PROTON MAGNETIC RESONANCE IN THULIUM ETHYL SULFATE

M. A. TEPLOV

Kazan' State University

Proton magnetic resonance spectra in thulium ethyl sulfate are studied experimentally and theoretically. It is shown that the spread of the proton spectrum may reach several hundred Oersteds at liquid-helium temperature, despite the fact that the ground state of the Tm^{3+} ion in the crystal is not paramagnetic. The experimental results are explained on the basis of the dipole-dipole interaction between the protons and electrons of the 4f shell of the Tm^{3+} ion.

INTRODUCTION

MAGNETIC resonance on the H^1 and F^{19} nuclei in paramagnetic crystals have been the subject of many investigations, but the experiments performed hitherto were made on substances such that the ground state of the paramagnetic ion was an electronic spin doublet. Examples are the NMR experiments on protons in $CuSO_4 \cdot 5H_2O$[1] and $CuCl_2 \cdot 2H_2O$[2], and on the F^{19} nuclei in compounds of the type MnF_2[3], $KMnF_3$[4], and CeF_3[5]1). The NMR spectra observed in these experiments are characterized by a large spread (hundreds of Oresteds), this being attributed either to the dipole-dipole interaction of the investigated nuclei with the large magnetic moments of the paramagnetic ions[1,2] or to the contact interaction of the electron and nuclear spins[3-5].

A paramagnetic ion in a singlet state has a small magnetic moment and it may appear at first glance that in those compounds in which the ground state of the ion is nondegenerate[6-9] the energy of the dipole interaction between the ion and the surrounding nuclei should be much lower at low temperatures than in the examples presented above. Indeed, in praseodymium sulfate[6] the NMR lines of the protons of the water of crystallization has a form characteristic of diamagnetic crystals. However, our experimental investigation of the proton magnetic resonance spectra (PMR) in single-crystal thulium ethyl sulfate (TmES) has shown that such an assumption is not always valid.

We present in this article the results of this experiment and their theoretical analysis.

EXPERIMENT

Single crystals of $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$ were obtained by free evaporation of saturated aqueous solution at room temperature, and had the form of plates about 3 mm thick, elongated along the hexagonal axis. Samples in the form of washers were cut from the crystals in such a way that the symmetry axis z of the crystal field was in a horizontal plane, and the orienta-

tion of the external magnetic field relative to the z axis could be readily changed by rotating an electromagnet.

The PMR spectra were obtained with an autodyne spectrometer at temperatures 1.5, 4.2, and 77°K and at frequencies from 4 to 18 MHz. Typical PMR signals are shown in the figure (solid line). We note the characteristic features of the behavior of these spectra: at
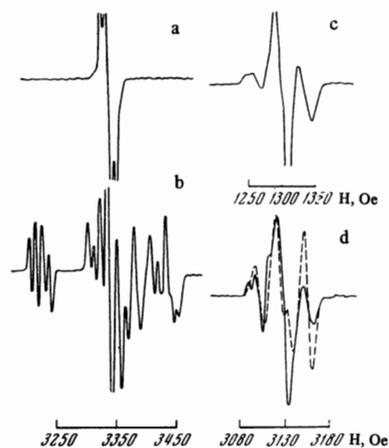
Proton resonance spectra in thulium ethyl sulfate, a) H‖z, T = 4.2°K, f = 14320 kHz; b) H⊥z, T = 4.2°K, f = 14230 kHz; c) H⊥z, T = 4.2°K, f = 5530 kHz; d) H⊥z, T = 77°K, f = 13325 kHz; the dashed line shows the calculated curve.

the orientation H ‖ z (see Fig. a), the spread of the spectrum is minimal (~20 Oe), and the shape of the curve is independent of the temperature; in the orientation H ⊥ z, the spread of the spectrum is maximal (see Fig. b) and is directly proportional to the applied magnetic field (see Fig. c), decreasing with increasing temperature (see Fig. d); the curves obtained at 1.5 and 4.2°K are practically indistinguishable.

DISCUSSION OF RESULTS

We shall attempt to explain the indicated features of the PMR spectrum in TmES single crystals as being due to only the dipole dipole interaction or protons with Tm^{3+} ions2), and will therefore retain in the Hamilton-

---

1)An exception in this series is praseodymium triflouride PrF_3 [5]. The low symmetry of the crystal field apparently leads to a complete lifting of the 9-fold degeneracy of the $^3H_4$ level; we recently succeeded in observing NMR of Pr^{141} on the ground-state singlet.

