M. A. Teplov. *Nuclear magnetic resonance, nuclear quadrupole resonance, and nuclear relaxation in high-temperature superconductors.* A possibility for two phases (conductive and dielectric) to exist in oxide superconductors has long been discussed.[1,2] Thus far the experiments on neutron diffraction on powders made it possible to establish that in superconductors La_2CuO_{4+x}, $Nd_{2-x}Ce_xCuO_4$, $La_{2-x}Sr_xCuO_4$ in a certain domain of values of x, a separation of phases actually occurs, and here the temperature of the transition to superconductive state, observed in the experiments, achieves its maximum at the boundary of the domain of phase coexistence.[3] In the domain of phase coexistence itself, a sample is a mixture of a superconductor of a fixed composition with a maximum value of T_s and a nonsuperconductor (a dielectric or a metal) of a different, but specified for the given x, composition. The available experimental data makes us assume that critical temperatures of oxide superconductors are limited by their phase instability. Therefore, it seems necessary to obtain detailed information on the electron structure of both phases of a substance. The present paper describes the results of experimental research by the method of nuclear magnetic resonance (NMR) of the two-phase $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ ($T_c = 24$ K) system. This substance belongs to the class of the so-called electronic superconductors $Ln_{2-x}M_xCuO_{4-y}$ (Ln = Pr, Nd, Sm, Eu; M = Ce, Th) with Nd_2CuO_4 structure.[4] A two-phase composition of the substance for $x = 0.15$ was determined earlier in the experiments with $Nd_{2-x}Ce_xCuO_{4-y}$ samples.[5]

NMR of copper. It is known,[6,7] that in antiferromagnetics Nd_2CuO_4 and Pr_2CuO_4 electric quadrupole interaction between copper nuclei is sufficiently strong ($\nu_Q = 13$–14 MHz) and in the case of doping of these compounds by cesium or thorium, copper centers appear, which are characterized by a very weak quadrupole interaction. While in a

superconductor with $x = 0.15$ these centers also exist on a level with others (having nuclear quadrupole resonance (NQR) frequencies in a wide spectrum from 20 to 60 MHz), they dominate in a nonsuperconductive metal phase ($x > 0.18$). A relative content of copper centers with a wide NQR spectrum is great in the domain of values of x, which corresponds to the observed great values of T_s and close to zero for $x \leqslant 0.05$ and $x = 0.2$.[6] Correlation of such a behavior with a concentration (x) dependence of a portion of superconductive phase[5] enables us to assign copper centers with a weak quadrupole interaction to a nonsuperconductive metal.

Let us dwell on the results of investigating copper NMR in the metal phase of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$. The spin-lattice relaxation of these nuclei at temperatures from 2.4 to 300 K is of Korringa nature: $T_1 T = 147$ ms K.[8] Experiments with an oriented powder[9] do not reveal any indication of an angular dependence of the time T_1; at the same time they show that in a crystal the spin-spin relaxation time T_2 in the case that the external field H is oriented along the c-axis must be significantly less than in the case $H \perp c$. The observed relationship between the relaxation times of two isotopes $^{63}T_2/^{65}T_2 > 1$ indicates that the mechanism of spin-spin relaxation of copper nuclei is of magnetic nature.

Calculations of different contributions to the gradient of the electric field (GEF) at the copper nuclei,[10] which take into account the effects of covalence and overlap of electron orbits of copper and oxygen, and also assume that there is a 15% admixture of a Cu^+ state, yield quadrupole frequency $\nu_Q = -34.5 - 16 + 53.2 = 2.7$ MHz; here the three contributions represent successively a ligand lattice, 3p- and 3d-electrons.[9] At liquid helium temperatures, narrow lines of copper NMR are observed on a "pedestal", where a diffuse quadrupole structure of the powder NMR spectrum, can be guessed at. Numerical simulation of the spectrum shows that it is described by a sum of four Gaussian curves (two narrow lines and two "pedestals"), and here the root-mean-square values of halfwidths of the "pedestals" are 800 kHz (^{63}Cu) and 700 kHz (^{65}Cu), i.e. they correspond to the root-mean-square values $(\nu_Q^2)^{1/2} = 1.6$ and 1.4 MHz, respectively. These values are close to the calculated frequency, however, the absence of any traces of nonmonotonic fall of the NMR signal strength at the line tails suggests that the "pedestals" were formed due to a random distribution of values near the zero mean value and that they may appear as a result of GEF dynamic fluctuations. In this case GEF fluctuations may also be expected in copper nuclear relaxation. Indeed, measurements of spin-lattice relaxation at liquid helium temperatures show[9] that the time $^{63}T_1$ of ^{63}Cu isotope is always less than $^{65}T_1$ as it should be with the quadrupole relaxation mechanism because of a greater value of the electric quadrupole moment of ^{63}Cu nuclei.

NMR of praseodimium. The ground state of the Pr^{3+} ($4f^2$, $^3H_4$, $J = 4$) ion in a crystalline electric field of symmetry D_{4h} is a singlet Γ_3 separated from the nearest excited state (a doublet Γ_5) by the energy interval of 119 cm^{-1}.[11] Therefore, it is possible to obtain additional information about the sample from the data of ^{141}Pr NMR (natural abundance ratio 100%, nuclear spin $I = 5/2$).[12-14] Splitting of energy levels of ^{141}Pr in a magnetic field is described by a spin Hamiltonian of axial symmetry: $H = -\gamma_\parallel \hbar H_z I_z - \gamma_\perp \hbar (H_x I_x + H_y I_y) + D[I_z^2 - I(I+1)/3]$. It follows from the spectra taken at 1.5–4.2 K that in the sample of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ there are two types of centers–rapidly relaxing (Pr1) and slowly relaxing (Pr2). The parameters of these spectra have close values: $\gamma_\parallel^{(1)}/2\pi \approx 1.84$ kHz/Oe, $|D^{(1)}/h| \approx 2.5$ MHz, $\gamma_\parallel^{(2)}/2\pi = 1.66 \pm 0.05$ kHz/Oe, $\gamma_1^{(2)}/2\pi = 5.1 \pm 0.5$ kHz/Oe, $|D^{(2)}/h| = 2.4 \pm 0.2$ MHz.

