetic field in the (100) plane. An RF coil of special construction was used in these experiments and made it possible to rotate the crystal about an axis situated in the plane of rotation of the electromagnet.

It is convenient to start the analysis of the experimental data with consideration of interactions in the system of  $\text{Tm}^{3+}$  ions. For simplicity we take into account initially only the excited state closest to the ground single  $|g\rangle$ , namely the doublet  $|d\rangle$  with energy  $E_d$ . It can then be assumed that the Hamiltonian of a pair of

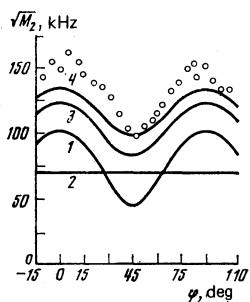


FIG. 4. Angular dependence of the square root of the second moment of the NMR lines of  $^{169}\text{Tm}$  at  $\theta = 7.5^\circ$ ; circles—experiment, the solid lines describe the contributions due to the different interactions (see Fig. 3).

ions (1 and 2) in the crystal electric field corresponds to four states:  $|g, g\rangle$  with zero energy,  $|g, d\rangle$  and  $|d, g\rangle$  with energy  $\Delta = E_d - E_g$ , and  $|d, d\rangle$  with energy  $2\Delta$ .

We obtain the Hamiltonian  $\mathcal{H}_{12}$  of the magnetic dipole-dipole interaction of the nuclei of this pair of ions by a perturbation method, writing down the perturbation operator in the form

$$V_{12} = a_J \bar{J}_1 \bar{I}_1 + a_J \bar{J}_2 \bar{I}_2 + \mathcal{H}_{1,11} + \mathcal{H}_{1,12} + \mathcal{H}_{1,13} + \mathcal{H}_{1,14}. \quad (3)$$

The first two terms represent here the energy of the magnetic hyperfine interaction of the nuclei with the  $4f$  electrons of their own shells, and the remaining four terms represent the energies of the nuclear-nuclear, electron-electron, and electron-nuclear inter-ion interactions. Since the average value of the total angular momentum  $J$  of the electronic  $4f$  shell of the  $\text{Tm}^{3+}$  ion in the singlet state  $|g\rangle$  is zero, we obtain in first-order perturbation theory only the direct dipole-dipole interaction of the nuclear magnetic moments:

$$\mathcal{H}_{12}^{(1)} = \langle g, g | V_{12} | g, g \rangle = \mathcal{H}_{1,11}. \quad (4)$$

In second-order approximation, as a result of the combination of the operators  $a_J \bar{J}_1 \bar{I}_1$  and  $\mathcal{H}_{1,12}$  ( $a_J \bar{J}_2 \bar{I}_2$  and  $\mathcal{H}_{1,21}$ ), an additional term  $\mathcal{H}_{12}^{(2)}$  appears, in which the product  $I_{1x} I_{2x}$  is preceded by a coefficient

$$\frac{4a_J g_J \mu_B \gamma \hbar}{r_{12}^3 \Delta} |\langle g | J_{1z} | d \rangle|^2 = \frac{\gamma^2 \hbar^2}{r_{12}^3} \alpha, \quad (5)$$

$g_J$  is the Landé factor,  $r_{12}$  is the distance between the ions. Thus, the second-order "correction" turns out to be  $\alpha$  times larger than  $\mathcal{H}_{12}^{(1)}$  (we recall that  $\alpha_1 \sim 70$  in  $\text{LiTmF}_4$ ). Finally, in third-order approximation of perturbation theory we combine the operators  $a_J \bar{J}_1 \bar{I}_1$ ,  $\mathcal{H}_{1,12}$  and  $a_J \bar{J}_2 \bar{I}_2$  and obtain the largest contribution  $\mathcal{H}_{12}^{(3)}$ , which contains terms of the type  $(\gamma^2 \hbar^2 / r_{12}^3) \alpha^2 I_{1x} I_{2x}$ . Actually, the magnetic properties of the  $\text{Tm}^{3+}$  ions should be considered with account taken of not only the lowest but also of other excited states  $|e\rangle$ . Then the total Hamiltonian of the dipole-dipole interaction of the thulium nuclei ( $\mathcal{H}_{12}^{(1)} + \mathcal{H}_{12}^{(2)} + \mathcal{H}_{12}^{(3)}$ ) takes the universally accepted form

$$\mathcal{H}_{12} = (\gamma^2 \hbar^2 / r_{12}^3) (A + B + C + D + E + F). \quad (6)$$

