Spin–spin relaxation of $^{63}Cu(2)$ nuclei in connection with localized Cu^{2+} (2) centers in $YBa_2Cu_3O_{7-y}$

O. A. Anikeenok, M. V. Eremin, R. Sh. Zhdanov, V. V. Naletov, M. P. Rodionova, and M. A. Teplov
Kazan State University, 420008, Kazan

(Submitted 9 July 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **54**, No. 3, 154–159 (10 August 1991)

The spin–spin relaxation of copper nuclei has been studied at NQR frequencies in $YBa_2Cu_3O_{7-y}$ in weak magnetic fields at 4.2 K. Structural features observed in the relaxation of $^{63}Cu(2)$ nuclei in both compounds are explained as resulting from a spin–spin interaction of resonating Cu(2) nuclei with Cu^{2+} (2) centers localized nearby. It is suggested that the NQR of copper is observed in Zhang–Rice singlet states.

The acceleration of the spin–spin relaxation of Cu(2) nuclei at 35 K, which has been observed in several studies,[1–6] remains an interesting puzzle in the nuclear quadrupole resonance (NQR) of copper in $YBa_2Cu_3O_{7-y}$ ($y = 0$–0.1). The temperature dependence of the relaxation rate, $T_2^{-1}(T)$, and the width and shape of the Cu(2) NQR line has been studied in most detail by Yutaka *et al.*[6] They showed, in particular that at $T > T_c$ the ratio of the fourth moment of the NQR line to the square of the second moment (M_4/M_2^2) is approximately 3 (this line has a Gaussian shape). At $T < T_c$ this ratio lies in the interval 6–10 (and the line has a Lorentzian shape). It reaches a value ~ 10 not only at $T = 35$ K but also at liquid-helium temperatures. An unusual spin–spin relaxation of Cu(2) nuclei at $T = 4.2$ K was also noted in Ref. 3, where it was suggested that an additional spin–spin interaction (i.e., one in addition to the nuclear dipole–dipole interaction) occurs and is strengthened noticeably upon the imposition of a static field ~ 50 Oe, while it weakens as the field is raised further. In the present letter we are reporting experiments at NQR frequencies on the field dependence of the relaxation rates T_2^{-1} of $^{63}Cu(1)$ and $^{63}Cu(2)$ nuclei in ceramic samples of $YBa_2Cu_3O_{6.95}$ ($T_c = 93$ K, $\nu_{Cu1} = 22.0$ MHz, $\nu_{Cu2} = 31.5$ MHz) and $YbBa_2Cu_3O_{6.9}$ ($T_c = 83$ K, $\nu_{Cu1} = 22.05$ MHz, $\nu_{Cu2} = 30.9$ MHz) at 4.2 K. We conclude that there is a strong interaction of resonating Cu(2) nuclei with Cu^{2+} centers localized in CuO_2 planes.

The $YBa_2Cu_3O_{6.95}$ (Y) and $YbBa_2Cu_3O_{6.9}$ (Yb) samples were prepared by a known procedure.[7] The samples were monitored by x-ray diffraction to ensure that they consisted of a single phase. The transition temperature T_c was found from the temperature dependence of the magnetic susceptibility. The full widths at half-maximum of the NQR lines of ^{63}Cu were $\Delta\nu_{Cu1} = 400$ kHz and $\Delta\nu_{Cu2} = 600$ kHz in the Y sample and $\Delta\nu_{Cu1} = 1.3$ MHz and $\Delta\nu_{Cu2} = 1.6$ MHz in the Yb sample. A home-brew coherent pulsed spectrometer, on line with a DVK-3M computer, was used to measure the relaxation times T_2. The typical amplitude of the field H_1 in the rf coil was 150 Oe (the volume of the sample was 0.2 cm^3). The experimental data were analyzed under

