NMR of copper and praseodymium in the two-phase compound $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

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The NMR and nuclear-relaxation spectra of $^{63,65}Cu$ and ^{141}Pr in a magnetically oriented powder of a van-Vleck paramagnet—the high-T_c superconductor $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ ($T_c = 24$ K)—were investigated by the spin-echo method. The results of the investigations indirectly confirm the two-phase composition of the specimen. The NMR spectra of copper with traces of weak quadrupole interaction ($^{63}\nu_Q \approx 1.6$ MHz) and the well-pronounced Knight shift ($K_0 \approx +0.2\%$ and $K_\parallel \approx +0.5\%$ are the isotropic and anisotropic components of the shift) are attributed to the metallic nonsuperconducting phase. The quadrupole spin-lattice relaxation of copper nuclei, which is observed in this phase at temperatures of 1.5–4.2 K, is explained by fluctuations of the electric-field gradient owing to charge transfer (Ln^{4+} holes) along the system of rare-earth atoms. Manifestations of a strong unknown mechanism of spin-spin relaxation of copper nuclei were also observed at temperatures above 1 K; they are especially noticeable at low frequencies. The above spin-echo signals of two types of $^{141}Pr^{3+}$ centers ($Pr^{(1)}$—rapidly relaxing and $Pr^{(2)}$—slowly relaxing) are attributed to the superconducting phase, and in addition the $Pr^{(2)}$ nuclei were identified as belonging to clusters $CePr_4$. The behavior of the NMR spectrum and the spin-spin relaxation of $Pr^{(2)}$ nuclei at temperatures of 0.05–4.2 K can be explained by assuming that the cerium ions in the superconducting phase have a valence of +3. Anomalously high spin-lattice relaxation rates of praseodymium nuclei are observed at ultralow temperatures (0.05–0.2 K).

1. INTRODUCTION

At the beginning of 1989 Tokura, Takagi, and Uchida[1] discovered a new family of high-T_c superconductors with the structure Nd_2CuO_4 (T' phase) and critical temperatures $T_c \lesssim 24$ K. These materials were distinguished from the well-known high-T_c superconductors with the structure La_2CuO_4 (T phase) by the fact that in them the copper atoms in the CuO_2 planes had not a six-fold oxygen environment (octahedron) but rather a four-fold environment (square). The main difference was observed, however, in Hall and thermo-emf measurements: all new materials $Ln_{2-x}Ce_xCuO_{4-y}$ (Ln = Pr, Nd, Sm, and Eu) exhibited electronic-type conductivity. The new series of n-type high-T_c superconductors was supplemented with the compounds $Ln_{2-x}Th_xCuO_{4-y}$,[2] which also have a T' structure. The natural desire of researchers to determine the differences in the electronic structure of p- and n-type superconductors stimulated many experiments, including experiments using the powerful methods of high-energy spectroscopy (XAS, XPS, and EELS), but the results of these experiments and their interpretation by different authors were found to be very contradictory.[3,4] Without discussing these contradictions, we note that in the interpretation of the results of experiments with n-type high-T_c superconductors up to now no attempts have been made to look at the compound $Ln_{2-x}M_xCuO_{4-y}$ as a two-phase system. In the meanwhile, this approach appears to be necessary.

The possibility of coexistence of two phases in oxide superconductors was already discussed a few years ago by Gor'kov *et al.*[5,6] In their experiments on neutron diffraction by powders Jorgensen *et al.*[7,8] established that in the superconductors La_2CuO_{4+x}, $Nd_{2-x}Ce_xCuO_4$, and $La_{2-x}Sr_xCuO_4$ phase separation indeed occurs in a definite range of values of x, and the superconducting transition temperature observed in the experiments reaches a maximum precisely at the boundary of the region of coexistence of the phases. In the region of coexistence of the phases itself the specimen is a mixture of a superconductor with a fixed composition with maximum T_c and a nonsuperconductor (dielectric in the case of La_2CuO_{4+x} and metal in the case of $Nd_{2-x}Ce_xCuO_4$, and $La_{2-x}Sr_xCuO_4$) of a different but definite composition for a given value of x. It is clear that the superposition of the effects from two phases can introduce confusion into the experimental results and even result in an incorrect interpretation of the results, especially since the quantitative ratio of the phases strongly depends on the conditions under which the specimens were prepared. For this reason, it is necessary to employ methods of investigation which give an "interior" view of the two-phase system and can clearly separate the observed effects. From investigations of the compounds $YBa_2Cu_3O_{7-y}$ it is known that the nuclear resonance methods—NMR and NQR—are such methods.

The first experiments on NMR and NQR of copper in the compounds $Nd_{2-x}Ce_xCuO_{4-y}$,[9] $Nd_{2-x}Th_xCuO_{4-y}$, and $Pr_{2-x}Th_xCuO_{4-y}$,[10] which were performed even before the two-phase composition of $Nd_{2-x}Ce_xCuO_{4-y}$ was determined from the neutron diffraction patterns,[7] actually showed that there are two types of resonating copper centers in specimens with cerium (thorium) concentration $x = 0.10$ and 0.15, corresponding to the region of coexistence of two phases. Some centers are characterized by NQR frequencies in a wide spectrum from 20 to 60 MHz, while for others the quadrupole interaction is characteristically very weak ($\nu_Q \approx 1$ MHz). For comparison we note that in the antiferromagnetic dielectric Nd_2CuO_4 the electric quadrupole interaction of the copper nuclei is quite strong: $\nu_Q = 13$–14 MHz.[9-11]

Estimates of the intensity of resonance absorption

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showed[9] that the relative content of copper centers with a wide spectrum of NQR frequencies is high in the range of values of x corresponding to high observed values of T_c and is close to zero for $x \leqslant 0.05$ (in the dielectric) and $x = 0.2$ (in the nonsuperconducting paramagnetic metal). The correlation of this behavior with the concentration (x) dependence of the fraction of the superconducting phase[7] suggests that these centers belong to the superconductor while the copper centers with weak quadrupole interaction can be referred to the nonsuperconducting metallic phase. The fact that the latter centers should be referred to the metallic phase is also indicated by the Korringa character of their relaxation ($T_1T = 0.147$ s·K at $T = 2.4$–300 K) was established by the experiments of Kumagai *et al.*[12] with the compound $Pr_{2-x}Ce_xCuO_{4-y}$, in which the Pr^{3+} ions have a nonmagnetic ground state[13,14] [in neodymium compounds the large magnetic moments of the Nd^{3+} ions have a very strong effect on the spin-lattice relaxation of the copper nuclei, as a result of which the relaxation time T_1 is virtually independent of the temperature in a wide range of temperatures $T = 0.4$–250 K and is equal to approximately 10^{-3} s (Refs. 9, 12, and 15)].

In this paper we present the results of investigations of the NMR and nuclear relaxation spectra of copper and praseodymium in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at low temperatures from 0.05 to 4.2 K. These results indirectly confirm that this compound has a two-phase composition. In the crystal electric field (CEF) of praseodymium cuprate, which has D_{4h} symmetry, the Pr^{3+} ions ($4f^2$, $^3H_4$, $J = 4$) have a nondegenerate ground state. The isotope ^{141}Pr with spin $I = 5/2$ have a 100% natural abundance, so that praseodymium nuclei are[16,17] just as convenient nuclear probes as are the nuclei which are widely employed in investigations of high-T_c superconductors (^{63,65}Cu, ^{17}O, ^{89}Y, ^{205}Tl, etc.).

The main features of the resonance spectrum of the rare-earth (RE) ions in materials with a singlet $4f$ electronic ground state (such materials are called van Vleck paramagnets) are governed by the intensification of the magnetic field by the $4f$-shell on the rare-earth nucleus.[18-22] This intensification is described by a rank-2 tensor, reflecting the symmetry of the crystal electric field. In praseodymium compounds this intensification is not as large as in holmium and thulium compounds,[20,23] but it can still reach magnitudes of the order of 10, thereby providing a large gain in the intensity of the observed NMR signals. An additional advantage of ^{141}Pr as nuclear probes is that their spectral and relaxational parameters, which are very sensitive to the details of the structure of the local environment of the Pr^{3+} centers, contain information which can be employed for determining more accurately the crystal structure and the CEF potential.

