NMR spectra and nuclear relaxation in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at low temperatures

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The spin-echo method at frequencies of 16 and 23 MHz has been used to study the NMR spectra and the nuclear relaxation of ^{141}Pr and ^{65}Cu in a partially oriented powder of the "electron superconductor" $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at temperatures from 4.2 K down to 0.05 K. Two types of $^{141}Pr^{+3}$ centers (rapidly relaxing and slowly relaxing) were observed, in a concentration ratio 2:1, with approximately the same magnetic properties. The pronounced slowing of the nuclear relaxation observed at temperatures on the order of 0.5 K is attributed to the possible onset of superconductivity in a system of square Pr and Ce lattices.

The first observations of pulsed NMR of praseodymium and copper in the "electron superconductor" $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ ($T_c = 24$ K) in a limited interval of liquid-^4He temperatures were reported in Refs. 1 and 2. In the present paper we are reporting the results of more comprehensive experiments on this Van Vleck paramagnet over the temperature interval from 4.2 K down to 0.05 K. The partially oriented powder which was used in Refs. 1 and 2 was used again in these experiments. A refrigerator operating on the basis of a dissolution of ^3He in ^4He was used to reach temperatures below 1 K. The temperature was monitored with a (100-Ω) calibrated Speer thermoresistance. The basic results of these measurements are generalized below.

A. Spectra. 1) The NMR spectrum of ^{141}Pr ($I = 5/2$) in a field H_0 directed parallel to the c' direction, which is the direction of the predominant orientation of the crystallographic c axes of the grains of the PrCeCuO powder, has a "fine" structure which is more intense and more clearly defined than that in the spectrum in a field $H_0 \perp c'$ (Fig. 1a). All the experiments described below were thus carried out in a field $H_0 \| c'$.

2) The inhomogeneous NMR linewidth of ^{141}Pr increases with decreasing temperature, so the fine structure of the spectrum is seen less clearly at $T = 1.5$ K than at $T = 4.2$ K (Fig. 1a), and it disappears almost entirely at $T = 0.1$ K (compare Figs. 1b and 1c).

3) There are two types of $^{141}Pr^{3+}$ centers in the PrCeCuO sample: rapidly relaxing centers (Pr1) and slowly relaxing centers (Pr2). The NMR spectrum of Pr2 is described by an axisymmetric spin Hamiltonian $H = -\gamma_\| \hbar H_z I_z - \gamma_\perp \hbar (H_x I_x + H_y I_y) + D[I_z^2 - I(I+1)/3]$ with the parameters[2,3] $\gamma_\|^{(2)}/2\pi = (1.66 \pm 0.05)$ MHz/kOe, $\gamma_\perp^{(2)}/2\pi = (5.1 \pm 0.5)$ MHz/kOe, and $|D^{(2)}/h| = (2.4 \pm 0.2)$ MHz. The fine-structure components of the NMR spectrum of Pr1 are manifested only at small values of the time interval τ between the $\pi/2$ and π probing pulses; they are seen as