The anisotropic character of the interaction manifests itself in the fact that the corresponding expressions for  $A$ ,  $B$ ,  $C(D)$ , and  $E(F)$  differ from the known ones (see, e.g., Ref. 15) by the factors  $(1 + \alpha_{||})^2$ ,  $(1 + \alpha_{\perp})^2$ ,  $(1 + \alpha_{||})$ ,  $(1 + \alpha_{\perp})$ , and  $(1 + \alpha_{\perp})^2$ , which contain the components of the paramagnetic shift of the NMR line of thulium

$$\alpha_{||} = \frac{2a_J g_J \mu_B}{\gamma \hbar} \sum_e \frac{|\langle g | J_{1z} | e \rangle|^2}{E_e - E_g}, \quad \alpha_{\perp} = \frac{2a_J g_J \mu_B}{\gamma \hbar} \sum_e \frac{|\langle g | J_{1x} | e \rangle|^2}{E_e - E_g}.$$

Calculation of the second moment of the thulium NMR line broadened by the interaction of (6) leads to the expression

$$M_2 \text{Tm} [\Gamma \text{T}^2] = \frac{1}{4\pi^2} \frac{\gamma^4 \hbar^2}{[(1 + \alpha_{||})^2 \cos^2 \theta + (1 + \alpha_{\perp})^2 \sin^2 \theta]^2} \left\{ \frac{\Sigma_1}{16} [2(1 + \alpha_{||})^2 + (1 + \alpha_{\perp})^2] [2(1 + \alpha_{||})^2 \cos^2 \theta - (1 + \alpha_{\perp})^2 \sin^2 \theta]^2 + \frac{81}{2} \Sigma_2 (1 + \alpha_{\perp})^4 (1 + \alpha_{||})^4 \cos^2 \theta \sin^2 \theta + \frac{81}{32} (1 + \alpha_{\perp})^2 [\Sigma_3 + \Sigma_4 \cos 4\varphi + 4\Sigma_5 \sin 4\varphi] \sin^4 \theta \right\}, \quad (7)$$

TABLE I. Lattice sums for the crystal  $\text{LiTmF}_4$  (in units of  $10^{44} \text{ cm}^{-6}$ ).

$\Sigma$	$\Sigma_1$	$\Sigma_2$	$\Sigma_3$	$\Sigma_4$	$\Sigma_5$
Over the $\text{Tm}^{3+}$ ions in a sphere of radius 15 Å	9.627	4.488	7.628	5.33	0
Over the $\text{F}^-$ ions in a sphere of radius 15 Å	359.3	117.4	315.8	-190.7	-47.41

where  $\theta$  and  $\varphi$  are the polar angles of the vector of the external magnetic field in the crystallographic-axis system  $a, b, c$  and for the lattice sums over the ions with coordinates  $x_i, y_i, z_i$  we use the notation

$$\begin{aligned} \Sigma_1 &= \sum_i \left(1 - 3 \frac{z_i^2}{r_i^2}\right)^2 / r_i^6, & \Sigma_2 &= \sum_i \frac{z_i^2(x_i^2 + y_i^2)}{r_i^{10}}, \\ \Sigma_3 &= \sum_i \frac{(x_i^2 + y_i^2)^2}{r_i^{10}}, & \Sigma_4 &= \sum_i \frac{x_i^4 - 6x_i^2y_i^2 + y_i^4}{r_i^{10}}, \\ \Sigma_5 &= \sum_i \frac{(x_i^2 - y_i^2)x_iy_i}{r_i^{10}}. \end{aligned} \quad (8)$$

Table I lists the corresponding values of the lattice sums over the thulium ions.

The results of the calculation of  $M_{2\text{Tm}}^{1/2}$  are represented by curves 1 in Figs. 3 and 4. We see that the value of  $M_{2\text{Tm}}^{1/2}$  measured in the orientation  $\text{H} \parallel c$  is well accounted for by the interaction (6) alone. It is of interest to note that at  $\theta = 0$  a substantial contribution is made to the second moment (7) only by the operator  $B$ , which is responsible for the process of mutual reorientation of the nuclear spins (spin-spin relaxation).

We consider now the interaction of the thulium nuclei with the nuclei of the diamagnetic ligands. The Hamiltonian of the dipole-dipole interaction is written in a form similar to (6), with replacement of one (anisotropic) magnetic moment of the thulium  $\gamma \hbar (1 + \alpha) I_{\text{Tm}}$  by the magnetic moment  $\gamma_l \hbar I_l$  of the ligand nucleus. Calculation of the second moment of the  $^{169}\text{Tm}$  NMR line broadened by the dipole-dipole interaction of the thulium with the ligand nuclei yields

