^{141}Pr NMR in the "electron superconductor" $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

O. N. Bakharev, A. V. Egorov, R. Sh. Zhdanov, M. S. Tagirov, and M. A. Teplov
Kazan State University

(Submitted 22 June 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 2, 812–816 (10 August 1990)

The NMR of ^{141}Pr has been observed and studied in a partially oriented powder of the Van Vleck paramagnet $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ by a spin-echo method at liquid-helium temperature. The parameters of the nuclear spin Hamiltonian are found. The energy interval between the singlet ground state (Γ_3) and the singlet excited state (Γ_4) of the Pr^{3+} ion in the crystal electric field is estimated: $E(\Gamma_4) - E(\Gamma_3) = 815 \pm 90$ cm^{-1}. The rate of the spin-lattice relaxation of ^{141}Pr nuclei measured at a frequency of 23 MHz is about 600 s^{-1} and does not depend on the temperature over the interval 1.5–4.2 K.

According to the existing data on the magnetic susceptibility of the Pr_2CuO_4 crystal,[1] a low-lying energy level of the Pr^{3+} ion ($4f^2$, $^3H_4$, $J = 4$) should be nondegenerate in the crystal electric field. In such cases, a study of the NMR of rare-earth ions can, as we know, provide useful information about the crystal electric potential in Van Vleck paramagnets.[2-4] In this letter we are reporting the first experiments on the NMR of ^{141}Pr ($I = 5/2$) in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at temperatures of 1.5–4.2 K. We have studied the spectra and the nuclear relaxation at frequencies form 10 MHz to 23 MHz in fields up to 20 kOe. The experiments were carried out on a sample of a partially oriented powder in which the NMR of the copper had been studied previously.[5]

Figure 1 shows two spectra, recorded at frequencies of 10.7 MHz and 16.25 MHz through measurements of the spin-echo amplitude at fixed values of the external field. Figure 2a shows the same spectra at a frequency of 23 MHz, recorded for two values of the interval (τ) between the $\pi/2$ and π probe pulses. Comparing the last two curves, we conclude that the decay of the echo amplitude cannot be described by a simple law $A_{2\tau} \sim \exp(-2\tau/T_2)$. This conclusion seems quite natural, since we are dealing with a system of nonequidistant energy levels of a spin $I = 5/2$. A detailed study of the spin-spin relaxation of praseodymium nuclei at a frequency of 23 MHz (some of the results of this study are shown in Table I) showed that this relaxation is described by

$$A_{2\tau}/A_0 = (1-a)\exp(-2\tau/T_2') + a\exp(-2\tau/T_2''), \qquad (1)$$

where $A_{2\tau}$, A_0, a, and T_2' depend on the external field H. In particular, at fields above 6.5 kOe the relaxation is characterized by two approximately equal parameters T_2' and

T_2''; their average values (over 11 values of the field H) are 12.3 and 33.5 μs, respectively. In fields $H \leqslant 6$ kOe, the low echo intensity prevents a discrimination of the two exponential functions, but as H is reduced, we see an obvious tendency for the parameter a to vanish and for the time T_2' to decrease. Postponing a discussion of the reason for the field dependence $T_2'(H)$, we can specify the quantities T_2' and T_2'' empirically, and we can use the two curves in Fig. 1a, along with relation (1), to construct the field dependence of A_0. This quantity is the spin-echo amplitude corrected to a zero value of the interval τ. If the function $A_0(H)$ is constructed correctly, the shape of the NMR spectrum should be reproduced precisely. When T_2' and T_2'' are specified empirically, on the other hand, we can expect only a qualitative description of the intensities of the