The compound $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ employed in this work was prepared by the well-known method.[1] Measurements of the magnetic susceptibility showed that there is a distinct superconducting transition at $T_c = 24$ K, and x-ray phase analysis confirmed the absence of extraneous phases. We did not determine the relative content of the superconducting material in the specimen and the oxygen index of the compound. The experiments were performed in partially oriented powder, prepared as follows. The pulverized specimen was mixed with paraffin, inserted in a cylindrical container, and placed in a magnetic field (~ 10 kOe). The heated container was slowly rotated at a rate of 2 rpm. This resulted in the fact that because the material has a anisotropic paramagnetic susceptibility ($\chi_a > \chi_c$) the crystal c axes of the separate particles of powder become aligned predominantly along the rotational $\mathbf{c}'$ axis, i.e., perpendicular to the field $\mathbf{H}_0$, and was fixed in the solidified paraffin. All NMR measurements were performed with the help of a laboratory-built pulsed coherent spectrometer-relaxometer, connected to a DVK-3M computer. Low-intensity NMR spectra (at frequencies of ~ 10 MHz) were obtained by accumulating spin-echo signals with fixed values of the magnetic field and high-intensity spectra (at frequencies ~ 30 MHz) were recorded by slowly scanning (256 points per 50 min) the field. The decay of the transverse magnetization was recorded by Hahn's method, and the spin-lattice relaxation rate was estimated from the restoration curve of the longitudinal magnetization after the system was perturbed by a pair of $\pi/2 - \pi$ pulses. The typical widths of the $\pi/2$ pulses were equal to 3–4 μs for copper nuclei and 1 μs for praseodymium nuclei. Temperatures below 1 K were obtained with the help of a ^{3}He–^{4}He dilution refrigerator; the specimen was placed, together with the rf coil, directly into the solution.

2. COPPER NMR

In this work we studied NMR of only the copper centers for which the quadrupole interaction is weak. Below, we give and discuss the basic results of the experiments.

Spectra. At liquid-helium temperatures the narrow NMR line of copper are observed on a "pedestal," in which the diffuse quadrupole structure of the NMR spectrum of the powder can be discerned (Fig. 1). Numerical modeling of the spectrum shows that it is well described by a sum of four Gaussian curves (two narrow lines, corresponding to the transitions $|1/2\rangle \leftrightarrow |-1/2\rangle$ and two pedestals—the solid curve in Fig. 1), and in addition the rms half widths of the pedestals are equal to 800 kHz (^{63}Cu) and 700 kHz (^{65}Cu), i.e., they correspond to the rms values of the NQR frequen-

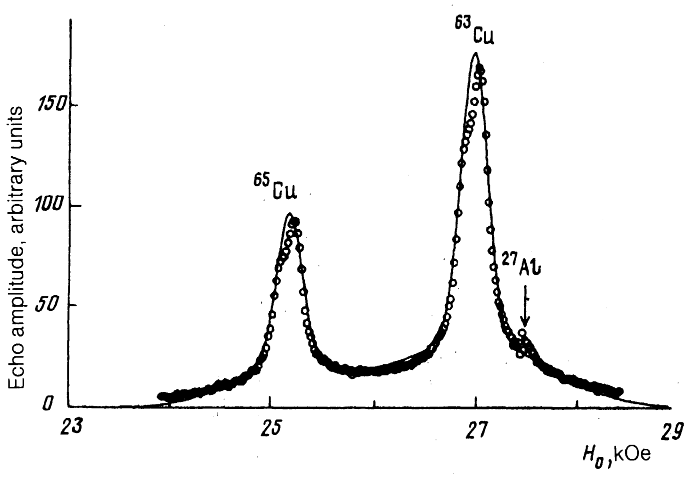

FIG. 1. NMR spectrum of copper in oriented $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ powder in the field $\mathbf{H}_0$ parallel to the predominant orientation $\mathbf{c}'$ of the $\mathbf{c}$ axes of the crystallites. $T = 4.2$ K, $\nu = 30.5$ MHz, the dots are the experimental points, the arrow indicates NMR of the ^{27}Al impurity, the $\pi/2$-pulse width $t_{\pi/2} = 3$ μs, the solid curve is the computed spectrum—the sum of two narrow Gaussian lines corresponding to the transitions $|1/2\rangle \leftrightarrow |-1/2\rangle$ and two Gaussian "pedestals" with rms half-width of 0.8 MHz (^{63}Cu) and 0.7 MHz (^{65}Cu).

cies $\langle \nu_Q^2 \rangle^{1/2} = 1.6$ and 1.4 MHz. The calculations of different contributions to the electric field gradient (EFG) at copper nuclei, which were performed, as in Ref. 24, taking into account the covalency and overlapping of the electronic orbitals of copper and oxygen as well as 15% admixture of the state Cu^+, give a quadrupole frequency $\nu_Q = -34.5 - 16 + 53.2 = 2.7$ MHz;[25] here the three contributions represent the ligand lattice, the $3p$ electrons, and the $3d$ electrons, respectively. As one can see, this frequency is close to the experimental; estimates are given above, but the lack of any indications of quadrupole satellites (nonmonotonic decay of the NMR signal intensity on the line wings) suggests that the pedestals can be formed as a result of random distribution of the quantities ν_Q around a zero average value, and in particular they can appear as a result of dynamic fluctuations of the EFG. In this case manifestations of fluctuations of the EFG can also be expected in nuclear relaxation of copper (see below).

The shape of the NMR lines at 22.5 and 30.5 MHz (Fig. 2) reveals the presence of an anisotropic Knight shift. Two important circumstances enabled us to determine this shift. First, in a field $\mathbf{H}_0$ oriented parallel to the direction $\mathbf{c}'$ of the predominant orientation of the c axes of the crystallites of the powder, the weak-field "shoulder" of the NMR line is much more pronounced than in the spectrum of the unoriented powder. Second, as was established previously in Ref. 25 in experiments at low frequencies (8.1 and 10.7 MHz), the spin-spin relaxation time of copper in PrCeCuO has an appreciable angular dependence: $T_2\,(\mathbf{H}_0 \| \mathbf{c}) < T_2(\mathbf{H}_0 \perp \mathbf{c})$. Using rf pulses with a lower than usual amplitude and longer duration ($\tau_{\pi/2} = 6$–$7\,\mu$s), we measured at the frequency 30.5 MHz the time T_2 at different points of the NMR line contour (Fig. 2b) and easily determined that the weak-field shoulder of the line corresponds to the signal from the powder particles whose axes make small angles with the field $\mathbf{H}_0$. In the absence of data on the character of the distribution of the particle orientations in the specimen under study, we cannot model accurately the form of the spectrum and for this reason we give the approximate magnitudes of the isotropic and anisotropic shifts, starting from a comparison with the form of the NMR spectrum of the unoriented powder (dashed line in Fig. 2b): $K_0 = +0.2\%$ and $K_\| = +0.5\%$. We note that the isotropic shift found here [measured according to the reference NMR line of ^{63}Cu of metallic copper, $^{63}K = +0.237\%$ (Ref. 26)] differs from the value $K_0 \approx 0$, found by Kumagai *et al.*[12] at temperatures $T < T_c$.

Relaxation. Experiments with oriented PrCeCuO powder, performed at frequencies from 8.1 to 30.8 MHz at temperatures of 1.5–4.2 K, showed that relaxation of the transverse magnetization of copper nuclei is described well by an exponential law $A_{2\tau}/A_0 = \exp(-2\tau/T_2)$ (see Fig. 3a). At low frequencies the relaxation rate is higher than can be provided by the dipole-dipole interaction of copper nuclei. The observed ratio of the relaxation rates of two isotopes $({}^{63}T_2^{-1}/{}^{65}T_2^{-1} < 1)$ indicates that the relaxation mechanism operating in addition to the dipole-dipole mechanism is of a magnetic nature, and in addition its effect is larger in a field oriented along the crystal $\mathbf{c}$ axis (see Ref. 25 and Fig. 2b) than in a field $\mathbf{H}_0 \perp \mathbf{c}$: $T_{2\|}^{-1} > T_{2\perp}^{-1}$. The additional mechanism of spin-spin relaxation is most efficient at low NMR frequencies; the relaxation time T_2 increases rapidly with increasing frequency. Thus, for example, measurements of the relaxation times of the isotope ^{63}Cu in a field $\mathbf{H}_0 \| \mathbf{c}'$, performed at a temperature of 4.2 K using narrow ($\tau_{\pi/2} = 3\,\mu$s) high-amplitude rf pulses, exciting practically all spins in a narrow NMR line, gave the value ${}^{63}T_{2\|} = 70\,\mu$s at 8.1 MHz and 170 μs at 30.8 MHz; for ^{65}Cu nuclei the corresponding times ${}^{65}T_{2\|}$ are equal to 66 and 160 μs. As the temperature of the specimen decreases from 4.2 to 1.5 K the times T_2 increase insignificantly (approximately by 15%), but when the specimens are cooled to ≈ 0.2 K they increase by a factor of two. Thus, for example, measurements of the times ${}^{65}T_{2\|}$ at 23 MHz gave values of 125, 200, and 250 μs at temperatures of 4.2, 0.5, and 0.17 K, respectively.

