Decrease in the rate of transverse relaxation of Cu nuclei in $YBa_2Cu_3O_{7-y}$ at $T<T_c$

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(Submitted 2 March 1988)

Pis'ma Zh. Eksp. Teor. Fiz. **47**, No. 8, 383–385 (25 April 1988)

Pulsed nuclear quadrupole resonance method was used to measure the uniform width of the ^{63}Cu lines in the ceramic compound $YBa_2Cu_3O_{7-y}$ ($y\approx 0.1$) at temperatures from 10 K to 200 K. The contraction of the NQR line of the copper atoms situated in the Cu–O planes, which was observed at $T<T_c$, is attributed to the formation of $Cu^{3+}-Cu^{3+}$ hole pairs due to the antiferromagnetic superexchange interaction.

In the $YBa_2Cu_3O_{7-y}$ structure the copper atoms are known to occupy the Cu1 and Cu2 crystallographic positions: the former form the Cu–O chains, which extend along the *b* axis, and the latter lie in the Cu–O planes perpendicular to the *c* axis. It has been unclear until now, however, the extent to which these two types of atoms are involved in the superconductivity. The results of the measurements of the uniform width NQR lines of ^{63}Cu, which we have carried out here, show that only the system of Cu2 atoms undergoes a transition to the superconducting state.

The ceramic samples were synthesized in 60 hours in air at a temperature of 950 °C. As the starting materials we used CuO, BaO, and Y_2O_3 oxides. The experiments were carried out using a pulsed coherent NQR relaxation meter which was coupled to a multichannel digital storage system. The temperature was monitored with a platinum resistance thermometer. The NQR frequencies of ^{65}Cu in the Cu1 and Cu2 positions varied respectively in the ranges 22.0–22.1 MHz and 31.6–31.3 MHz over the temperature interval from 10 K to 200 K (Ref. 2). The shape of nonuniformly broadened NQR lines was estimated from the measurements of the amplitude of the quadrupole echo as functions of the frequency. Experiments showed that nonuniform line broadening is totally independent of the temperature. The enormous nonuniform linewidth (up to 0.8 MHz for Cu2) apparently is attributable primarily to the scatter of the electric field gradient on copper nuclei because of the defects in the crystal structure.

The uniform linewidth ($1/T_2$) was estimated from the decay of the echo signal as a result of the increase of the time interval τ between the sensing rf pulses: $A_{2\tau} = A_0\exp[-(2\tau/T_2)^n]$. The measurements showed that n lies in the range 1.3–1.7 for both copper positions; i.e., the shape of the uniformly broadened NQR lines is somewhere between the Gaussian shape ($n=2$) and the Lorentzian shape ($n=1$). For comparison with the calculation, we evaluated the results of the measurements under the assumption that $n=2$. These data are shown in Fig. 1; the straight lines in this figure represent the calculated values $1/T_2=(M_2/2)^{1/2}$. In calculating M_2, the

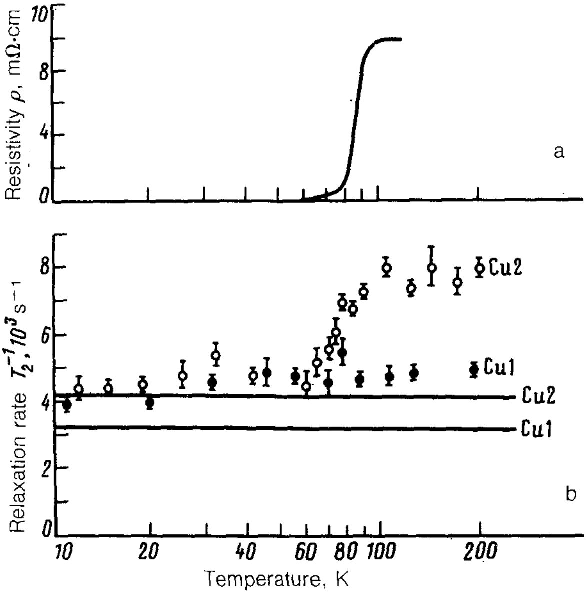

FIG. 1. Temperature dependence of the resistivity of the $YBa_2Cu_3O_{7-y}$ sample (a) and of the uniform width of the NQR line of ^{63}Cu in two crystallographic positions (b); straight lines—contribution to the uniform width of the NQR lines due to the magnetic dipole-dipole interaction of ^{63}Cu nuclei.

second moment of the NQR line which was broadened due to a magnetic dipole-dipole interaction of the identical spins of ^{63}Cu, we assumed,[3] to simplify the calculation, that the electric field gradient of the copper nuclei has an axial symmetry. This assumption is justifiable only in the case of Cu2 atoms, for which the asymmetry parameter of the electric field gradient is small enough ($\eta = 0.14$; Ref. 2). As can be seen in Fig. 1b, in the superconducting phase the NQR lines of Cu1 and Cu2 have approximately the same uniform width, which can be fully explained by the dipole-dipole interaction of the nuclear magnetic moments of copper. Upon transition of the material to the normal state, the uniform width of the NQR line of Cu1 remains constant, whereas the NQR line of Cu2 almost doubles in width. This circumstance leads us to conclude that superconductivity of the material is linked with the Cu2 atoms.

