Radio-Spectroscopic Studies of Magnetic Properties of High Temperature Superconductors *

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We have performed ^{17}O and ^{63}Cu NMR measurements in $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.15$) oriented powder samples at CuO_2 plane sites Cu(2) and O(2, 3) in the temperature range 10–300 K. The temperature dependent Knight shift $K(T)$ and spin lattice relaxation rate T_1^{-1}–(T) of O(2, 3) yield $K^2 T_1 T$ = const in accordance with the presence of free carriers at plane oxygen sites. A sharp decrease of T_1^{-1} of Cu(2) below 120 K is associated with the opening of a gap in the spectrum of antiferromagnetic spin fluctuations of localized copper 3d^9 electrons. The comparison of different temperature dependences of spin densities at the Cu and O sites shows the presence of two nearly independent spin systems. A close similarity of $YBa_2Cu_3O_{7-\delta}$ with heavy fermion superconductors is discussed.

Introduction

The electronic states at the Fermi energy (ε_F) play a very important role in studies of the nature and mechanism of high temperature superconductivity (HTSC). According to the data of photoelectron spectroscopy [1], the conductivity band consists predominantly of the 2p states of oxygen, and the 3d states of copper are localized and do not exceed ε_F. On the other hand, copper NMR data show that at $T < T_c$ the components of the magnetic hyperfine shift of copper in the CuO_2 plane site Cu(2) (K_{aa} and K_{bb}) decrease by half while K_{cc} remains constant [2], and the spin-lattice relaxation rate T_1^{-1} of Cu(2) decreases without enhancement below T_c by 2 to 3 orders of magnitude [3, 4]. This has been attributed to opening of the superconducting gap in the spectrum of electronic states of copper.

Oxygen ^{17}O NMR provided new results [5, 6]:

1) The relaxation rate T_1^{-1} of oxygen O(2, 3) in the plane sites was found to show enhancement just below T_c, as expected for usual singlet S-wave superconductivity [7].

2) At $T > T_c$, oxygen $T_1^{-1}(T)$ follows the usual Korringa law $T_1^{-1} \propto T$, in accordance with the existence of free carriers at oxygen orbitals [1].

For correct interpretation of the copper NMR results, parallel measurements of ^{17}O and ^{63}Cu NMR shift and relaxation data using the same sample are essential.

Experimental

The pellet of $YBa_2Cu_3O_{7-\delta}$ was prepared with standard methods. The gas exchange process consisted of removal of ^{16}O from the initial sample and exposing a pellet to ^{17,18}O gas (22 atom% of ^{17}O, 63 atom% of ^{18}O) at 500 °C during 5 days. The weight increase of the initial pellet (1.7%) suggests a nearly complete exchange of ^{16}O in all oxygen positions of the lattice. The pellet was crushed into fine powder with the grain size less than 2 μm, mixed with epoxy, and the mixture was hardened in 11.7 T magnetic field during 12 hours. Thus we got a solid sample where the $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.15$) microcrystals were oriented with the crystal axis ***c*** aligned in one direction. The onset temperature of the superconducting transition in zero field T_c^0 was 91 K. The NMR measurements were performed in the 8.5 T field of a Bruker CXP-360 FT spectrometer. The spin-lattice relaxation times T_1 were calculated from the recovery of the magnetization after a train of saturating pulses. The magnetic shift of Cu(2) was measured from the resonance frequency of solid copper iodide CuI and the magnetic shift of ^{17}O from that of H_2O.

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Results

The NMR spectrum of the central $(1/2 \leftrightarrow -1/2)$ transition of ^{63}Cu in the Cu(2) site shows the line with the full width at half height FWHH = 70 kHz ($\boldsymbol{c} \parallel \boldsymbol{H}$) and the magnetic shift $K_{cc} = 1.27\%$ at $T = 295$ K, in excellent agreement with the data measured in $YBa_2Cu_3O_7$ single crystal [8, 9]. With decreasing temperature the linewidth increases to FWHH = 100 kHz at $T = 100$ K, but the magnetic shift remains constant with an accuracy of 0.01% in the $T_c < T < 295$ K range. The transverse components of the magnetic shift K_{aa}, $K_{bb} = K_{\perp} = 0.6\%$ in the $120 < T < 295$ K range begin to decrease at $T < 120$ K and reach the value $K_{\perp} \simeq 0.2\%$ at $T \leq 40$ K. The temperature dependence of T_1^{-1} of Cu(2) at the orientation $\boldsymbol{c} \perp \boldsymbol{H}$ is presented in Figure 1. Over the whole temperature range, except the $T = 200$ to 220 K region, the magnetization recovery function was established to be

