Nuclear magnetic resonance of copper in the superconductor $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

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The nuclear magnetic resonance of ^{63}Cu and ^{65}Cu was observed in an "electronic superconductor" $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ at the frequencies of 8.1 and 10.7 MHz and at temperatures of 1.5 K and 4.2 K. The spin-echo method was used to observe this effect. It follows from the experiment that the relaxation of the longitudinal magnetization of ^{63,65}Cu is determined by a quadrupole mechanism.

Interest of high-T_c superconductivity research in "electronic superconductors" of the composition $Ln_{2-x}M_xCuO_{4-y}$ (Ln = Pr, Nd, Sm; M = Ce, Th), which have been discovered relatively recently,[1] is evident in the rapidly increasing number of papers. There are, however, not many papers dealing with the NQR or NMR studies,[2–4] and the experimental results have so far not been explained adequately. The electric quadrupole interaction of copper nuclei was found[3,4] to be fairly strong in the antiferromagnet Nd_2CuO_{4-y} ($\nu_Q^{63} = 14$ MHz, $\nu_Q^{65} = 13$ MHz) and a doping of this compound with Ce4$^+$ or Th^{4+} ions in an amount sufficient to attain superconductivity ($x = 0.15$; $T_c = 24$ K) gives rise to copper centers, with a typically very weak quadrupole interaction. If these centers in the superconductor with $x = 0.15$ share an equal footing with other centers (whose NQR frequencies cover a broad spectrum from 20 MHz to 60 MHz), then their concentration is the dominant concentration in the nonsuperconducting metallic phase ($x \geqslant 0.18$). The small electric field gradient of the copper nucleus in a crystal of tetragonal symmetry may be the result of the compensation for the contributions from the lattice and from the 3*p* and 3*d* electrons, which are of different magnitude and different sign.[5] The Mössbauer studies of the paramagnetic iron oxide compounds[6] showed that there is an averaging of the electric field gradient because of the motion of charges (fluctuation of the Fe^{2+}–Fe^{3+} valence). The real reason for the inordinately weak quadrupole interaction of copper nuclei evidently stems from the particular features of the electronic structure of $Ln_{2-x}M_xCuO_{4-y}$. To determine it, new experimental information, including data on the nuclear relaxation, must be obtained.

In the present letter we report the results of an experimental study of the pulsed NMR of ^{63}Cu and ^{65}Cu in the ceramic compound $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ which was prepared according to the standard procedure.[1] The measurement of the magnetic susceptibility of the sample showed that $T_c = 24$ K and an x-ray phase analysis confirmed that there are no extraneous phases. The experiments were carried out with a partially oriented powder which was prepared as follows. The powdered sample was mixed with melted paraffin and placed in a cylindrical container in a ~10-kOe magnetic field. By slowly rotating (2 rpm) the heated container in a magnetic field we were able to align the crystallographic c axes of single powder particles principally along the turning c' axis, i.e., at right angles to the $\overline{\mathbf{H}}_0$ field, because of the anisotropy of the paramagnetic susceptibility of the material ($\chi_L > \chi_{\parallel}$). The NMR measurements were carried out at the frequencies of 8.1 and 10.7 MHz at the temperatures of 1.5 K and 4.2 K, and the typical pulse lengths of the $\pi/2$ and π pulses were 7 and 14 μs. The NMR spectra were recorded by measuring the amplitude of the spin echo signals at fixed values of the magnetic field (Fig. 1). The paramagnetic NMR (Knight) shift measured in this manner was $+0.1\%$. The decay of the envelope of the echo signals (Fig. 2) in all cases could be reconciled with the simple relation $A(2\tau) = A(0)\exp(-2\tau/T_2)$, while we had to use the two-exponential approximation, $1 - A(t)/A(\infty) = \lambda \exp(-t/T_1') + (1-\lambda)\exp(-t/T_1'')$, to describe the spin-lattice relaxation (Fig. 3). Let us discuss the results of the measurements (see Table I).

