Effect of magnetostriction on the NMR spectra of Van Vleck paramagnets

S. A. Al'tshuler, A. A. Kudryashov, M. A. Teplov, and D. N. Terpilovskiĭ
V. I. Ul'yanov (Lenin) Kazan' State University

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An anisotropy of the Van Vleck paramagnetic susceptibility in the (001) plane of the tetragonal crystal $LiTmF_4$ has been detected by an NMR method. The susceptibility oscillation depth varies in proportion to H^2 and has the value 1.3×10^{-2} in a field $H = 6.7$ kOe. Perturbation-theory calculations show that the anisotropy of χ results from a magnetostriction of the crystal and a mixing of the Tm^{3+} wave functions in a magnetic field.

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Ioffe *et al.*[1] have reported observing an anisotropy of the transverse component of the magnetization of the tetragonal crystal $TmPO_4$ in fields from 10 to 130 kOe. Using the NMR method in relatively weak magnetic fields, we have observed a corresponding effect in the $LiTmF_4$ crystal, which has attracted attention because of its giant magnetostriction[2] at liquid-helium temperatures. It has been shown previously[3] that the shift α_{ij} of the NMR line of rare-earth ions in Van Vleck paramagnets is proportional to the paramagnetic susceptibility and can reach very high values (~ 100). In particular, the magnetic resonance of ^{169}Tm nuclei (spin $I = \frac{1}{2}$) in the $LiTmF_4$ crystal is described by the spin Hamiltonian

$$\mathcal{H}_I = -\gamma_I \hbar (1+a_\parallel) H_z I_z - \gamma_I \hbar (1+a_\perp)(H_x I_x + H_y I_y). \quad (1)$$

The parameters α_i of this Hamiltonian are proportional to the corresponding components χ_{ii} of the susceptibility tensor; i.e., they increase as the crystal is cooled, and at $T<5$ K they are independent of the temperature ($[\alpha_\parallel^{(0)} = 1.74, \alpha_\perp^{(0)} = 67.5; \gamma_I = 2\pi 352]$ s^{-1} Oe^{-1} is the gyromagnetic ratio of the "free" thulium nuclei). Since the resonant fields can be measured highly accurately, it would be natural to expect that slight variations in the paramagnetic susceptibility of $LiTmF_4$ resulting from changes in the energy of the crystal due to a magnetostrictive deformation could be detected as a variation of the paramagnetic NMR shift of ^{169}Tm at high frequencies.

The experiments were carried out at 4.2 K. The nuclear magnetic resonance was detected by an autodyne detector at frequencies near the resonant frequency of the coaxial lead to the cryostat. To eliminate the effect of the demagnetizing field, we used an $LiTmF_4$ sample whose surface had the shape of a small ball ~4 mm in diameter. At the beginning of each experiment, we adjusted the inclination of the cryostat in the gap of the electromagnet to bring the *c* axis of the crystal into coincidence with the rotational axis of the electromagnet. The *a* axis of the crystal was oriented in the rotation plane of the electromagnet on the basis of the shape of the NMR spectrum of ^{19}F (in a magnetic field making an angle $\varphi = 22°$ from the *a* axis, the fluorine spectrum becomes a single line). Figures 1 and 2 show the measured values of the effective gyromagnetic ratio

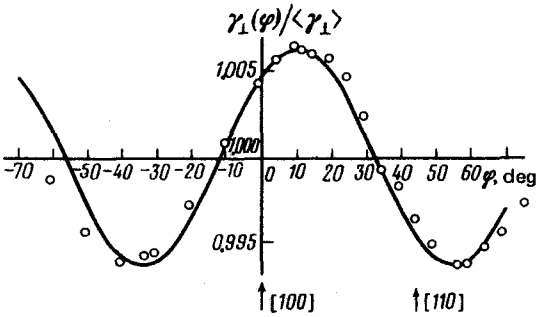

FIG. 1. Angular dependence of the effective gyromagnetic ratio of ^{169}Tm nuclei in the $LiTmF_4$ crystal. The magnetic field is oriented perpendicular to the c axis of the crystal; the temperature is 4.2 K; the frequency is 162 MHz. Here $\langle\gamma_\perp\rangle = 2\pi \times 2.4 \times 10^4$ s^{-1} Oe^{-1} is the average value of $\gamma_\perp$. Curve–$\gamma_\perp(\varphi)/\langle\gamma_\perp\rangle = 1 + (1.08\cos 4\varphi + 0.926 \sin 4\varphi)10^{-10} H^2$ [cf. (8)].

$\gamma_\perp(\varphi) = \gamma_I [1 + \alpha_\perp(\varphi)]$ of thulium nuclei at the frequencies 123, 140, and 162 MHz. We see that $\gamma_\perp$ oscillates as the orientation of the external field is varied in the (001) plane; the oscillation depth, $(\gamma_\perp^{max} - \gamma_\perp^{min})/\langle\gamma_\perp\rangle$, increases with increasing resonant field, in proportion to H^2 (Fig. 2).