The results of our experiment can be qualitatively interpreted on the basis of the following model. The hole conductivity in the normal phase occurs as a result of migration of the holes which are related to the Cu^{3+} ions ($S = 1$). This migration occurs along the planes of the superexchange-bound Cu^{2+} ions ($S = 1/2$) which are in the $d_{x^2-y^2}$ state. The exchange interaction of Cu^{2+} and Cu^{3+} ions is distinguished by the fact that the energy of the double exchange[4] in the $d_{3z^2-r^2}$ states is comparable in order of magnitude to the antiferromagnetic coupling through the semioccupied $d_{x^2-y^2}$ states of Cu^{2+} and Cu^{3+} ions (see Fig. 2). Calculation of the exchange interaction in the $Cu^{2+} - Cu^{3+}$ pair shows that the energy of the state with a total spin $S = 3/2$ is $\pm (1/2)I_\sigma$, where I_σ is the electron-transport integral over the σ bonds of the O^{2-} ion. The energy of the states with a total spin $S = 1/2$, on the other hand, is determined by solving a cubic equation

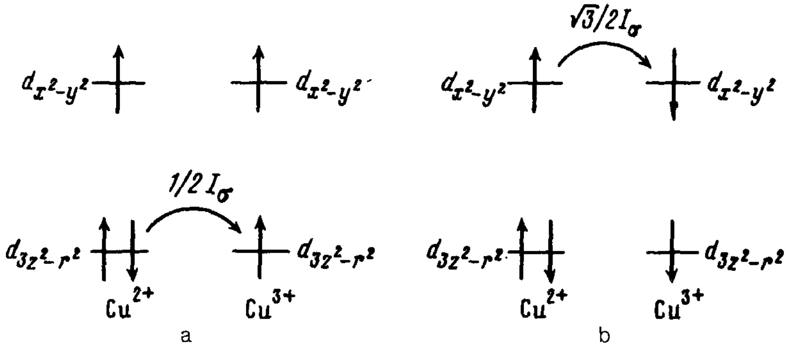

FIG. 2. (a) Schematic diagram of the double exchange which accounts for the parallel orientation of the Cu^{2+} and Cu^{3+} spins; (b) schematic of the hopping of an electron from the Cu^{2+} ion to Cu^{3+} ion, which accounts for the antiparallel spin ordering.

$$(\Delta - \epsilon)\left(\epsilon^2 - \frac{1}{16}I_\sigma^2\right) + \frac{9}{8}I_\sigma^2\,\epsilon = 0, \tag{1}$$

where Δ is the energy of the excited configuration of the pair (Fig. 2b) relative to the ground-state configuration (Fig. 2a). We easily see that for real values of $\Delta(\Delta \sim I_\sigma)$ the energy of the ground state with $S = 1/2$ is also on the order of $-(1/2)I_\sigma$. Consequently, the dynamic antiferromagnetic correlations in the $Cu^{2+} - O^{2-}$ plane do not prevent migration of the Cu^{3+} ion. These correlations account for the pairing of the hole carriers in the superconducting phase. A possible configuration of such a pair is shown in Fig. 3. It should be noted that the model we are proposing here is similar to the model described in Ref. 5.

The hyperfine magnetic field fluctuations on copper nuclei, which stem from fast motion of the holes (Cu^{3+}), contribute additionally to the width of the NQR line of Cu2. Using the measured value of the abrupt change in the transverse relaxation time of Cu2 nuclei ($3.5 \times 10^3\ s^{-1}$), we can estimate the correlation time τ_c from the rela-

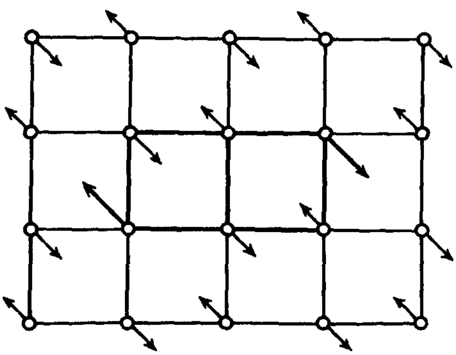

FIG. 3. Possible configuration of a nonmagnetic ($S = 0$) hole pair $Cu^{3+} - Cu^{3+}$ in the antiferromagnetic plane of the Cu^{2+} ions; long arrows—Cu^{3+} ions ($S = 1$); short arrows— Cu^{2+} ions ($S = 1/2$). The O^{2-}-ion positions are omitted.

tion[6]

$$1/T_2 = (A/\hbar)^2 \tau_c , \tag{2}$$

which holds for fast fluctuations ($\omega^2\tau_c^2 \ll 1$, where ω is the NQR frequency). Assuming the hyperfine structure constant to be $A = -6.43\times 10^{-3}$ cm^{-1} (as in the case of Cu^{3+} ions in Al_2O_3; Ref. 7), we find $\tau_c \approx 2\times 10^{-15}$ s. On the other hand, we can crudely estimate the hopping time of the hole on the basis of the indeterminacy relation, $\tau \sim \hbar/\Delta E$. Assuming $\Delta E = (\sqrt{3/2})I_\sigma = 3000$ cm^{-1} (see Ref. 8), we again find $\tau_c \approx 2\times 10^{-15}$ s. As a result of transition to the superconducting state, the additional contribution to the uniform width of the NQR line of Cu2 disappears because the Cu^{3+} holes combine into pairs with a zero total spin.

We wish to thank A. S. Borovik-Romanov for interest in this study. We also thank N. V. Zavaritskiĭ and S. V. Petrov for helping us master the method of synthesizing the samples.

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Translated by S. J. Amoretty