$$M(\infty) - M(0) = A\,e^{-\tau/T_1} + B\,e^{-6\tau/T_1}\,, \qquad (1)$$

corresponding to a wholly magnetic relaxation mechanism of the quadrupolar $I = 3/2$ nuclei [10]. The nearly constant relaxation rate T_1^{-1} in the $120 < T < 295$ K range with an anomaly between 200 to 220 K closely follows the data for the $YBa_2Cu_3O_7$ single crystal [11]. A sharp decrease of T_1^{-1} begins below $T^* \simeq 120$ K, some 40 K higher than the transition temperature into the superconducting state at $T_c^{\perp} = 81$ K in the magnetic field used. Between $40 < T < 120$ K the relaxation rate $T_1^{-1} \propto T^{\alpha}$ ($\alpha = 3$ to 4). There is a certain instability of T_1^{-1} at $T = 100$ K, but no anomaly in the vicinity of $T = T_c^{\perp}$ was found.

The NMR spectrum at 295 K of the central transition of ^{17}O consists of three lines (see Fig. 2), denoted by α, β, and γ. As the spectrum recorded in the $\boldsymbol{c} \parallel \boldsymbol{H}$ orientation should not contain any broadening due to the anisotropy of the quadrupolar and magnetic shift interactions, the intensity ratio 4:2:1 of the lines α, β, and γ, respectively, corresponds to the already established [12, 13] assignment. Therefore the line α corresponds to oxygens in the CuO_2 plane sites O(2, 3), β to the oxygen bridging the CuO planes and chains O(4), and the smeared line γ to the oxygen in the CuO chains, O(1). According to the measured values of the quadrupolar interaction parameters, the frequency shift due to the second order quadrupolar interaction ($\boldsymbol{c} \parallel \boldsymbol{H}$) is less than 0.01%. Therefore we ignore the quadrupolar contribution to the shift and attribute the frequency shift to the Knight shift component in the c axis direction. The Knight shift of O(4) oxygens $K \simeq 0.095\%$ does not depend on temperature in the $120 < T < 295$ K range. At $T < 120$ K the overlapping of lines α and β makes the separation of lines impossible. The inhomogeneously broadened line of

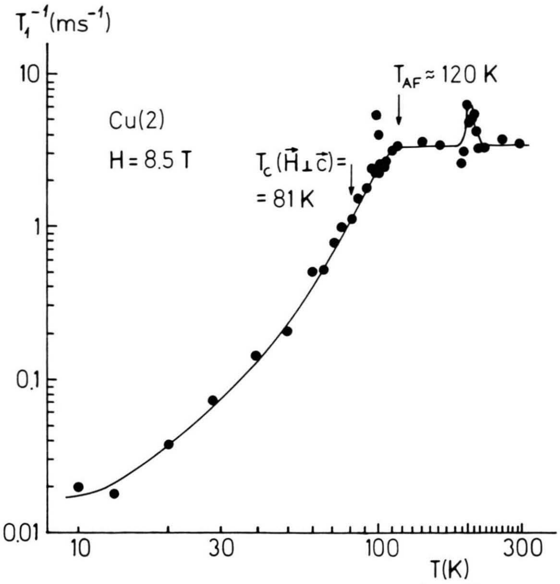

Fig. 1. The temperature dependence of T_1^{-1} of ^{63}Cu at the Cu(2) site, orientation is $\boldsymbol{c} \perp \boldsymbol{H}$.

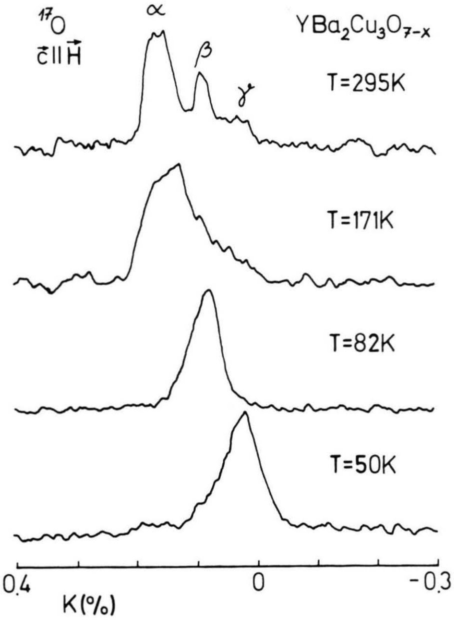

Fig. 2. The temperature dependence of the ^{17}O NMR spectrum at the orientation $\boldsymbol{c} \parallel \boldsymbol{H}$. We have assigned the α-oxygen to O(2, 3) sites, the β line to the bridge oxygen O(4) and the γ line to the chain oxygen O(1).