The Hamiltonian of the Tm^{3+} ion ($4f^{12}$, $^3H_6$) may be written

$$\mathcal{H} = \mathcal{H}_{cr} + \mathcal{H}_z + \mathcal{H}_{ep}, \qquad (2)$$

where $\mathcal{H}_{cr}$ is the energy of the ion in the crystal electric field, $\mathcal{H}_z$ is the Zeeman energy, and $\mathcal{H}_{eff}$ is the operator representing the electron-phonon interaction (given explicitly in Ref. 4). The crystal field splits the lower level $^3H_6$ of the ground multiplet of the Tm^{3+} ion into a series of doublets and singlets. Aukhadeev *et al.*[5] have calculated the Stark structure of the $^3H_6$ state for $LiTmF_4$ in the system of crystallographic axes. They also gave the wave functions for the Tm^{3+} ion. At low temperatures the excited energy levels of the Tm^{3+} ion are not populated, so that the paramagnetic susceptibility of the

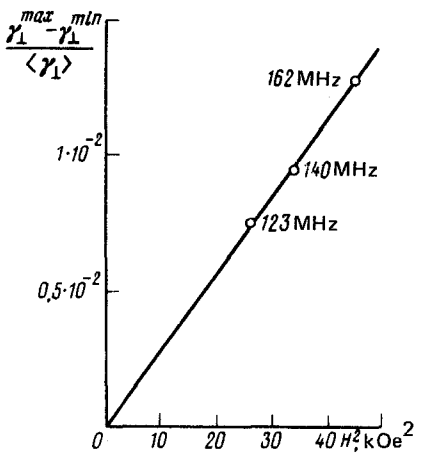

FIG. 2. Depth of the oscillation of the gyromagnetic ratio as a function of H^2. Line–$(\gamma_\perp^{max} - \gamma_\perp^{min})/\langle\gamma_\perp\rangle = 2.9 \times 10^{-10} H^2$.

crystal, $\chi = -\partial^2 E/\partial H^2$, is determined by only the energy (E) of the (singlet) ground state. For the weak magnetic fields of interest here ($\mathcal{H}_z \ll \mathcal{H}_{cr}$) the energy of the ground singlet can be determined by perturbation theory. Calculations[1)] using the wave functions of Ref. 5 yield the following expression for the increment in the ground-state energy of the Tm^{3+} ion in a magnetic field $H \perp c$:

$$\Delta E = E_z^{(2)} + E_z^{(4)} + E_{z-\text{ep}}^{(3)} . \tag{3}$$

Here

$$E_z^{(2)} = -3{,}28 \times 10^{-25} \tag{4}$$

is the correction of second order in $\mathcal{H}_z$, which causes the Van Vleck susceptibility $\chi_\perp^{(2)}$, which is isotropic in the (001) plane;

$$E_z^{(4)} = -(3{,}20 \cos 4\varphi + 2.82 \sin 4\varphi - 4{,}27) \times 10^{-36} H^4 \tag{5}$$

is the correction of fourth order in $\mathcal{H}_z$, which makes an anisotropic contribution $\chi_\perp^{(4)}$ to the transverse component of the susceptibility; and

$$E_{z-\text{ep}}^{(3)} = -(9{,}81 \cos 4\varphi + 8{,}31 \sin 4\varphi + 12{,}70) \times 10^{-36} H^4 \tag{6}$$

is the third-order correction, which results from the combination of $\mathcal{H}_z$ (twice) and $\mathcal{H}_{ep}$ and which generates the magnetostrictive contribution to the susceptibility, $\chi_\perp^{(3)}$.

Since the paramagnetic shift of the nuclear magnetic resonance, $\alpha_\perp$, is much larger than unity, while $\chi_\perp^{(3)}$ and $\chi_\perp^{(4)}$ are small in comparison with $\chi_\perp^{(2)}$, the variations in the effective gyromagnetic ratio of the thulium nuclei reproduce the changes in the paramagnetic susceptibility of $LiTmF_4$ quite accurately:

$$\Delta\gamma_\perp / \langle \gamma_\perp \rangle \cong (\chi_\perp^{(3)} + \chi_\perp^{(4)}) / \chi_\perp^{(2)} . \tag{7}$$

Differentiating (4)-(6) twice with respect to H, and substituting the result into (7), we find

$$\Delta\gamma_\perp / \langle \gamma_\perp \rangle \cong (2.38 \cos 4\varphi + 2{,}04 \sin 4\varphi + 1{,}55) \times 10^{-10} H^2 . \tag{8}$$

According to (8), the effective gyromagnetic ratio of the thulium nuclei should have a maximum at $\varphi_{max} = 10.1°$. Our measurements (Fig. 1) yield $\varphi_{max} \cong 11°$, in excellent agreement with the prediction. The measured oscillation depth $(\gamma_\perp^{max} - \gamma_\perp^{min})/\langle\gamma_\perp\rangle$ is $2.9 \times 10^{-10} H^2$ (Fig. 2); i.e., it is roughly half the calculated value of $6.27 \times 10^{-10} H^2$ [see (8)]. Since the energy levels and wave functions of the Tm^{3+} ion in $LiTmF_4$ are well known, so that the magnetic correction $E_z^{(4)}$ to the energy of the ground singlet can be calculated quite accurately, the reason for the discrepancy between theory and experiment should be identified as an error in the estimate of $E_{z\text{-ep}}^{(3)}$. Evidently, the magnetostrictive correction does not actually exceed the magnetic correction by a factor of 3 [as would follow from (5) and (6)] but is instead approximately equal to the magnetic correction.

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[1)]The procedure for calculating the magnetostrictive deformation is described in Ref. 4.

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