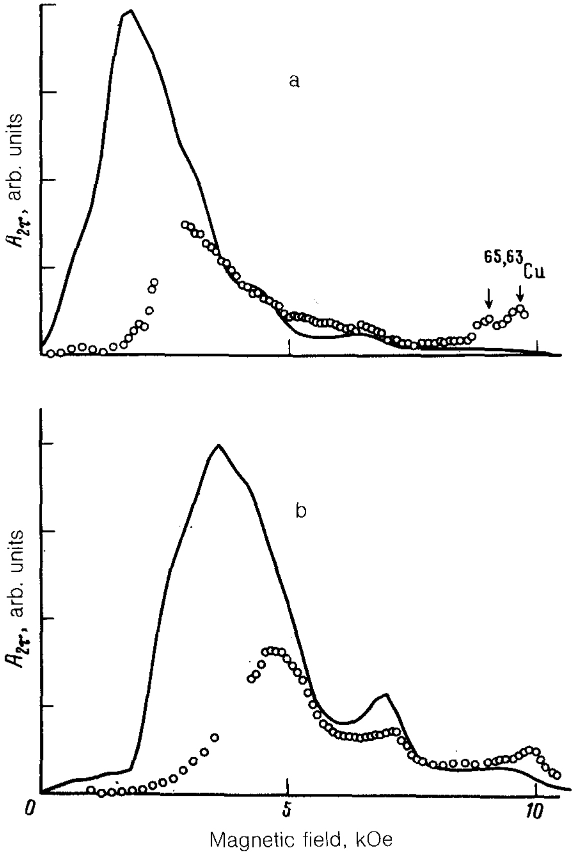

FIG. 1. Amplitude of the spin echo of ^{141}Pr nuclei as a function of the magnetic field at a temperature of 1.5 K. O: Experimental. a—$\nu = 10.7$ MHz, probe pulse lengths $\tau_1 = 1$ μs and $\tau_2 = 2$ μs, interval $\tau = 15$ μs; b—$\nu = 16.25$ MHz, $\tau_1 = 1.2$ μs, $\tau_2 = 2.4$ μs, $\tau = 11$ μs. The field H is parallel to the c' direction, which is the direction of the predominant orientation of the c crystallographic axes of the powder grains. There are no experimental points in the region of the NMR of the protons of paraffin. Solid lines: Theoretical NMR spectra with the parameter values in (4) and (5). The shape of an individual NMR line of a crystallite is assumes to be Gaussian. The linewidth at half-maximum is $\Delta H = 330$ Oe.

various parts of the spectrum. For the NMR frequency $\nu = 23$ MHz we thus set $T_2'' = 33.5\ \mu s$, the same for all values of H, while we assign the time T_2' the following behavior:

$$T_2'(\mu s) = \begin{cases} 6, \text{ for } H < 3 \text{ kOe}, \\ 6 + 6{,}3\,(\text{H}-3 \text{ kOe})/3{,}5 \text{ kOe} \quad \text{for } 3 \text{ kOe} \leqslant H \leqslant 6{,}5 \text{ kOe}, \\ 12{,}3, \text{ for } H > 6{,}5 \text{ kOe} \end{cases} \tag{2}$$

(we were able to detect the minimum value $T_2' = 6\ \mu s$ at a frequency of 10.7 MHz in fields below 1.5 kOe). We then reconstruct the function $A_0(H)$ (the upper curve in Fig. 2b). We see that a characteristic feature of the actual NMR spectrum of ^{141}Pr in a

