Cu and O NMR studies of the magnetic properties of $YBa_2Cu_3O_{6.63}$ ($T_c = 62$ K)

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The microscopic magnetic properties of the CuO_2 planes in $YBa_2Cu_3O_{6.63}$ ($T_c = 62$ K) have been investigated in Cu and O NMR experiments. Unlike the fully oxygenated Y-Ba-Cu-O_7 ($T_c \simeq 90$ K), the various components of the Cu and O Knight-shift tensors show strong but identical temperature dependences in the normal state. This supports the picture that there is only one spin component in the CuO_2 planes. The spin susceptibility deduced from Knight-shift results shows significant reduction with decreasing temperature in the normal state. The temperature dependences of the nuclear-spin-relaxation rates ($1/T_1$) are very different for the Cu and the O sites. $1/(T_1T)$ at the O sites is nearly proportional to the spin susceptibility. $1/(T_1T)$ at the Cu sites shows a broad peak around 150 K. We discuss these relaxation behaviors based on a model of the dynamical spin susceptibility proposed by Millis, Monien, and Pines.

I. INTRODUCTION

The role played by magnetism, particularly the nature of spin fluctuations, is one of the central issues of the high-T_c copper oxide superconductors. The importance of magnetism is suggested by the proximity of the superconducting phase to the antiferromagnetic insulating phase as the composition is changed. In the antiferromagnetic insulators such as La_2CuO_4 and $YBa_2Cu_3O_6$, each Cu atom in the two-dimensional (2D) CuO_2 layers has 2+ valence ($3d^9$ configuration). The ground state and the magnetic excitations of these compounds are well described by a 2D, $s = \frac{1}{2}$ Heisenberg model.[1-3] The long-range antiferromagnetic order is easily destroyed by doping a small number of additional holes into the CuO_2 planes. For sufficient doping the system becomes metallic and superconducting. Various high-energy spectroscopic data show that these doped holes mostly occupy the O $2p$ states leaving the Cu valence to be 2+.[4,5] ^{17}O and ^{89}Y Knight-shift results on $YBa_2Cu_3O_7$ strongly support the fact that doped holes go into the O $2p_\sigma$ states.[6,7]

Neutron-scattering experiments performed on $La_{2-x}Sr_xCuO_4$ (Ref. 8) and $YBa_2Cu_3O_{7-y}$ (Ref. 9) revealed that short-range antiferromagnetic correlations persist into the superconducting phase. However, an appropriate description of the magnetic correlations is still a subject of controversy. An important problem here is whether the Cu $3d$ and O $2p$ holes have distinct spin degrees of freedom and different spin dynamics[10] or whether the hybridization between these states is so strong that the system is described by a single spin component with unique dynamics. A particular model of the latter case was presented by Zhang and Rice.[11] They proposed that the spin of a doped hole forms a local singlet state with the neighboring Cu spin with such a large singlet binding energy that O $2p$ holes make no contribution to the spin susceptibility. It may also be possible that the superconducting materials are already so heavily doped that the charge-transfer gap is not clearly defined and the states near the Fermi level are properly described by the Cu d and O p hybridized band in a way similar to the heavy electron materials.[12] In this case, the magnetic properties are described also by a single-spin component.

Nuclear magnetic and quadrupole resonance (NMR and NQR) have been extensively used as microscopic probes of the magnetic properties of high-T_c compounds. The unique power of these techniques lies in their capability to distinguish behaviors at different atoms and different crystallographic sites. The most extensive resonance studies have been done in the $YBa_2Cu_3O_{7-y}$ system, particularly on the fully oxygenated ($y \simeq 0$) material, using $^{63,65}Cu$, ^{17}O, and ^{89}Y nuclei. A significant feature of this system is that one can control the concentration of doped holes and the superconducting transition temperature (T_c) by changing the oxygen content y.[13] In particular, two homogeneous phases are known so far, one with $y \simeq 0$ ($T_c \simeq 90$ K) and the other with $y = 0.3$–0.5 ($T_c \simeq 60$ K).

