Nuclear magnetic resonance of ^{17}O and ^{63}Cu in oriented $YBa_2Cu_3O_{7-x}$

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The NMR data have shown that there are carriers at the oxygen orbitals, that these carriers are paired at $T < T_c^{II} \approx 80$ K, and that copper and oxygen electron subsystems are independent subsystems.

Identification of the high-T_c superconductivity mechanism is closely related to the determination of the electron spectrum near the energy ϵ_F. The NMR method, which makes it possible to selectively determine the local electron density and its low-frequency dynamics near the nucleus, can be used for this purpose. The results obtained by this method using copper nuclei, which proved that $3d^9$ electron pairing occurs at $T < T_c$ (Ref. 1), are at variance, however, with the most recently obtained NMR data on ^{17}O (Refs. 2–4 and 8) and on the photoelectron spectroscopy as to whether the carriers have a preferentially oxygen nature. In view of this circumstance, the question arises as to whether the experimental data have been interpreted correctly and whether a parallel study of the NMR of ^{17}O and ^{63}Cu should be carried out with the same sample.

To carry out such an experiment, we have synthesized a $YBa_2Cu_3O_{7-x}$ ceramic sample enriched with an oxygen isotope ^{17}O in the gas phase for 5 days at 500 °C. Substitution of ^{16}O for a 22% mixture of ^{17}O and 63% mixture of ^{18}O caused the weight of the pellet to increase by 1.7%, suggesting that the substitution of the original ^{16}O is nearly complete at all the oxygen sites in the $YBa_2Cu_3O_7$ lattice. The pellet was then ground into a powder ($\lesssim 2$ μm diam) and mixed with an epoxy resin in the ratio 2:3. This mixture, shaped into a parallelepiped, was allowed to harden for 12 h in a magnetic field $H = 11.7$ T. We have thus obtained a uniaxially oriented sample comprised of fine crystals of $YBa_2Cu_3O_{7-x}$. The critical temperature of the onset of the superconducting transition in the absence of a field, measured from the screening signal of an NMR tansducer, was $T_c^O = 91$ K. Comparing the measured curve with the corresponding $\chi(T)$ curves at $T < T_c$ for the compounds $YBa_2Cu_3O_{7-x}$ with various values of x (Ref. 5), we concluded that the oxygen concentration in the test sample is 6.85. To estimate the quality of the sample, we compared the position of ν_0 and the width at half-maximum $\Delta\nu$ of the NMR line of copper in the CuO plane of $^{63}Cu(2)$ at $\mathbf{H}\|\mathbf{c}$ with the data obtained using a single crystal.[6] We found that at $T = 295$ K, ν_0 and $\Delta\nu$ coincide with the results obtained for a single crystal (96.6 MHz and 80 kHz, respectively), and that the disorientation of the c axis is no greater than 5^0. The NMR measurements were carried out using a Bruker CXP spectrometer in a 8.5-T field. The spin-lattice relaxation time T_1 was measured by the method of reconstruction of the nuclear magnetization after saturating the sample with a train of rf pulses.

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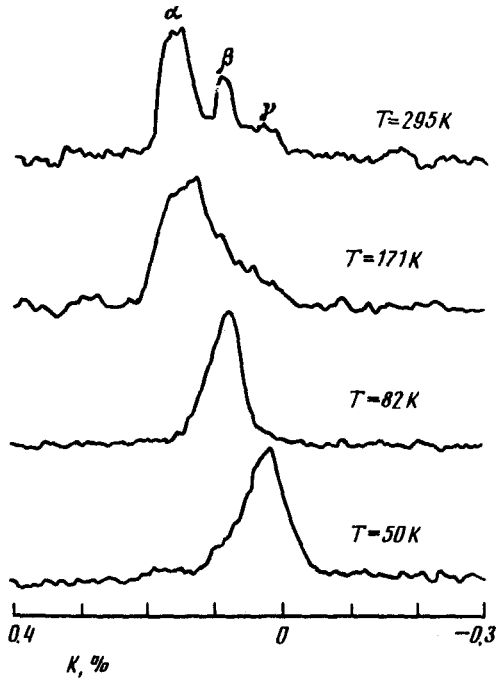

FIG. 1. NMR spectra of ^{17}O in $YBa_2Cu_3O_{7-x}$ ($x \approx 0.15$); the O(2, 3) α line, planes; the O(1) β line, bridges; the O(4) γ line, chains, with the orientation $\mathbf{H} \| \mathbf{c}$.