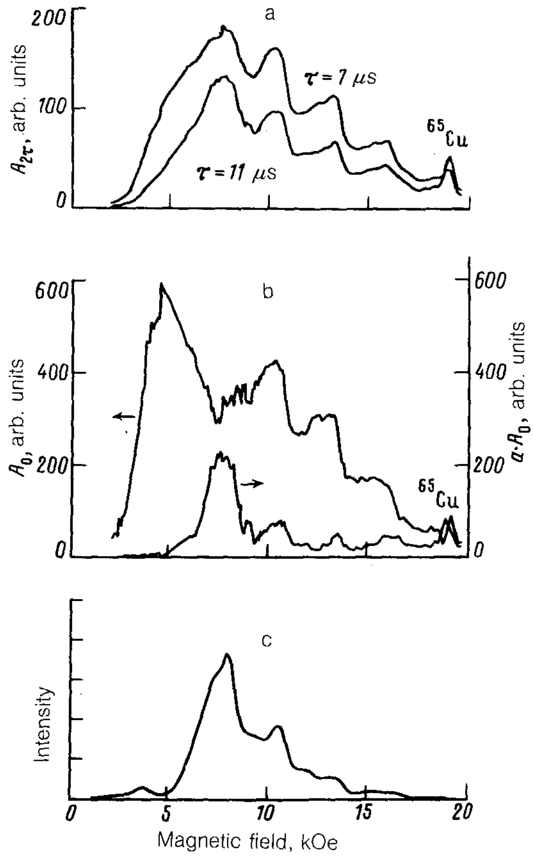

FIG. 2. a,b: Field dependence of the spin-echo amplitude. c: Theoretical spectrum of the ^{141}Pr NMR at a frequency of 23 MHz. a—$H \| c'$, $T = 1.5$ K, $\tau_1 = 1.1\ \mu s$, $\tau_2 = 2.2\ \mu s$, $\tau = 7\ \mu s$ (upper curve) or $\tau = 11\ \mu s$ (lower curve); b—the function $A_0(H)$, which gives an approximate description of the complete NMR spectrum, and the function $a(H) \times A_0(H)$, which is the component of this spectrum with the time scale $T_2'' = 33.5\ \mu s$, both reconstructed from the experimental data; c—theoretical NMR spectrum of ^{141}Pr of powder grains with angles $\theta \leqslant 40°$. The parameter values in (4) and (5) were used in the calculations. The shape of an individual NMR line of a crystallite was assumed to be Gaussian with a linewidth $\Delta H = 330$ Oe at half-maximum.

$Pr_{1.85}Ce_{0.15}CuO_{4-y}$ powder should be an intense line (or group of lines) with short time scales T_2 in weak fields.

To pursue the analysis, we make two assumptions. (1) The NMR spectrum of ^{141}Pr in a crystal with axial symmetry should be described by a spin Hamiltonian[2]

$$\mathcal{H} = -\gamma_{\parallel}\hbar H_z I_z - \gamma_{\perp}\hbar(H_x I_x + H_y I_y) + D[I_z^2 - \frac{1}{3}I(I+1)], \tag{3}$$

where $\gamma_{\parallel} = \gamma_I(1+\alpha_{\parallel})$, $\gamma_{\perp} = \gamma_I(1+\alpha_{\perp})$, $\gamma_I/2\pi = +1.26$ MHz/kOe is the gyromagnetic ratio of the praseodymium nuclei,[3] and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the components of the paramagnetic-NMR-shift tensor in an external field **H** directed respectively parallel to and perpendicular to the c axis of the crystal. Since the values of α_i are usually proportional to the corresponding components (χ_i) of the paramagnetic-susceptibility tensor,[4] and since we have $\chi_{\parallel} < \chi_{\perp}$ in Pr_2CuO_4 (Ref. 1), we set $\gamma_{\parallel} < \gamma_{\perp}$, and we assign the group of lines in fields above 6.5 kOe to those powder grains for which the c crystallographic axes do not make excessively large angles with the field **H** (say, $\theta \leqslant 40°$). (2) Working from existing data[4] on the anisotropy of the spin-spin relaxation time of the nuclei of rare-earth ions in Van Vleck paramagnets, and also working from the results of our own measurements, which show that the relative weight (a) of the slow relaxation of ^{141}Pr nuclei in fields $H < 6.5$ kOe falls to zero, we assume that the relation $T_2(\theta = 90°) < T_2(\theta = 0)$ holds in our system, and we assign the longest of the observed relaxation times $T_2 = T_2''$ to the powder grains with angles $\theta \leqslant 40°$. The spectral component with the time scale $T_2'' = 33.5\ \mu s$ extracted from the experimental data (Fig. 2a) is shown by the lower curve in Fig. 2b. This curve agrees fairly well (cf. Fig. 2c) with the results calculated for the spectrum of a powder containing crystallites with angles $\theta \leqslant 40°$ for the following values of the spin-Hamiltonian parameters:

$$\gamma_{\parallel}/2\pi = (1.66 \pm 0.05)\ \text{MHz/kOe}, \quad D/h = (2.4 \pm 0.2)\ \text{MHz}. \tag{4}$$