It has already been reported that the magnetic properties of the 60-K phase are very different from those of fully oxygenated material. The magnetic susceptibility $\chi(T)$ of the 60-K phase decreases with decreasing temperature,[14] in contrast to the T-independent Pauli-like susceptibility in the $y = 0$ material, as shown in Fig. 1. This T dependence is partly associated with the spin susceptibility of the CuO_2 plane as revealed by the ^{89}Y and ^{63}Cu Knight-shift data.[7,15,16] The ^{89}Y and ^{63}Cu nuclear relaxation rates also show quite different behaviors from the $y \simeq 0$ material.[7,17,18] Since the detailed magnetic properties depend on the sample preparation method as well as the precise value and homogeneity of the oxygen content, it is important to make various NMR measurements on a single sample. This motivation led us to perform ^{63}Cu and ^{17}O NMR experiments on a well-characterized $YBa_2Cu_3O_{6.63}$ ($y = 0.37$) sample, the results of which are presented below.

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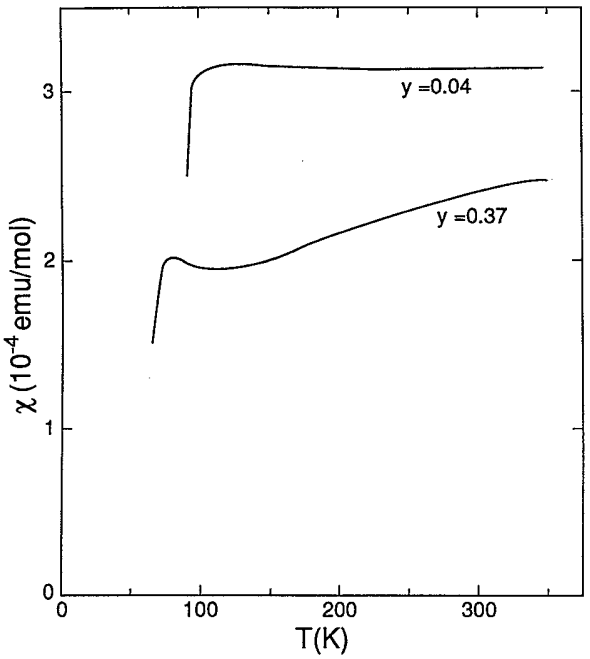

FIG. 1. Magnetic susceptibility of $YBa_2Cu_3O_{7-y}$ powder sample measured at 3 T. The $y=0.37$ sample was used in the present NMR experiments.

In Sec. II we describe the method of sample preparation and the experimental details. In Sec. III we present the NMR spectra and the Knight-shift results at the planar Cu(2) and O(2,3) sites and discuss the static magnetic properties. It is shown that the various components of the spin Knight shift at the Cu and O sites follow the same T dependence, strongly supporting the existence of a single-spin component in the CuO_2 plane. Section IV is devoted to discussions of spin dynamics based on the results of the nuclear relaxation rate $(1/T_1)$ at the planar Cu(2) and O(2,3) sites. It is shown that the results can be understood in the framework of T-dependent antiferromagnetic (AF) correlations among Cu spins, similar to the models presented to explain the data in the $y=0$ material.[19,20] A few concluding remarks are given in Sec. V.

A preliminary account of the present results is given in Ref. 21. More quantitative analysis of the relaxation data using a phenomenological model of the dynamical spin susceptibility in Ref. 19 will be given by Monien, Pines, and Takigawa.[22]

II. EXPERIMENTAL

The powder sample of $YBa_2Cu_3O_{6.63}$ used in this study was prepared as follows. A powder sample of fully oxygenated $YBa_2Cu_3O_{7-y}$ was made by the standard ceramic method. Isotopic ^{17}O was then introduced by annealing the powder in O_2 gas with 45 at. % ^{17}O at 670 °C for 25 h. The oxygen content was determined by iodometric titration to be $y=0.04$. Zr gettering was employed to reduce oxygen content as described by Cava *et al.*[13] A proper amount of the fully oxygenated powder and Zr foil were sealed in an evacuated quartz tube and annealed at 490 °C for 50 h followed by slow cooling to room temperature in 100 h. Such low-temperature annealing and slow cooling seem to be important to obtain good homogeneity and oxygen ordering. Both the titration analysis and the weight change of the Zr foil gave the same value of the oxygen content $y=0.37\pm0.02$.