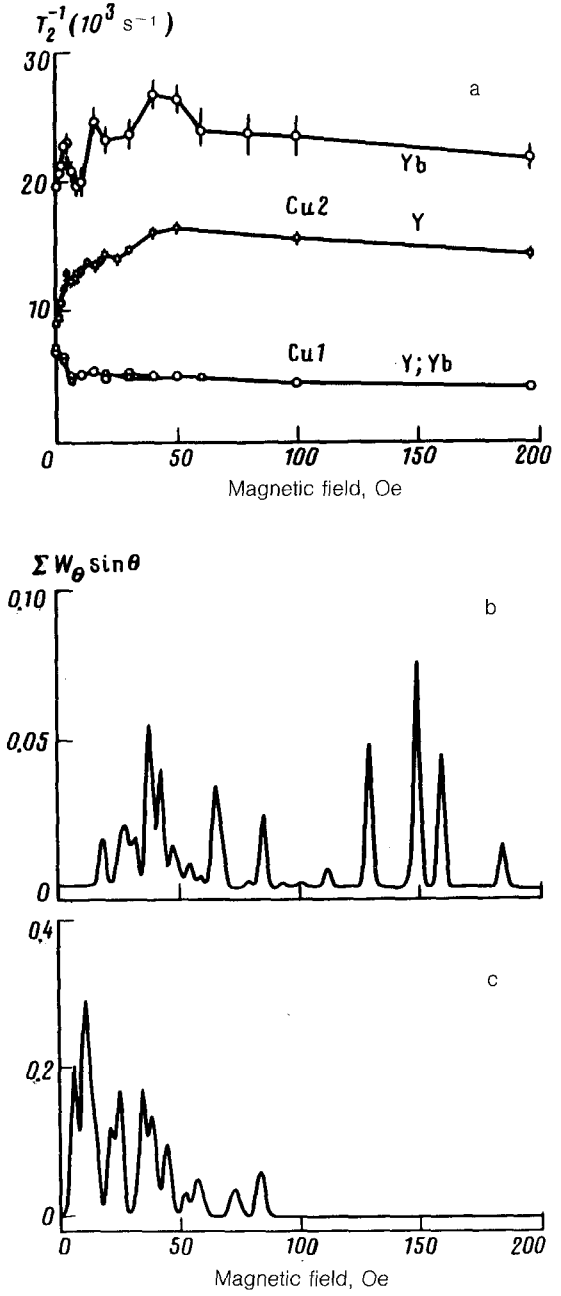

FIG. 1. a—Rate of the spin–spin relaxation of copper nuclei in YBaCuO and YbBaCuO in a weak magnetic field at 4.2 K, measured at NQR frequencies; b,c—results of a numerical simulation with the parameter values in (2) and (4), respectively, of the total probability for electronic transitions at the frequency $\nu_{Cu2} = 31.2$ MHz in the system of electron–nucleus energy levels of localized $^{63}Cu^{2+}$ centers in a YBaCuO powder (see the text proper).

the assumption of a Lorentzian lineshape. Figure 1a shows the results of the measurements of the rates T_2^{-1} in fields from 0 to 200 Oe. Let us take a look at the most important features of this relaxation.

Cu(1). The relaxation rate in the Y and Yb samples decreases upon the imposition of a field. This decrease agrees with the idea that the dipole–dipole interaction of the copper nuclei weakens upon a splitting of the nuclear doublets $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ by a magnetic field. The replacement of diamagnetic Y^{3+} ions by paramagnetic Yb^{3+} ions does not lead to a significant increase in T_2^{-1}. This result is understandable, since the interatomic distances R(Yb–Cu1) are large.

Cu(2). The relaxation rate in the Y sample increases upon the imposition of a field, goes through a maximum at $H = 40$–50 Oe, and then falls off. There are some small but clearly distinguishable peaks at $H \sim 5$ and 15 Oe. In the Yb sample the rate T_2^{-1} in a field $H = 0$ is significantly higher than that in the Y sample. This result can be explained in a natural way as resulting from a strong spin–spin interaction of Cu(2) nuclei with nearby magnetic Yb^{3+} ions ($g_a = 3.5$, $g_b = 3.7$, $g_c = 3.1$; Ref. 8). The general shape of the $T_2^{-1}(H)$ curve in the Yb sample is the same as that in the Y sample [this similarity extends to the same increase in the rate ($\approx 7 \times 10^3$ s^{-1}) as the field is raised from 0 to 40 Oe]. The peak at $H \sim 5$ Oe increases in size.