The third parameter of Hamiltonian (3),

$$\gamma_{\perp}/2\pi = (5.1 \pm 0.5)\ \text{MHz/kOe}, \tag{5}$$

is found from the position of the maximum (Fig. 2b) of the weak-field line of the spectrum, under the assumption that this maximum corresponds to the transition $|1/2\rangle \leftrightarrow |-1/2\rangle$ for those powder grains for which the c axes make angles $\theta > 40°$ with the field **H**. The validity of the parameter values found for the Hamiltonian from our experiments at a frequency of 23 MHz, i.e., the values in (4), is confirmed by measurements of other frequencies (Fig. 1).

Since the ground state of the Pr^{3+} ion in the crystal field of PrCeCuO, of symmetry D_{4h} (C_{4v}), should be a singlet,[1,6] $|\Gamma_3\rangle = (1/\sqrt{2})(|2\rangle + |-2\rangle)$ and since the value of the parameter $\alpha_{\parallel} = (\gamma_{\parallel}/\gamma_I - 1)$ is determined by the energy interval between the ground state and the excited singlet $|\Gamma_4\rangle = (1/\sqrt{2})(|2\rangle - |-2\rangle)$ and has the value[2]

$$\alpha_{\parallel} = \frac{2A_J g_J \mu_B}{\gamma_I \hbar}\,\frac{\langle \Gamma_3 | J_z | \Gamma_4 \rangle^2}{E(\Gamma_4) - E(\Gamma_3)} \tag{6}$$

$[A_J/h = +1093$ MHz (Ref. 3) is the hyperfine-interaction constant of the free

TABLE I. Parameters of the spin-spin and spin-lattice relaxation of praseodymium nuclei in a partially oriented $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ powder according to measurements at a frequency of 23 MHz and a temperature of 1.6 K.

H (kOe)	4,5	6,0	6,5	7.5	9,0	10.4	11.6	13,3	15.8
a	0	0,23 ± 0,11	0,19 ± 0,03	0.32 ± 0,03	0,16 ± 0,03	0,18 ± 0.04	—	0,20 ± 0,04	0.40 ± 0,06
T_2' (μs)	11,6 ± 0,3	9,3 ± 2.6	12,8 ± 1,0	12,4 ± 1.1	12.3 ± 1,1	11.2 ± 1,0	—	13,6 ± 0,8	10.6 ± 2,3
T_2'' (μs)		23.6 ± 5,3	33,8 ± 3,0	31,4 ± 1.8	33.2 ± 4,1	31,9 ± 4.5	—	37.0 ± 4,2	31.3 ± 3,4
λ	0,34 ± 0.03	0.52 ± 0,02	—	0,64 ± 0.03	—	0,34 ± 0,02	0.40 ± 0,03	0.34 ± 0,02	0.44 ± 0,04
T_1' (ms)	0.17 ± 0,02	0.20 ± 0.02	—	0.11 ± 0,02	—	0.16 ± 0,01	0,27 ± 0.03	0.16 ± 0.01	0,21 ± 0.03
T_1'' (ms)	1,61 ± 0,10	1.70 ± 0,06	—	1.59 ± 0,03	—	1,71 ± 0.08	2.17 ± 0.18	1,56 ± 0,07	1,62 ± 0.13