The spin-lattice relaxation of copper nuclei is of special interest. As should happen for spins $I = 3/2$, the restoration of the longitudinal magnetization in our system is a two-exponential process with decay times differing by a factor of six. It is known that in the case of large quadrupole splittings the relative weight of the slow process (relaxation with the true time T_1), recorded on the transition $|1/2\rangle \leftrightarrow |-1/2\rangle$, is equal to only 10%. In our experiments, however, this quantity, which depends, as it turned out, on the NMR frequency, amplitude, and width of the rf pulses, was always significantly larger—from 30 to 55%. The typical results of measurements of T_1 are presented in Fig. 3b. We have already mentioned in the introduction that Kumagai *et al.*[12] found that the temperature dependence of the spin-lattice relaxation of ^{63}Cu in PrCeCuO corresponds to Korringa's law. The results of their experiments and the approximating straight line

$$T_1^{-1} = 6{,}8 \qquad (\mathrm{s}^{-1}) \tag{1}$$

are shown in Fig. 4. We note that at temperatures below T_c all experimental points[12] lie above the straight line. Our measurements at 22.5 MHz (open circles in Fig. 4) confirmed the approximation (1) at 0.8 K, but it turned out that the experimental points obtained at $T = 1.4$ and 4.2 K also

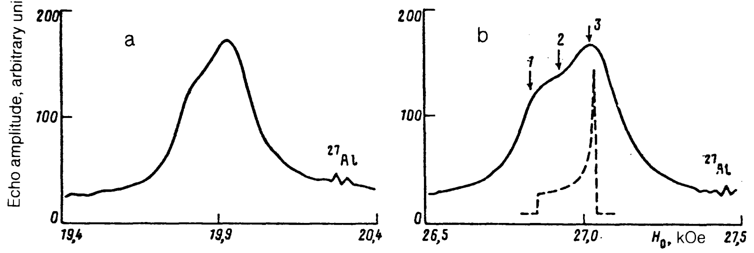

FIG. 2. Shape of the NMR line of ^{63}Cu at frequencies of 22.5 MHz (a) and 30.5 MHz (b). $\mathbf{H}_0 \| \mathbf{c}'$, $t = 4.2$ K, $t_{\pi/2} = 3\,\mu$s, the dashed curve is the computed spectrum of ^{63}Cu of the unoriented powder with the parameters $K_0 = +0.19\%$ and $K_\| = +0.46\%$, and the arrows *1*, *2*, and *3* indicate the points of the NMR line contour at which $T_2 = 135$, 152, and 179 μs, respectively ($t_{\pi/2} = 7\,\mu$s).

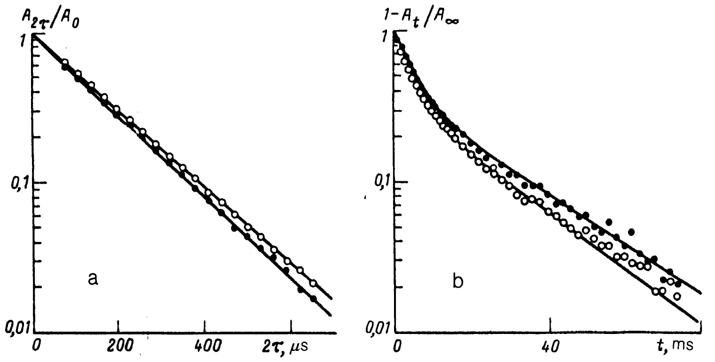

FIG. 3. Decay of the transverse magnetization (a) $A_{2\tau}/A_0 = \exp(-2\tau/T_2)$ and restoration of the longitudinal magnetization (b) $1 - A_t/A_\infty = (1-\lambda)\exp(-t/T_1') + \lambda\exp(-t/T_1)$ of copper nuclei in oriented PrCeCuO powder. $\mathbf{H}_0 \| \mathbf{c}'$, $\nu = 30.8$ MHz, $T = 4.2$ K, $t_{\pi/2=3}$ μs, ○—^{63}Cu, ●—^{65}Cu; solid lines: a) $^{63}T_2 = 170(1)$ μs (top line), $^{65}T_2 = 160(1)$ μs (bottom line); b) $^{63}T_1' = 4.4(1)$ μs, $^{63}T_1 = 23.4(6)$ ms, $\lambda = 0.34(1)$ (bottom line); $^{65}T_1' = 4.7(1)$ ms, $^{65}T_1 = 25.7(7)$ ms, $\lambda = 0.37(1)$ (top line).

lie above the straight line (1). It was first pointed out in Ref. 25 that the relaxation times T_1 of ^{63}Cu nuclei measured at low frequencies (8.1 and 10.7 MHz) at temperatures of 1.5–4.2 K are systematically shorter than the relaxation times of the ^{65}Cu nuclei, and in this connection it was suggested that the nuclear-spin-lattice relaxation operates by the quadrupole mechanism. In experiments at higher frequencies (22.5 and 30.8 MHz) the difference in the times T_1 of the two copper isotopes is not as large as at low frequencies and the relaxation times themselves increase [in the field $\mathbf{H}_0 \| \mathbf{c}'$ at a temperature of 4.2 K $^{63}T_1$ changes from 13.6(6) ms at 10.7 MHz (Ref. 25) to 21.5(8) ms at 30.8 MHz while the time $^{65}T_1$ changes from 15.5(9) ms to 23.5(14) ms, respectively], but the inequality $^{63}T_1^{-1}/^{65}T_1^{-1} > 1$ continues to hold (see Fig. 3b). These observations show that the estimates of the quadrupole relaxation rate must be treated with great care.

In the compound PrCeCuO the copper-oxygen planes CuO$_2$ are separated by "sandwiches" consisting of Pr–O–Pr planes, in which the Ce^{4+} ions occupy some of the rare-earth sites. It is thought that the cerium ions give up electrons to the copper-oxygen planes, as a result of which the material becomes an n-type conductor. We shall further assume, on the basis of the well-known capability of praseodymium to exist in a tetravalent state (the oxide PrO$_2$ is an example), that Ln^{4+} holes are not localized on the cerium atoms but rather are distributed over the praseodymium-cerium planes. The presence of tetravalent praseodymium in Pr_2CuO_4 and $Pr_{1.85}Ce_{0.15}CuO_4$ was noted in Ref. 4. Charge transfer in the rare-earth subsystem gives rise to fluctuations of the electric-field gradient on the copper nuclei in adjacent CuO$_2$ planes and can give rise to spin-lattice relaxation with the rate[27]

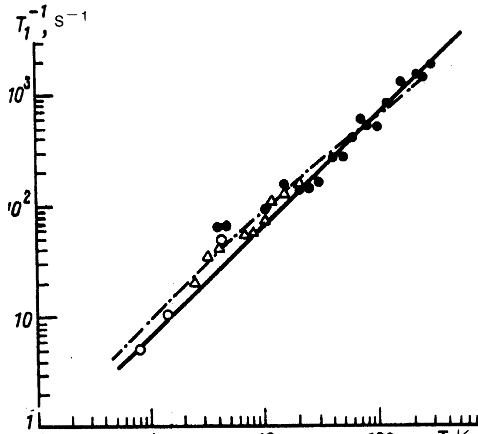

FIG. 4. Temperature dependence of the spin-lattice relaxation rate of ^{63}Cu nuclei in $Pr_{2-x}Ce_xCuO_{4-y}$: ● (70 MHz), △ (12 MHz)—data from Ref. 12, (22.5 MHz)— our measurements; the straight line is Korringa's law (1); the dot-dashed line is $T_1^{-1} = T_{1Q}^{-1} + 4.6T$ (see text).

$$T_{1Q}^{-1} = {}^2/_5(w_1 + 4w_2), \tag{2}$$

where w_1 and w_2 are the probabilities of transitions with $\Delta m = \pm 1$ and ± 2, respectively. We shall estimate the rate of this relaxation.

We represent in the following form[28] the Hamiltonian describing the interaction of the nucleus with the electrons:

$$\mathscr{H} = \frac{e^2Q}{I(2I-1)} \sum_q r^{-3}(-1)^q F_{-q}^{(2)} C_q^{(2)}(\theta, \varphi), \tag{3}$$

where it is assumed that the nucleus is located at the origin of the coordinate system; r, θ, φ are the spherical coordinates of the electron; $C_q^{(2)}(\theta,\varphi)$ is a spherical tensor; and, $F_q^{(2)}$ designate the components of a tensor constructed from the nuclear-spin operators:

$$\begin{gathered} F_0^{(2)} = {}^1/_2[3I_z^2 - I(I+1)], \\ F_{\pm 1}^{(2)} = \mp({}^3/_8)^{1/2}(I_zI_\pm \pm I_\pm I_z), \\ F_{\pm 2}^{(2)} = ({}^3/_8)^{1/2} I_\pm^2. \end{gathered} \tag{4}$$

Let the electronic density of states in the $4f$ band of width W be described by the parabolic law

$$\rho(\varepsilon) = \frac{8}{\pi W^2}[\varepsilon(W-\varepsilon)]^{1/2}. \tag{5}$$

Then, after summing over the current-carrier states (i.e., over the states of the thermostat absorbing energy from the nuclear Zeeman reservoir) we obtain

$$T_{1Q}^{-1} = \frac{2\pi}{\hbar}\cdot\frac{2}{5}\int \rho^2(\varepsilon) f(\varepsilon-\mu)[1 - f(\varepsilon-\mu)](w_1' + 4w_2')d\varepsilon. \tag{6}$$