Looking at the set of data, we can assert that the Cu(2) nuclei are coupled by a strong spin–spin interaction with paramagnetic centers of some sort. We believe that the absence of an effect of these centers on the relaxation of Cu(1) nuclei, combined with the very strong effect on the relaxation of Cu(2) (as in the case of the Yb^{3+} ions), is unambiguous evidence that these centers are localized in CuO_2 planes. We suggest that these centers are Cu^{2+} ions which are immediate neighbors of resonating Cu(2) nuclei belonging to the superconducting phase of the substance. Arguments in favor of the existence of localized Cu^{2+} centers in CuO_2 planes have been raised previously (see, for example, Refs. 9 and 10). Let us examine the energy levels of the Cu^{2+} ion in weak fields. We write the Hamiltonian of the ion $^{63}Cu^{2+}$ ($S = 1/2$, $I = 3/2$) in a field **H**, which makes an angle θ with the c axis of the crystal, as follows:

$$\mathcal{H} = g_{\parallel}\mu_B H \cos\theta S_z + g_{\perp}\mu_B H \sin\theta S_x + A_{\parallel} S_z I_z$$

$$+A_{\perp}(S_x I_x + S_y I_y) + (h\nu_Q/2)[I_z^2 - I(I+1)/3]. \qquad (1)$$

We choose the values $g_{\parallel} = 2.2$ and $g_{\perp} = 2.05$, which are typical of the Cu^{2+} ion. We take the parameters of the hyperfine interaction from Ref. 11:

$$A_{\parallel} = -59.4 \cdot 10^{-4} \text{ cm}^{-1}, \quad A_{\perp} = 13.9 \cdot 10^{-4} \text{ cm}^{-1}. \qquad (2)$$

We take the quadrupole frequency $\nu_Q = -22.87$ MHz from Ref. 12 (the sign of ν_Q was found by a calculation[3]). Figure 2 shows the electron–nucleus energy levels for the angle $\theta = 60°$. The vertical lines are transitions at the frequency $\nu_{Cu2} = 31.5$ MHz for those pairs of states ψ_k, ψ_l between which the electron–spin operator has a large matrix element $|\langle\psi_k|S_y|\psi_l\rangle|^2$. We see that the electronic transitions which are capable of leading to a flip-flop $S_{\pm} I_{\mp}$ and an exchange of energy between $^{63}Cu^{2+}$ ions and

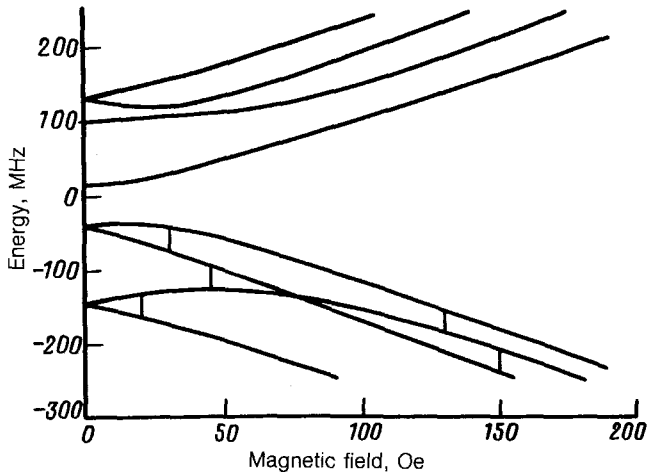

FIG. 2. Electron–nucleus energy levels of $^{63}Cu^{2+}$ for the case in which the field H makes an angle $\theta = 60°$ with the c axis of the crystal.

the resonating $^{63}Cu(2)$ ions fall in the magnetic-field region of interest here. To demonstrate the situation which prevails in a powder of randomly oriented particles, we select nine fixed values of θ (10°,20°,...,90°), and for each we construct a function (3a)

$$W_\theta \sin\theta = \sum_{\cdot} | < \psi_k(\theta, H_i)|S_y|\psi_l(\theta, H_i) > |^2 g(H - H_i)\sin\theta \qquad (3)$$

($g(H-H_i) = (1/\sqrt{2\pi}\Delta)\exp[-(H-H_i)^2/2\Delta^2]$ is a Gaussian form factor). We then sum all the probabilities, approximating the integral $\int W(\theta)\sin\theta d\theta$ over the angular distribution with a probability density $\sin\theta$. The results of the calculations (Figs. 1b and 3a) show that the H regions in which electron–nucleus flip-flop transitions, and hence the acceleration of the relaxation of Cu(2) nuclei, are most probable, are near 50 and 150 Oe (this conclusion is consistent with the experimental data). However, there are no peaks near $H \sim 5$ Oe. The parameter values in (2) were found for resonating $^{63}Cu^{2+}$ (2) centers, while in the case at hand we are dealing with centers which are neighbors of these resonating centers and whose NQR we do not observe. We would naturally expect that the parameters of interest here, $A_\parallel$ and $A_\perp$, would have different values. For example, Mehran *et al.*[13] have observed a hyperfine structure in the ESR of Cu^{2+} in YBaCuO which was described by the parameter values $|A_\parallel| \sim 90$ Oe (87×10^{-4} cm^{-1}) and $|A_\perp| \sim 75$ Oe (72×10^{-4} cm^{-1}). Our estimates of these parameters of the basis of the standard Abragam–Bleaney formulas,[14] with allowance for covalency effects,[15] yield