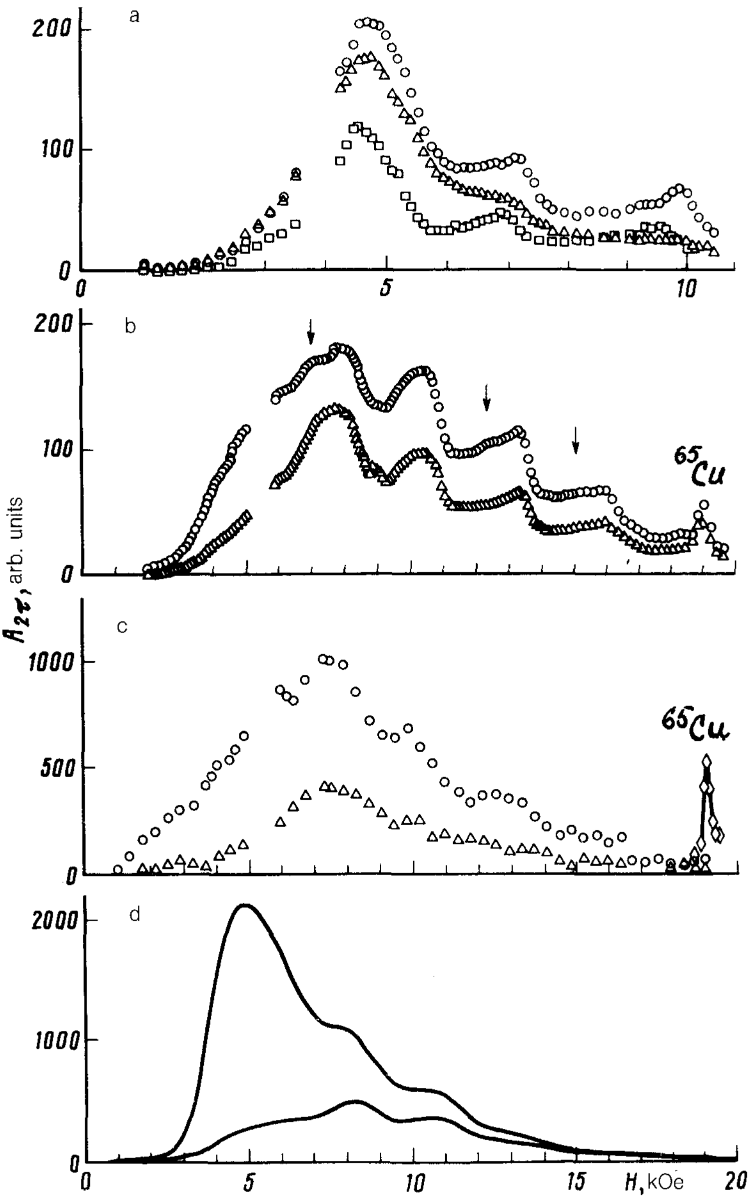

FIG. 1. NMR spectra of ^{141}Pr in powdered $Pr_{1.85}Ce_{0.15}CuO_{4-y}$. a: Frequency $\nu = 16.25$ MHz. ○—$T = 1.5$ K, $H_0 \| c'$; Δ—$T = 1.5$ K, $H_0 \perp c'$, $\tau = 11$ μs; □—$T = 4.2$ K, $H_0 \| c'$, $\tau = 11$ μs. b: $\nu = 23$ MHz, $T = 1.6$ K, with $\pi/2$ and π pulses with respective lengths of 1.1 and 2.2 μs. ○—$\tau = 7$ μs, Δ—$\tau = 11$ μs, and the arrows show the components of the fine structure of the NMR spectrum of the rapidly relaxing Pr1 centers. c: $\nu = 23$ MHz, $T = 0.1$ K, and the lengths of the probing pulses are 0.9 and 1.8 μs. ○—$\tau = 10$ μs; Δ—$\tau = 50$ μs; ◇—NMR of ^{65}Cu ($\tau = 50$ μs, and the lengths of the probing pulses are 5 and 10 μs). d: Calculated dependence of the echo amplitude $A(2\tau)$ of the Pr2 nuclei in an unoriented PrCeCuO powder on the magnetic field for $\nu = 23$ MHz, $\gamma_{\|}/2\pi = 1.66$ MHz/kOe, $\gamma_{\perp}/2\pi = 5.1$ MHz/kOe, $D/h = 2.4$ MHz, $T_{2\|}^{(2)} = 300$ μs, and $T_{2\perp}^{(2)} = 30$ μs. Upper curve—$\tau = 10$ μs; lower curve—$\tau = 50$ μs. The width of an individual NMR line (of Gaussian shape) is assumed to be 660 Oe.

weak-field satellites on the components of the NMR spectrum of Pr2 (see the arrows in Fig. 1b). Estimates suggest values of the parameters of the spin Hamiltonian which are close to those given above: $\gamma_{\parallel}^{(1)}/2\pi \simeq 1.84$ MHz/kOe and $|D^{(1)}/h| \simeq 2.5$ MHz. The relative numbers of Pr1 and Pr2 atoms could be determined reliably from relaxation measurements at ultralow temperatures: $n(\text{Pr1})/n(\text{Pr2}) \simeq 2$ (see Subsections B1 and C1).