Here $f(\varepsilon - \mu)$ is the Fermi distribution function, μ is the chemical potential, and w_1' and w_2' are determined by the squared matrix elements of the operator (3) on the wave functions of the copper nucleus and the conduction electrons. We estimate the width of the $4f$ band as follows:

$$W \approx 4\lambda_{4f\sigma}^2 U. \tag{7}$$

Here $\lambda_{4f\sigma}$ is the hybridization parameter for the $4f$ electrons hybridized with the $2p\sigma$-states of oxygen and U is the Coulomb repulsion energy of the electrons. Taking $\lambda_{4f\sigma} = 0.042$ and $U = 8.6 \cdot 10^4$ K (Ref. 29) we find $W = 600$ K. Next, as in the first work on nuclear quadrupole relaxation in metals,[30] we write the Hamiltonian (3) in the second-quantized representation:

$$\mathscr{H} = \sum_{\bar{k}\bar{k}'\sigma} B^q_{\bar{k}\bar{k}'} F^{(2)}_q a^+_{\bar{k}\sigma} a_{\bar{k}'\sigma}. \tag{8}$$

In our case, in contrast to Ref. 30, the coefficients $B^q_{\bar{k}\bar{k}'}$ are best sought in the strong-coupling approximation using the well-known expansion

$$\exp(i\bar{k}\bar{R}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kR)(-1)^m Y_l^{-m}(\theta_k, \varphi_k) Y_l^m(\theta_R, \varphi_R), \tag{9}$$

where

$$j_l(x) = x^l \left(-\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x}$$

are spherical Bessel functions. As a result we have

$$B^q_{\bar{k}\bar{k}'} = 4\pi \frac{e^2 Q(1-\gamma_\infty)}{I(2I-1)N} \times \sum_{l_1 m_1 l_2 m_2} (i)^{l_1 - l_2 + 2m_1 + 2m_2 - 2q} b_{kk'}(l_1 m_1 l_2 m_2, 2q) \times Y_{l_1}^{m_1}(\theta_k, \varphi_k) Y_{l_2}^{m_2}(\theta_{k'}, \varphi_{k'}), \tag{10}$$

where

$$b_{kk}'(l_1 m_1 l_2 m_2, 2q) = 4\pi \sum j_{l_1}(kR) j_{l_2}(k'R) \times Y_{l_1}^{-m_1}(\theta_R, \varphi_R) Y_{l_2}^{-m_2}(\theta_R, \varphi_R) C^{(2)}_{-q}(\theta_R, \varphi_R), \tag{11}$$

and N is the number of Ln atoms.

We assume that the number of holes in the praseodymium subsystem is small, and we estimate the sum (11) only for small values of k. Table I gives the results of the calculation of the three sums with $l_1 = l_2 = 1$:

$$\sum\nolimits_1 = \sum j_1^2(kR) \frac{z^2(x^2+y^2)}{R^7}, \quad \sum\nolimits_2 = \sum j_1^2(kR) \frac{(x^2+y^2)^2}{R^7}, \quad \sum\nolimits_3 = \sum j_1^2(kR) \frac{x^4 - 6x^2y^2 + y^4}{R^7}. \tag{12}$$

Analysis shows that the sums in Eqs. (12) can be approximated by the following expression:

$$\sum\nolimits_i = a_i \operatorname{th}(b_i k^2). \tag{13}$$

Here $a_1 = 89.5$; $a_2 = 332.5$; and $a_3 = -23.3$ (in 10^{20} cm^{-3}) and $b_1 = 678.3$; $b_2 = 511.2$; and $b_3 = 1032$ (in Å^2).

Transferring next from summation over k and k' to integration over the energy ε, we obtain the formula (6) for the relaxation rate, where

$$w_1' + 4w_2' = 6[3\pi e^2 Q(1-\gamma_\infty)]^2 \left[4\sum\nolimits_1^2 + \left(\sum\nolimits_2 + \sum\nolimits_3\right)^2\right]. \tag{14}$$

Strictly speaking, when determining the chemical potential μ the hybridization of the states of praseodymium with the copper-oxygen planes must be taken into account. Assuming this hybridization to be weak, we shall assume that the number of holes in the praseodymium subsystem is constant. Then the chemical potential will be determined by solving the equation

$$1 - \frac{n}{2} = \int_0^W \rho(\varepsilon) f(\varepsilon - \mu)\, d\varepsilon, \tag{15}$$

where n is the number of holes per praseodymium atom. An example of the solution of this equation with $W = 600$ K and $n = 0.06$ is presented in Table II (column 2).

In calculating the quadrupole relaxation rate T_{1Q}^{-1} we employed the quadratic dispersion relation for quasiparticles in the subsystem of Ln atoms near the top of the band:

$$W - \varepsilon = (\Omega W / 32\pi) k^2 \approx 1{,}54\, W k^2$$

where $\Omega = V/N$ is the unit-cell volume and k is given in angstroms. The computational results are presented in column 3 of Table II [$^{63}Q = -0.211$ b, $1 - \gamma_\infty = 12.3$ (Ref. 24)]. In order to obtain agreement with the experimental data, we retain also the magnetic contribution to the relaxation rate $T_{1M}^{-1} = 4.6/T$ (s^{-1}) [1.5 times smaller than (1)]. The temperature dependence of the resulting rate, $T_1^{-1} = T_{1Q}^{-1} + T_{1M}^{-1}$, is shown by the dot-dashed line in Fig. 4.

At first glance, our proposed description of the experimental results does not have any obvious advantages over the approximation by the standard Korringa straight line (1). We note, however, if we had not invoked the quadrupole relaxation mechanism we would not have been able to explain either the fact that in the temperature range 2–20 K the measured rates are systematically higher than the values given by Eq. (1) or the main observation itself that

TABLE I. Lattice sums Σ_1, Σ_2, and Σ_3 for Pr_2CuO_4 (in 10^{20} cm^{-3}).

k, Å^{-1}	Σ_1	Σ_2	Σ_3	k, Å^{-1}	Σ_1	Σ_2	Σ_3
0,01	7,1	20,0	−2,8	0,07	82,6	311,6	−12,9
0,02	23,2	67,5	−8,7	0,08	84,2	323,7	−10,4
0,03	42,7	130,4	−14,9	0,09	85,2	328,7	−9,7
0,04	60,2	194,5	−18,6	0,10	86,1	330,2	−10,8
0,05	72,4	248,7	−18,9	0,15	89,6	332,5	−23,3
0,06	79,3	287,7	−16,4				

TABLE II. Chemical potential μ and nuclear relaxation rate of ^{63}Cu in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$.

T, K	μ, K	T_{1Q}^{-1}, s^{-1}	T_{1M}^{-1}, s^{-1}	T, K	μ, K	T_{1Q}^{-1}, s^{-1}	T_{1M}^{-1}, s^{-1}
0,5	558,7	2,5	2,3	60	637	155	273
1,5	558,7	7,4	6,8	100	739	186	455
4,2	559,0	20,5	19,1	120	796	195	545
10	560,8	46,5	45,5	200	1046	211	910
20	568	82	91	300	1377	218	1364
40	596	127	182				

$^{63}T_1^{-1}/^{65}T_1^{-1} > 1$. This latter relation can be realized only when the rates of the relaxation transitions thanks to the fluctuations of the EFG ($^{63}T_{1Q}^{-1}/^{65}T_{1Q}^{-1} = {}^{63}Q^2/^{65}Q^2 = 1.17$ exceed the magnetic relaxation rates ($^{63}T_{1M^{-1}}/^{65}T_{1M^{-1}} = {}^{63}\gamma^2/^{65}\gamma^2 = 0.87$).

3. PRASEODYMIUM NMR

Spectra. Most works on NMR spectroscopy of rare-earth ions in van Vleck paramagnets[22,23] have still have performed by stationary NMR methods and, as a rule, the specimens consisted of single crystals of rare-earth compounds. In those cases when large crystals were difficult to prepare and their use did not promise any advantages (for example, owing to the skin effect in conducting materials), the specimens usually[20] consisted of powders of compounds with cubic structure and in which one NMR line, characterized by the single parameter $\gamma = \gamma_I(1+\alpha)$, where γ_I is the gyromagnetic ratio of a free nucleus of a rare-earth ion and α is the paramagnetic NMR shift, was observed (once again by stationary methods).