The NMR spectrum of the central transition ($1/2 \leftrightarrow -1/2$) of ^{17}O of a sample with $\mathbf{c} \| \mathbf{H}$ at $T = 295$ K shows that there are three lines denoted by α, β, and γ in Fig. 1. The integrated intensities of these lines satisfy the relationship 4:2:1. Since there is no interaction anisotropy in the spectrum in this orientation, the strongest α line with a shift $\delta_1 = 0.16\%$ (relative to the ^{17}O resonance in water) can be assigned to the oxygens in the O(2,3) plane, the β line with $\delta_2 = 0.09\%$ can be assigned to the oxygen in the O(1) bridge position, and the diffuse γ line with $\delta_3 \approx 0.02\%$ can be related to the oxygen in the O(4) chains. The shifts and the line assignments are in agreement with the data of Refs. 3, 7, and 8. Since the estimate of the frequency shift due to a second-order quadrupole interaction does not exceed $\sim 0.01\%$, and since $\delta_1 \to 0$ as $T \to 0$ (Fig. 2a), we can assume that shifts δ_i which we determined are the K_{cc} components of the Knight-shift tensors of the various positions of oxygen in the $YBa_2Cu_3O_{7-x}$ lattice. The Knight shift and the shape of the maximum of the α line, K_M, depend strongly on the temperature (Fig. 2a). At $T = 295$ K the Knight shift $K_M = 0.16\%$ decreases to half its value: $K_M = 0.08\%$ at $T_c^{\|} = 75$ K, and follows the dependence $K_M \sim T^{0.6}$ over the temperature interval $T = 80$–200 K. The rf limit of this line, $K_0 \approx 0.18\%$, in this case remains in the same position in the temperature interval $T = 120$–295 K. At $T \lesssim 120$ K the NMR line narrows down and the Knight shift rapidly decreases to zero in the superconducting region (Fig. 2a). The bridge-oxygen line with a temperature-independent Knight shift $K_{cc} = 0.09\%$, which is clearly observed at high temperatures, merges with the O(2,3) line at $T \lesssim 100$–120 K (Fig. 2a).

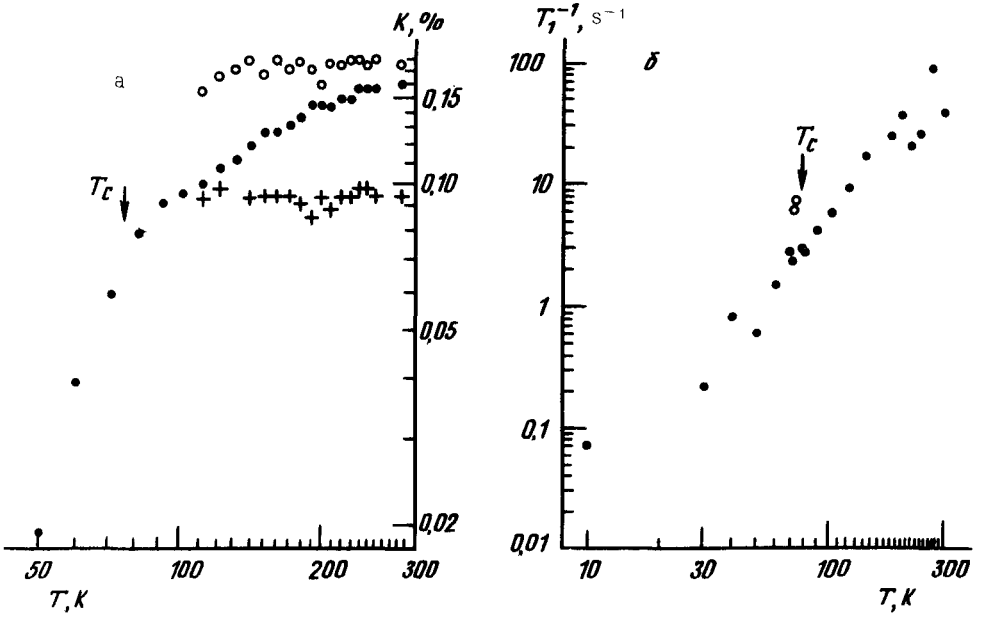

FIG. 2. (a) Positions of the ^{17}O lines vs the temperature. ○—The K_0 shift of the rf edge of the α line; ●—K_M shift at the maximum of the α line; + —shift of the β line; (b) Temperature dependence of the spin-lattice relaxation rate T_1^{-1} of 0(2, 3) oxygens, measured at the frequency of the maximum of the α line.

The recovery of the nuclear magnetization of ^{17}O was approximated by the relation which holds for a magnetic relaxation channel for nuclei with spin $I = 5/2$. The spin-lattice relaxation time T_1 of oxygen nuclei was determined from experimental data using Eq. (1) for numerical fitting. The temperature dependence of the spin-lattice relaxation, measured at the frequency of the maximum of the α line, is shown in Fig. 2c. In the normal phase $T_1^{-1} \sim T^{2.5}$.