4) Because of the pronounced anisotropy of the transverse relaxation time, described by $T_2(\theta = 90°) \ll T_2(\theta = 0)$ (θ is the angle between the magnetic field H_0 and the c axis of the PrCeCuO crystal), the NMR spectrum of the ^{141}Pr in the powder, recorded by measuring the spin-echo amplitude as a function of the field H_0 at a constant value of τ, is distorted. Specifically, its high-field part, which is due to powder grains with small angles θ, is clearly identifiable, while its weak-field part (corresponding to grains with large angles θ) is suppressed (compare Figs. 1b and 1c). As the weak-field part of the spectrum is restored as a result of an increase in the time T_2 during the cooling of the sample (the upper curve in Fig. 1c), the large width of this part of the spectrum becomes apparent. This large width is probably evidence of significant distortions of the crystal electric field and of a scatter in the values of $\gamma_{\perp}(\gamma_x, \gamma_y)$ from 3 to 8 MHz/kOe.

B. Relaxation of the transverse magnetization. 1) Since the NMR spectra of Pr1 and Pr2 are superimposed, the relaxation of the resultant magnetization of the ^{141}Pr nuclei is described by the two-exponential law

$$A_{2\tau}^{\mathrm{Pr}}/A_0^{\mathrm{Pr}} = (1-a)\exp(-2\tau/T_2^{(1)}) + a\exp(-2\tau/T_2^{(2)}),$$

where $T_2^{(1)} < T_2^{(2)}$. Measurements at a frequency of 23 MHz in a field of 7.5 kOe (corresponding to the transition $|m_I = -5/2\rangle \leftrightarrow |-3/2\rangle$ for powder grains with small angles θ) yielded the following values for the parameters at temperatures of 1.6, 0.09, and 0.05 K, respectively: $a = 0.32 \pm 0.03$, 0.33 ± 0.03, and 0.35 ± 0.02; $T_2^{(1)} = 12.4 \pm 1.1$ μs, 22 ± 3 μs, and 24 ± 2 μs; $T_2^{(2)} = 31.4 \pm 1.8$ μs, 300 ± 26 μs, and 374 ± 18 μs. At 1.6 K, the values of $T_2^{(1)}$ and $T_2^{(2)}$ are the same in all fields $H_0 \geqslant 7.5$ kOe.

2) At frequencies below 20 MHz the NMR signal from the rapidly relaxing Pr1 centers cannot be distinguished. The decay of the transverse magnetization follows the simple law $\exp(-2\tau/T_2)$, with T_2 several times shorter in weak fields than in strong fields. Above the resonant field for the transition $|-5/2\rangle \leftrightarrow |-3/2\rangle$ for grains with small angles θ (i.e., to the right of the intensity peak in the observed spectrum), the time T_2 is nearly independent of the field. With increasing frequency, however, the NMR obviously increases: At $T = 1.5$ K we have a time $T_2 \approx 17$ μs at a frequency of 10.7 MHz and a time of 22 μs at 16 MHz.

3) The transverse relaxation rate of the Pr2 nuclei slows down markedly as the material is cooled (Fig. 2a). The most pronounced changes occur in the temperature interval between 0.5 and 0.17 K. The nature of these changes is reminiscent of the temperature dependence $T_2^{-1}(T)$ of the Cu(2) copper nuclei in the high-T_c superconductor[4] $YBa_2Cu_3O_{7-\delta}$ at $T \simeq T_c = 93$ K and of that in the heavy-fermion superconductor[5] $CeCu_2Si_2$ at $T \simeq T_c = 0.6$ K. In this same temperature interval near 0.5 K