The pulsed method of NMR (spin echo) has not been employed in spectroscopy primarily because of the short spin-spin relaxation times T_2 of the nuclei of rare-earth ions, though it has been employed for studying the relaxation characteristics of nuclei in several dielectric crystals of praseodymium and thulium compounds.[21,23] Metallic van Vleck paramagnets were regarded as especially unsuitable for investigations performed by the pulsed method.[19] As far as we know, Sato, Kitaoka, Yasuoka, *et al.*[31] were able to observe a spin echo at frequencies of 55–140 MHz only in the compound $PrIn_3$ (with the cubic structure of $AuCu_3$) and they were able to measure the relaxation time of the ^{141}Pr nuclei: $T_1 = 225\,\mu$s and $T_2 = 0.43\,\mu$s at $T = 1.2$ K. It is obvious that such short times T_2 left little hope that the pulsed method of NMR of rare-earth ions could be successfully employed in investigations of high-T_c superconductors. However, in the first experiments with the compounds $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (Refs. 16, 17, 32) and $TmBa_2Cu_3O_{7-y}$ (Ref. 33) it was found that the times T_2 of the nuclei of rare-earth ions in high-T_c superconductors can have the most unexpected values and, in particular, at temperatures $T \ll T_c$ they can reach hundreds of microseconds. Under these conditions the main problem becomes not so much the observation itself of the spin echo with extremely short time intervals τ between the $\pi/2$ and π pulses as interpretation of the NMR spectrum of the powder, and in order to facilitate interpretation it is simply necessary to employ magnetically oriented powder. The NMR spectrum ^{141}Pr in a field $\mathbf{H}_0$ parallel to the direction c' of predominant orientation of the crystallographic c axes of particles of the powder PrCeCuO has a higher intensity and a more pronounced fine structure than the spectrum in a field $\mathbf{H}_0 \perp \mathbf{c}'$.[17] For this reason all experiments described below were performed with a field $\mathbf{H}_0 \| \mathbf{c}$.

The form of the spectrum $A_{2\tau}(H_0)$ at the temperatures of liquid helium ^{4}He (Fig. 5) is strongly distorted by the field dependence $T_2(H_0)$: in strong fields one can see well all five "lines" ($I = 5/2$) belonging to powder particles whose c axes make small angles θ with the external field and for which comparatively long nuclear relaxation times ($T_2 = 10$–$30\,\mu$s) are characteristic, but the group of NMR lines determined by crystallites with large angles θ and weak resonance fields is practically excluded from the spectrum owing to their very short times T_2 ($< 5\,\mu$s). This group of unresolved lines is observed only when the spectrum is recorded with the minimum admissible interval τ between the $\pi/2$ and π pulses (compare the two weak-field curves in Fig. 5). Our apparatus made it possible to perform measurements with the minimum values $\tau = 6$, 7, and 15 μs at fre-

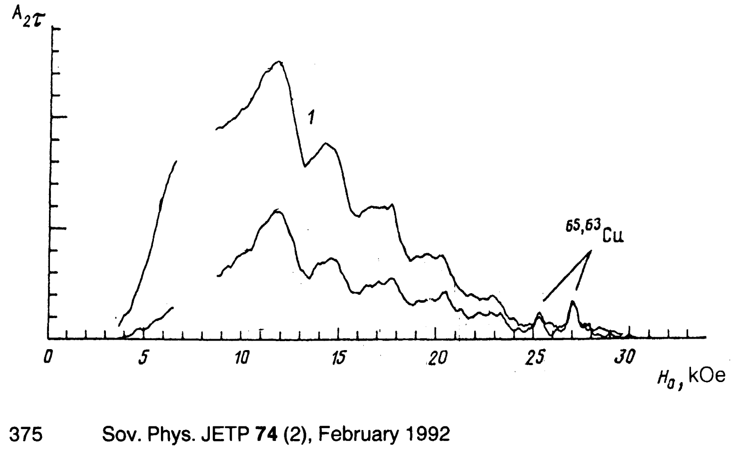

FIG. 5. NMR spectra of ^{141}Pr in oriented PrCeCuO powder at a frequency of 30.5 MHz, $\mathbf{H}_0 \| \mathbf{c}'$, $T = 2.35$ K, $t_{\pi/2} = 1\,\mu$s, $\tau = 6\,\mu$s (curve *1*) and 15 μs (curve *2*); the five "steps" correspond to $|-5/2\rangle \leftrightarrow |-3/2\rangle$, $|-3/2\rangle \leftrightarrow |-1/2\rangle$, $|-1/2\rangle \leftrightarrow |1/2\rangle$, $|1/2\rangle \leftrightarrow |3/2\rangle$, $|3/2\rangle \leftrightarrow |5/2\rangle$. The fragments of the spectrum in the region of the NMR of the paraffin protons (6.5–8.5 kOe) were excluded.

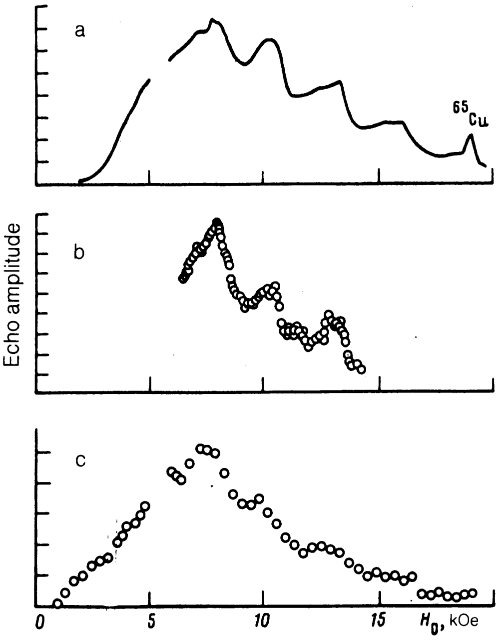

FIG. 6. NMR spectra of ^{141}Pr in oriented PrCeCuO powder at a frequency of 23 MHz in a field $\mathbf{H}_0 \| \mathbf{c}'$; a) $T = 1.6$ K, $t_{\pi/2} = 1.1$ μs, $\tau = 7$ μs; b) $T = 1.05$ K, $t_{\pi/s} = 1$ μs, $\tau = 7$ μs; c) $T = 0.10$ K, $t_{\pi/2} = 0.9$ μs, and $\tau = 10\,\mu$s.

quencies of 30, 20, and 10 MHz, respectively. Interpretation of the spectra, similar to those shown in Figs. 5 and 6a, using the methods of numerical modeling showed[16,17] that the compound PrCeCuO has two types of $^{141}\text{Pr}^{3+}$ centers—rapidly relaxing $\text{Pr}^{(1)}$ and slowing relaxing $\text{Pr}^{(2)}$. The NMR spectrum of $\text{Pr}^{(2)}$ at $T = 1.5$–4.2 K is described by an axisymmetric spin Hamiltonian

$$\mathscr{H}_I = -\gamma_\| \hbar H_z I_z - \gamma_\perp \hbar (H_x I_x + H_y I_y) + D[I_z^2 - I(I+1)/3] \quad (16)$$

with the following parameters:

$$\gamma_\|^{(2)}/2\pi = 1{,}66(5)\ \text{kHz/Oe}, \quad \gamma_\perp^{(2)}/2\pi = 5{,}1(5)\ \text{kHz/Oe}, \quad |D^{(2)}/h| = 2{,}4(2)\ \text{MHz}. \quad (17)$$

These parameters correspond to the components of the NMR paramagnetic shift $\alpha_i = (\gamma/\gamma_1 - 1)$:

$$\alpha_\| = 0.317(40) \quad \text{and} \quad \alpha_\perp = 3.05(40); \quad (18)$$

where $\gamma_I/2\pi = 1.26$ kHz/Oe is the gyromagnetic ratio of the praseodymium nuclei.[34] Because the times T_2 are short the intensity of the NMR spectrum of $\text{Pr}^{(1)}$ is very weak, and the components of the fine structure of this spectrum (five wide lines) are observed only with the shortest time intervals τ as weak-field satellites of the components of the $\text{Pr}^{(2)}$ spectrum and correspond to the parameters $\gamma_{(\|)}^{(1)}/2\pi \approx 1.84$ kHz/Oe and $|D^{(1)}/h| \approx 2.5$ MHz. The relative content of $\text{Pr}^{(1)}$ and $\text{Pr}^{(2)}$ atoms cannot be determined from the form of the spectra, but it can be determined reliably from the results of relaxation measurements at ultralow temperatures: $n^{(1)}/n^{(2)} \approx 2$ (see below).

Calculation of the crystal-field Stark effect using four sets of parameters of the crystal electric field (CEF), which were proposed in Refs. 35–38, shows that the ground state of the Pr^{3+} ion in PrCeCuO must be a singlet state $|^3H_4, \Gamma_3\rangle = 2^{-1/2}(|4,2\rangle + |4,-2\rangle)$. If only the $4f$ states with $J = 4$ are considered, then the energy splitting $E(\Gamma_4) - E(\Gamma_3)$ can be estimated with the help of (18) and the expression for the paramagnetic shift in a field $H_0 \| c$ $(T = 0)$:

$$\alpha_\| = \frac{2A_J g_J \mu_B}{\gamma_I \hbar} \frac{\langle ^3H_4, \Gamma_3 | J_z | ^3H_4, \Gamma_4 \rangle^2}{E(\Gamma_4) - E(\Gamma_3)}, \quad (19)$$

where $A_J/h = 1093$ MHz is the hyperfine interaction constant of a free Pr^{3+} ion,[28] $g_J = 4/5$ is the Landé factor, and $|^3H_4, \Gamma_4\rangle = 2^{-1/2}(|4,2\rangle - |4,-2\rangle)$ is the wave function of the excited singlet state. Such an estimate gives the value 815(90) cm^{-1}. It turned out that the energy of the singlet state Γ_4 close to this value can be obtained only with one of the above-mentioned sets of parameters of the CEF, namely, with the set proposed by Nekvasil[38] for describing the observed properties of Nd^{3+} ions in Nd_2CuO_4. If the CEF Hamiltonian is represented in the form

$$\mathscr{H}_{\text{cr}} = \Sigma \chi_n C_n^m O_n^m,$$

where $\chi_n = \alpha, \beta, \gamma$ are Stevens coefficients and O_n^m are equivalent operators, then the parameter set of Ref. 38 will be as follows (in cm^{-1}):

$$C_2^0 = -257, \quad C_4^0 = -242, \quad C_4^4 = 2090, \quad C_6^0 = 37{,}1, \quad C_6^4 = \bar{1}103. \quad (20)$$

The energies and wave functions of the states $^3H_4$ calculated with these parameters are given in the left-hand half of Table III. Using them we find the paramagnetic shift $\alpha = 0.2904$ and the effective gyromagnetic ratio $\gamma_\|/2\pi = 1.626$ kHz/Oe, which agree fairly well with the measured values.

