Models for quadrupole-resonance centers of copper nuclei in $YBa_2Cu_3O_{7-\delta}$

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(Submitted 27 January 1989; resubmitted 24 February 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **49**, No. 8, 446–448 (25 April 1989)

The spin-spin relaxation and spin-lattice relaxation of ^{63}Cu nuclei have been studied at a frequency of 31.5 MHz at temperatures of 120 K and 4.2 K in polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ with $\delta = 0.11$–0.43. A sharp change in the relaxation rates is observed at $\delta = 0.3$. Some models for the electronic structure of Cu(1) and Cu(2) centers are proposed on the basis of an analysis of the experimental data and calculations of the electric-field gradients.

Although the problem of identifying the nuclear-quadrupole-resonance (NQR) lines of copper in $YBa_2Cu_3O_{7-\delta}$ is very important to the study of the electronic structure and dynamics of the high-temperature superconductors, this problem remains only partially solved because of its complexity. Here are the conclusions which have been solidly established (we will cite the data only on the isotope ^{63}Cu): 1) The line at the frequency $\nu_Q = 30$ MHz in antiferromagnetic $YBa_2Cu_3O_6$ (Refs. 1 and 2) corresponds to $Cu^+(1)$ centers in CuO chains. These centers occupy positions with a double coordination (Fig. 1A). 2) In the same compound, the nuclei of $Cu^{2+}(2)$ ions, which belong to CuO_2 planes, are acted upon by the strong hyperfine magnetic field from the $3d$ electrons and resonate at frequencies near 90 MHz (Refs. 1–3) (89.9 MHz for the transition $+1/2 \leftrightarrow -1/2$). 3) The two lines near $\nu_Q = 22.1$ MHz and 31.5 MHz in $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0$–0.1) correspond to Cu(1) and Cu(2) centers.[4] With regard to the electronic structure of the Cu(1) and Cu(2) centers which we mentioned in conclusion 3), the literature reveals more than a few contradictory opinions. Our primary purpose in the present letter is to refine the models of these centers. The analysis below is based on two assumptions: a) The NQR line with $\nu_Q = 31.5$ MHz is due to centers of a single type, Cu(2), for all values of δ from 0 to 0.45. b) All of the NQR lines of copper which have been described in the literature, at frequencies from 20 to 32 MHz, are due to nonmagnetic states of copper (the homogeneous NQR linewidth of single Cu^{2+} centers[5] is usually much greater than the homogeneous NQR linewidth which is observed in $YBa_2Cu_3O_{7-\delta}$, because of fluctuations in the hyperfine field[6]).

We begin our analysis with the line $\nu_Q = 31.5$ MHz. The ground state of the quintuply coordinated $Cu^{2+}(2)$ ion is a $d_{x^2-y^2}$ hole state. Let us assume that the Cu(2) center in which we are interested consists of a Cu^{2+}–O^- hole-hole pair, which forms a local singlet.[7] We will calculate the NQR frequency of ^{63}Cu, allowing for the contributions to the electric-field gradient from all of the lattice ions and from the electrons of the $3d^9$ shell. We make use of x-ray structural data from Ref. 8. The "lattice" (γ_∞) and "atomic" (R) antiscreening factors required for these calculations

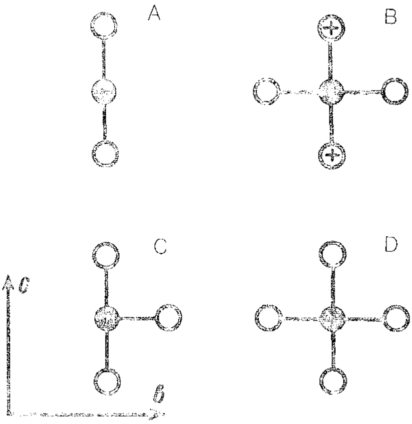

FIG. 1. Models of the nearest neighborhood of $Cu^+(1)$ in the $YBa_2Cu_3O_{7-\delta}$ structure. ●—Cu^+; ○—0^{2-}; ⊕—0^-. The x, y, and z axes run parallel to the a, b, and c crystallographic axes. A: $\delta = 1$, $\nu_Q = 30$ MHz, $\eta = 0$. B: $\delta = 0$, $\nu_Q = 22.1$ MHz, $V_{xx} = -V_{yy}$, $V_{zz} = 0$. C: $\delta = 0.2$, $\nu_Q = 24.7$ MHz, $\eta = 0.7$. D: $\delta = 0$, $\nu_Q = 28.7$ MHz, $\eta = 0.17$; $\delta = 0.5$, $\nu_Q = 28.5$ MHz, $\eta = 0.18$.

can be found by comparing the theoretical and observed quadrupole splittings of the NMR lines of Cu(2) in antiferromagnetic $YBa_2Cu_3O_6$ (Refs. 1–3) and La_2CuO_4 (Ref. 9). With the parameter values $1-\gamma_\infty = 23.4$ and $\langle 1/r^3 \rangle (1-R) = 5.6$ a.u. found in this manner, we find electric-field gradients from the lattice ions and from the electrons of the $3d^9$ valence shell which are of the same order of magnitude but differ in sign. With $\delta = 0.2$, for example, we find $V_{zz}^{(3d)} = -1.69 V_{zz}^{(latt)}$, and the NQR frequency turns out to be 32.0 MHz, in good agreement with experiment. The effective charges of the oxygen ions in the CuO_2 planes were assumed to be $-1.85e$. When we change the effective charge to $-2e$, i.e., when the hole current carriers disappear, we find that the NQR frequency of Cu(2) decreases to 22.9 MHz.

