# Magnetic resonance in the Van Vleck paramagnets Tm(C₂H₅SO₄)·9H₂O and LiTmF₄ under uniaxial and hydrostatic compression

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Nuclear magnetic resonance of $^{169}$Tm and EPR of $Er^{3+}$ impurity ions is used to investigate the effect of uniaxial and hydrostatic compression on the crystal electric field in thulium ethyl sulfate TmES and in the double fluoride LiTmF₄ at 4.2 K. It is established that the point-charge model predicts correctly the changes of the most pressure-sensitive parameter $C_2^0$ of the crystal field in TmES. The anisotropy of the compressibility of TmES is estimated. It is found that under a hydrostatic pressure of the order of 1 kbar a structural phase transition takes place in LiTmF₄ and the crystal symmetry is lowered. It is proposed that the cooperative Jahn-Teller effect is responsible for this transition.

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Investigations of the dependence of the magnetic properties of paramagnets with singlet ground states on the hydrostatic pressure have been intensively pursued in recent years and have yielded interesting results. In particular, the investigation of the van Vleck susceptibility and of the paramagnetic shift of the NMR lines of rare-earth ions have shown that the point-charge model previously used successfully to interpret the results of neutron spectroscopy of monopnictides of praseodymium and thulium[1] do not explain even qualitatively the magnetic properties of these compounds under hydrostatic compression.[2,3] The causes of the observed inconsistency of the point-charge model as applied to intermetallic compounds have not yet been established, although some authors[2,3] believe that effects due to the conduction electrons must be taken into account.

We report here the results of a study of NMR of $^{169}$Tm and of EPR of the impurity $Er^{3+}$ ions in the dielectric crystals TmES and LiTmF₄ under a hydrostatic pressure $P$ and a uniaxial pressure $p$. To observe the NMR we used an autodyne spectrometer operating at frequencies up to 30 MHz; the EPR spectra were registered at 35 GHz. All the measurements were made at a 4.2 K. The hydrostatic compression was produced in a high-pressure vessel made of Br-B2 beryllium bronze, with a construction close to that previously described.[4] The pressure-transmitting medium was a mixture of transformer oil and dehydrated kerosene, which made it possible to obtain a highly uniform hydrostatic pressure at low temperatures.[5] At room temperature, the pressure in the vessel was measured with a manganin pickup calibrated against the secondary standard of the All-Union Research Institute of Physicotechnical and Radiotechnical Measurements. At 4.2 K the pressure was determined from the graduation curve of Ref. 5.

The TmES and LiTmF₄ crystals are very similar in their magnetic properties[6]: the ground state of the Tm³⁺ ion in the crystal electric field is in both cases a singlet $|s\rangle$, and the closest excited state is a doublet $|d\rangle$ separated from the singlet by an energy gap $E_d - E_s$ of the order 30 cm⁻¹. The Zeeman splitting of the nuclear energy levels of $^{169}$Tm (spin $I = 1/2$) is described for both crystals by the simple spin Hamiltonian

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

whose two parameters (the components of the paramagnetic shift of the NMR line) are proportional to the paramagnetic susceptibility of the medium and are consequently constant at low temperatures. The paramagnetic shift of the NMR line of $^{169}$Tm in a magnetic field perpendicular to the $c$ axis of the crystal is determined mainly by the two lower states of the $4f$ electron shell of the Tm³⁺ ion, so that at low temperatures we have

$$\alpha_{\perp}=(4g_J\mu_Ba_J/\gamma\hbar)\frac{|\langle s|J_x|d\rangle|^2}{E_d-E_s}; \tag{2}$$

where $g_J = 7/6$ and $a_J = -h \cdot 393.5$ MHz (Ref. 7) are the Landé factor and the hyperfine-interaction constant of the free Tm³⁺ ion, and $J_x$ is the $x$ component of the operator of the angular momentum of the $4f$ electron shell ($J = 6$). We observed values of $\alpha_{\perp}$ in TmES and LiTmF₄ (73.3 and 67.9, respectively) agree well with the calculated ones obtained using the known potentials of the crystal electric field in these compounds.[8,9]

The deformation of the crystal lattice under the influence of pressure leads to distortion of the crystal potential and consequently to a change of the energies and of the wave functions of the states of the $4f$ electrons, and to an additional shift of the NMR lines of $^{169}$Tm. Since these changes are small, they can be calculated by a perturbation method. Thus, if the compression does not disturb the symmetry of the crystal, and causes only a small increment $\delta C_n m$ of the crystal-field parameter $C_n^m$, then the paramagnetic shift to $\alpha_{\perp}(P)$ is described as before by formula