$$A_\parallel = -83,5 \cdot 10^{-4}\text{cm}^{-1}, \quad A_\perp = 57 \cdot 10^{-4}\text{cm}^{-1}. \qquad (4)$$

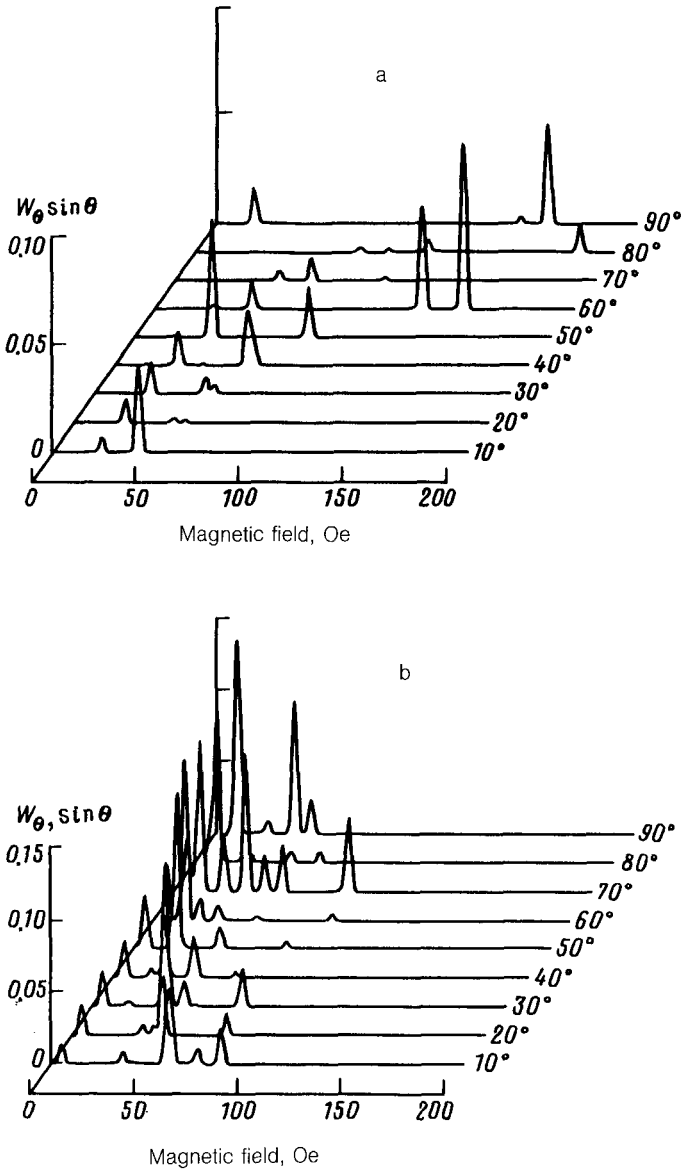

FIG. 3. a,b—Results of a numerical simulation with the parameter values in (2) and (4), respectively, of the probabilities for electronic transitions at the frequency 31.5 MHz in the system of electron–nucleus energy levels of $^{63}Cu^{2+}$ in a YBaCuO crystal for various orientations of the magnetic field ($\Delta = 1.3$ Oe).

Repeating all the calculations with the parameter values in (4), we find results (Figs. 1c and 3b) which also explain the appearance of the T_2^{-1} peak at $H \sim 5$ Oe.