Strictly speaking, since the excited multiplet level $^3H_5$ lies above $^3H_1$ by only 2100 cm^{-1},[28] the paramagnetic NMR shifts must be calculated taking into account J mixing. The results of diagonalization of the total energy matrix of the states $^3H_4$ and $^3H_5$ in a crystal field are presented on the right-hand side of Table III (only for the lower group of levels). As one can see, the state $|^3H_4, \Gamma_4\rangle$ is shifted downward by almost 100 cm^{-1} and its wave function acquires a significant admixture of the state $|^3H_5, \Gamma_4\rangle$. Because of the downwards shift of the level the paramagnetic shift $\alpha_\|$ increases. This increase, however, is compensated by the decrease of the Zeeman interaction matrix element, proportional to $\langle \Gamma_3 | L_z + 2S_z | \Gamma_4 \rangle$, so that the value of the paramagnetic shift $\alpha_\|$ is even lower (0.2885). The calculation of the shift due to the higher-lying state $|^3H_5, \Gamma_4\rangle$ with energy 2360 cm^{-1} gives $\alpha' = -0.0069$, as a result of which, taking into account all effects due to J mixing, we obtain

$$\alpha_\| = 0{,}2816, \quad \gamma_\|/2\pi = 1{,}615\ \text{kHz/Oe}. \quad (21)$$

Comparing the computed value of $\gamma_\|/2\pi$ (21) and our measurement of this quantity for the $\text{Pr}^{(2)}$ nuclei (17) shows that the choice (20) for the CEF potential for Pr^{3+} ions in $\text{Pr}^{(2)}$ positions is correct. We shall not analyze the quantities $\gamma_\perp^{(2)}$ and $\gamma_\|^{(1)}$, since in the experiments they were determined with a large error. We only note that the singlet state $|^3H_4, \Gamma_4\rangle$ should lie significantly lower in the group of energy levels of the ions $\text{Pr}^{(1)}$ than in the group of levels of $\text{Pr}^{(2)}$.

TABLE III. Energy levels and wave functions of the ion Pr^{3+} in the crystal electric field in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$.

$^3H_4$ state			$^3H_4$ state with an admixture of $^3H_5$	
Energy, cm^{-1}	Wave function		Energy, cm^{-}	Wave function
891,8	Γ_4	$-0,707\,|2\rangle + 0,707\,|-2\rangle$	795,1	$-0,689\,|4,2\rangle + 0,689\,|4,-2\rangle$ $+0,160\,|5,2\rangle + 0,160\,|5,-2\rangle$
871,3	$\Gamma_1^{(2)}$	$0,690\,|4\rangle + 0,222\,|0\rangle$ $+0,690\,|-4\rangle$	825,5	$0,699\,|4,4\rangle - 0,073\,|4,0\rangle$ $+0,699\,|4,-4\rangle + 0,097\,|5,4\rangle$ $-0,097\,|5,-4\rangle$
859,6	Γ_2	$-0,707\,|4\rangle + 0,707\,|-4\rangle$	783,6	$-0,691\,|4,4\rangle + 0,691\,|4,-4\rangle$ $+0,112\,|5,4\rangle + 0,145\,|5,0\rangle$ $+0,112\,|5,-4\rangle$
731,0	$\Gamma_5^{(2)}$	$0,547|\pm 3\rangle - 0,837|\mp 1\rangle$	640,5	$-0,617\,|4,\pm 3\rangle + 0,757\,|4,\mp 1\rangle$ $\pm 0,179\,|5,\pm 3\rangle$ $\pm 0,010\,|5,\mp 1\rangle$ $\pm 0,120\,|5,\mp 5\rangle$
555,6	$\Gamma_1^{(1)}$	$-0,159\,|4\rangle + 0,975\,|0\rangle$ $-0,159\,|-4\rangle$	556,0	$0,036\,|4,4\rangle + 0,986\,|4,0\rangle$ $+0,036\,|4,-4\rangle + 0,111\,|5,4\rangle$ $-0,111\,|5,-4\rangle$
128,8	$\Gamma_5^{(1)}$	$0,837\,|\pm 3\rangle + 0,547\,|\mp 1\rangle$	99,4	$0,785\,|4,\pm 3\rangle + 0,607\,|4,\mp 1\rangle$ $\pm 0,081|5,\pm 3\rangle \pm 0,055|5,\mp 1\rangle$ $\pm 0,078\,|5,\mp 5\rangle$
0	Γ_3	$0,707\,|2\rangle + 0,707\,|-2\rangle$	0	$0,706\,|4,2\rangle + 0,706\,|4,-2\rangle$ $+0,044\,|5,2\rangle - 0,044\,|5,-2\rangle$

We now discuss the origin of two types of Pr^{3+} centers. Boothroyd *et al.*[37] actually observed two types of rare-earth sites in their experiments on inelastic neutron scattering by Nd^{3+} ions in $Nd_{1.85}Ce_{0.15}CuO_{4-y}$. Analyzing the experimental data of Ref. 37, Furrer *et al.*[39] introduced the idea of "undisturbed" (located far from Ce^{4+} ions) and "disturbed" (lying close to Ce^{4+} ions) Nd sites and proposed two slightly different sets of parameters for a CEF with tetragonal symmetry. Using this approach, the relative content of undisturbed and disturbed Nd^{3+} centers, estimated from the experiment of Ref. 37, is found to be approximately the same as in our case, i.e., $\sim$2:1. This agreement suggests that the disturbed $Ln^{(2)}$ centers are most likely belong to the four-fold nearest-neighbor environment of the cerium atoms in the rare-earth plane. The formula of the compound $Ln_{1.85}Ce_{0.15}CuO_{4-y}$ can then be represented in the form $Ln^{(1)}_{1.25}(CeLn_4^{(2)})_{0.15}CuO_{4-y}$, whence there naturally follows the ratio $n^{(1)}:n^{(2)} \approx 2:1$.

As we have already seen, in the superposition of the $Pr^{(1)}$ and $Pr^{(2)}$ spectra, which is observed by the pulsed NMR method, the intensity of the echo signal is determined primarily by the $Pr^{(2)}$ centers. For this reason, it can be expected that the form of the spectra will largely depend on the charge state of the cerium ions. The Ce^{4+} ions ($4f^0$) are diamagnetic, so that the form of the NMR spectrum of $Pr^{(2)}$ should remain constant as a function of the temperature. The Ce^{3+} ions ($4f^1, {}^2F_{5/2}, J = 5/2$), on the contrary, have a quite large magnetic moment. In the crystal field (20) the lower energy level should be the doublet $|\pm 1/2\rangle$ with g factors $g_\parallel = 6/7 = 0.857$ and $g_\perp = 18/7 = 2.571$. At sufficiently high temperatures, when the degree of polarization of the cerium spins $P_0 = \tanh(g\mu_B H_0/2kT)$ is small and the local fields generated by these spins at the neighboring nuclei are averaged to zero owing to the rapid electronic spin-lattice (and spin-spin) relaxation processes, the NMR spectra should not react much to a change of the temperature. Under the conditions of high polarization ($P_0 \approx 1$), however, the fine structure of the spectrum can be smoothed as a result of the spread of the local fields, if the latter are equal in magnitude to $|D^{(2)}/\gamma_\parallel^{(2)}\hbar| = 1.4$ kOe. Experiment shows (Figs. 5 and 6) that the fine structure of the spectrum is present in the temperature range of liquid ^{4}He (right up to 1 K), but when the sample is cooled to 0.1 K it vanished almost completely. We are inclined to interpret this fact as an indication of the existence of Ce^{3+} ions in the superconducting phase of PrCeCuO. The presence of Ce^{3+} ions in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ was also established by means of EELS.[4]

Relaxation. Before we present and discuss the results of relaxation mechanisms, we underscore once again the fact that they all refer to the superconducting phase of PrCeCuO. Indeed, if the above-proposed model of formation of the $4f$ band of praseodymium in the metallic phase is correct, then the relaxation rate of the transverse magnetization of Pr nuclei in the field $\mathbf{H}_0 \| \mathbf{c}$ can be approximately estimated as

$$T_2^{-1} \approx \Delta\omega_l^2 \tau, \tag{22}$$

where $\tau \sim \hbar/W$ is the correlation time of fluctuations of the longitudinal hyperfine magnetic field on the nucleus, W is the width of the $4f$ band, and $\Delta\omega_l = A_J/\hbar$ (we recall that the ground state of the Pr^{4+} ions, just as for the Ce^{3+} ion, should be the doublet $|\pm 1/2\rangle$). Substituting into the approximation (22) the quantities $A_J/\hbar = 1093$ MHz and $W = 600$ K (see above), we find $T_2^{-1} = 6 \cdot 10^5\ s^{-1}$ or $T_2 = 1.7\ \mu s$. If in our estimates the width of the band is too high, then in reality the time T_2 should be even shorter. These simple arguments, as all previous investigations of metallic van Vleck paramagnets, show that in order to observe pulsed NMR of praseodymium in a nonsuperconducting metal it is necessary to use a special apparatus in which the sensitivity of the detector has a very short sensitivity-restoration time.