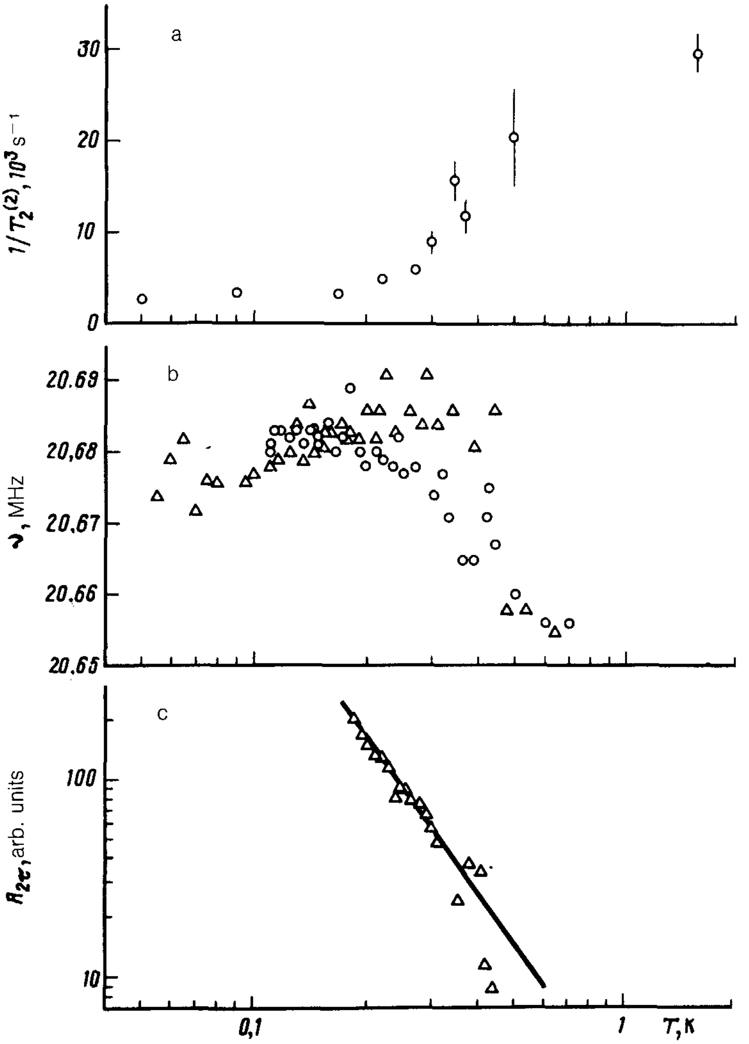

FIG. 2. Temperature dependence of the relaxation rate of the transverse relaxation of Pr2 nuclei at $\nu = 23$ MHz, $H_0 = 7.9$ kOe, with probing pulses 0.9 and 1.8 μs long. b: Changes in the frequency of an autodyne generator (Δ) during a cooling of a PrCeCuO sample (for 1 h) from 0.64 K to 0.055 K and (O) during a heating of the sample (for 2 h) from 0.11 K to 0.70 K. c: Temperature dependence of the spin-echo amplitude of ^{141}Pr nuclei with $\nu = 23$ MHz, $H_0 = 4.8$ kOe, and $\tau = 10\,\mu$s. The lengths of the probing pulses are 0.9 and 1.8 μs. The straight line is a Curie law.

we see a significant decay of the magnetic susceptibility of the sample, which is manifested (in particular) as an increase in the frequency of an autodyne generator (Fig. 2b), because of a decrease in the inductance of the coil during the cooling of the sample in the absence of a magnetic field.

4) The anisotropy of the times T_2 of the ^{141}Pr nuclei is seen particularly vividly at

low temperatures. At $T = 0.17$ K, for example, the time $T_2^{(2)}$ measured at a frequency of 23 MHz is 310 ± 16 μs in a field of 7.9 kOe (the transition $|-5/2\rangle \leftrightarrow |-3/2\rangle$ for crystallites with small angles θ), while it is 30.4 ± 4.0 μs in a field of 4.8 kOe (the center of the weak-field group of lines from crystallites with large angles θ). Since the ratio of the limiting relaxation rates, $(1/T_{2\parallel}^{(2)})/(1/T_{2\perp}^{(2)}) = 0{,}1$, is equal to the ratio of the squares of the corresponding components of the tensor $\tilde{\gamma}$ ($\gamma_\parallel^2/\gamma_\perp^2 = 1.66^2/5.1^2 \simeq 0.1$), one might suggest that for an arbitrary orientation of a crystallite in a field H_0 the relaxation rate $1/T_2^{(2)}(\theta)$ is proportional to the quantity $\gamma^2 = \gamma_\parallel^2 \cos^2\theta + \gamma_\perp^2 \sin^2\theta$. The qualitative similarity between the calculated NMR spectra of Pr2 in an unoriented powder (Fig. 1d), on the one hand, and the experimental spectra (Fig. 1c), on the other, confirms the validity of this suggestion. We cannot claim a quantitative comparison here, since we were dealing with an oriented PrCeCuO powder in these experiments.

5) The transverse relaxation time of the ^{141}Pr nuclei in weak fields also increases rapidly with decreasing temperature. As a result, the amplitude of the spin echo increases more rapidly than the nuclear magnetization in the temperature interval 0.5–0.3 K (Fig. 2c).

