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MAGNETIC RESONANCE ON Pr^{141} *NUCLEI IN A* $Pr_2(SO_4)_3 \cdot 8H_2O$ *SINGLE CRYSTAL*

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Nuclear magnetic resonance of Pr^{141} in a $Pr_2(SO_4)_3 \cdot 8H_2O$ single crystal is studied experimentally. It is shown that the NMR spectra can be described by the nuclear spin Hamiltonian (1) with the values of coefficients of Eq. (4). The quadrupole interaction parameters are determined (5). The experimental method is described and the results are discussed.

1. INTRODUCTION

In 1956, Zaripov[1] proposed to investigate transitions between nuclear sublevels of singlet electronic levels of paramagnetic ions and showed that the results of such investigations can yield information on the magnetic-dipole and the electric-quadrupole moments of the nucleus, and also on the wave functions of the excited states. Subsequently Elliott[2] published calculations of the Zeeman splitting of the energy levels of the Eu^{3+} ion (ground state $^7F_0$) in the crystal field of ethyl sulfate. It followed from the calculations that, owing to the contribution from the excited states ($^7F_1$), the magnetic moment of the nucleus decreases strongly, to approximately 10% of its real value, and therefore the experiment entails considerable difficulties.

The possibility of observing NMR on simple electronic levels of ions of the 3d and 4f groups was discussed in subsequent theoretical papers;[3-6] calculations performed for a number of concrete cases pointed to the feasibility of organizing an experiment aimed at observing this effect. The conclusions of the theory were experimentally confirmed in investigations of the ion V^{3+} in corundum[7, 8] and of the ion Pr^{3+} in praseodymium sulfate.[9]

In this article we describe procedures for an experimental study of the magnetic-resonance spectra of the nuclei Pr^{141} in single-crystal $Pr_2(SO_4)_3 \cdot 8H_2O$, and discuss the results.

Already back in the thirties, measurements of the magnetic susceptibility of crystalline powder $Pr_2(SO_4)_3 \cdot 8H_2O$, performed by Gorter and by de Haas, have shown that the lower electronic level is nondegenerate.[10] This circumstance, as well as the relative simplicity of obtaining single crystals of praseodymium sulfate,[11] induced us to choose this compound for our study. The symmetry class of this crystal is monoclinic-prismatic and the unit cell contains four molecules.[11] We observed in the experiment the NMR spectra of two types of Pr^{3+} ions; the magnetic properties of the ions of both types are described by the same spin Hamiltonian, but the principal axes of the γ tensors are rotated relative to each other.

The ground multiplet level $^3H_4$ of the Pr^{3+} is split by a crystal field of low symmetry in such a way that the lower Stark sublevel is singlet. The remaining degeneracy with respect to the nuclear spin ($I = {}^5\!/_2$) is partly lifted by the hyperfine and quadrupole interactions and fully lifted by the magnetic field. A study of the transitions between these nuclear sublevels was indeed the purpose of the present work.

To interpret the results we use the spin-Hamiltonian method.[1, 2] We choose as the basis states the eigenstates of the Hamiltonian of the Pr^{3+} ion in a crystal field of rhombic symmetry, the perturbation Hamiltonian taking the form

$$\hat{V} = g\beta \mathbf{HJ} + a\mathbf{JI} + g_N\beta_N \mathbf{HI} + P[I_z^2 - {}^1\!/_3 I(I+1) + {}^1\!/_3 \eta (I_x^2 - I_y^2)],$$

where a is the hyperfine interaction constant, P the quadrupole-coupling constant, $\eta = (\varphi_{xx} - \varphi_{yy})/\varphi_{zz}$ is the asymmetry parameter, and φ_{xx}, φ_{yy}, and φ_{zz} are the components of the tensor of the gradient of the electric field at the nucleus.

