JETP LETTERS VOL 5, NO 7 1 APRIL 1967

NUCLEAR MAGNETIC RESONANCE AT SIMPLE ELECTRONIC LEVELS OF RARE EARTH IONS

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Submitted 23 December 1966
JETP Pis'ma 5, No. 6, 209-212 (1 April 1967)

Magnetic resonance at paramagnetic-ion nuclei whose ground state in the crystalline field is an electronic spin singlet is discussed in [1-4]. An experimental confirmation of the theoretical deductions was obtained so far only in one case, in an investigation of the ion V^{3+} in corundum [5]. The absence of the EPR effect in a large number of crystals containing rare-earth ions with an even number of electrons gives grounds for assuming that the lower state is here, too, singlet and that magnetic resonance can be observed for the rare-earth ion nuclei. Owing to the large values of the hyperfine structure constant and of the total angular momentum J in crystals with rare-earth ions, the influence of the excited levels on the ground level should be more noticeable than in the iron group, and the effect of absorption of radio frequency energy should be stronger. The absorption spectra contain in these cases information concerning the excited states, which, together with the information obtained from optical spectroscopy, may turn out to be quite valuable in determining the system of energy levels of the ions in the crystal and the parameters of the crystalline field.

We report in this note observation of magnetic resonance for Pr^{141} nuclei in single-crystal praseodymium sulfate octahydrate $Pr_2(SO_4)_3 \cdot 8H_2O$. Praseodymium sulfate is a monoclinic crystal [6]. Experiment shows that each unit cell contains two magnetically equivalent but differently oriented complexes. The crystalline field (which is apparently rhombic or of lower symmetry) lifts the degeneracy of the ground level $^3H_4(4f^2)$ in such a way that the lower level turns out to be simple; this is confirmed by the absence of the EPR effect. Owing to the hyperfine interaction, the presence of closely-lying excited levels lifts the sixfold degeneracy (in the nuclear spin) of the lower Stark sublevel to doublets. A noticeable role is played here apparently also by quadrupole interaction. The measurements were made with an autodyne video spectroscope at 1.5°K. To ensure that the crystalline axes were aligned with the direction of the constant magnetic field, a system was constructed for vertically rotating the crystal inside the radio frequency coil. According to the measurements, the spacings in zero field are:

$\pm 1/2 \leftrightarrow \pm 3/2$ transition: 13 390 ± 10 kHz,

$\pm 3/2 \leftrightarrow \pm 5/2$ transition: 22 860 ± 20 kHz.

We used frequencies from 4 to 24 MHz and varied the magnetic field from 0 to 8500 Oe. These conditions correspond to the most difficult case, that of intermediate fields. The interpretation of the spectra in different orientations reduced to a diagonalization of 6-th order matrices; the calculations were made with an electronic computer. The results of [7] turned out to be very useful for the results of preliminary estimates.

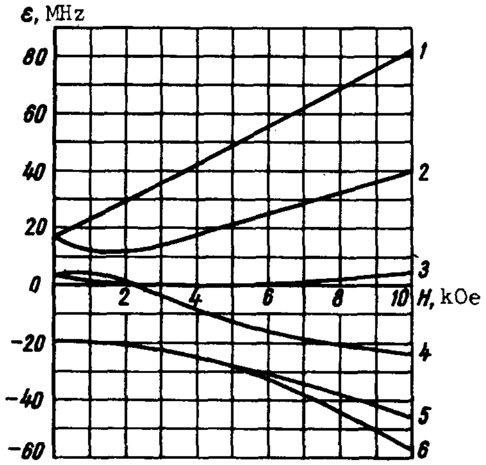

Fig. 1. Plot of $|\epsilon_i - \epsilon_k|$ vs. H for $Pr_2(SO_4)_3 \cdot 8H_2O$; H ∥ γ, $|\gamma_y| = 2.71$ kHz/Oe. Lines - theory, circles - experiment.

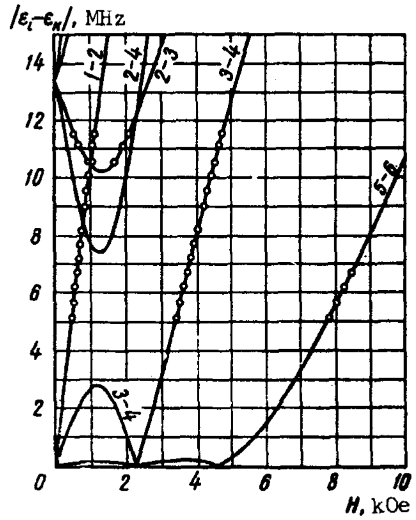

Fig. 2

Summarizing the preliminary experimental data reduction, we can state that the spectrum is described by a spin Hamiltonian of the form:

$$\mathcal{H} = \gamma_x H_x I_x + \gamma_y H_y I_y + \gamma_z H_z I_z + D[I_z^2 - 1/3I(I+1)] + E(I_x^2 - I_y^2),$$

where $|\gamma_x| = 4.640 \pm 0.050$ kHz/Oe, $|\gamma_y| = 2.710 \pm 0.010$ kHz/Oe, $|\gamma_z| = 12.0 \pm 2.0$ kHz/Oe, $|D| = 5865 \pm 5$ kHz, and $|E| = 730 \pm 1$ kHz. The figures illustrate the method of determining the spin-Hamiltonian constants: Figure 1 shows the symmetry of the nuclear energy levels in the "y" orientation *, and Fig. 2 shows the plots of the frequencies of the various transitions against the magnetic field. The numbering of the energy levels makes it easy to find the required transition in Fig. 2.

The magnetic moment of the Pr^{141} nucleus is +4.28 nuclear magnetons [8], and the gyromagnetic ratio γ_{nuc} is +1.310 kHz/Oe. From a comparison of the latter quantity with the γ factors given above it follows that the contribution of the electronic magnetism to the diamagnetic ground state is quite large here. The rather strong anisotropy of the γ factor prevents a more accurate determination of $|\gamma_z|$.

A detailed discussion of the procedure and results of the experiment will be published later.

In conclusion, the authors are grateful to O. I. Mar'yakhina for help in reducing the experimental data and L. A. Sherbakova for preparing the crystal.

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* In the diagonalization of the spin Hamiltonian we have assumed that the constants D and E are negative.

ERRATA

In the article by S. A. Al'tshuler and M. A. Teplov, Vol. 5, No. 7, p. 168, the caption of Fig. 1 belongs to Fig. 2.