Spin Dynamics at Oxygen Sites in $YBa_2Cu_3O_7$

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We report NMR measurements of the nuclear relaxation rate at all copper and oxygen sites in magnetically aligned powder samples of $YBa_2Cu_3O_7$. Comparison of the oxygen and copper relaxation reveals a characteristic temperature greater than T_c. The copper relaxation rate is enhanced by antiferromagnetic copper spin fluctuations which are undiminished in the superconducting state. The absence of a coherence peak indicates that the superconductive pairing is not of the conventional BCS type.

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The nature of spin fluctuations in the high-temperature superconducting copper oxides and their possible role in superconductive pairing are problems of central importance in our understanding of these materials. Nuclear-magnetic-relaxation-rate (T_1^{-1}) measurements microscopically probe spin dynamics at the atomic sites and so provide crucial insight into this question. Accordingly we have measured the relaxation rate at all oxygen and copper sites in magnetically aligned powders[1] of $YBa_2Cu_3O_7$.

Comparison of the copper and oxygen NMR relaxation rates shows that the large magnitude of the copper relaxation rate in the normal state is due to antiferromagnetic copper spin fluctuations and that these antiferromagnetic spin fluctuations persist into the superconducting state. The behavior of these fluctuations changes at a characteristic temperature slightly above T_c. In addition to probing the microscopic dynamics, nuclear relaxation can provide information about the nature of the superconducting condensate: The coherence peak[2] in T_1^{-1} just below T_c is a hallmark indicator of BCS superconductivity. Our measurements clearly show the absence of any increase of relaxation just below T_c at *any* of the four oxygen sites. The absence of this peak supports the possibility that the pairing in $YBa_2Cu_3O_7$ is *d* wave.

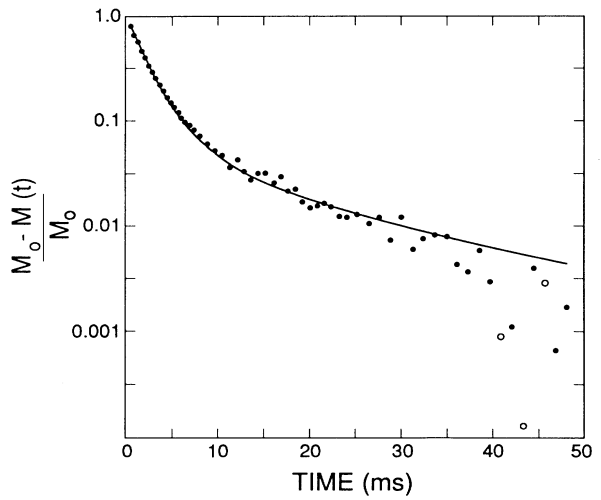

FIG. 1. Time dependence at 110 K of the recovery of the spin-echo intensity from the first high-field O(2) and O(3) satellites at 40.2 MHz in a 7.017-T field applied parallel to the crystal *c* axis. Both satellites fall within the spectrometer bandwidth. The open circles indicate points for which the measured signal magnitude exceeded the equilibrium ($t = \alpha$) value as determined by the fit. The solid line is the fit described in the text.

The preparation of the sample in which ^{17}O was substituted for ^{16}O by conventional gas-phase exchange has been described in an earlier publication[3] in which we show an NMR spectrum. T_c is 93 K in a 10-mT field and the sample exhibits close to 100% shielding. The ^{17}O (^{63}Cu) relaxation measurements were made in a 7.0- (7.4-) T field which reduces T_c to 86 K when the field direction is parallel to the crystal *c* axis ($\mathbf{H} \| \mathbf{c}$). The ^{17}O (nuclear spin $I = \frac{5}{2}$) $\mathbf{H} \| \mathbf{c}$ measurements were made on the quadrupole satellites to ensure that signals from a single site only were detected; such measurements are more reliable than those made on the central transition in which lines from all sites overlap. The spin-echo intensity was measured at varying times following a single 90° saturating pulse to determine the relaxation rate. In Fig. 1 we show the time dependence of the recovery of the magnetization at the O(2) and O(3) sites [since the relaxation rates at the two sites are identical, we will refer to both sites as O(2,3)] at $T = 110$ K and the three-parameter fit of the expected[4] five-component exponential recovery to the data. Figure 2 shows the relaxation data for all oxygen and copper sites with $\mathbf{H} \| \mathbf{c}$. It is immediately evident that there is no increase or peak in the oxygen relaxation rate below T_c at any site. This contradicts earlier results[5,6] obtained in randomly oriented powder samples. We feel that the distinction between our results and the earlier ones lies in our use of the quadrupole satellites in aligned crystalline samples. The alignment procedure fixes the powder grains to prevent accidental changes in alignment and ensures that we detect signals from a single site only, as shown by the quality of the fit (Fig. 1) by the predicted five-component exponential.