Unfortunately, we do not yet have a clear picture of the state of those copper atoms in the high-T_c superconductors at whose nuclei the NQR and NMR are ob-

served. The structure of the energy bands of the copper–oxygen layers is formed primarily by three interactions: the Coulomb repulsion of copper electrons (or holes), the exchange interaction of copper holes with oxygen holes, and a superexchange interaction. The Coulomb interaction of copper holes is known to be the strongest. It forms Hubbard subbands. The lowest band is completely filled in the insulating phase. Doping of the planes with holes results in a predominant filling of oxygen–hole states which lie at distance $\Delta \sim 2$ eV away from the lowest Hubbard band.[16]

The interaction coming next in importance is the exchange interaction of the holes due to virtual hops of oxygen holes into the upper Hubbard band of copper. The operator for this interaction is

$$\mathcal{H}_{dp} = -\sum_{fjj'\sigma\sigma'} \frac{t_{jf}t_{fj'}}{(U-\Delta)}(-1)^{\sigma_1-\sigma_1'} X_f^{\sigma_1,\bar{\sigma}_1'} c_{j\sigma}^{+} c_{j'\sigma'}. \tag{5}$$

The integral t_{jf} represents the hop of a hole from an oxygen σ state to a copper x^2-y^2 state; the Hubbard operator $X_f^{\sigma_1,\sigma_1'}$ corresponds to the copper site with index f; the operator $c_{j\sigma}^{+}$ creates an oxygen hole at site j with a spin projection σ; and U is the repulsion energy of the holes at a copper site. Although the operator in (5) is exceedingly complex, it can be diagonalized easily at a fixed site index f. The ground state turns out to be a singlet state—a Zhang–Rice singlet.[17] It is likely that the NQR and MNR of copper are observed in singlet states of this type. However, our experiments show that these states in the CuO_2 planes coexist with ordinary localized Cu^{2+} centers.

In conclusion, the reason for the acceleration of the spin–spin relaxation of Cu(2), which we mentioned at the beginning of this paper, may be a spin–lattice relaxation of localized Cu^{2+} centers, which goes at a rate $\tau_1^{-1} = \alpha T^9$ at $T \gtrsim 10$ K. The coefficient α has values ranging from 2×10^{-6} to 3×10^{-3} in different materials.[18] At a certain temperature T^* in the interval 16–36 K, the rate τ_1^{-1} may thus become comparable to the value of $\omega_{Cu2} = 2\pi\times31.5\times10^6\ s^{-1}$. At $T > T^*$, the structure of the energy levels is painted over completely, and the nuclear relaxation rate should decrease. As we approach T^* from below, this rate should increase if τ_1^{-1} is greater than the spin–spin relaxation rate τ_2^{-1} of localized Cu^{2+} centers.

We thank A. F. Andreev for a discussion of this paper. This work is supported by the Scientific Council of Problems of High-Temperature Superconductivity and is being carried out within the framework of Project 333 of the State Program "High Temperature Superconductivity."

[1]A. V. Bondar', M. Ryabchenko, Yu. V. Fedotov, and A. A. Motuz, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 133 (1989) [JETP Lett. **50**, 146 (1989)].
[2]O. N. Bakharev, R. Sh. Zdanov, A. V. Egorov, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 383 9 (1988) [JETP Lett. **47**, 458 (1988)].
[3]A. Yu. Zavidonov *et al.*, Sverkhprovodimost' (KIAE) **3**, 1597 (1990) [Superconductivity **3**, 1274 (1990)].
[4]M. Tei *et al.*, Z. Naturforsch. a **45**, 429 (1990).
[5]K. Kumagai *et al.*, J. Phys. Soc. Jpn. **59**, 2336 (1990).

[6]I. Yutaka *et al.*, J. Phys. Soc. Jpn. **59**, 3463 (1990).
[7]T. Wada *et al.*, Ceram. Soc. **72**, 2000 (1989).
[8]M. V. Eremin *et al.*, Sverkhprovodimost' (KIAE) **4**, 716 (1991) [Superconductivity **4**, 625 (1991)].
[9]Y. Hayashi *et al.*, Physica B **165**, 1317 (1990).
[10]N. E. Phillips and R. A. Fisher, Mag. Mag. Materials (to be published).
[11]T. Imai, J. Phys. Soc. Jpn. **59**, 2508 (1990).
[12]H. Yasuoka *et al.*, J. Phys. Soc. Jpn. **57**, 2659 (1988).
[13]F. Mehran *et al.*, Solid State Commun. **66**, 299 (1988).
[14]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
[15]J. A. Aramburu and M. Moreno, J. Chem. Phys. **83**, 6071 (1985).
[16]H. Eskes *et al.*, Phys. Rev. B **41**, 288 (1990).
[17]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[18]K. J. Staudley and R. A. Vaughan, *Electron Spin Relaxation Phenomena in Solids*, London NWI, 1969.

Translated by D. Parsons