Magnetization measurements on the $y=0.37$ sample at 10 Oe show the onset of a superconducting transition at 62 K, with a transition width of 5 K determined from the midpoint of the M-T curve. The Meissner fraction was about 40% of the shielding fraction, the latter being about 70% of that of the $y\simeq0$ material.

For NMR measurements, magnetic alignment was employed to obtain a high degree of c-axis orientation, and the sample was fixed in epoxy as described in Ref. 23. Cu and O NMR spectra were obtained by integrating the spin-echo signal with a boxcar integrator, while sweeping the applied magnetic field. Oxygen NMR spectra for the magnetic field along the c axis were obtained also from the Fourier transform of the spin-echo signal, since the resonance line was sufficiently narrow. Nuclear spin-lattice relaxation rates $(1/T_1)$ were measured by recording the spin-echo intensity at varying times following a single 90° saturating rf pulse. Magnetization measurements on the aligned sample at high magnetic field up to 50 kOe along the c axis show that T_c decreases at a rate $dT_c/dH=0.07\pm0.03$ K/kOe. This rate will be smaller for $\mathbf{H}\perp\mathbf{c}$. Therefore, at the typical field used in the NMR measurements (60–70 kOe), T_c is expected to be reduced only by 5 K or less from the zero-field value.

III. NMR SPECTRA AND KNIGHT SHIFT

A. Cu results

Figure 2(a) shows the ^{63}Cu NMR spectrum of the quadrupole split central transition $(-\frac{1}{2}\leftrightarrow\frac{1}{2})$ lines with the magnetic field along the c axis ($\mathbf{H}\|\mathbf{c}$). In addition to the relatively sharp planar Cu(2) resonance line, a broad line at lower field and a sharp line at higher field are observed. The position of the broad line is close to that for the chain Cu(1) site in the $y=0$ material. Therefore, this line is assigned to the Cu(1) sites that have four oxygen neighbors, two at the bridging O(4) sites and two at the chain O(1) sites [$Cu(1)_4$]. The sharp line shows a small magnetic shift and is easily saturated by fast repetition (20 msec). This signal is assigned to those Cu(1) sites that do not have O(1) nearest neighbors [$Cu(1)_2$], in accordance with previous work.[24] The shift of the Cu(2) resonance field was proportional to the resonance frequency, indicating a vanishing quadrupole shift and hence an axially symmetric electric field gradient (EFG) around the c axis at the Cu(2) site.[23]

The ^{63}Cu NMR spectrum of the high-field quadrupole satellite ($\frac{1}{2}\leftrightarrow\frac{3}{2}$ transition) for the Cu(2) and $Cu(1)_2$ sites is shown in Fig. 2(b). The Cu(2) spectrum shows a central peak and shoulders on both sides, indicating a certain distribution of EFG's. For the ideal superstructure with complete oxygen ordering in the alternative sequence of filled and empty chains, one would expect only two inequivalent Cu(2) sites. We have prepared a few samples

with varying oxygen content and indeed found that the Cu(2) satellite shows a double-peak structure when the oxygen content becomes closer to 6.5. The spectrum in Fig. 2(b) implies that the oxygen ordering in the present $y=0.37$ sample is somewhat different from the ideal structure. This is inferred also from the oxygen content. Nevertheless, the magnetic properties of the CuO_2 plane appear to be quite homogeneous as we discuss below, based on the O NMR spectra.

The Cu(2) central line NMR spectrum for $\mathbf{H}\perp\mathbf{c}$ is shown in Fig. 2(c). This line shape is well accounted for by the second-order effects of the distribution of EFG's, which appear in the satellite spectrum, Fig. 2(b). This means that the distribution of the Knight shift is much smaller than the line width. The Cu(2) Knight shift for $\mathbf{H}\perp\mathbf{c}$ is determined from the central peak position of the spectrum after correcting for the quadrupolar shift as described in Ref. 23. In this procedure, a weak T-linear variation of the quadrupole coupling ν_Q [defined as the largest component of $\nu_\alpha=(1/2h)|eQ|(\partial^2V/\partial\alpha^2)$, where Q is the nuclear quadrupole moment and $\partial^2V/\partial\alpha^2$ is the α component of EFG] determined from the position of the satellite spectrum (29.13±0.04 MHz at 50 K and 28.89±0.04 MHz at 250 K) was taken into account.