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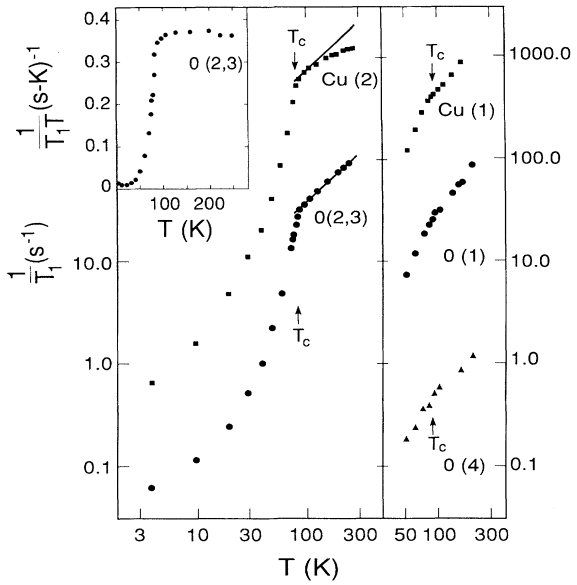

FIG. 2. The relaxation rates at all four oxygen sites and both copper sites in a field of 7.0 T ($^{17}T_1^{-1}$) or 7.4 T ($^{63}T_1^{-1}$) applied parallel to the crystal c axis plotted on a logarithmic scale for both axes. The solid lines indicate a linear relationship between relaxation rate and temperature. The contrast between copper and oxygen relaxation is evident. The inset emphasizes the linear temperature dependence of oxygen relaxation above T_c.

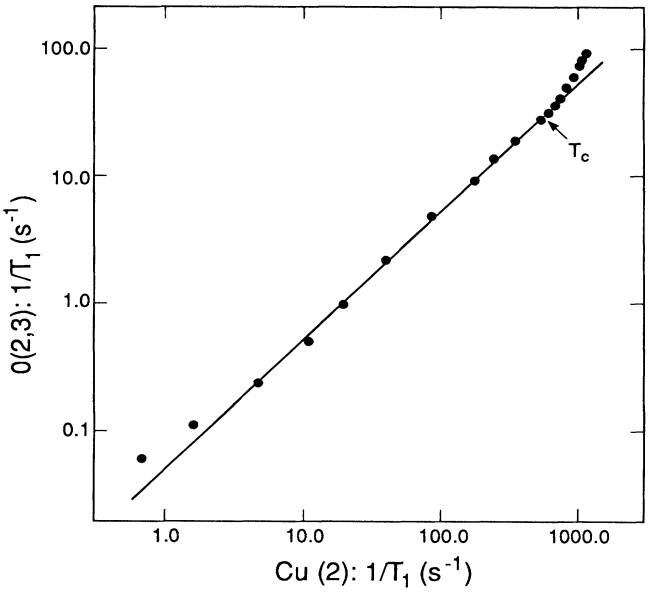

FIG. 3. $^{17}T_1^{-1}$ is plotted against $^{63}T_1^{-1}$ with temperature as an implicit parameter. Temperature ranges from 4 to 250 K. The solid line of unity slope indicates the relationship $^{63}T_1^{-1}/^{17}T_1^{-1}=19.3$. The data deviate from this relationship above $T=110$ K demonstrating the existence of a characteristic temperature other than T_c.

We will concentrate on results from the planes: the relaxation rates at the O(2,3) sites, $^{17}T_1^{-1}$, and at the Cu(2) site, $^{63}T_1^{-1}$. The Cu(2) results are largely in agreement with those of Imai *et al.*[7] obtained in zero-field measurements. The linear relationship between $^{17}T_1^{-1}$ and temperature above T_c is emphasized in the inset of Fig. 2. The magnitude of the relaxation is very close to that predicted by Korringa,[8] as will be discussed below. In the same temperature regime $^{63}T_1^{-1}$ exceeds $^{17}T_1^{-1}$ by as much as a factor of 20 and has a much weaker temperature dependence. Below T_c both relaxation rates drop very rapidly ($\sim T^5$ initially). In Fig. 3 we compare $^{17}T_1^{-1}$ with $^{63}T_1^{-1}$, plotting with temperature as an implicit parameter. The temperature dependences of both rates are identical for 20 K $< T <$ 110 K as shown by the solid line of unity slope indicating the relationship $R=^{63}T_1^{-1}/^{17}T_1^{-1}=19.3$. We emphasize two important features. First is the existence of a characteristic temperature above T_c. The second is that below this characteristic temperature both rates have identical temperature dependences; in particular, the oxygen rate decreases just as rapidly as the copper rate. The significance of this point will be discussed further below.