(2), in which we must now

$$(E_d - E_s)_P = (E_d - E_s) + [\langle d|\chi_n O_n{}^m|d\rangle - \langle s|\chi_n O_n{}^m|s\rangle]\delta C_n{}^m,$$

$$|s\rangle_P = |s\rangle + \delta C_n{}^m \sum_e \frac{\langle s|\chi_n O_n{}^m|e\rangle}{E_s - E_e}|e\rangle, \qquad (3)$$

$$|d\rangle_P = |d\rangle + \delta C_n{}^m \sum_e \frac{\langle d|\chi_n O_n{}^m|e\rangle}{E_d - E_e}|e\rangle.$$

Here $\chi_n$ is the corresponding Stevens coefficient, $O_n{}^m$ is an equivalent operator, and $|e\rangle$ are the unperturbed wave functions of the excited states of the $Tm^{3+}$ ion. Neglecting the corrections quadratic in $C_n{}^m$, we can obtain from (2) and (3) the dependence of the paramagnetic shift on the pressure in the form

$$\alpha_\perp(P) = \alpha_\perp(0)[1 + (\lambda_{nm}' - \lambda_{nm}'')\delta C_n{}^m/C_n{}^m], \qquad (4)$$

where $\lambda_{nm}'$ and $\lambda_{nm}''$ characterize respectively the contributions due to the change of the wave functions and to the shift of the energy levels.

Figure 1 shows the results of measurements of the paramagnetic shift $\alpha_\perp$ under hydrostatic compression in both crystals. Since these results differ greatly, we shall discuss them separately. The monotonic character of the $\alpha_\perp(P)$ dependence in TmES allows us to interpret the experimental data on the basis of the arguments presented above. The potential of the crystal electric field in TmES contains four parameters[8]: $C_2^0 = 30.5$ cm$^{-1}$, $C_4^0 = -65.9$ cm$^{-1}$, $C_6^0 = -28.6$ cm$^{-1}$, and $C_6^6 = 427.3$ cm$^{-1}$, which are subjected to the action of the pressure to different degrees. A rough estimate of the influence of the hydrostatic pressure on the crystal potential can be obtained by using the point-charge model.

Starting from the distinguishing structural features[10] of TmES (the thulium ions are arranged about 0.70 nm apart in chains along the crystallographic $c$ axis; the distance between the ions in neighboring chains is 0.87 nm), it is natural to assume that the compressibility of the crystal along the $c$ axis is less than the compressibility in the transverse direction. In the preliminary estimate of the influence of the pressure on the crystal potential in the point-charge model we have assumed for simplicity that the compressibility of the
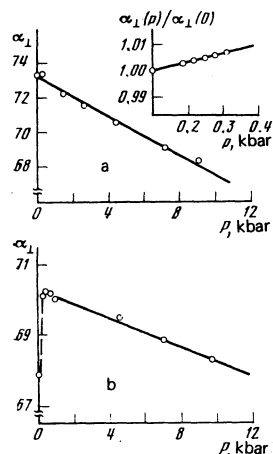
crystal along the $c$ axis is zero, and found that the most sensitive to the change of the interatomic distance is the crystal-field parameter $C_2^0$. This conclusion agrees with piezo-optical spectroscopy data on $Pr^{3+}$ ions in an LaES crystal.[11] Assuming further that the changes of the paramagnetic shift $\alpha_\perp$ with changing pressure are due to the change of $C_2^0$, we have calculated with the aid of (2) and (3) the coefficients in formula (4):

$$\lambda_{20}' = 0.094, \quad \lambda_{20}'' = 0.281 \qquad (5)$$

and obtained from a comparison of (4) with the measurement results (Fig. 1a) a relative increment $(\delta C_2^0/C_2^0)_P = +4.5\%$ kbar$^{-1}$. Finally, using the obtained value of $(\delta C_2^0/C_2^0)_P$, we estimated by the point-charge model the compressibility of the crystal in a direction perpendicular to the $c$ axis, and obtained a value $7.5 \times 10^{-3}$ kbar$^{-1}$, which does not contradict the available data on the compressibility of crystal hydrates.[12]

Since the point-charge model predicts correctly not only the sign but also the order of magnitude of the increment $(\delta C_2^0/C_2^0)_P$ in the TmES crystal under the influence of hydrostatic pressure, it is of interest to determine the anisotropy of the compressibility of this substance on the basis of measurements of the paramagnetic shift $\alpha_\perp$ as a function of the uniaxial pressure $p$ along the $c$ axis (upper inset in Fig. 1a). Assuming as before that the observed changes of $\alpha_\perp$ with changing pressure

$$\alpha_\perp(p) = \alpha_\perp(0)(1 + 1.60 \cdot 10^{-2} p[\text{kbar}]) \qquad (6)$$

are due only to a change in the parameter $C_2^0$, we have calculated $C_2^0$ by the point-charge model and found that relations (6) and (4) with the coefficient (5) are satisfied for a Poisson coefficient

$$\sigma = \varepsilon_{xx}/\varepsilon_{zz} = -0.1. \qquad (7)$$

In the calculation we have assumed, on the basis of data on the elastic properties of the related cerium-magnesium nitrate crystal,[13] a deformation along the $c$ axis $\varepsilon_{zz} = -2.5 \times 10^{-3}$ kbar$^{-1}$.