$$\begin{aligned} M_{2l}^{\text{dip}} &= \frac{I_l(I_l+1)\gamma^2\gamma_l^2\hbar^2}{12\pi^2[(1+\alpha_l)^2\cos^2\theta + (1+\alpha_{\perp l})^2\sin^2\theta]} \left\{ \frac{\Sigma_1}{4} [2(1+\alpha_{\parallel l})^2\cos^2\theta \right. \\ &\quad \left. - (1+\alpha_{\perp l})^2\sin^2\theta] + [(1+\alpha_{\parallel l})^2 + (1+\alpha_{\perp l})^2]^2 \frac{9}{2} \Sigma_2 \sin^2\theta \cos^2\theta \right. \\ &\quad \left. + (1+\alpha_{\perp l}) \cdot \frac{9}{8} [\Sigma_3 + \Sigma_4 \cos 4\varphi + 4\Sigma_5 \sin 4\varphi] \sin^4\theta \right\}. \end{aligned} \quad (9)$$

The values of the lattice sums over the nuclei  $^{19}\text{F}$  ( $I_{\text{F}} = \frac{1}{2}$ ) are given in Table I, while the solid lines 2 in Figs. 3 and 4 show the angular dependences of  $(M_{2\text{F}}^{\text{dip}})^{1/2}$ . The second moment  $M_{2\text{F}}^{\text{dip}}$  is not plotted in the figures, since it does not exceed 2% of  $M_{2\text{F}}^{\text{dip}}$ .

From a comparison of the experimental data in Figs. 3 and 4 with curves 3, which represent the summary effect  $(M_{2\text{Tm}}^{\text{dip}} + M_{2\text{F}}^{\text{dip}})^{1/2}$ , it is seen that the interactions that we took into account do not suffice to explain the observed values of  $M_{2\text{Tm}}^{1/2}$ . It was shown in Ref. 10 that besides the dipole-dipole interaction there is in the  $\text{LiTmF}_4$  crystal also an indirect interaction of the nuclear moments of thulium and fluorine, due to the overlap of the electron orbits of these ions. The Hamil-

TABLE II. Parameters of the interaction (10) of the nuclear magnetic moments of  $^{169}\text{Tm}$  and  $^{19}\text{F}$ , due to overlap of the electron orbits of the  $\text{Tm}^{3+}$  and  $\text{F}^-$  ions (in kHz).

Parameter	Position		Parameter	Position	
	$\text{F}_1$	$\text{F}_2$		$\text{F}_1$	$\text{F}_2$
$A_1$	0.98	1.15	$C_4$	+0.42	1.64
$B_1$	-2.19	9.87	$D_1$	+0.95	0.42
$B_2$	14.57	-8.99	$D_2$	+0.15	0.07
$B_3$	4.25	-3.68	$D_3$	-1.63	0.51
$B_4$	-0.15	-1.63	$E_1$	-14.02	8.64
$C_1$	+15.42	-1.48	$E_2$	5.73	-4.99
$C_2$	-4.63	-0.83	$E_3$	-10.83	-9.02
$C_3$	+17.67	-6.20	$E_4$	0.15	0.05

Note. The designations of the positions of the fluorine atoms  $\text{F}_1$  and  $\text{F}_2$  are the same as in Ref. 10. The signs of the parameters  $C_1$  and  $D_1$  are determined by the sign of the coordinate  $z$  of the fluorine relative to the thulium ion; the signs given in the table correspond to  $z(\text{F}) - z(\text{Tm}) > 0$ .

tonian of this interaction in a tetragonal crystal can be written in the form

$$\begin{aligned} \mathcal{H}_{\text{Tm-F}}^{\text{indir}} &= A_l I_{\text{Tm}} I_{\text{F}} + (B_1 + B_2 e^{4i\varphi} + B_3 e^{-4i\varphi} + B_4 e^{8i\varphi}) I_{\text{Tm}} I_{\text{F}} \\ &+ (C_1 e^{-i\varphi} + C_2 e^{3i\varphi} + C_3 e^{-5i\varphi} + C_4 e^{7i\varphi}) I_{\text{Tm}} I_{\text{F}} + (D_1 e^{-i\varphi} + D_2 e^{3i\varphi} + D_3 e^{-5i\varphi}) I_{\text{Tm}} I_{\text{F}} \\ &+ (E_1 e^{-2i\varphi} + E_2 e^{2i\varphi} + E_3 e^{-6i\varphi} + E_4 e^{6i\varphi}) I_{\text{Tm}} I_{\text{F}} + \text{c.c.} \end{aligned} \quad (10)$$

where  $\varphi$  is the polar angle of the  $\text{Tm} + \text{F}$  pair. The values of the parameters  $A_1, B_1, \dots, E_4$  for the  $\text{LiTmF}_4$  crystal, calculated from the data of Ref. 10, are given in Table II.