The sought spin Hamiltonian is written in the form

$$\mathcal{H} = \gamma_x H_x I_x + \gamma_y H_y I_y + \gamma_z H_z I_z + D[I_z^2 - {}^1\!/_3 I(I+1)] + E(I_x^2 - I_y^2). \tag{1}$$

The first and second perturbation-theory approximations lead to the following expressions for the spin-Hamiltonian parameters:

$$D = D_a + P, \quad E = E_a + \eta P/3,$$
$$D_a = a\left(\frac{\Lambda_{xx} + \Lambda_{yy}}{2} - \Lambda_{zz}\right), \quad E_a = a\frac{\Lambda_{yy} - \Lambda_{xx}}{2}, \tag{2}$$

Here

$$\gamma_i = (g_N\beta_N - 2g\beta\Lambda_{ii})/h.$$

$$\Lambda_{ii} = \sum_{n \neq 0} \frac{a|\langle 0|J_i|n\rangle|^2}{\mathcal{E}_n - \mathcal{E}_0}, \tag{3}$$

$\mathcal{E}_n$ and $|n\rangle$ are the energy and wave function of the n-th level, and $\langle 0|$ is the wave function of the singlet under consideration. It is easy to note that in the absence of quadrupole interaction, only three out of the five spin-Hamiltonian parameters are independent.

2. EXPERIMENT

In view of the fact that the investigated crystal could not be oriented in the proper manner prior to the experiment, it was convenient to use a device which made it possible to rotate the sample inside the radio-frequency coil. By rotating the sample about the horizontal axis and rotating the electromagnet in the horizontal plane, it was possible to make the constant magnetic field parallel to any direction in the crystal.

All the measurements were made at a temperature 1.5°K with an autodyne video spectroscope (the Pound-Knight scheme). The spectra were plotted at frequencies from 4 to 24 MHz in fields up to 8500 Oe. It turned out that the case of intermediate fields, which is the most difficult to interpret, is realized under these conditions. The spectra were interpreted by the methods used in EPR (see, for example, [12]), and the sixth-order matrices were diagonalized with the aid of an electronic computer.

For the spin-Hamiltonian constants we obtained the following numerical values:

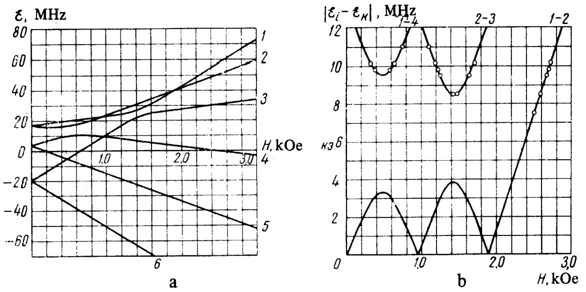
$$|\gamma_x| = 4{,}64 \pm 0{,}05 \text{ kHz/Oe} \; |\gamma_y| = 2{,}71 \pm 0{,}01 \text{ kHz/Oe} \quad (4)$$
$$|\gamma_z| = 12{,}35 \pm 0{,}15 \text{ kHz/Oe} \; |D| = 5865 \pm 5 \text{ kHz} \quad |E| = 730 \pm 1 \text{ kHz}$$

Figure 1a shows the nuclear energy levels in the orientation H ∥ z for negative values of D and E, while Fig. 1b shows the corresponding plots of the transition frequency against the magnetic field; the circles denote the experimental points.[1] The determination of the crystal axes is made difficult in our case by such specific peculiarities of the phenomenon in question as the weak intensity of the absorption line and the large anisotropy of the γ factor. We shall describe in this connection the procedure used to find the principal orientations.

The y orientation can be easily determined, since the γ factor has in this case a smaller absolute value than for the other two, and the resonant fields for strong-field transitions assume maximal values in the vicinity of y.

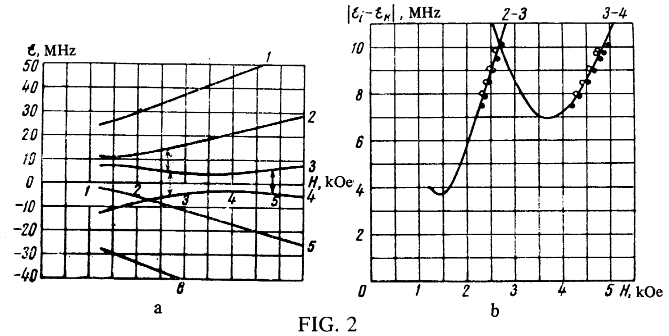
To determine the x orientation, we used the strong-field y line; this line has a maximum intensity in the xy plane, the x orientation corresponding to the minimum of the resonant field of the transition in question in this plane.