The dependence of the paramagnetic shift of the NMR



FIG. 1. Paramagnetic shift of the NMR line of $^{169}$Tm in the crystals TmES (a) and LiTmF$_4$ (b) under uniaxial pressure $p$ and hydrostatic pressure $P$.
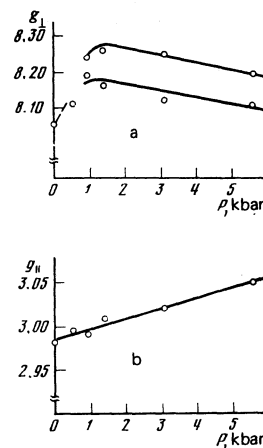


FIG. 2. Dependence of the $g$-factors of the ground-state doublet of the Er$^{2+}$ ions in an LiTmF$_4$ crystal on the hydrostatic pressure.
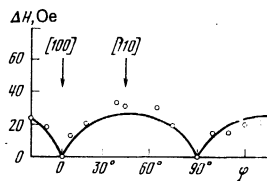
FIG. 3. Angular dependence of the splitting of the EPR line of $Er^{3+}$ ion in $LiTmF_4$ under hydrostatic compression; $H \perp c$, $P = 2.8$ kbar.

of $^{169}Tm$ in the $LiTmF_4$ crystal on the hydrostatic pressure (Fig. 1b) is anomalous and cannot be explained if it is assumed that its crystal-field parameters vary linearly with pressure. The abrupt increase of $\alpha_\perp$ at low pressures, accompanied by an increase in the line width from 13.5 Oe at $P = 0$ to 17.5 Oe at $P \gtrsim 0.2$ kbar,[1)] is evidence of a jumplike change of the crystal potential and forces us to assume that hydrostatic compression produces a structural phase transition in the $LiTmF_4$ crystal. The NMR data also allow us to assume that the transition is accompanied by a decrease of the symmetry of the crystal; favoring this assumption is the broadening (unresolved splitting?) of the NMR line of $^{169}Tm$ under pressure. In experiments with uniaxial pressure $p \leqslant 0.5$ kbar along the $c$ direction, we did not observe any changes of $\alpha_\perp$. This means that an important role in the structural transition is played by compression in the $ab$ plane.

Proof of the validity of our assumption concerning the structural phase transition was obtained by investigating the EPR spectra of impurity $Er^{3+}$ ions in an $LiTmF_4$ crystal (Fig. 2). It turned out that hydrostatic compression influences most strongly the ERP spectrum of $Er^{3+}$ in a magnetic field perpendicular to the crystal axis: at pressures above 1 kbar no hyperfine structure of the spectrum is seen, and the ground-state line is split into two components with an interval $\Delta H$ (the two values of $g_\perp$ in Fig. 2a). The dependence of $g_\perp$ on the pressure is nonmonotonic and correlates well with the $\alpha_\perp(P)$ dependence for the thulium nuclei. On the contrary, the quantity $g_\parallel$ changes with pressure linearly (Fig. 2b), and the EPR spectrum of $Er^{3+}$ retains a normal form up to $P = 5.9$ kbar. From the form of the EPR spectrum in the $H \perp c$ orientation it follows that at pressures $P > 1$ kbar the rare-earth ions occupy in the $LiTmF_4$ lattice two nonequivalent positions, and this in turn means that the symmetry of the crystal becomes lower than $I4_1/a$. The nonequivalence of the positions of the $ER^{3+}$ ions manifests itself clearly in the dependence of the splitting $\Delta H$ of the principal line on the orientation of the magnetic field relative to the crystallographic axes $a$ and $b$. It is seen from Fig. 3 that there is no

splitting (the spectra coincide) if the magnetic field is directed along $a$, and reaches a maximum in the [110] direction.

Although the available data are insufficient to draw a definite conclusion concerning the character of the structural phase transition in $LiTmF_4$, we are inclined to assume its most probable cause to be the cooperative Jahn-Teller effect.[14] An indirect confirmation of the strong spin-phonon coupling in the $LiTmF_4$ was obtained by us in a pulsed NMR experiment; it turned out that in the presence of a constant magnetic field $H \perp c$ the radiofrequency field pulse $H_1$ causes intense magnetostriction oscillations similar to those observed in strong magnets.[15]

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[1)]In TmES, the NMR line width of $^{169}Tm$, measured as the interval between the maximum and minimum of the absorption derivative, is approximately 5.5 Oe and is practically independent of the pressure right up to 9 kbar.

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