Nuclear acoustic resonance of Pr^{141} in a F_3 Van Vleck paramagnet

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Observations are given for the first time for the nuclear acoustic resonance of Pr^{3+} ions in the singlet ground electronic state in a PrF_3 crystal. The experiment was carried out at 4.2 K using ~21 and ~36 MHz ultrasonic frequencies.

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Earlier studies of pulsed nuclear magnetic resonance (NMR) in a number of Van Vleck paramagnets earlier have shown[1] that, in the spin-lattice relaxation of paramagnetic ion nuclei at liquid helium temperatures and higher, two-phonon relaxation processes by excited Stark levels in paramagnetic ions play a dominant role. The participation of a paramagnetic ion unfilled electron shell in nuclear relaxation is not unexpected, since nuclear relaxation transitions may be induced by hyperfine magnetic field fluctuations produced by the perturbing effect of lattice vibrations on electron orbital motion. It would naturally be expected that, in the relaxation of paramagnetic ion nuclei with a singlet ground state at low temperatures, as in electron spin-lattice relaxation, a single-phonon (direct) process occurs. However, numerical values[2] of the single-phonon relaxation rate T_{1d}^{-1} give a value on the order of 10^{-11} sec^{-1} at liquid helium temperatures, and leave no hope for the possibility of observing such a slow relaxation process in actual crystal which always contain an admixture of rapidly-relaxing paramagnetic ions. Under these conditions, the nuclear acoustic resonance technique[3] is suitable for studying nuclear spin-phonon interactions. Resonance absorption of ultrasound is essentially the reverse of magnetic relaxation which occurs by single-phonon processes. Therefore, to obtain an approximate value for the absorption of sound α we may use the equation[4]

$$\alpha = \frac{h^2 N v^2 g(\nu)}{16\pi (kT)^2} T_{1d}^{-1}, \qquad (1)$$

in which N is the paramagnetic ion density, v is the speed of sound, $g(\nu)$ is the resonance line shape function, and T_{1d}^{-1} is the single-phonon relaxation rate. Substituting typical values of the Van Vleck parameters in this equation $N \sim 10^{22}$ cm^{-3}, $v \sim 5 \times 10^5$ cm/sec, $g(\nu) \approx (1/\Delta\nu) \sim 10^{-5}$ sec, for $T = 4.2$ K, we obtain the completely determined value $\alpha \sim 10^{-6}$ cm^{-1}.

In this paper we report the detection of nuclear acoustic resonance (NAR) of Pr^{141} (nuclear spin $I = 5/2$) in a PrF_3 monocrystal at a temperature of 4.2 K. Praseodymium trifluoride and also lanthanum trifluoride crystallize in a hexagonal system.[5] The low-symmetry crystalline electric field splits the ground multiplet level in the Pr^{3+}

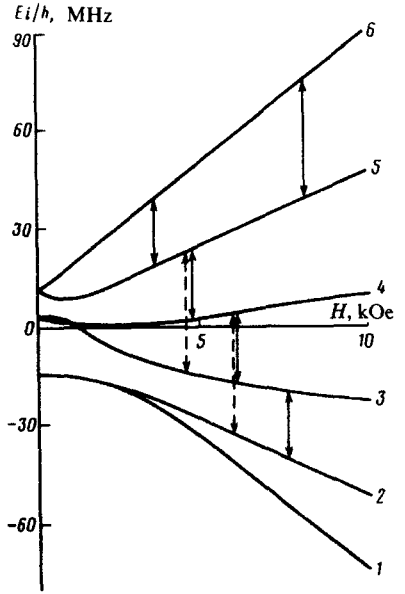

FIG. 1. Nuclear energy levels for Pr^{141} in a PrF_3 crystal in a magnetic field $H \| c$.

ion ($4f^2, {}^3H_4$) into nine singlets. According to neutron spectroscopy data,[6] the closest excited Stark levels in the Pr^{3+} ions are separated from the ground state singlet by 59.5 and 69.1 cm^{-1} energy intervals. The study of NMR spectra in Pr^{141} at a temperature of 4.2 K showed that Pr^{3+} ions in the crystal occupy three magnetically-nonequivalent positions, differing only by local axis orientation. The observed NMR spectra are described by a nuclear spin Hamiltonian with rhombic symmetry

$$\mathcal{H} = -\hbar \sum_{i=x,y,z} \gamma_i H_i I_i + D\left[I_z^2 - \frac{1}{3} I(I+1)\right] + E\left(I_x^2 - I_y^2\right) \qquad (2)$$

with the parameters $|\gamma_x/2\pi| = 3.32(2)$ kHz/Oe, $|\gamma_y/2\pi| = 3.24(2)$ kHz/Oe, $|\gamma_z/2\pi| = 10.03(5)$ kHz/Oe, $|D/h| = 4.31(1)$ MHz, and $|E/h| = 0.30(1)$ MHz.