The second moment of the NMR line of thulium, which is connected with the nuclear spins of the fluorine by dipole-dipole and indirect interactions, is too cumbersome to be written out in an analytic form similar to (9). In numerical form we have

$$\begin{aligned} M_{2\text{F}}^{\text{dip+indir}} [\text{kHz}^2] &= (x^2 \cos^2 \theta + \sin^2 \theta)^{-1} \{ 18.8x^2 \cos^4 \theta + 8324 \sin^2 \theta \cos^2 \theta \\ &\quad + (12\,217 - 4348 \cos 4\varphi - 4147 \sin 4\varphi) \sin^4 \theta \}, \end{aligned} \quad (11)$$

where  $x = (1 + \alpha_{\parallel}) / (1 + \alpha_{\perp}) = 0.040$ .

As seen from Figs. 3 and 4, the calculated values of  $(M_{2\text{Tm}} + M_{2\text{F}}^{\text{dip+indir}})^{1/2}$  are in fair agreement with experiment. We might have possibly obtained complete agreement with experiment by considering in addition the interaction of the nuclear moments of thulium with the electronic moments of the extraneous paramagnetic impurities (according to EPR measurements, the investigated crystal contained approximately 0.05% Er, 0.001% Th and 0.0001% Gd). However, the question of the role of impurities in the broadening of NMR lines of the principal paramagnetic ions in van Vleck paramagnets is outside the scope of the present article and can be subject of special theoretical and experimental research.

Generalizing the foregoing, we can draw the following conclusions. The interaction of the nuclear magnetic moments of  $^{169}\text{Tm}$  in the tetragonal crystal  $\text{LiTmF}_4$  is via the  $4f$ -electron shells of the  $\text{Tm}^{3+}$  ions and has the same anisotropic character as in the  $xy$  model. Its energy is  $(1 + \alpha_{\perp})^2 \approx 5000$  times larger than the energy of the direct dipole-dipole interaction of the nuclei, and the expected temperature of the nuclear ordering is  $\sim 5 \cdot 10^{-6}$  K. Obviously, the enhancement of the dipole-dipole interaction of nuclei by the electron shells of

paramagnetic ions is a characteristic feature of all van Vleck paramagnets. It must be borne in mind, however, that an estimate of the interaction energy on the basis of the measured (or calculated) values of  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , in the case of ions with large ionic radii (such as  $\text{Pr}^{3+}$ ) may be too low, since it does not take into account the additional enhancement of the interaction by the kinetic exchange of the  $4f$  electrons.

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<sup>1</sup>In principle, the fact that the second moment of a paramagnetic-resonance line depends on the direction of the external magnetic field relative to a crystallographic axis has been known for a long time (see, e.g., Refs. 13 and 14). The difference in the present paper is that this angular dependence is used here to study nuclear spin-spin interactions.

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## Parametric excitation of spin waves by noise pumping

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A new method is proposed for parametric excitation of spin waves by noise pumping. The principal characteristics of the subthreshold regime are determined with the aid of Wyld's diagram technique and the above-threshold state is examined. The ineffectiveness of the "phase mechanism" of the above-threshold limitation is demonstrated and the role of various dissipative mechanisms is analyzed.

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Besides ferromagnetic resonance, it is possible to excite parametrically spin waves in ferroelectric crystals by applying an external alternating magnetic field parallel to the static magnetization of the crystal. The absorption of the energy in this pumping method is due to production of pairs of spin waves (SW) with opposite wave vectors and with a frequency close to half the pump frequency.<sup>1</sup> Measurements of the resonance threshold and investigations of the properties of the subthreshold state of the spin system is by now the subject of an extensive literature (see, e.g., Refs. 2-5).

Parametric excitation of waves is close to the known effect of parametric excitation of an oscillator, explained way back by Rayleigh.<sup>6</sup> This effect is the basis of the action of ordinary swings: if the length of the mathematical pendulum is periodically varied at the frequency equal to double the natural frequency of the pendulum, then an exponential buildup of oscillations sets in when the external action exceeds a certain

threshold intensity.<sup>1</sup> It is not quite obvious that parametric excitation of an oscillator can be produced also by a random (noise) variations of its parameters with time (see, e.g., Ref. 7).

We analyze in this paper the features of parametric excitation of spin waves by noise pumping in the subthreshold and in the (nonlinear) above-threshold regime.

### 1. NOISE PUMPING

Let  $h(t)$  be the alternating magnetic pump field. To describe its properties it is convenient to consider the autocorrelation function<sup>2)</sup>

$$g(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T h(t)h(t+\tau)dt \quad (1)$$

and its frequency spectrum

$$g(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} g(\tau)e^{i\omega\tau}d\tau. \quad (2)$$