The following procedure for identifying the Cu(1) centers is based on an analysis of our experimental data on the nuclear relaxation of Cu(2) centers in samples with various oxygen concentrations. It ends with a calculation which confirms the observed values of the NQR parameters. In our experiments, samples with $\delta = 0.11$, 0.17, and 0.23 were synthesized by the standard solid-phase synthesis procedure.[10] Four other samples were synthesized from the original samples by annealing in air at 500–680 °C for 4 h. The measurements revealed that the spin-spin relaxation rates T_2^{-1} at temperatures of 120 K and 4.2 K decrease with increasing δ (Fig. 2a). The most interesting result is the decrease in the additional broadening $\Delta\omega = T_2^{-1}(120\mathrm{K}) - T_2^{-1}(4.2\mathrm{K})$ with a decrease in the oxygen concentration (Fig. 2b). Bakharev *et al.*[6] have discussed the additional homogeneous linewidth $\Delta\omega = (A/\hbar)^2\tau$ as a consequence of fast fluctuations in the hyperfine magnetic field at copper nuclei (A is the hyperfine interaction constant, and τ is the correlation time of the fluctuations). If we assume that the NQR at the frequency of 31.5 MHz is observed from localized moments of copper, which are coupled in a singlet fashion with an O^- hole which is "smeared" over oxygen positions, we define τ as the reciprocal of the probability for the escape of an 0^- hole from a resonating copper center. The value $A/h \sim 250$ MHz (Ref. 9; the energy of the interaction of the nuclear magnetic moment with the hyperfine magnetic field of the $3d^9$ shell of Cu^{2+}) must not depend on δ, so we attribute the observed decay of $\Delta\omega$ at $\delta \sim 0.3$ to a sharp increase in the probability

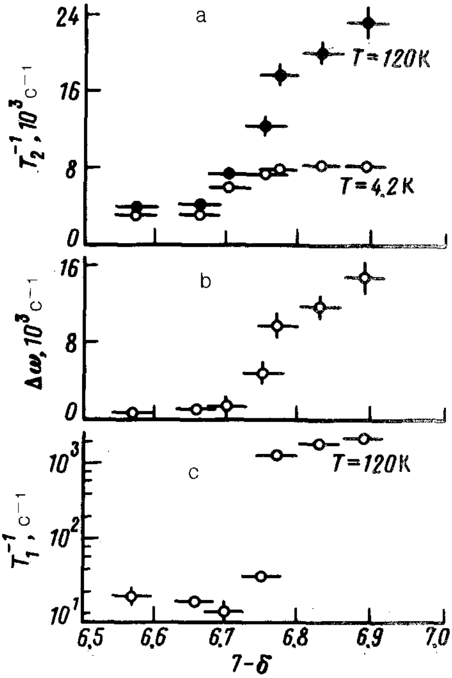

FIG. 2. Spin-spin relaxation and spin-lattice relaxation of ^{63}Cu nuclei in $YBa_2Cu_3O_{7-\delta}$ at an NQR frequency of 31.5 MHz. The relaxation rate T_2^{-1} was found under the assumption that the NQR line has a Lorentzian shape. $\Delta\omega = T_2^{-1}(120K) - T_2^{-1}(4.2K)$.

for the escape of an O^- hole, and we link it with the possibility that a hole jumps from a CuO_2 plane into adjacent BaO planes. This migration of oxygen holes is manifested most clearly in the spin-lattice relaxation rate T_1^{-1} measured at $T = 120$ K (Fig. 2c). It is not difficult to reach the conclusion that a "freezing" of jumps between CuO_2 and BaO planes at $\delta < 0.3$ may then mean that the BaO planes are saturated with holes and that stable $Cu^+(1)$ centers with the structure in Fig. 1B appear. The NQR frequency of these centers can be calculated by making use of the Sternheimer antiscreening parameter for Cu^+ ions extracted from a comparison of the theoretical and observed NQR frequencies of doubly coordinated $Cu^+(1)$ centers in $YBa_2Cu_3O_6$ (Fig. 1A). Using the parameter value found by this method, $1 - \gamma_\infty = 6.61$, we find for the centers of interest here (Fig. 1B) the frequency $\nu_Q = 22.1$ MHz and the components $V_{xx} = -V_{yy}$ and $V_{zz} = 0$ of the electric-field gradient. These results are in excellent agreement with experiment.[11] We know[2] that the resonance at 22.1 MHz is observed in specific substances which have a high oxygen concentration ($\delta = 0$–0.3). This result can serve as support for the hypothesis offered here regarding the structure of the Cu(1) centers. The frequencies $\nu_Q = 24.7$ MHz and 28.7 MHz, calculated in this fashion for the centers shown in Figs. 1C and 1D, are close to the positions of maxima in the observed NQR spectra.[2,12]

The agreement of the oxygen concentration ($\delta = 0.3$), which corresponds to the jump in the relaxation rates (Fig. 2) with the concentration at which T_c increases from 60 K to 90 K (Ref. 13), is hardly fortuitous. It apparently means that some restructuring of the crystal structure is occurring. It is at $\delta = 0.3$ that one observes the anomalous changes in the lattice constants and Young's modulus.[13,14]

We note in conclusion that according to our conceptual understanding, the decrease in the relaxation rates of the Cu(2) centers at $T < T_c$ in $YBa_2Cu_3O_{7-\delta}$ samples ($\delta = 0$–0.1) (Refs. 4 and 6) means that the fluctuation-relaxation mechanism "turns off." This decrease may be viewed as an indication that $Cu^{2+}(2)$–0^- singlet hole pairs in CuO_2 planes become stable formations in the superconducting phase.

We wish to thank N. V. Zavaritskiĭ for interest in this study and for useful discussions.

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Translated by Dave Parsons