TABLE I.

Transition		5 – 6	4 – 5	F^{19}	3 – 4	2 – 3	1 – 2
Magn. field, kOe		3.69	4.82	5.25	6.12	7.66	9.84
Linewidth, kHz	NAR	180	145	—	275	310	—
	NMR	211	294	285	417	504	808
Rel. intensity	NAR	0.06	0.3	0	1.0	2.1	—
	NMR	0.71	1.05	0.43	1.00	0.47	0.45

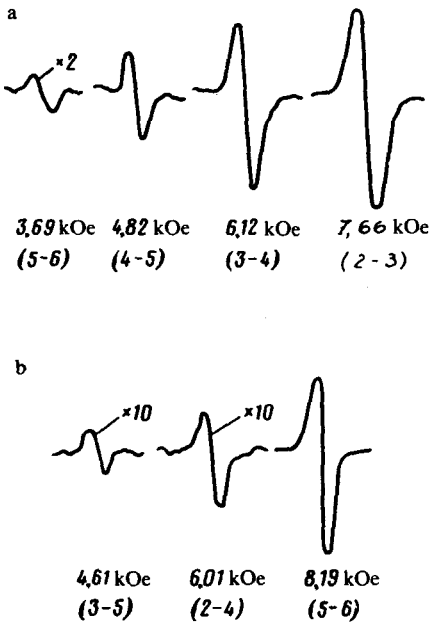

FIG. 2. Nuclear acoustic resonance signals of the Pr^{141} nucleus at two frequencies: (a) $\nu_1 = 21049$ kHz; (b) $\nu_2 = 36427$ kHz. Signals for the 5–6 and 3–5, 2–4 transitions are shown on a scale increased along the vertical by factors of two and ten, respectively.

The local "x" axes are directed perpendicular to the crystal cleavage plane *ac*, and the "z" axes coincide with the hexagonal axis *c*.

The acoustic experiment was carried out with magnetic field orientation $H \| c$; the nuclear energy levels corresponding to this case for Pr^{141} are shown in Fig. 1. Nuclear acoustic resonance was observed with an autodyne spectrometer[7] connected to an acoustic measuring unit. The unit contains a sample in the shape of an acoustic resonator with its axis parallel to the *c*-axis of the crystal with a glued-on quartz converter of *X*-cut which generated longitudinal sound waves at one of the characteristic frequencies of the component resonator. Measurements were made at frequencies of 21049 and 36427 kHz. Nuclear acoustic resonance lines in Pr^{141} (Fig. 2a) were found at the first of these, corresponding to the transitions 2–3, 3–4, 4–5 and 5–6 with a magnetic quantum number change $\Delta m_I = \pm 1$; the value of the resonance field for the 1–2 transition turned out to be outside the capability of our electromagnet. The results of the NMR experiments at the 21049-kHz frequency are shown in Table I (the line at half-height is given). The absence of an F^{19} NAR line, and also the difference in width and relative intensities of the NMR and NAR lines of Pr^{141}, definitely indicate that absorption by ultrasonic and not electromagnetic waves was recorded in the acoustic experiments. A value for the absorption coefficient α along with the measured value for the speed of sound $v_l \approx 6.2 \times 10^5$ cm/sec gave a value of the order of 10^{-6} cm^{-1} for the 2–3 transition.

At the 36427-kHz frequency, besides the 5–6 line, we succeeded in detecting the relatively less intense NAR lines (Fig. 2b) corresponding to the transitions 2–4 and 3–5 with $\Delta m_I = \pm 2$ (dashed lines in Fig. 1). Comparing the intensities of the 5–6 lines

at the two frequencies, and taking into account the quadratic variation of the absorption coefficient with frequency, we found that α depends on the magnetic field approximately as H^2. It is not difficult to understand the origin of such a field relationship: in the Hamiltonian for the nuclear spin-phonon interaction, the bilinear operator according to the field and nuclear spin is the most important, appearing as the result of the combined hyperfine, electron-Zeeman and orbital-lattice interactions in third-order perturbation theory. The weaker absorption of ultrasound at transition with $\Delta m_I = \pm 2$ is related to the presence of a quadratic component in terms of the nuclear spin Hamiltonian, arising in the third-order as a result of the combined orbital-lattice and hyperfine interactions.

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