The search for the z orientation was effected in two stages. We first determined roughly the value of $|\gamma_z|$ form the form of the spectrum in oblique orientation, belonging to the yz line. We then established by calculation the transitions for which the resonant fields are most sensitive to variations of the angle in the vicinity of z. It turned out here that, in spite of the expectations, the resonant field of the transition 1 – 2 (Fig. 1) can have here a saddle point, whereas the resonant field of the 2 – 3 transition has a minimum for the weak-field branch and a maximum for the strong-field branch. The exact position of the z axis was determined with the aid of the 2 – 3 transition.



a b

FIG. 1



a b

FIG. 2

During the course of the study of the spectra we observed the following fact: a certain direction ξ in the crystal, which did not coincide with any of the principal directions of both complexes, has that property that when H ∥ ξ the resonant fields of the observed lines have a clearly pronounced maximum. It turned out subsequently that this direction belongs to the yz plane of one of the complexes, and that the angle between y and ξ is equal to 12°30' ± 30'. The form of the spectrum in the ξ orientation was used for a preliminary rough determination of $|\gamma_Z|$. Figure 2a shows the course of the energy levels, when a magnetic field was directed along ξ; the calculations were made for $|\gamma_Z| = 12.0$ kHz/Oe. Figure 2b illustrates the dependence of the frequency of the transitions noted in Fig. 2a by the arrows, on the magnitude of the magnetic field. We shall return later to a discussion of some of the peculiarities of these figures.

We note an interesting detail. The strong-field line in the y orientation reveals, upon closer examination, a structure consisting of a central line and two symmetrically located satellites of lower intensity, the distance between satellites being on the order of 30 Oe. The structure of the line can be observed in the xy plane, but the least deviation in the z direction (~0.5°) causes it to disappear immediately. We were unable to find a satisfactory explanation for the observed splitting of the line into three components.

3. DISCUSSION OF RESULTS

1. According to [13], the magnetic moment of the Pr^{141} nucleus is $\mu_N = +4.28\beta_N$; we therefore obtain for the gyromagnetic ratio

$$_{\text{nuc}} = \mu_N / hI = +1.31 \text{ kHz/Oe}$$

Inasmuch as the hyperfine interaction constant is positive ($a = -1093$ MHz[13]), the sums Λ_{ii} (3) are also positive and the values of the γ factors in the algebraic sense should be smaller than the purely nuclear value γ_{nuc}. But it follows from the experiment that γ_i is larger in absolute magnitude than γ_{nuc}; we therefore conclude that the spin-Hamiltonian constants γ_x, γ_y, and γ_z are negative, i.e.,

$$\gamma_x = -4.64 \pm 0.05 \text{ kHz/Oe} \; \gamma_y = -2{,}71 \pm 0{,}01 \text{kHz/Oe}$$
$$\gamma_z = -12.35 \pm 0.15 \text{ kHz/Oe}$$

The pseudoquadrupole-interaction constants are then found to be (see (2)):

$$D_a = -4230 \pm 100 \text{ kHz}, \; E_a = -470 \pm 20 \text{ kHz}.$$

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[1] We have omitted experimental points due to the presence of nonequivalent ions.

Comparison of these two quantities with the constants D and E, which were determined from experiment, shows an appreciable discrepancy; we ascribe this discrepancy to the presence of quadrupole interaction. Thus, it becomes possible to determine, albeit indirectly, the quadrupole-interaction constants. However, inasmuch as the signs of the experimental parameters D and E are unknown, the next step should be some assumption concerning the relative magnitudes of the true and pseudoquadrupole interactions. Recognizing that the quadrupole moment of the nucleus is quite small ($Q = -0.0589$ b[13]), we propose that the first of the compared quantities is smaller than the second. This assumption is confirmed in the case of praseodymium ethyl sulfate, where the pseudoquadrupole interaction is several times larger than the true one.[14]