Because the NMR spectra of $Pr^{(1)}$ and $Pr^{(2)}$ are superposed the relaxation of the longitudinal and transverse magnetizations of ^{141}Pr nuclei in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ is described by a two-exponential law:[16,17]

$$1 - A_t/A_\infty = (1-\lambda)\exp(-t/T_1^{(1)}) + \lambda\exp(-t/T_1^{(2)}), \tag{23}$$

$$A_{2\tau}/A_0 = (1-a)\exp(-2\tau/T_2^{(1)}) + a\exp(-2\tau/T_2^{(2)}). \tag{24}$$

The NMR signal from the rapidly relaxing $\mathrm{Pr}^{(1)}$ centers can be separated only at frequencies above 20 MHz. Measurements at 23 MHz and 1.6 K show that above the resonance field of the transition $|-5/2\rangle\leftrightarrow|-3/2\rangle$ for crystallites with small angles θ (to the right of maximum intensity of the spectrum in Fig. 6) all four relaxation rates are independent of the field. Their temperature dependence, measured at $H_0 = 7.5$ kOe (maximum intensity), is shown in Fig. 7 (light-colored symbols). The least-squares approximations of the measured relaxation rates (in $\sec^{-1}$) are as follows:

$$T_2^{-1}(\mathrm{Pr}^{(1)}) = 3{,}6\cdot 10^4 + 3{,}7\cdot 10^4\ T, \tag{25}$$

$$T_2^{-1}(\mathrm{Pr}^{(2)}) = 2{,}3\cdot 10^3 + 1{,}7\cdot 10^4\left(1-\mathrm{th}^2\frac{0{,}36}{T}\right) + 0{,}75\cdot 10^4\ T, \tag{26}$$

$$T_1^{-1}(\mathrm{Pr}^{(1)}) = 45 + 2{,}0\cdot 10^3\ T\left(1-\mathrm{th}^2\frac{0{,}57}{T}\right), \tag{27}$$

$$T_1^{-1}(\mathrm{Pr}^{(2)}) = 1{,}5 + 1{,}0\cdot 10^2\ T\left(1-\mathrm{th}^2\frac{0{,}56}{T}\right). \tag{28}$$

We call attention to the most important, in our opinion, features of the relaxation of praseodymium.

1. All relaxation rates are temperature-independent in the interval from 0.05 to 0.2 K. The measurements at 0.05 K show that the $\mathrm{Pr}^{(2)}$ nuclei make virtually the same contributions to the longitudinal and transverse components of the observed magnetization of praseodymium,

$$\lambda = 0{,}36(5),\quad a = 0{,}35(2), \tag{29}$$

whence we find the ratio $n^{(1)}/n^{(2)} \approx 2$, which suggest that the $\mathrm{Pr}^{(2)}$ atoms belong to the clusters $\mathrm{CePr}_4^{(2)}$.

2. At ultralow temperatures the relaxation rate $T_2^{-1}(\mathrm{Pr}^{(1)})$ is close, in order of magnitude, to the rate $T_{2d}^{-1}(\mathrm{Pr})$ which the interaction of the dipole magnetic moments of $^{141}\mathrm{Pr}$ nuclei, enhanced by the $4f$ electrons,[21,23] can give in a regular crystal lattice, while the rate $T_2^{-1}(\mathrm{Pr}^{(2)})$ is much shorter than T_{2d}^{-1}. If the relaxation of the transverse magnetization of $\mathrm{Pr}^{(2)}$ nuclei is also determined by the dipole-dipole interaction and the assumption that $\mathrm{CePr}_4^{(2)}$ clusters exist is correct and the cerium ions have a valance of three, then the ratio $T_2^{-1}(\mathrm{Pr}^{(2)})/T_2^{-1}(\mathrm{Pr}^{(1)})$ should be approximately equal to the relative cerium concentration $C = x/2$. Indeed, in a field $\mathbf{H}_0$ which is not parallel to the crystal c axis and which destroys the magnetic equivalents of the $\mathrm{Pr}^{(2)}$ positions within a single cluster (for most resonating particles of the powder $\mathbf{H}_0\|\mathbf{c}$, though $\mathbf{H}_0\|\mathbf{c}'$), only energy exchange between equivalent nuclei from different clusters will be significant, and the dipole-dipole interaction energy of the nuclei will be only a small fraction ($\sim C$) of its initial value. The ratio $T_2^{-1}(\mathrm{Pr}^{(2)})/T_2^{-1}(\mathrm{Pr}^{(1)}) = 0.064$ measured at ultralow temperatures is very close to the value $C = 0.15/2 = 0.075$, and this gives us another argument in favor of the existence of trivalent cerium in the superconductor PrCeCuO.

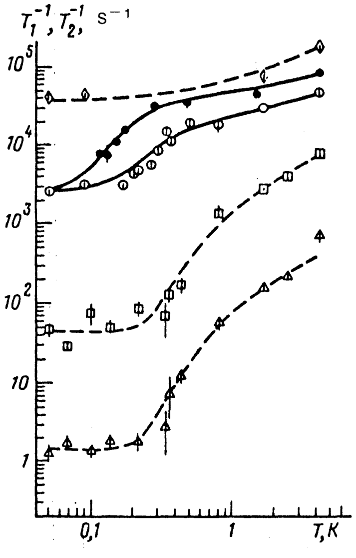

FIG. 7. Temperature dependence of the relaxation rates of $\mathrm{Pr}^{(1)}$ nuclei (◇—T_2^{-1}, □—T_1^{-1}) and $\mathrm{Pr}^{(2)}$ (○, ●—T_2^{-1}, △—T_1^{-1}). $\mathbf{H}_0\|\mathbf{c}$, the light-colored symbols correspond to $\nu = 23$ MHz, $H_0 = 7.5$ kOe; the dark-colored symbols correspond to $\nu = 15.6$ MHz, $H_0 = 4.2$ kOe; the approximating curves (top to bottom) correspond to the formulas (25), (31), (26), (27), and (28).

3. In the temperature range 0.2–0.5 K the relaxation rates of the praseodymium nuclei change radically. The character of the changes in $T_2^{-1}(\mathrm{Pr}^{(2)})$ is reminiscent of the analogous step in the temperature dependence of the relaxation rate $T_2^{-1}(T)$ of copper nuclei in a system with heavy fermions $\mathrm{CeCu_2Si_2}$,[40] so that it can be conjectured that the observed jump in $T_2^{-1}(\mathrm{Pr}^{(2)})$ is related with the superconducting transition.[17,32] However the spin polarization of the Ce^{3+} ions is still the most likely reason for the sharp slowing down of the transverse relaxation of $\mathrm{Pr}^{(2)}$ on cooling. The nuclear relaxation rate, owing to fast fluctuations of the local magnetic field h from the paramagnetic ion, are determined by the following expressions:[23]

$$T_1^{-1} = \gamma^2 h_t^2 \tau (1 - P_0^2), \tag{30a}$$

$$T_2^{-1} = \gamma^2 h_l^2 \tau (1 - P_0^2) + {}^1/_2 T_1^{-1}. \tag{30b}$$

Here h_l and h_t are the amplitudes of the longitudinal and transverse components of the local field, τ is the correlation time of the fluctuations (in magnetically concentrated materials it is the spin-spin relaxation time of the paramagnetic ions), $P_0 = \tanh(\delta/2kT)$ is the polarization factor of electronic spins, and δ is the Zeeman splitting of the energy levels of a paramagnetic ion. The second term in the formula (26), describing the transverse relaxation of $\mathrm{Pr}^{(2)}$ nuclei from $\mathrm{CePr}_4^{(2)}$ clusters, has the same form as Eq. (30b), and the quantity $\delta/2 = 0.36$ K in Eq. (26) with an effective field $H_0 = 7.5$ kOe corresponds to the effective value $g = 1.4$, as if the magnetic field made an angle of ≈ 25 with the z axis of the $\tilde{g}$ tensor of the Ce^{3+} ion. This can be taken as the average value of the angle θ in our specimen of magnetically oriented powder with the field orientation $\mathbf{H}_0\|\mathbf{c}'$.

