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^{17}O NMR STUDY OF $YBa_2Cu_3O_{7-\delta}$

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We present our ^{17}O NMR experimental results in a magnetically aligned powder sample of $YBa_2Cu_3O_{7-\delta}$ (T_c = 93 K). The sign of the anisotropic Knight shift shows that the spin density resides mainly on the p_σ orbitals at the planar O(2,3) and bridging O(4) sites. About 30 % of the total spin susceptibility is attributed to the oxygen $2p_\sigma$ states. The Knight shift at the O(2,3) sites decreases more rapidly than that at the chain O(1) sites, indicating a larger gap in the planes. The nuclear relaxation rate at the O(2,3) sites shows linear-T (Korringa) behavior above T_c, in contrast to the much weaker temperature dependence at the planar Cu(2) sites. However, these two rates show identical temperature dependence below about 110 K, indicating that an important change in the spin dynamics takes place above T_c.

1. INTRODUCTION

In the high T_c superconducting copper oxides, the magnetic interaction between Cu d-holes and oxygen p-holes has been considered to be a key issue. The rapid reduction of the Knight shift[1] and the nuclear relaxation rate[2] below T_c at the Cu sites in $YBa_2Cu_3O_{7-\delta}$ clearly indicates that a gap appears in the spin excitations of the Cu d-hole system in the superconducting state. Since NMR is a site specific probe, it is highly desirable to perform detailed oxygen NMR studies to compare with the Cu results. In this paper we describe the results of ^{17}O NMR experiments in a magnetically aligned powder sample of fully oxygenated $YBa_2Cu_3O_{7-\delta}$ (T_c = 93 k). The method for the isotope exchange and magnetic alignment as well as the details of the NMR experiments are described in earlier publications.[3,4]

2. NMR SPECTRUM AND KNIGHT SHIFTS

Fig. 1 shows the ^{17}O NMR spectrum at 160 K obtained by sweeping the applied magnetic field along the c-axis at a fixed NMR frequency (49.8 MHz). The technique of magnetic alignment allowed us to obtain well separated resonance lines for the inequivalent oxygen sites, as shown in Fig. 1. The assignment of these resonance lines to different oxygen sites and the procedures to deduce the principal components of the electric field gradient (EFG) and the Knight shift (K) tensors are desribed in detail in ref. 3.

The components of the EFG and K along the a- and b- axes were determined from spectra with the field applied perpendicular to the c-axis.

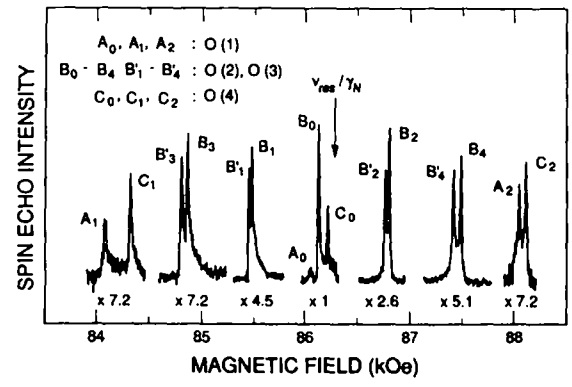

Figure 1. ^{17}O NMR spectrum at 160 K and 49.8 MHz with the magnetic field along the c-axis. Each piece of the spectrum was taken with dufferent gain as shown under the spectrum.

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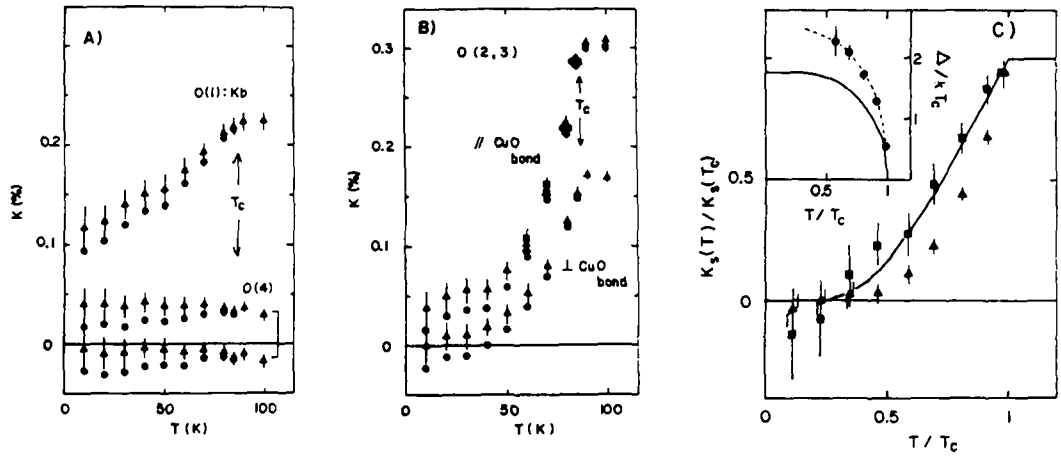