It follows from the foregoing that the signs of the experimental parameters D and E should coincide with the signs of D_a and E_a, i.e.,

$$D = -5865 \pm 5 \text{ kHz}, \quad E = -730 \pm 1 \text{ kHz}.$$

For the quadrupole-coupling constant P and for the asymmetry parameter η we then obtain the following numerical values:

$$P = -1635 \pm 100 \text{ kHz}, \quad \eta = 0.477 \pm 0.070. \tag{5}$$

2. Although it has been experimentally proved that the assumption that the crystal field of praseodymium sulfate has cubic symmetry is incorrect, it is nevertheless of interest to calculate the γ factor with the aid of the cubic-field potential, since it describes very well the behavior of the static susceptibility of the $Pr_2(SO_4)_3 \cdot 8H_2O$ powder at low temperatures.[10] In accordance with [10], only operators of the fourth degree are taken into account in the potential of the crystal field, and the total Stark splitting of the $^3H_4$ level is 389 cm^{-1}. Recognizing that the contribution to the γ factor of the singlet ground state is made only by the nearest triplet, we write out[15] the wave functions of the states under consideration:

$$\begin{aligned} \Gamma_1 &\to 0.4564|4\rangle + 0.7638|0\rangle + 0.4564|-4\rangle, \\ \Gamma_4 &\to 0.3536|\pm 3\rangle + 0.9354|\mp 1\rangle, \\ &\quad 0.7071|4\rangle - 0.7071|-4\rangle. \end{aligned} \tag{6}$$

The level Γ_4 lies higher than Γ_1 by 100 cm^{-1}.

Calculation by means of formulas (2) and (3) with allowance for (6) yields $\gamma_{cub} = -4.07$ kHz/Oe. Comparing γ_{cub} with the γ factors obtained from experiment, we note that γ_{cub} approaches in absolute magnitude the mean value of the three values γ_x, γ_y, and γ_z, and agrees with them in sign.

3. We call attention to the following two facts in Fig. 2b.

a) In the ξ orientation we do not see the second branch of the strong-field line (dashed arrow on Fig. 2a). Computer calculations have shown that the probabilities of transitions between levels 3 and 4 in the weak-field branch are smaller by a factor 5–10 than in the strong-field branch. If we take into consideration the fact that the line corresponding to the strong-field branch of the transition 3–4 is observed at a signal/noise ratio on the order of 5, the absence of a weak-field line can be attributed simply to its insufficient intensity.

b) The experimental points denoted in Fig. 2b by light and filled circles, pertain to two different orientations, ξ_+ and ξ_-, which differ from each other in the fact that one of them is obtained by deflection from the y axis in the +z direction and the other in the −z direction. The observed difference in the spectra ($\Delta H \sim 150$ Oe for $H_{res} = 4500$ Oe) certainly is beyond the limits of possible experimental errors, and cannot be explained if the allowance for the contribution to the magnetism of the ground state from the excited electronic states is confined only to corrections of second order of perturbation theory.

If fourth-order corrections are taken into account,[2)] then the observed anomaly can be explained, for example, as being due to the presence in the spin Hamiltonian of an operator in the form O_4^3 with a rather large coefficient. However, numerical estimates show that a more probable cause of the difference between the spectra is apparently the appearance in the spin Hamiltonian of terms of the type $\alpha H_i^2 H_k I_i$. Such terms introduce in the γ factors corrections that depend on the orientation of the magnetic field. These corrections are of the order of $(g\beta HJ)^3 aK/(\Delta\mathscr{E})^3$, where K is the coefficient that takes into account the summation of the products of different matrix elements $\langle m|J_k|n\rangle$; the number of terms in the sum depend on the concrete form of the wave functions and may be large, particularly for triclinic symmetry of the crystal field. Assuming $K \sim 10^2$ and $\Delta\mathscr{E} \sim 100$ cm^{-1}, we find that the fourth-approximation corrections to the γ factors can amount to 1/100 of the main quantity. In addition, the fourth-order approximation contributes to the energy of the pseudoquadrupole interaction, and the corrections also depend on the orientation of the magnetic field.

In conclusion we note that the results of the experiment indicate a low symmetry of the crystal field in single-crystal $Pr_2(SO_4)_3 \cdot 8H_2O$, but do not make it possible to determine whether the symmetry is rhombic or triclinic.

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