It is obvious that as the constant field H_0 (and the NMR frequency) change the temperature range in which the polarization effect of the electronic moments of Ce^{3+} is manifested should be displaced. We observed this displacement, repeating the measurements of $T_2^{-1}(\mathrm{Pr}^{(2)})$ at a lower frequency (15.6 MHz in the field 4.2 kOe; the dark circles in Fig. 7); the results of these measurements are approximated by the expression

$$T_2^{-1}(\mathrm{Pr}^{(2)}) = 2{,}3\cdot 10^3 + 4{,}0\cdot 10^4\left(1 - \mathrm{th}^2\frac{0{,}21}{T}\right) + 1{,}0\cdot 10^4\, T, \tag{31}$$

in which the first and third terms have remained the same as in Eq. (26), while the splitting δ in the second term has decreased as the ratio of the magnetic fields (0.21 K $\approx$ 0.36 K·4.2/7.5). Thus the temperature dependence of the transverse relaxation rate of $\mathrm{Pr}^{(2)}$ nuclei also agrees with the hypothesis that in the superconductor PrCeCuO the cerium ions are in a trivalent state.

4. The relaxation of the longitudinal nuclear magnetization of praseodymium has an unusual functional temperature dependence which does not agree with the idea of relaxation via paramagnetic impurities [compare Eqs. (27) and (28) with Eq. (30a)]. The high and virtually temperature-independent relaxation rates of both types of nuclei at temperatures $T \lesssim 0.2$ K are especially unusual. At the present time we cannot give satisfactory explanations of these facts; they require more thorough experimental and theoretical investigation. We note, however, that the comparatively high values of the rates T_1^{-1} indicate that there exists a relaxation mechanism that is probably related with the motion of charges in the superconductor and is capable of giving rise to fluctuations of the hyperfine magnetic fields on praseodymium nuclei even at ultralow temperatures. We also note that the large difference between the relaxation rates T_1^{-1} and T_2^{-1} of $\mathrm{Pr}^{(2)}$ nuclei, which was observed not only at ultralow temperatures but also at temperatures above 1 K [see Fig. 7 and the formula (30)], is consistent with the hypothesis that the state of the cerium ions is magnetic: the $\mathrm{Pr}^{(2)}$ nuclei lie in the same plane as the Ce^{3+} ion, so that the transverse components h_t of the local fields are small, if the c axes of the crystallites make small angles with the external field $\mathbf{H}_0$.

4. CONCLUSIONS

The main facts and conclusions can be formulated as follows.

1. The NMR spectra of copper, characterized by the weak quadrupole interaction (${}^{63}\nu_Q \approx 1.6$ MHz) and the well-pronounced Knight shift ($K_0 \approx +0.2\%$ and $K_\parallel \approx +0.5\%$ are the isotropic and anisotropic components of the shift), must be referred to the metallic nonsuperconducting phase of the compound $\mathrm{Pr}_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_{4-y}$. This is indicated by the temperature dependence of the spin-lattice relaxation rate of copper nuclei, which, as was established previously in Ref. 12 for the temperature range $T = 2.4$–300 K and confirmed in this work down to $T = 0.8$ K, agrees fairly well with Korringa's law and does not have any significant peculiarities at temperatures $T \lesssim T_c = 24$ K. At the temperatures of liquid helium ^{4}He the spin-lattice relaxation rate ${}^{63}T_1^{-1}$ of ^{63}Cu nuclei is higher than the relaxation rate ${}^{65}\mathrm{T}_1^{-1}$ of ^{65}Cu nuclei; this indicates manifestation of the quadrupole mechanism of relaxation. As theoretical analysis shows, quadrupole relaxation can be explained by fluctuations caused in the electric-field gradient on copper nuclei by charge transfer (Ln^{4+} holes) along the system of rare-earth atoms.

2. The spin-spin relaxation of copper nuclei is of a magnetic nature (${}^{63}T_2^{-1} < {}^{65}T_2^{-1}$) and is characterized by appreciable anisotropy ($T_2^{-1}(\mathbf{H}_0 \| \mathbf{c}) > T_2^{-1}(\mathbf{H}_0 \perp \mathbf{c})$). At temperatures of 1.5–4.2 K the relaxation rate is significantly higher than the rate that can be supported by the magnetic dipole-dipole interaction of copper nuclei. This is especially clearly seen in measurements at low frequencies ($10 \lesssim$ MHz). As the NMR frequency increases and also as the sample is cooled to temperatures below 0.5 K, the effect of the additional channel of spin-spin relaxation of copper nuclei becomes weaker and the times T_2 reach values of the order of 200–250 μs. The nature of the additional mechanism of spin-spin relaxation of the copper nuclei at low temperatures.

3. It follows from measurements of the NMR spectra and relaxation of praseodymium nuclei at temperatures much lower than T_c that two types of magnetically nonequivalent centers ${}^{141}\mathrm{Pr}^{3+}$ are present in the PrCeCuO lattice: rapidly relaxing $\mathrm{Pr}^{(1)}$ and slowly relaxing $\mathrm{Pr}^{(2)}$ present in the quantitative ratio $n^{(1)}:n^{(2)} \approx 2:1$. Because of the unusually long, for metallic van Vleck paramagnets, relaxation times T_2 of ^{141}Pr nuclei we referred both types of observed centers to the superconducting phase of PrCeCuO, and the slowly relaxing $\mathrm{Pr}^{(2)}$ centers were identified as belonging to CePr_4 clusters in the rare-earth planes. The parameters of the NMR spectra of $\mathrm{Pr}^{(1)}$ and $\mathrm{Pr}^{(2)}$ differ little from one another and agree quite well with the existing representations of a tetragonal crystal electric field.[38]

4. Measurements of spin-lattice relaxation in a field of 7.5 kOe ($\mathbf{H}_0 \| \mathbf{c}'$, frequency of 23 MHz) showed that the times T_1 of $\mathrm{Pr}^{(1)}$ and $\mathrm{Pr}^{(2)}$ nuclei at low temperatures ranging from 4.2 to 0.2 K increase approximately by 100 and 400 times, respectively, while at ultralow temperatures ranging from 0.2 to 0.05 K they hardly change at all and remain unusually short: $T_1(Pr^{(1)}) \approx 20$ ms and $T_1(\mathrm{Pr}^{(2)}) \approx 700$ ms. Although the spin-lattice relaxation mechanisms are still unknown, on the basis of experimental results it can still be concluded that even at ultralow temperatures the ^{141}Pr nuclei in the superconductor PrCeCuO are affected by the fluctuating hyperfine magnetic fields perpendicular to the c axis of the crystal. Since at these temperatures all localized spins are completely polarized by the external field, the fluctuations of the hyperfine fields must apparently be considered as resulting from the motion of the charges.

5. The spin-spin relaxation rate of $\mathrm{Pr}^{(1)}$ nuclei at ultralow temperatures ($\approx 4\cdot 10^4\ \mathrm{s}^{-1}$) is close to the rate that can be expected from the dipole-dipole interaction of ^{141}Pr nuclei, enhanced by the $4f$ electrons, while the relaxation rate of $\mathrm{Pr}^{(2)}$ nuclei is approximately 15 times shorter. Such significant weakening of the dipole-dipole coupling of the nuclear moments of $\mathrm{Pr}^{(2)}$ as well as the characteristic temperature dependence of the relaxation rate $T_2^{-1} \propto [1 - \tanh^2(g\mu_B H_0/2kT)]$ and the vanishing of the fine structure in the NMR spectrum of $\mathrm{Pr}^{(2)}$ at $T = 0.1$ K can be explained by one factor: the cerium ion has a valance of three (at least at temperatures $T \lesssim 0.5$ K) and the ground state in the crystal field is a doublet $|M_J = \pm 1/2\rangle$ with the parameters $g_\parallel = 0.86$ and $g_\perp = 2.57$.

Thus, although the investigations of the NMR spectra and nuclear relaxation of copper and praseodymium performed in this work do not give direct proof of the two-phase composition of the compound $\mathrm{Pr}_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_{4-y}$, they indirectly confirm the existence of superconducting and nonsuperconducting phases in the specimen. Moreover, our data show that the cerium ions in these two phases have a different valence and, being triply charged in the superconducting phase they cannot be donors, and for this reason the charge carriers responsible for the superconductivity of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ must be holes and not electrons. Recently Wong *et al.*,[41] who observed large positive values of the Hall constant in a number of single crystalline specimens of $Nd_{2-x}Ce_xCuO_{4-y}$ at low temperatures, arrived at an analogous conclusion. Thus doubts in the "electronic character" of the superconductor $Pr_{2-x}Ce_xCuO_{4-y}$ have now been added to the same doubts for the superconductor $Nd_{2-x}Ce_xCuO_{4-y}$, first stated two year ago[42] and persisting to this day. The resolution of these doubts must be sought in independent experiments, and in particular heat-capacity measurements at ultralow temperatures.

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