6) The relaxation of the transverse magnetization of the copper nuclei is exponential: $A_{2\tau}^{\mathrm{Cu}}/A_0^{\mathrm{Cu}} = \exp(-2\tau/T_2)$. The time $^{65}T_2$, corresponding to the isotope ^{65}Cu, measured at a frequency of 23 MHz, is 250 μs at 0.17 K, 200 μs at 0.5 K, and far shorter at higher sample temperatures (at a frequency of 10.7 MHz, the time $^{65}T_2$ is 83 μs at $T = 1.5$ K and 69 μs at 4.2 K).

C. Relaxation of the longitudinal magnetization. 1) For the ^{141}Pr nuclei, this process (like the relaxation of the transverse magnetization) is observed in a two-exponential form: $1 - A_t^{\mathrm{Pr}}/A_\infty^{\mathrm{Pr}} = (1-\lambda)\exp(-t/T_1^{(1)}) + \lambda \exp(-t/T_1^{(2)})$, where $T_1^{(1)} \ll T_1^{(2)}$. Table I shows the results of measurements carried out at a frequency of 23 MHz in a field of 7.5 kOe. We see that the times $T_1^{(1)}$ and $T_1^{(2)}$ vary only slightly within the temperature intervals 4.2–1.6 K and 0.1–0.05 K, but when the sample is cooled from 1.6 K to 0.1 K, they increase by more than two orders of magnitude. The implication is that some powerful relaxation mechanism has diminished its effect. We also note that at the lowest temperature, $T = 0.05$ K, the parameters a and λ are the same, supporting the suggestion that there exist two types of centers (Pr1 and Pr2), in a concentration ratio 2:1.

2) The experiments at a frequency of 23 MHz and a temperature of 1.6 K in fields

TABLE I. Parameters of the spin-lattice relaxation of ^{141}Pr nuclei in PrCeCuO.

Parameter	Temperature			
	4,2 K 1)	1,6 K 1)	0,1 K 2)	0,05 K 2)
λ	0.37± 0,03	0.64± 0,03	0,43± 0,05	0,36 ± 0.05
$T_1^{(1)}$, ms	0.15± 0,02	0,11± 0,02	13± 4	21 ± 4
$T_1^{(2)}$, ms	1,40± 0.08	1.59± 0.03	710± 130	760 ± 200

1) $\tau = 7$ μs; 2) $\tau = 20$ μs.

$H_0 \geqslant 4.5$ kOe showed that the times $T_1^{(1)}$ and $T_1^{(2)}$ are essentially independent of the value of H_0.

3) The restoration of the longitudinal magnetization of the copper nuclei is also a two-exponential process: $1 - A_t^{\mathrm{Cu}}/A_\infty^{\mathrm{Cu}} = (1 - \lambda_{\mathrm{Cu}})\exp(-t/T_1') + \lambda_{\mathrm{Cu}} \times \exp(-t/T_1'')$. The times T_1' and T_1'' of the ^{65}Cu nuclei become longer, equally dramatically, as the temperature is lowered. For example, at a frequency of 10.7 MHz and at temperatures $T = 4.2$ and 1.5 K, the relaxation parameters are, respectively, $\lambda_{\mathrm{Cu}} = 0.39 \pm 0.04$ and 0.53 ± 0.04, $T_1' = 2.49 \pm 0.19$ and 2.95 ± 0.22 ms, and $T_1'' = 15.5 \pm 0.9$ and 17.6 ± 0.6 ms. At low temperatures, 0.17 K and 0.065 K (from measurements at a frequency of 23 MHz), the same parameters have the values $\lambda_{\mathrm{Cu}} = 0.51 \pm 0.07$ and 0.5 ± 0.05, $T_1' = 65 \pm 25$ and 320 ± 60 ms, and $T_1'' = 2.1 \pm 0.4$ and 8.1 ± 2.1 s, respectively. The dependence of the times T_1' and T_1'' on the NMR frequency is weak.

We should point out in conclusion that experiments on NMR in the "electron superconductor" $\mathrm{Pr_{1.85}Ce_{0.15}CuO_{4-y}}$ provide evidence of a phase transition at a temperature on the order of 0.5 K. Its external manifestations (Subsections B3, B5, C1, and C3) remind one of a transition to a superconducting state. It is possible that the observed effects stem from the onset at $T \simeq 0.5$ K of a superconductivity in a system of square lattices consisting of Pr and Ce atoms.

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