If we consider the imaginary part of the wave-vector- (q) and frequency- (ω) dependent electronic spin susceptibility $\chi''(q,\omega)$, we can write a general expression[9] for the relaxation rate

$$T_1^{-1}=(\gamma^2 k_B T/2\mu_B^2)\lim_{\omega\to 0}\sum_q |A(q)|^2\chi''(q,\omega)/\omega\,, \quad (1)$$

where $A(q)$ is the hyperfine coupling between the electronic spin and the nuclear spin having gyromagnetic ratio γ. The Korringa[8] relation $(K^2T_1T)^{-1}=\pi\hbar k_B\gamma^2/\mu_B^2$, which relates the Knight shift K and the relaxation rate, describes relaxation of nuclei coupled to conduction electrons in a metal. Derived from a single-electron theory of electron dynamics, it predicts a specific and temperature-independent relationship between the static, uniform spin susceptibility χ and $\langle\chi''(q)\rangle_q$ [the zero-frequency limit of the average of $\chi''(q,\omega)/\omega$ over all q spanning the Fermi surface] proportional, respectively, to the Knight shift[10] and the relaxation rate.[11] Electron-electron interactions can increase $\chi(q)$ at nonzero q and hence $\langle\chi''(q)\rangle_q$ while having little effect on $\chi(q=0)$; this will result in an enhancement of $(K^2T_1T)^{-1}$ with respect to $\pi\hbar k_B\gamma^2/\mu_B^2$.

To estimate the enhancement of the copper relaxation we compare the $\mathbf{H}\perp\mathbf{c}$ relaxation rate at 100 K (2850 s^{-1}) (Ref. 12) to the fraction of the $\mathbf{H}\parallel\mathbf{c}$ spin Knight shift[5] attributable to the on-site d-spin hyperfine fields (0.44%) since fluctuations of the on-site spin make the dominant contribution to $^{63}T_1^{-1}$ for $\mathbf{H}\perp\mathbf{c}$ (assuming the four nearest-neighbor contributions fluctuate incoherently). Because the orbital character is almost exclusively $d_{x^2-y^2}$, orbital relaxation makes little contribution. The

on-site hyperfine field in the a-b plane[13] is very small due to accidental cancellation. Taking account of this extreme anisotropy introduces a factor of $\frac{1}{2}$ in estimating the enhancement with respect to the ideal Korringa value: We compare $(K^2T_1T)^{-1}$ to $\frac{1}{2}\pi\hbar k_B\gamma^2/\mu_B^2$. We estimate an enhancement of 11 at 100 K. Unlike copper, oxygen relaxation is linear in temperature implying [Eq. (1)] a temperature-independent dynamical susceptibility. From the Knight shift[5] we know that the dominant hyperfine coupling is isotropic ($K_{\rm iso}=6.3K_{\rm axial}$). The core polarization field for oxygen[14] is small ($\sim$30 kOe/μ_B) and cannot account for the Knight shift. In the insulating transition-metal oxides[15] the O-2s orbital is coupled to the 3d orbital through hybridization. In the present case we cannot exclude the possibility of O-2s coupling to neighboring O-2p orbitals as well. Using the measured isotropic Knight shift[5] and relaxation rate above T_c, we estimate that there is only a slight enhancement of $^{17}T_1^{-1}$: $(K^2T_1T)^{-1}$ is 1.4 times the ideal Korringa value.