Linewidth. The increase in $\Delta\nu_{1/2}$ (the width at half-maximum) with decreasing frequency ν_0 suggests that the linewidth may be linked with the second-order quadrupole shifts:[7]

$$\delta\nu^{(2)}_{1/2,-1/2} = -(3\nu_Q^2/16)(1-\cos^2\theta)(9\cos^2\theta - 1), \qquad (1)$$

where $\nu_Q = e^2qQ/2h$ is the NMR frequency, and θ is the angle between the c axis of a single crystallite and the field $\overline{\mathbf{H}}_0$. Calculating the second moment of the NMR line of the powder as the square of the shift (1), averaged over the angle θ, and assuming that

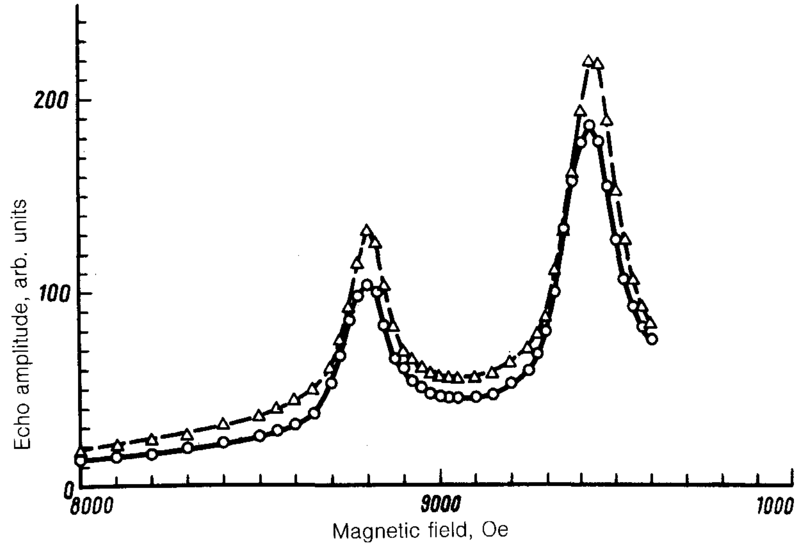

FIG. 1. NMR Spectra of ^{63}Cu and ^{65}Cu in a partially oriented powder of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$; the temperature is 1.5 K; the frequency is 10.7 MHz; O—$H_0 \| \mathbf{c}'$; Δ—$\mathbf{H}_0 \perp \mathbf{c}'$.

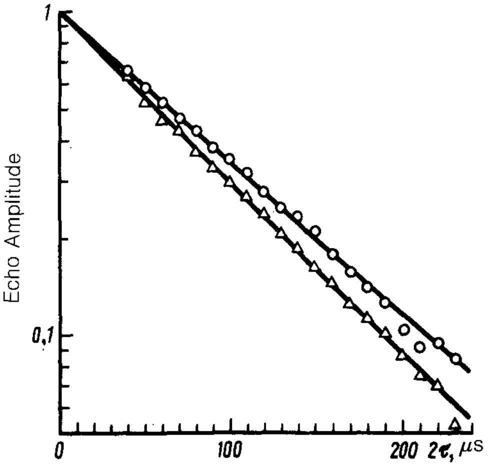

FIG. 2. Decay of the amplitude of the echo signals of ^{63}Cu (O) and ^{65}Cu (Δ) in a partially oriented powder of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$; $T = 1.5$ K, $\nu_0 = 10.7$ MHz, $H_0 \| c'$.

the line has a Gaussian shape, we find that the value $\Delta\nu_{1/2}\nu_0 \approx 2$ MHz^2 which we observed should correspond to the parameter $\nu_Q \approx 1.1$ MHz. Although the spectrum in Fig. 1 does not contain a clearly identifiable satellite separated from the ^{65}Cu line by the internal $\Delta H = \nu_Q(\pi/\gamma) = 0.45$ kOe, the position of this satellite approximately

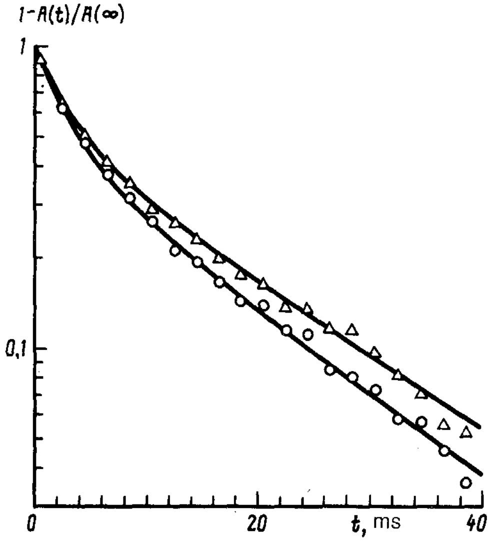

FIG. 3. Relaxation of the longitudinal magnetization of ^{63}Cu (O) and ^{65}Cu (Δ) in a partially oriented powder of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$; $T = 1.5$ K, $\nu_0 = 10.7$ MHz, $H_0 \| c'$.