2)Calculations show that the maximum PMR line shift that can result from the dipole-dipole interaction of protons with Tm^{169} nuclei amounts to approximately 10 Oe.

ian of the "thulium-proton" system only the terms that are significant for the subsequent analysis

$$\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 = g\beta HJ + g_N\beta_N HI + \frac{gg_N\beta\beta_N}{r^3}\left[(JI) - \frac{3(Jr)(Ir)}{r^2}\right].$$

Here $\mathcal{H}_1$ and $\mathcal{H}_2$ are respectively the electronic and nuclear Zeeman terms, and $\mathcal{H}_3$ describes the dipole-dipole interaction of the proton with the rare-earth ion. Going over to the nuclear spin Hamiltonian for H^1 and using perturbation theory, up to the second approximation, for the determination of the corrections to the proton energy, we can write for any temperature T

$$\mathcal{H} = g_N\beta_N HI + \frac{\sum_m \exp(-E_m/kT)\exp(-g\beta\langle m|HJ|m\rangle/kT)\mathcal{H}^{(m)}}{\sum_m \exp(-E_m/kT)\exp(-g\beta\langle m|HJ|m\rangle/kT)}, \quad (1)$$

where

$$\mathcal{H}^{(m)} = \langle m|\mathcal{H}_3|m\rangle$$
$$+ \sum_n{}' \frac{\langle m|\mathcal{H}_1|n\rangle\langle n|\mathcal{H}_3|m\rangle + \langle m|\mathcal{H}_3|n\rangle\langle n|\mathcal{H}_1|m\rangle}{E_m - E_n}, \quad (2)$$

E_m are the energy levels of the ion with total angular momentum J in the crystal field, and $|m\rangle$ are the corresponding wave functions. The prime in (2) denotes that the term with index m is missing from the sum.

Expressions (1) and (2) are valid for any rare-earth ion. The level $^3H_6$ of the Tm^{3+} ion splits in the crystal field of the ethyl sulfate (symmetry point group C_{3h}) into five singlets and four doublets. An essential fact here is that a magnetic field applied perpendicular to the z axis does not split the doublets.

The Hamiltonian (1) can be represented in the form

$$\mathcal{H} = g_N\beta_N \sum_{j=x,y,z} (1-\Delta_j)H_j I_j. \quad (3)$$

We shall consider two particular cases.

1. The magnetic field is perpendicular to the crystal axis z ($H_x = H$, $H_y = H_z = 0$) and is parallel to the radius vector r joining the Tm^{3+} ion with the proton. After simple transformations we obtain for the parameter Δ_x in (3) the expression

$$\Delta_x = \frac{4(g\beta)^2}{r^3}\sum_m \exp\left(-\frac{E_m}{kT}\right)\sum_n{}' \frac{|\langle m|J_x|n\rangle|^2}{E_m - E_n}\Bigg/ \sum_m \exp\left(-\frac{E_m}{kT}\right). \quad (4)$$

It follows from (3) and (4) that in the case of the orientation $H \perp z$ the swing of the PMR spectrum is proportional to the constant magnetic field.

2. The magnetic field is parallel to the crystal axis z ($H_x = H_y = 0$, $H_z = H$) and is parallel to the radius vector r. In this case

$$\Delta_z = \frac{2g\beta}{r^3 H}$$

$$\times \frac{\sum_m \exp(-E_m/kT)\exp(-g\beta H\langle m|J_z|m\rangle/kT)\langle m|J_z|m\rangle}{\sum_m \exp(-E_m/kT)\exp(-g\beta H\langle m|J_z|m\rangle/kT)}$$

$$+ \frac{4(g\beta)^2}{r^3}\sum_m \exp\left(-\frac{E_m}{kT}\right)\sum_n{}' \frac{|\langle m|J_z|n\rangle|^2}{E_m - E_n}\Bigg/\sum_m \exp\left(-\frac{E_m}{kT}\right). \quad (5)$$

For numerical estimates we have used the system proposed in[10] for the energy levels and wave functions of the Tm^{3+} ions in the crystal field of the ethyl sulfate (see the table).