Because the discussion of the relaxation data depends on the model one chooses to describe the doped holes, we will use the so-called two-band[16] and single-band[17] models as frameworks for discussion. Our major conclusions do not depend on the framework we choose. The two-band picture[16] allows the holes occupying the 2p orbitals on oxygen to have degrees of freedom independent of the d holes. The doped holes are mobile and carry spin; calling their dynamical susceptibility $\chi''_{\rm O\text{-}p}(q,\omega)/\omega$ and that of the copper d spins $\chi''_{d,1}(q,\omega)/\omega$ we expect

$$^{17}T_1^{-1}=(^{17}\gamma^2k_BT/2\mu_B^2)\times\lim_{\omega\to 0}\Big[\sum_q|A_{\rm O\text{-}p}(q)|^2\chi''_{\rm O\text{-}p}(q,\omega)/\omega+\sum_q|A_d(q)|^2\chi''_{d,1}(q,\omega)/\omega\Big] \quad (2)$$

in a simplified picture. $A_{\rm O\text{-}p}$ is the Fermi contact coupling to the O-2s orbital which is assumed to carry some doped-hole spin density through hybridization. $A_d(q)$ is the coupling to the neighboring copper spin. The oxygen is symmetrically located between neighboring coppers so hyperfine fields from antiparallel spins on the neighboring coppers will cancel at the oxygen site: $A_d(q_a)\propto\cos(q_a\pi/2Q_{\rm AF})$ (a corresponds the Cu-O bond axis direction).

In the single-band picture[17] holes having primarily 2p character hybridize strongly with copper d holes of opposite spin forming a local singlet. If we call the dynamical susceptibility of the copper d spins in this system $\chi''_{d,2}(q,\omega)/\omega$ we expect

$$^{17}T_1^{-1}=(^{17}\gamma^2k_BT/2\mu_B^2)\lim_{\omega\to 0}\sum_q|A_d(q)|^2\chi''_{d,2}(q,\omega)/\omega. \quad (3)$$

Although the following discussion will be in the framework of Eq. (2), it carries through almost unchanged for the model of Eq. (3) as will be discussed below. The large enhancement of $^{63}T_1^{-1}$ shows that the increase of $\langle\chi''(q)\rangle_q$ is large compared to that of $\chi(q=0)$. The negligible enhancement of $^{17}T_1^{-1}$ shows that $\chi''_{d,1}(q)$ must be strongly peaked in the vicinity of $q=Q_{\rm AF}$ where the hyperfine coupling of $\chi''_{d,1}(q)$ to the oxygen nuclear spin vanishes. In Eq. (2) the first term is dominant then and $^{17}T_1^{-1}$ probes the mobile-hole spin dynamics: These are very similar to those of a simple metal. In contrast, the temperature dependence of the copper relaxation shows that $\langle\chi''_{d,1}(q)\rangle_q$ is increasing with decreasing temperature. However, from the copper Knight shift[18] we know that $\chi_{d,1}(q=0)$ is temperature independent above T_c, showing that it is the large-q component of $\chi''_{d,1}(q,\omega)$ which is increasing. The Kramers-Kronig sum rule relates the real, static susceptibility, $\chi_{d,1}(q)$, and $\chi''_{d,1}(q,\omega)/\omega$. Assuming a Lorentzian frequency dependence, the temperature dependence of $\chi''_{d,1}(Q_{\rm AF},\omega)/\omega$ indicates that $\chi_{d,1}(Q_{\rm AF})$ is increasing with decreasing temperature. Figure 3 shows that $^{17}T_1^{-1}$ and $^{63}T_1^{-1}$ have identical temperature dependences below approximately 110 K; this strongly suggests that some coupling between $\chi''_{\rm O\text{-}p}(q,\omega)$ and $\chi''_{d,1}(q,\omega)$ sets in at this temperature. At this point the increase of $\chi_{d,1}(Q_{\rm AF})$ ceases and, like $\chi''_{\rm O\text{-}p}$, it becomes temperature independent. We note that a change in the copper relaxation behavior is seen in zero-field measurements in the vicinity of 110 K in fully oxygenated[7] and oxygen-deficient[19] $YBa_2Cu_3O_x$. We have shown that the oxygen nuclear spin does not couple well to the antiferromagnetic copper spin fluctuations. The rapid decrease of copper relaxation cannot be due to the loss of the antiferromagnetic spin fluctuations since this would have little effect on the oxygen relaxation; in fact the oxygen relaxation rate decreases equally sharply.