Figure 2. Temperature dependences of the Knight shift at all oxygen sites with magnetic field applied perpendicular to the c-axis. A) Circles denote raw data and triangles represent data corrected for diamagnetism. Data for O(1) sites were taken with field along direction of largest EFG, most likely the b-axis. The O(4) data are shown for two field orientations. B) Circles and triangles: O(2) data corrected and uncorrected for diamagnetism; diamonds and squares O(3) data corrected and uncorrected for diamagnetism. O(2) and O(3) overlap at low T(K). C) Normalized spin Knight shift at O(1) (squares) and O(2,3) (|| Cu-O bond, triangles). Solid line is the Yosida function. Inset shows value of isotropic gap determined from the experimental Knight shift at O(2,3). Solid line shows calculated gap temperature dependence for weak coupling BCS model.

Although we cannot assign these components a priori to either the a or b axis, detailed analysis of the EFG tensor at the planar O(2) and O(3) sites shows that the largest component of the EFG corresponds to the Cu-O bond direction, i.e. the a-axis for O(2) and the b-axis for O(3).[3,5] Based on this analysis, the larger component of K at O(2,3) in the ab-plane is also assigned to the Cu-O bond direction.

The observed Knight shift is the sum of the spin and orbital contributions $K = K_s + K_{orb}$. K_{orb}, which is expected to be temperature independent, is determined from the residual Knight shift at low temperatures below T_c, assuming[1] that K_s vanishes due to singlet spin pairing.

The temperature dependence of K_s in the superconducting state also yields important information about the magnitude and the symmetry of the gap. Fig. 2 A), B) show the temperature dependence of K_a and K_b for all oxygen sites. Because the NMR spectra were taken in the vortex state, we need to make corrections for the field produced by the diamagnetic screening current in order to determine K, as has been done in the Cu Knight shift study.[1] The details of this correction will be described elsewhere. We discuss the temperature dependence of K only with the $H \perp c$ data since the diamagnetic magnetization is much smaller for this direction ($M_c \sim 5M_{a,b}$). Therefore, possible errors in these corrections are small.

The most remarkable feature of this data is that the O(2,3) and O(1) sites show different temperature dependences of K. K at the O(2,3) sites decreases much more rapidly below T_c than at O(1). The difference is shown more clearly in the normalized $K_s(T)/K_s(T_c)$ vs. T/T_c plot shown in Fig. 2 C). The O(1) result is well explained by the Yosida function[6] for the weak coupling BCS model ($\Delta(0) = 1.76\ kT_c$). The more rapid decrease of $K_s(T)/K_s(T_c)$ at the O(2,3)

sites is naturally explained by a larger gap. Similar data for K_c at O(2,3) has been reported by Horvatic et al.[7] The magnitude of the gap is estimated from the experimental data of $K_s(T)/K_s(T_c)$ at each temperature assuming an isotropic gap and is plotted in the inset of Fig. 2 C). The zero temerature value of the gap in this model appears to be around $2.5k_BT_c$.

K_a and K_b at O(2,3) show similar temperature dependence and there is no clear indication of linear-T dependence at low temperaturs as was found in the Cu(2) Knight shift.[1] As reported in a separate paper[8] Cu(2) shows large anomalous line widths when the field is applied perpendicular to the c-axis. Since we do not understand the reason for this large line width, it is not clear whether the temperature variation of the peak field of the resonance is entirely associated with changes of the spin susceptibility.

A larger energy gap for the spin excitations in the planes than in the chains is also inferred from the Cu relxation rate.[2] It will be important to take these differences into account when comparing values of the gap obtained from various experimental methods.

We now turn to discuss K_s in the normal state. At the O(2,3) sites, K_s is axial symmetric around the Cu-O bond direction and larger along this direction. The anisotropic part of K_s is associated with the dipolar field from the spin density on the oxygen 2p orbitals. The observed sign of the anisotropy of K_s immediately leads to the conclusion that the spin density at the O(2,3) sites mainly resides on the p_σ orbitals which have lobes along the CuO bond axis. The same argument applies for the bridging O(4) sites which show almost zero K_s in the ab-plane and positive K_s along the c-axis (0.06%). We therefore conclude that the spin density at O(4) resides on the P_σ orbitals extending along the c-axis.

The chain O(1) sites, however, show nearly isotropic K_s (0.1 %) and very large K_{orb} (0.13 %). The large difference in the symmetry and the magnitude of K_s and K_{orb} between the O(1) and the O(4) sites is in contrast to the similarity of the O(2) and O(3) Knight shifts (except for the different symmetry axes). This fact indicates that the planes and chains have quite different electronic structure in spite of the similarity of the four-fold oxygen coodination around each Cu.