The T dependences of the Cu(2) Knight shift (denoted as ^{63}K) for $\mathbf{H}\|\mathbf{c}$ (K_c) and $\mathbf{H}\perp\mathbf{c}$ (K_{ab}) are shown in Fig. 3 together with the results for the $y\simeq0$ material (solid line) reported by Barrett *et al.*[25] No correction was made for the local field produced by diamagnetic shielding currents below T_c in the data for $y=0.37$. A large difference can immediately be seen in the behavior of K_{ab} for the $y\simeq0$ and $y=0.37$ materials. In the $y\simeq0$ material, K_{ab} is T independent in the normal state and rapidly decreases below T_c, while in the $y=0.37$ material, K_{ab} depends strongly on temperature in the normal state and the overall change below T_c is relatively small. On the other hand, K_c is T independent and takes almost the same value for the two materials. These results largely agree with the previous measurements of the Cu(2) Knight shift results in the $y=0.52$ material by Shimizu *et al.*[16] and in the $y=0.36$ material by Walstedt *et al.*[15]

Quite generally the observed Knight shift is the sum of the spin and orbital parts,

$$K_\alpha=K_{\alpha,\mathrm{spin}}+K_{\alpha,\mathrm{orb}}\ , \tag{1}$$

where K_{orb} is proportional to the Van Vleck orbital susceptibility and is generally T independent. The results in the $y=0$ material were analyzed assuming that $K_{\mathrm{spin}}=0$ at $T=0$.[23,25] The magnitude and the anisotropy of K_{spin} in the normal state were explained by two types of hyperfine coupling,[26]

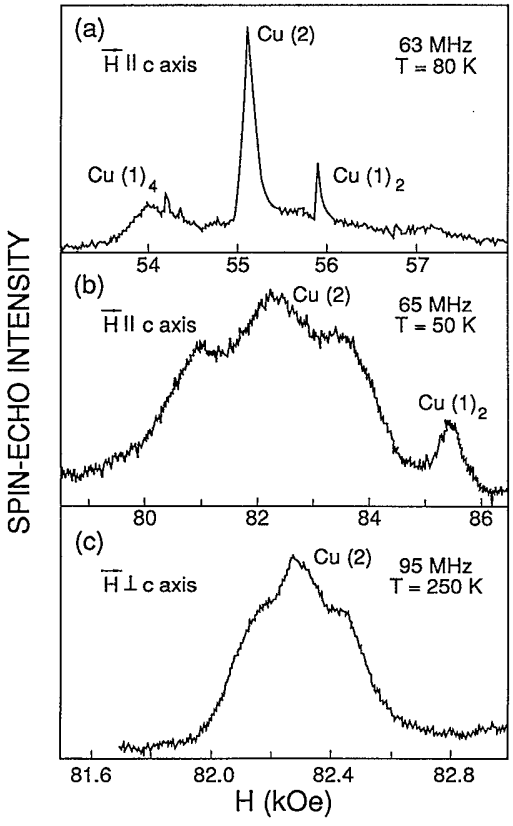

FIG. 2. ^{63}Cu NMR spectra of the center (a) and (c) the quadrupole satellite (b) lines. The planar Cu site is denoted as Cu(2). $Cu(1)_4$ [$Cu(1)_2$] denotes the chain Cu sites that have two (no) oxygen nearest neighbors along the chain.