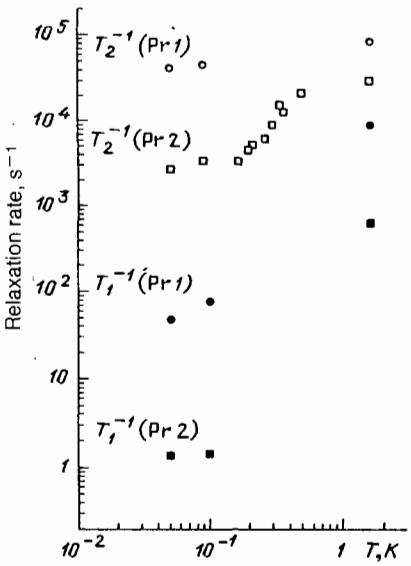

FIG. 4.

Owing to the anisotropy of γ, in the powder spectrum the lines of praseodimium NMR, corresponding to the orientations of $H \| c$ and $H \perp c$ are separated by the field and this makes it possible to study the angular dependence of the nuclear relaxation rate. Figure 4 shows the results of measuring relaxation rates $T_{1\|}^{-1}$ and $T_{2\|}^{-1}$ at temperatures from 0.05 to 1.6 K in the field $H \| c$ at the frequency of 23 MHz; these rates remain practically unchanged in the wide range of fields from 7.5 kOe to the upper boundary of the spectrum (19 kOe). As is clear, relaxation characteristics of Pr1 and Pr2 nuclei differ sharply, in contrast to spectrum parameters. Slowing down of relaxation of transverse magnetization of Pr2 nuclei with cooling attracts attention. Such a behavior is similar to the temperature dependence $T_2^{-1}(T)$ of Cu(2) nuclei in $YBa_2Cu_3O_{6.9}$[15] and copper nuclei in the system with heavy fermions $CeCu_2Si_2$[16] when these compounds go over to the superconducting state. The rates of spin-lattice relaxation of Pr1 and Pr2 nuclei decrease with cooling from 1.6 to 0.05 K by approximately 200 and 500 times. For $T = 0.05$ K the relative portion of praseodimium nuclei with greater T_2 is 0.35 ± 0.02 and the relative portion of the nuclei with greater T_1 is 0.36 ± 0.05. Coincidence of these values confirms once more that there are two types of centers (Pr1 and Pr2) with a relative content 2:1 in the sample.

The analysis of experimental NMR data for copper and praseodimium in the $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ sample enables us to draw the following conclusions:

1. NMR data confirm that there are two phases in the sample.

2. Narrow lines of copper NMR with weakly expressed traces of quadrupole interaction belong to copper nuclei in a

metal (nonsuperconducting) phase of the sample. An important feature of this phase is the quadrupole character of copper nuclear relaxation.

3. Praseodimium NMR is observed, most probably, from the superconducting phase. High rates of praseodimium nuclear relaxation at low temperatures can be explained by fluctuations of intra-atomic (hyperfine) magnetic fields, which in turn may arise due to valence fluctuations of $Pr^{3+} - Pr^{4+}$.

4. On the basis of the observed relative content of two types of praseodimium centers Pr2 atoms may be ascribed to the nearest fourfold surrounding of Ce atoms.

[1] V. A. Borodin, L. P. Gor'kov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **46**, (Suppl.) 211 (1987). [JETP Lett. **46**, (Suppl.)S181 (1987)].
[2] L. P. Gor'kov and A. V. Sokol, *ibid.*, 333 [JETP Lett. **46**, 420 (1987)].
[3] J. D. Jorgensen *et al.*, Proc. Third Intern. Symposium on Superconductivity. Sendai. Japan, November 6–9 (1990).
[4] Y. Tokura, H. Takagi, and S. Uchida, Nature (London), **337**, 545 (1989).
[5] P. Lightfoot *et al.*, Physica. Ser. C, **168**, 627 (1990).
[6] M. Abe *et al.*, *ibid.*, **160**, 8 (1989).
[7] Y. Kohori *et al.*, J. Phys. Soc. Jpn., **58**, 3493 (1989).
[8] K. Kumagari *et al.*, Physica. Ser. B, **165–166**, 1297 (1990).
[9] O. N. Bakharev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 571 (1990) [JETP Lett. **51**, 649 (1990)].
[10] A. Yu. Zavidonov *et al.*, **3**, 1597 (1990).
[11] V. Nekvasil, Physica. Ser. C, **170**, 469 (1990).
[12] O. V. Bakharev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 812 (1990) [JETP Lett. **52**, 179 (1990)].
[13] O. N. Bakharev *et al.*, *ibid.*, 1012. [*ibid.*, 405].
[14] O. N. Bakharev *et al.*, Proc. Third German-Soviet Bilateral Seminar on HTSC.–Karlsruhe, FRG, October 8–12, 1990, p. 9.
[15] O. N. Bakharev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 383 (1988) [JETP Lett. **47**, 458 (1988)].
[16] D. E. Mac Laughlin *et al.*, Phys. Rev. B **30**, 1577 (1984).