The local spin susceptibility associated with these oxygen 2p states can be estimated from the anisotropy of K_s, using the appropiate hyperfine coupling constant $A_{2p} = (2/5)\mu_B\langle r^{-3}\rangle \approx 91\text{kOe}/\mu_B$ (70 % of the free atom value[9]). We obtain $\chi_{p,pl} = 1.7 \times 10^{-5}$, $\chi_{p,br} = 1.1 \times 10^{-5}$ (emu/mole.atom) for the O(2,3) and O(4) sites, respectively. The local p_σ spin susceptibility on the oxygen sites accounts for about 30 % of the total spin susceptibility, neglecting the contribution from the chain O(1) sites. This indicates that the dominant part (70 %) of the spin susceptibility is associated with Cu d-states.

3. NUCLEAR SPIN RELAXATION RATES

While the Knight shift provides a measure of the static spin susceptibility, the nuclear relaxation rate ($1/T_1$) is determined by the low frequency spin fluctuations. The temperature dependences of $1/T_1$ at the O(2,3) and Cu(2) sites are shown in Fig. 3 $1/T_1$ at O(2,3) follows the Korringa relation (T_1T = const.) above T_c with a only slightly enhanced value of $(T_1T\,K_s^2)^{-1}$ (about 1.4 times the Korringa value $\hbar k_B\gamma_N^2/\mu_B^2$), in strong contrast to the weaker temerature dependence and greatly enhanced value of $1/T_1$ at Cu(2). The most striking result is that these two sites show an identical temperature dependence of $1/T_1$ below about 110 K, in spite of large differences in magnitude.

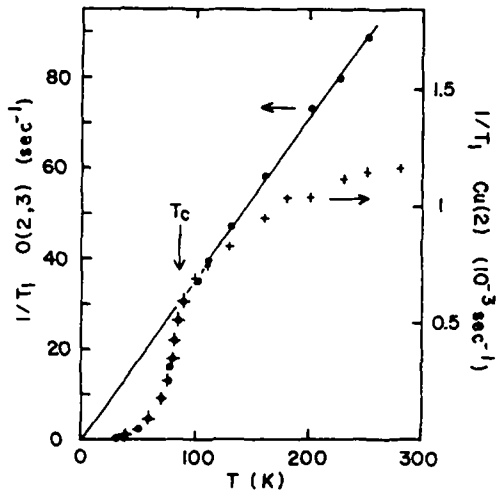

Figure 3. Temperature dependence of $1/T_1$ at the O(2,3) (solid dots) and the Cu(2) (crosses) sites.

The implication of these results are discussed in detail in separate papers.[4,10] We summarize the important points here. The different temperature dependences of $1/T_1$ at high temperature can be explained if the spin dynamics of the itinerant oxygen p-holes, responsible for the Korringa behavior of oxygen $1/T_1$, is different from that of Cu d-holes.[11,12] The large Cu(2) enhancement of $1/(T_1T K_S^2)$ over the Korringa value implies an enhancement of the dynamical susceptibility $\chi''(q,\omega)/\omega$ of Cu d-holes at large q, which must be temperature dependent in order to be consistent with the weak temperature dependence of $1/T_1$ ($\alpha T \sum_q \chi''(q,\omega_o)/\omega_o$). These two spin systems become strongly coupled below 110 K, as implied by the same temperature dependence of the two relaxation rates.

The Cu d-spins could also relax the oxygen nuclei through the transferred hyperfine interaction. The antiferromagnetic fluctuations of Cu d-spins do not couple to the oxygen nuclei because of the symmetric position of O(2,3), however. Therefore, the small q parts of the dynamical susceptibility, which will be weakly temperature dependent, may dominate the oxygen relaxation rate, giving a Korringa-like behavior. Thus the different temperature dependences of the two relaxation rates above 110 K may not rule out the possibility of a single band picture.[13]

4. CONCLUDING REMARKS

The single band and the two band pictures mentioned above also have different consequenses for the fractional spin susceptibility of the oxygen 2p-states. In the single band picture, the itinerant oxygen p-holes are tightly coupled to neighboring Cu d-spins to form local singlet states.[13] In this case, the observed oxygen 2p spin density must be entirely due to the covalency effect. We would then expect the same (30 %) fractional spin density in the oxygen deficient insulating materials. On the other hand, the oxygen p-holes and Cu d-spins contribute independently to the spin susceptibility in the two-band picture. In this case, the fraction of oxygen 2p spin susceptibility is expected to be much smaller in the insulating systems. This would provide a crucial check whether the single- or two-band description is appropriate.

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