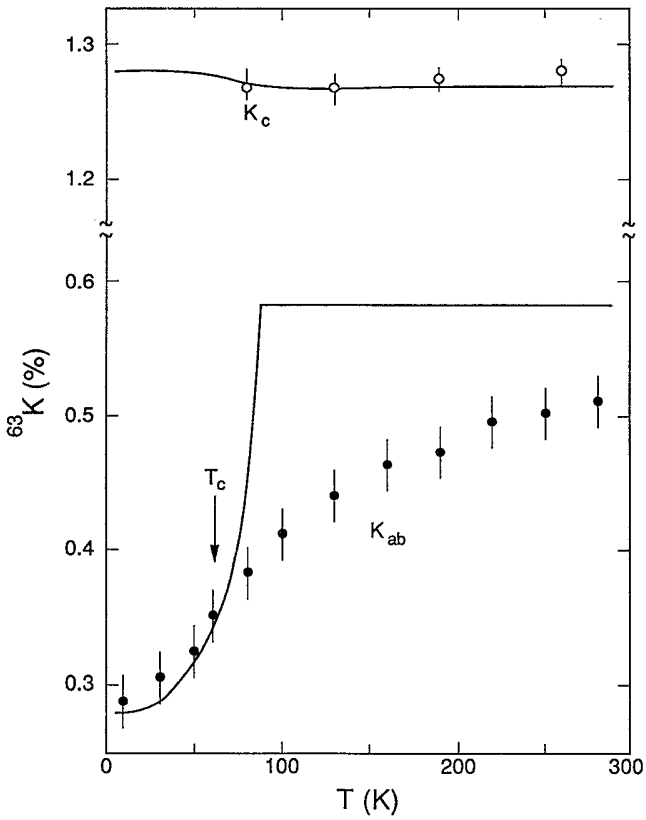

FIG. 3. Temperature dependence of the Cu(2) Knight shift (^{63}K) for $H\|\mathbf{c}$ (K_c) and $\mathbf{H}\perp\mathbf{c}$ (K_{ab}) together with the results in the $y\simeq0$ material reported by Barrett *et al.* (Ref. 25) (solid line). The arrow indicates the value of T_c at 10 Oe.

$$K_{\alpha,\text{spin}}=(A_\alpha+4B)\chi_d \quad (\alpha=c \text{ or } ab)\,, \tag{2}$$

where the first and the second term represent the hyperfine coupling to the on-site and the nearest-neighbor Cu $3d$ spin, respectively, and χ_d is the partial spin susceptibility associated with the Cu $3d$ states. A T-independent K_c below T_c in the $y\simeq 0$ material indicates that $K_{c,\text{spin}}=0$ and the cancellation of two terms: $A_c+4B=0$. The almost identical value of K_c for the $y\simeq 0$ and $y=0.37$ material means that this cancellation holds in the $y=0.37$ material as well.

It has been proposed that there is also a hyperfine coupling to the second spin component (O p hole spin):[25,27]

$$K_{\alpha,\text{spin}}=(A_\alpha+4B)\chi_d+B_h\chi_h\,. \tag{3}$$

The fact that $K_{c,\text{spin}}$ is equal to zero independent of T and y, however, indicates that χ_h, if it exists, has the same T and y dependence as χ_d. We will see more direct evidence for this in the oxygen Knight shift. The transferred hyperfine interaction, $4B\chi_d$ and $B_h\chi_h$ terms, are mainly due to the polarization of Cu $4s$ states slightly hybridized with neighboring O p states and will be isotropic. Therefore, the spin part of the anisotropic Knight shift K_c-K_{ab} is exclusively coupled to the Cu d spin even if the second spin component exists. Since $K_{c,\text{spin}}=0$, $K_{ab,\text{spin}}$ will be proportional to χ_d.

B. Oxygen results

The ^{17}O NMR spectra at 160 K are shown in Fig. 4 for **H**$\parallel$c and in Fig. 5 for **H**$\perp$c. These spectra are very similar to those observed in the $y\simeq 0$ material.[6] For **H**$\parallel$c two distinct central transition lines corresponding to the plane O(2,3) and bridging O(4) sites are identified [Fig. 4(a)]. The line width of the O(2,3) central transition is about the same as or even smaller than that in the $y\simeq 0$ material, indicating good microscopic homogeneity of the spin susceptibility in the CuO_2 plane in spite of a certain structural disorder that appears in the ^{63}Cu satellite spectrum. The line width of the first quadrupole satellite for the O(2,3) sites shown in Figs. 4(b) and 4(c) is only slightly larger than that in the $y\simeq 0$ material. The Knight shift at the O(2,3) sites for **H**$\parallel$c was determined from the Fourier transformed spectra of the spin-echo signal at a fixed magnetic field (73 kOe) with varying temperature.