O(2, 3) shows a remarkable temperature dependence (Figs. 2 and 3). The Knight shift of the maximum of the line, K_M, decreases with the decreasing of temperature from $K_M \simeq 0.16\%$ at 295 K to $K_M \cong 0.08\%$ at $T_c'' = 75$ K. At temperatures between $90 < T < 200$ K, $K_M \propto T^{0.6}$. The high frequency shoulder at the O(2, 3) line exhibits a constant value of $K_0 \simeq 0.18\%$ between $120 < T < 295$ K. At $T < 120$ K the line of O(2, 3) narrows and the Knight shift of the whole line decreases rapidly to zero in the superconducting state. The temperature dependence of the relaxation rate T_1^{-1} measured at the frequency of K_M is shown in Figure 4. At all temperatures the magnetization recovery was approximated by the function

$$M(\infty) - M(\tau) - A\,e^{-\tau/T_1} + B\,e^{-6\tau/T_1} + C\,e^{-15\tau/T_1}, \quad (2)$$

as expected for a purely magnetic relaxation mechanism for quadrupolar nuclei with spin $I = 5/2$ [10]. The temperature dependence of the relaxation rate can be described by the function $T_1^{-1}(T) \propto T^{\alpha}$ ($\alpha = 2$ to 3) and shows no maximum below T_c'', in contrast with the opening of a BCS-like gap at the Fermi energy.

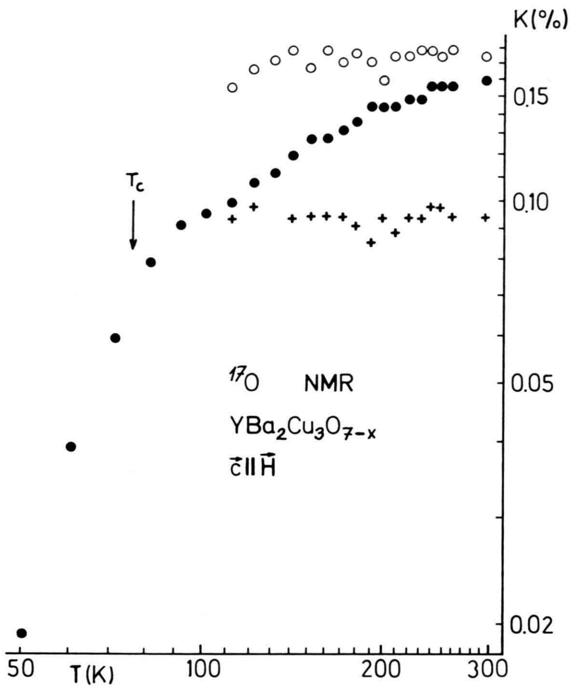

Fig. 3. The temperature dependence of the Knight shifts of ^{17}O in the O(4) site (+) and in the O(2, 3) sites (o: the high frequency edge, K_0; •: the maximum of the line, K_M).

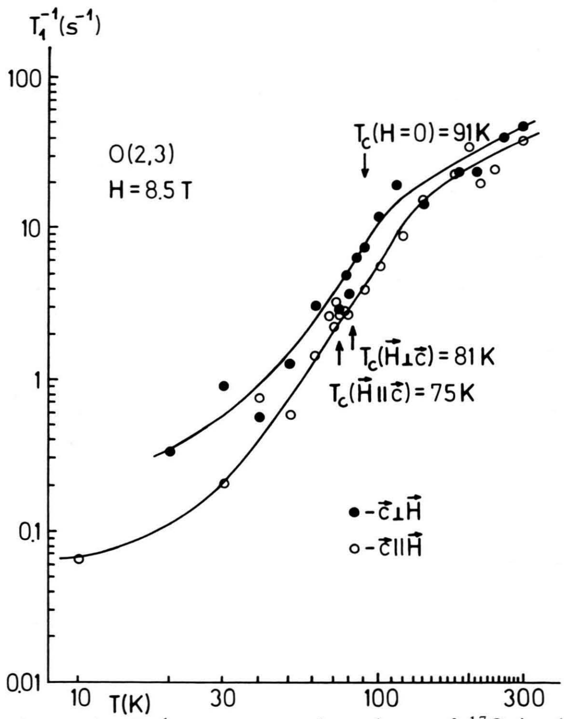

Fig. 4. The T_1^{-1} temperature dependence of ^{17}O in the O(2, 3) site, measured at K_M.