Level number	Energy, cm^{-1}	Wave function
8	300.1	$-0.707\,|-3\rangle+0.707\,|+3\rangle$
7	273.6	$\{-0.446\,|-2\rangle+0.895\,|+4\rangle$
		$\ \ 0.895\,|-4\rangle-0.446\,|+2\rangle$
6	221.0	$0.697\,|-6\rangle-0.168\,|0\rangle+0.697\,|+6\rangle$
5	214.8	$-0.707\,|-6\rangle+0.707\,|+6\rangle$
4	198.1	$\{-0.305\,|-1\rangle+0.953\,|+5\rangle$
		$\ \ -0.953\,|-5\rangle+0.305\,|+1\rangle$
3	157.1	$0.707\,|-3\rangle+0.707\,|+3\rangle$
2	114.0	$\{0.895\,|-2\rangle+0.446\,|+4\rangle$
		$\ \ 0.446\,|-4\rangle+0.895\,|+2\rangle$
1	31.3	$\{0.305\,|-5\rangle+0.953\,|+1\rangle$
		$\ \ 0.953\,|-1\rangle+0.305\,|+5\rangle$
0	0	$0.119\,|-6\rangle+0.986\,|0\rangle+0.119\,|+6\rangle$

The good approximation of the crystal-field model in TmES[10] was confirmed once more by NMR experiments on Tm^{169} in this crystal[8]. Calculations based on formulas (4) and (5) for two fixed temperatures show that $\Delta_x/\Delta_z \sim 200$ at T = 4.2°K and $\Delta_x/\Delta_z \sim 15$ at T = 77°K.

Thus, at low temperatures, the local field produced by the electronic of shell of the Tm^{3+} ion at the neighboring protons, and consequently also the entire spread of the proton spectrum is much larger than at the orientation $H \perp z$ at the orientation $H \parallel z$. This is confirmed by our experiment (Figs. a and b) and is due to the fact that the doublet state

$$0,305\,|-5\rangle + 0.953\,|+1\rangle$$
$$0.953\,|-1\rangle + 0.305\,|+5\rangle,$$

which makes the main contribution to the local field when $H \perp z$ lies quite close to the ground state.

It is seen from the table that at temperatures 1.5 and 4.2°K only the lower singlet level is populated in practice, and therefore the PMR spectra should be identical at these temperatures.

The protons belonging to the ethyl groups and to the molecules of the water of crystallization occupy in the unit cell of the ethyl sulfate different positions relative to the rare earth ion, and are therefore in different local fields. As a result we observe the PMR spectrum in lieu of one line.

Let us calculate now the form of the PMR spectrum for the magnetic-field orientation $H_0 \parallel x$. Let the Tm^{3+} ion be at the origin of a spherical coordinate system, let it be surrounded by K protons, and let r_i, ϑ_i and φ_i be the coordinates of the i-th proton. By the same procedure as for the single "thulium-proton" pair, we obtain the Hamiltonian for a system of K protons:

$$\mathcal{H}_x = g_N\beta_N H_0 \sum_{i=1}^K \left[I_{ix} + \frac{2(g\beta)^2}{r_i^3}\Lambda(a_i I_{ix} + b_i I_{iy} + c_i I_{iz})\right], \quad (6)$$

where

$$a_i = 1 - 3\sin^2\vartheta_i\cos^2\varphi_i, \quad b_i = -3\sin^2\vartheta_i\sin\varphi_i\cos\varphi_i,$$
$$c_i = -3\sin\vartheta_i\cos\vartheta_i\cos\varphi_i,$$

$$\Lambda = \left[\sum_m{}' \exp\left(-\frac{E_m}{kT}\right)\right]^{-1}\sum_m \exp\left(-\frac{E_m}{kT}\right)\sum_n{}' \frac{|\langle m|J_x|n\rangle|^2}{E_m - E_n}. \quad (7)$$

The eigenvalues of the Hamiltonian (6) are determined by the equations

$$\varepsilon_i^2 = \left(\frac{g_N\beta_N H_0}{2}\right)^2\left[1 + \frac{4(g\beta)^2}{r_i^3}\Lambda a_i + \frac{4(g\beta)^4}{r_i^6}\Lambda^2(a_i^2 + b_i^2 + c_i^2)\right]. \quad (8)$$

It follows from simple estimates that the terms containing the operators I_{iy} and I_{iz} in (6) make a small

contribution to the proton energy (8), so that Eq. (6) can be rewritten in the simple form:

$$\mathcal{H}_x = g_N\beta_N H_0 \sum_{i=1}^{K}\left[\ 1 + 2(g\beta)^2\Lambda\frac{a_i}{r_i^{\cdots}}\ \right]I_{ix}.$$