Despite the temperature-dependent Knight shift $T_M \sim T^{0.6}$ in the normal phase, the Corringa product $K_M^2 T_1 T \approx 1.6 \times 10^{-5}$ s·K (T = 100 K) depends only slightly on $T > T_c$ and is in good agreement with the theoretical value of ^{17}O: $K^2 T_1 T = (h/4\pi K_B)(\gamma_e/\gamma_n)^2 \approx 1.4 \times 10^{-5}$ s·K. We thus conclude that the nuclear spin of ^{17}O interacts with the free carriers from the oxygen 0(2,3) orbitals. This case is similar to that of an ordinary metal, with the exception that the spin density at ϵ_F depends on the temperature. An acceleration of T_1^{-1} at $T \lesssim T_c$, which was observed in Refs. 2 and 4, and also by us (Fig. 2c), should probably be attributed to the artifacts of the experiment which are the result of an abrupt change in the impedance during the superconducting transition. A nonuniform broadening of the α line suggests that the spin density at the 0(2, 3) sites is distributed nonuniformly because of a possible nonuniform filling of the CuO chains chains by oxygen. As a result, in addition to oxygen-rich clusters which cause a Knight shift $K_0 \approx 0.18\%$, there are also some clusters with

a lower oxygen concentration which cause a temperature-dependent Knight shift $K_M \approx 0.16\%$ (Fig. 2a).

The NMR data on ^{63}Cu(2) are strongly at variance with the results for oxygen.

1. The magnetic shifts $K_{\parallel} = 1.27\%$ $\mathbf{H}\|\mathbf{c}$ and $K_{\perp} = 0.6\%$ ($\mathbf{H}\|\mathbf{c}$) do not depend on the temperature at $T = 120$–300 K, since they cannot sense the change in the spin density at ϵ_F, which is seen for O(2, 3) oxygen (Fig. 2a). It can thus be concluded that the "oxygen carriers" in the plane are slightly hybridized with the $3d^9$ electrons of Cu(2) copper. At $T < 100$ K, we see that $K_{\perp}$ decreases rapidly to 0.2% at $T = 10$ K, a behavior which is usually attributed to the formation of a superconductivity gap in the band comprised of neighboring Cu(2) orbitals. The K_{cc} component anomalously does not undergo any changes near $T = 10$–300 K, a situation which can obviously be attributed to its orbital nature which is insensitive to the superconducting pairing.[9]

2. The time T_1 for Cu (2) was found from the experimental data by numerical fitting according to the formula $M(\infty) - M(\tau) = A \exp(-\tau/T_1) + B \exp(-6\tau/T_1)$ which can be used for a magnetic channel for the relaxation of nuclei with spin $I = 3/2$. The invariance of T_1^{-1} at $T > 120$ K and the anomalous behavior in the temperature region $200 < T < 200$ K (Fig. 3) reproduce well the results of experimental studies with single crystals.[10] At $T \approx 100$ K the anomalous behavior of T_1^{-1} in the case $\mathbf{H}\perp\mathbf{c}$ cannot be attributed to the superconducting transition. At $T < T^* = 120$ K, T_1^{-1} decreases by 2–3 orders of magnitude in accordance with $T_1^{-1} \sim T$, which is usually attributed to the presence of a superconducting gap. It should be noted, however, that the T_1^{-1} (T) dependence of Cu(2) in our case does not undergo any changes or exhibit any structural features near the actual superconducting phase transition at $T = T_c^{\perp} = 81$ K (Fig. 3). Consequently, the gap in the $3d^9$ electron spectrum

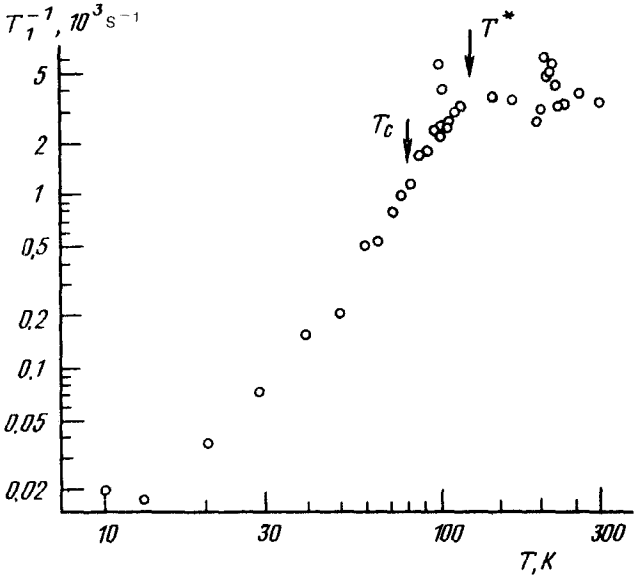

FIG. 3. Dependence of the spin-lattice relaxation rate T_1^{-1} of Cu(2) copper with $\mathbf{H}\perp\mathbf{c}$.

which appears at $T \lesssim T^*$ cannot be attributed to the superconducting gap. The results of Ref. 11, where $YBa_2Cu_3O_{6.7}$ with $T_c = 60$ K has also exhibited a decay of T_1^{-1} at $T \lesssim 100$ K, confirm our viewpoint. A decrease in T_1^{-1} at $T < T^*$ can probably be attributed to the formation of a gap in the spectrum of antiferromagnetic fluctuations of $3d^9$ copper electrons from the CuO planes.

We should note in conclusion that electron spin subsystems of oxygens and Cu(2) copper are relatively independent of each other at high temperatures ($T > T^*$) and couple dynamically at $T < T_c$, as can be deduced from such $T_1^{-1}(T)$ dependences of Cu(2) and O(2,3) (Figs. 2c and 3) in the superconducting region.

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