Pr^{3+} ion, and $g_J = 0.8054$ (Ref. 3) is the Landé factor], we can estimate this energy interval:

$$E(\Gamma_4) - E(\Gamma_3) = (815 \pm 90)\ \text{cm}^{-1}. \tag{7}$$

Various authors have proposed four sets of crystal-field parameters to describe the Stark splitting of the energy levels of the Nd^{3+} and Pr^{3+} ions in the crystal fields of compounds with the Nd_2CuO_4 structure.[1,6–8] Some of these parameters satisfy condition (7), $E(\Gamma_4) - E(\Gamma_3) = 776\ \text{cm}^{-1}$, but overestimate the value of $\gamma_\perp/(2\pi)$ (6.06 MHz/kOe). Values of the spin-Hamiltonian parameters similar to our own are found from calculations based on the crystal electric potential proposed in Ref. 1 ($\gamma_\parallel/2\pi = 1.54$ MHz/kOe, $\gamma_\perp/2\pi = 5.52$ MHz/kOe), but the energy of the Γ_4 singlet is too large ($1186\ \text{cm}^{-1}$).

The identification of the "lines" in the NMR spectrum offered in this letter is supported in a qualitative way by studies of the spin-lattice relaxation of ^{141}Pr nuclei. The restoration of the longitudinal nuclear magnetization observed experimentally agrees fairly well with a two-exponential dependence

$$1 - A(t)/A(\infty) = (1 - \lambda)\exp(-t/T_1') + \lambda\exp(-t/T_1''). \tag{8}$$

On the other hand, we know[9] that a system of nonequidistant energy levels of a spin $I = 5/2$ has five characteristic times: T_1, $T_1/3$, $T_1/6$, $T_1/10$, and $T_1/15$.

It can be seen from Table I that the largest relative weight (0.64) of the slowest relaxation process is found in a field of 7.5 kOe, as it should be[9] in the case of $|5/2\rangle \leftrightarrow |3/2\rangle$ transition, while the smallest relative weight is found at fields of 4.5 kOe, 13.3 kOe (the transition $|1/2\rangle \leftrightarrow |-1/2\rangle$), and 10.4 kOe (the transition $|3/2\rangle \leftrightarrow |1/2\rangle$).

It was mentioned in Ref. 5 that the spin-lattice relaxation of ^{63}Cu and ^{65}Cu nuclei in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at $T = 1.5$–4.2 K is determined by a quadrupole mechanism. The ^{141}Pr nuclei also have quadrupole moments, but regarding the mechanism for their relaxation we can say nothing more at present than that this mechanism leads to an essentially constant relaxation rate $1/T_1 = 1/T_1'' \approx 600\ \text{s}^{-1}$ over the temperature interval from 1.5 to 4.2 K.

This work is supported by the Scientific Council on the Problem of High-Temperature Superconductivity and is carried out within the framework of Project 333 of the State Program "High-Temperature Superconductivity."

---

[1] P. Allenspach *et al.*, Z. Phys. B **77**, 185 (1989).

[2] M. A. Teplov, in *Crystal Field Effects in Metals and Alloys* (ed. A. Furrer), Plenum Press, New York, 1977, p. 318; S. A. Al'tshuler and M. A. Teplov, in *Problems of Magnetic Resonance*, Nauka, Moscow, 1978, pp. 14–30.

[3] B. Bleaney *et al.*, J. Phys. C **11**, 3059 (1978).

[4] L. K. Aminov and M. A. Teplov, Usp. Fiz. Nauk **147**, 49 (1985) [Sov. Phys. Usp. **28**, 762 (1985)]; L. K. Aminov and M. A. Teplov, Sov. Sci. Rev. Phys. A **14**, 1 (1990).

[5] O. H. Bakharev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 571 (1990) [JETP Lett. **51**, 649 (1990)].

[6] P. A. Alekseev *et al.*, Sverkhprovodimost' (KIAE) **2**, 44 (1989) [Superconductivity **2**, 39 (1989)].

[7] A. T. Boothroyd *et al.*, Phys. C **165**, 17 (1990).
[8] Y. Nekvasil, Preprint 1990, submitted to Physica C.
[9] W. W. Simmons *et al.*, Phys. Rev. **127**, 1168 (1962).

Translated by D. Parsons