The resonant field of the i-th proton is then equal to

$$H_i = H_0\left[1 - 2(g\beta)^2\Lambda\frac{a_i}{r_i^3}\right], \qquad (9)$$

and if $G(H - H_i)$ is the line-shape function, then the absorption curve is given by

$$f(H) = \sum_{i=1}^{K} G(H - H_i). \qquad (10)$$

The crystal structure of the ethyl sulfates of rare earths was investigated by Ketelaar[11], but the positions of the C_2H_5 radicals and of the H_2O molecules were not determined exactly. This does not allow us to assign exact values to the quantities a_i and r_i in (9). However, Ketelaar noted that the nine water molecules constitute the nearest surrounding of the rare-earth ion and proposed a probable model for the surrounding of the Ce^{3+} ion. From this model, assuming that the parameters of the thulium ethyl sulfate unit cell are $a_0 = 13.875$ Å and $c_0 = 7.02$ Å, we obtain the positions of the nine oxygen atoms belonging to the nine molecules of the water of crystallization: three oxygen atoms in the plane containing the Tm^{3+} ion at $(R_1, \pi/2, \varphi)$, where $R_1 = 2.46$ Å and $\varphi = 0, 2\pi/3$, and $4\pi/3$; three oxygen atoms at $(R_2, \vartheta, \varphi)$ and three oxygen atoms at $(R_2, \pi - \vartheta, \varphi)$, where $R_2 = 2.53$ Å, $\vartheta = 40.5°$, and $\varphi = \pi/3, \pi$, and $5\pi/3$.

Inasmuch as the distances from the Tm^{3+} ion to the protons of the ethyl group is larger than the distance to the protons of the water of crystallization, certain important characteristics of the PMR spectrum, viz., the positions of the outermost lines and the total spread of the spectrum, will apparently be determined only by the coordinates of the water of crystallization. Disregarding the ethyl-group protons, we calculated the form of the derivative of the PMR spectrum under the following assumptions: the "triangles" of H_2O molecules lie in planes perpendicular to the z axis, the protons of one molecules being equidistant from the Tm^{3+} ion, the H—H distance inside the molecule equals 1.58 Å (as in gypsum), and the HOH angle equals 108°; the constant magnetic field is perpendicular to the z axis ($H_0 \parallel x$) and is oriented along one of the three Tm—O directions; the NMR line of a single proton has a Gaussian shape, and the distance between the maximum and minimum of its derivative equals 10 Oe.

From calculations by means of formulas (7), (9),

and (10) for $T = 4.2°K$ and $f = 14230$ kHz it follows that the distance between the outermost lines of the PMR spectrum should be 226 Oe, whereas experiment yields (see Fig. b) 238 Oe. In accordance with the foregoing estimates, the local field produced by the Tm^{3+} ion at the protons, at $T = 4.2°K$ and $H_0 \parallel z$, amounts to approximately 1/200th of the local field in the $H_0 \perp z$ orientation. The cause of the splitting of the PMR lines in the $H_0 \parallel z$ orientation (see Fig. a) is therefore probably the dipole-dipole interaction of the protons with one another. The calculated curve for $T = 77°K$ and $f = 13325$ kHz is shown by the dashed line in Fig. d, together with the corresponding experimental curve.

The good agreement between the experimental and the theoretical results, obtained under rather arbitrary assumption, leads to the following conclusion: The characteristics of the PMR spectra in single-crystal thulium ethyl sulfate can be obtained from an analysis of the dipole-dipole interaction of the protons surrounding the Tm^{3+} ion with its unfilled 4f shell.

Its seems natural to pose the inverse problem, that of determining the exact positions of the protons with the aid of the PMR spectrum. However, the large number of protons (33 per ethyl sulfate molecule) makes this an exceedingly laborious task.

[1] N. Bloembergen, Physica 16, 95 (1950).

[2] N. J. Poulis and G. E. C. Hardeman, Physica 18, 201 (1952).

[3] R. G. Shulman and V. Jaccarino, Phys. Rev. 108, 1219 (1957).

[4] R. G. Shulman and K. Knox, Phys. Rev. 119, 94 (1960).

[5] S. P. Gabuda, A. G. Lundin, Yu. V. Gagarinskiĭ, L. R. Batsanova, and L. A. Khripin, Zh. Eksp. Teor. Fiz. 51, 707 (1966) [Sov. Phys.-JETP 24, 469 (1967)].

[6] M. A. Teplov, Zh. Eksp. Teor. Fiz. 53, 1510 (1967) [Sov. Phys.-JETP 26, 872 (1968)].

[7] E. D. Jones, Phys. Rev. Lett. 19, 432 (1967).

[8] M. A. Teplov, Fiz. Tverd. Tela 10, 2548 (1968) [Sov. Phys.-Solid State 10, 2009 (1969)].

[9] E. D. Jones, J. Phys. Chem. Solids, in print.

[10] R. G. Barnes, R. L. Mossbauer, E. Kankeleit, and J. M. Poindexter, Phys. Rev. 136, A175 (1964).

[11] J. A. A. Ketelaar, Physica 4, 619 (1937).