TABLE I. NMR parameters of ^{63}Cu and ^{65}Cu in a partially oriented powder of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ measured at the freqency $\nu_0 = 10.7$ MHz (8.1 MHz).

Isotope	Field orientation	Linewidth $\Delta\nu_{1/2}$ (kHz)	T_2 (μs)	λ	T_1' (ms)	T_1'' (ms)
			Temperature 1.5 K			
^{63}Cu	$H_0 \parallel c'$	280	93.0 ± 1,1	0,51 ± 0.04	2,84 ± 0,20	15,7 ± 0.6
	$H_0 \perp c'$	235	–	(0.52 ± 0.02)	(3.01 ± 0.20)	(15,0 ± 0.9)
^{65}Cu	$H_0 \parallel c'$	250	82,7 ± 1.3	0.47 ± 0,04	2,95 ± 0,22	17,6 ± 0.6
	$H_0 \perp c'$	215	–	(0,51 ± 0,06)	(2.77 ± 0.40)	(15,1 ± 1,8)
			Temperature 4.2 K			
^{63}Cu	$H_0 \parallel c'$	205 (250)	79,9 ± 1,4	0,65 ± 0,03	2.27 ± 0,12	13,6 ± 0,6
	$H_0 \perp c'$	180 (250)	98.9 ± 1,4	0.73 ± 0.04	2,53 ± 0,16	15,2 ± 1.3
^{65}Cu	$H_0 \parallel c'$	220	68,7 ± 0.7	0,61 ± 0,04	2,49 ± 0.19	15,5 ± 0,9
	$H_0 \perp c'$	190	89,8 ± 1,0	0,65 ± 0,05	2,37 ± 0,18	14,0 ± 1,1

corresponds to the midpoint on the weak-field wing of the spectrum. The absence of satellites in the NMR spectra is apparently attributable to the scatter of ν_Q near the mean value of ~ 1 MHz because of the nonuniformity of the electric field gradient.

Electric field gradient. The calculations of various components of the electric field gradient induced by copper nuclei in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$, carried out in Ref. 5 with the parameters $\gamma_\infty = -11.34$ and $R = 0.19$, with allowance for the covalence and overlapping of the electronic orbits of copper and oxygen, and also under the assumption that the Cu^+ state impurity is considerable (0.15), give the result

$$\nu_Q = -34{,}5 - 16 + 53{,}2 = 2{,}7\ \text{MHz}, \tag{2}$$

in which the three components are respectively the ligand lattice, the $3p$ electron, and the $3d$ electron.

Spin–spin relaxation. The relaxation rate increases appreciably as the temperature is raised from 1.5 K to 4.2 K. Its angular dependence implies that in a crystal the rate T_2^{-1} is higher when $\mathbf{H}_0 \| \mathbf{c}$ than when $\mathbf{H}_0 \perp \mathbf{c}$. The ratio $(T_2^{63}/T_2^{65}) \approx (\gamma^{65}/\gamma^{63})^2$ which we observed suggests that the mechanism of the spin–spin relaxation of copper nuclei is magnetic in nature.

Spin-lattice relaxation. In the presence of three multilevel spin systems $[I({}^{63,65}\mathrm{Cu}) = 3/2,\ I({}^{141}\mathrm{Pr}) = 5/2]$ we naturally link the fast process $(T_1' \approx 2.5\ \mu\mathrm{s})$ with the balancing of the spin temperature in these systems, and we link the slow process (T_1'') with its relaxation to the "lattice" temperature. The decrease of the relative weight of the short exponential function with decreasing temperature (from 0.65 at $T = 4.2$ K to 0.5 at $T = 1.5$ K) seems to suggest that the heat capacity of the reservoir, arbitrarily called here a "lattice," decreases. The ratio $(T_1''^{63}/T_1''^{65}) \approx (Q^{65}/Q^{63})^2$, observed when $\mathbf{H}_0 \| \mathbf{c}'$, is a strong argument in favor of the quadrupole relaxation mechanism which assumes that the electric field gradient fluctuates. This result, in our view, deserves a very close scrutiny.

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