Discussion

Inhomogeneous broadening of the O(2, 3) line shows a distribution of spin densities at the O(2, 3) sites which can be caused, as was proposed in [13], by the presence of oxygen deficient clusters of $YBa_2Cu_3O_{6.7}$ type in our sample. The temperature dependence of the Knight shift $K_M \propto T^{0.6}$ is in accordance with the temperature dependence of the density of states in the case of a linear temperature dependence of the concentration of carriers within a closed Fermi surface. According to the Korringa relation for free carriers, $K^2 T_1 T$ is constant. In our case, the K_M temperature dependence yields $T_1^{-1} \propto T^{2.2}$ in rough agreement with the dependence shown in Figure 4. Therefore we can conclude that the data of ^{17}O NMR correspond to the case of free carriers at O(2, 3) orbitals.

The sharp decrease of the relaxation rate T_1^{-1} of copper in the Cu(2) site was already reported for $YBa_2Cu_3O_{6.7}$ [14] below $T^* \simeq 100\ \text{K} > T_c$. We believe that the temperature T^* cannot be attributed to the opening of the superconductivity gap. Most probably the gap is opening at $T = T^*$ in the spectrum of copper antiferromagnetic fluctuations, because the main relaxation mechanism of Cu(2) is due to the quantum mechanical fluctuations of localized $3d^9$

electrons [8]. This circumstance underlines the close similarity of the phenomenon of HTSC to the superconductivity in heavy fermion compounds (e.g. $CeCu_2Si_2$), where at $T^* > T_c$ the correlation gap opens and in the superconducting phase the nuclear spin-lattice relaxation rate T_1^{-1} follows the T^3 law [15]. In the absence of the correlation gap the superconductivity does not occur in these systems [16]. Taken together, all this means a magnetic mechanism of high temperature superconductivity in doped CuO_2 layers.

[1] H. Katayama-Yoshida, T. Takahashi, H. Matsuyama, Y. Okabe, Y. Kitaoka, K. Ishida, K. Asayama, H. Fujimoto, and H. Inokuchi, Int. J. Modern Phys. **B 1,** 1273 (1988).
[2] M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, and R. B. Schwarz, Phys. Rev. B **39,** 300 (1989).
[3] M. Mali, D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, and Hulliger, J. Phys. Lett. **A 124,** 112 (1987).
[4] T. Imai, T. Shimizu, T. Tsuda, H. Yasuoka, T. Takabatake, Y. Nakazawa, and M. Ishikawa, J. Phys. Soc. Japan **57,** 1771 (1988).
[5] K. Ishida, Y. Kitaoka, K. Asayama, H. Katayama-Yoshida, Y. Okabe, and T. Takahashi, J. Phys. Soc. Japan **57,** 2897 (1988).
[6] P. Wzietek, D. Köngeter, P. Auban, D. Jérome, J. P. Contures, B. Dubois, and Ph. Odier, Europhys. Lett. **8,** 363 (1989).
[7] The latest result of P. C. Hammel, M. Takigawa, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. Lett., in press, show no enhancement of T_1^{-1} below T_c for the O(2, 3) site.
[8] C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. **B 39,** 274 (1989); ibidem, 2902 (1989).
[9] I. A. Heinmaa, A. M. Vainrub, J. O. Past, V. O. Miidel, A. V. Miller, I. F. Štšegolev, and G. A. Jemeltšenko, Pis'ma v JETP **48,** 171 (1988).
[10] A. Narath, Phys. Rev. **162,** 320 (1967).
[11] A. V. Miller, A. M. Vainrub, I. A. Heinmaa, A. V. Reinhold, E. T. Lippmaa, and I. F. Štšegolev, Pis'ma v JETP **49,** 211 (1989).
[12] C. Coretsopoulos, H. C. Lee, E. Ramli, L. Reven, T. B. Rauchfuss, and E. Oldfield, Phys. Rev. B **39,** 781 (1989).
[13] M. Horvatić, Y. Berthier, P. Butand, Y. Kitaoka, P. Segransan, C. Berthier, H. Katayama-Yoshida, Y. Okabe, and T. Takahashi, Physica C, submitted.
[14] W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, R. J. Cava, R. Tycko, R. F. Bell, and G. Dabbagh, Phys. Rev. Lett. **62,** 1193 (1989).
[15] Y. Kitaoka, K. Ueda, T. Kohara, and K. Asayama, Solid State Commun. **51,** 461 (1984).
[16] F. Steglich, in: Theory of heavy fermions and valence fluctuations (T. Kasuya and T. Saso, eds.), Springer-Verlag, Berlin 1985.