Because the oxygen relaxation is not dominated by $\langle\chi''_{d,1}(q)\rangle_q$ the complete absence of any peak in the relaxation rate immediately below T_c is significant. Seen[4] in s-wave superconductors, this peak results from the piling up of states at the gap edge. In d-wave superconductivity it will be absent: The existence of quasiparticle states in the gap reduces the accumulation of states at the gap edge and the coherence factor will be zero for the simplest d-wave states one might consider for a square Fermi surface. Electron-phonon scattering[20] can broaden the peak in the density of states, thus smearing the peak in T_1^{-1}. In the case of strong scattering one would expect severe broadening, but the complete absence of a peak seems unlikely. However, angle-resolved ultraviolet-photoemission-spectroscopy measurements[21] at 20 K have observed the peak in the density of states predicted by BCS. Nonetheless, the absence of the peak suggests that the pairing is not of the ordinary s-wave BCS type.

In the picture of Eq. (3), the strongly enhanced copper relaxation tells us that $\chi''_{d,2}(q,\omega)$ is peaked at large q. The hyperfine coupling of oxygen nuclei to $\chi''_{d,2}(q,\omega)$ is the same as for the two-band model; $\chi''_{d,2}(q,\omega)$ must be

sharply peaked around $q = Q_{AF}$. Thus the difference in the temperature dependences of the oxygen and copper relaxation rate does not rule out the single-band picture. This implies that the large-q component of $\chi''_{d,2}(q,\omega)$ increases with decreasing temperature, while the small-q components of $\chi''_{d,2}(q,\omega)$ are temperature independent. At the characteristic temperature 110 K all wave-vector components of $\chi''_{d,2}(q,\omega)$ become temperature independent. The same argument as above allows us to deduce the temperature dependence of $\chi_{d,2}(Q_{AF})$ from $^{63}T_1^{-1}$. As in the two-band picture, the enhancement due to $\chi''_{d,2}(Q_{AF})$ remains in the superconducting state.

Figure 3 suggests a third model to describe the relationship between doped and d holes. This picture takes the two-band model as a starting point for $T > 110$ K. We have seen that in a two-band model we must have some coupling between $\chi''_{O\text{-}p}$ and $\chi''_{d,1}$ which sets in at 110 K. It is possible that this could result from a strengthening of the coupling between doped holes and the d holes themselves. This situation would bear some similarity to the heavy-fermion systems[22] in which a change occurs from a system comprised of two independent but interacting spin systems to one made up of a single Fermi sea of spins. The analogy is certainly not complete; for instance, in the present case the uniform susceptibility is temperature independent but $\chi(Q_{AF})$ grows with decreasing temperature much as the uniform susceptibility does in the heavy fermions.

We turn briefly to the relaxation results in the chains shown in Fig. 2. Both O(1) and O(4) (the chain and bridging sites) show the same temperature dependence as the chain copper, Cu(1): Above T_c the temperature dependence is stronger than linear and there is a clear but weak change in behavior associated with T_c. For both O(1) and O(4) there is little enhancement of the relaxation rate. The very small values of both the isotropic Knight shift[5] and T_1^{-1} for O(4) indicate that the fractional occupation of the $2s$ state on O(4) is smaller than for other sites. It is not understood why this should occur. Because the anisotropic hyperfine field due to p orbitals is comparable to the contact coupling, the O(4) relaxation rate is anisotropic: The $\mathbf{H} \perp \mathbf{c}$ rate exceeds the $\mathbf{H} \| \mathbf{c}$ rate by a factor of 2.2. From the similar temperature dependences at all chain sites we conclude that the doped holes are strongly bound to the Cu(1) holes to form a single band. As in the planes, neither the O(1) nor O(4) sites show a peak in T_1^{-1} below T_c, again supporting the possibility of d-wave pairing.

From simple geometrical considerations we have shown that the oxygen relaxation rate is sensitive only to low-q fluctuations of the copper spin susceptibility. The minimal enhancement of oxygen relaxation shows that the large enhancement of copper relaxation rate must result from *antiferromagnetic* (large q) fluctuations. Well above T_c, $\chi_d(Q_{AF})$ is increasing with decreasing temperature, becoming temperature independent at 110 K. Comparing oxygen and copper relaxation rates, we see this to be a characteristic temperature below which both rates exhibit identical temperature dependences while decreasing by almost 3 orders of magnitude. The rapid decrease of the copper relaxation rate in the vicinity of T_c cannot be due to the loss of antiferromagnetic spin fluctuations since in this case the decrease of oxygen relaxation would be slight: The *antiferromagnetic spin fluctuations do not diminish in the superconducting state.*

Finally, the clear absence of a coherence peak in $^{17}T_1^{-1}$ supports the possibility of d-wave superconductive pairing.

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