The O(2,3) Knight shift in the a or b direction was determined from the position of the singularities in the first quadrupole satellite spectra for **H**$\perp$c shown in Figs. 5(b) and 5(c). These spectra show a two-dimensional powder pattern, since the resonance field depends on the direction of the external field in the ab plane. Following the same analysis as has been used for the $y\simeq 0$ material,[6] the singularities originating from the O(2,3) sites are assigned as shown in the figure, where $\theta=0°$ ($\theta=90°$) corresponds to the field direction parallel (perpendicular) to

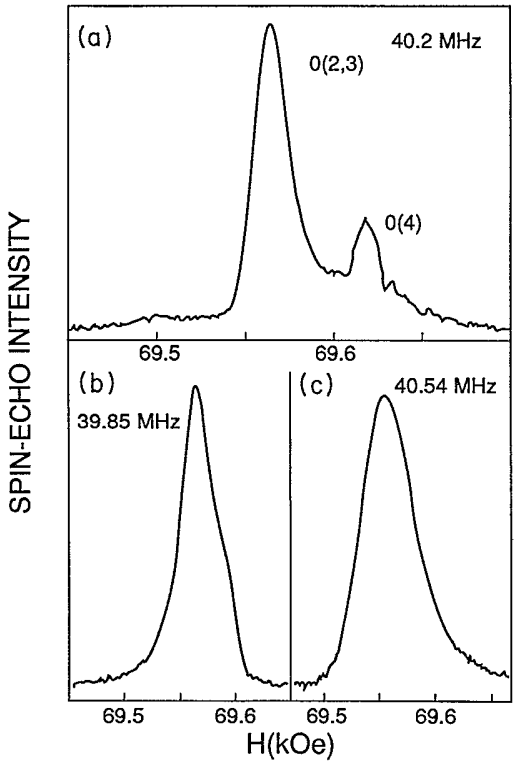

FIG. 4. ^{17}O NMR spectra of the center lines from the O(2,3) and the O(4) sites (a) and the first high-field (b) and low-field (c) satellite lines from the O(2,3) sites obtained at 160 K with **H**$\parallel$c.

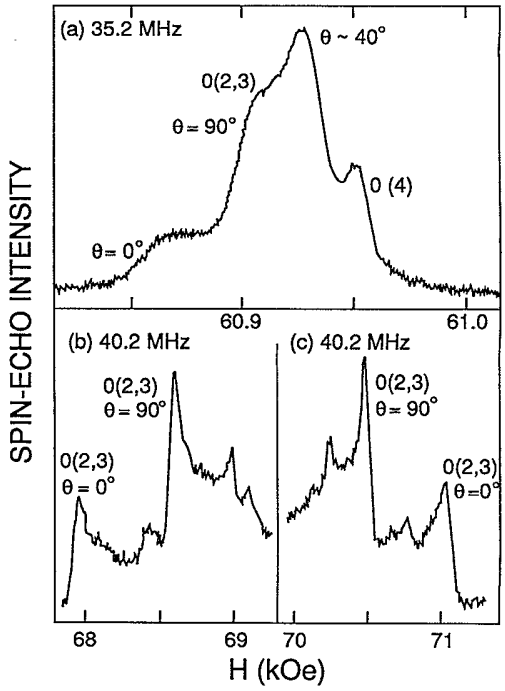

FIG. 5. ^{17}O NMR spectra of the center lines (a) and the first low-field (b) and high-field (c) satellite from the O(2,3) and O(4) sites obtained at 160 K with **H**$\perp$c. The O(2,3) center line spectrum (a) shows three singularities corresponding to different values of the angle between external field and the Cu—O bond axis (θ). The O(2,3) satellite spectra (b) and (c) show singularities at $\theta=0°$ and 90°.

the Cu—O bond axis, which is the a (b) axis for the O(2) [O(3)] sites. The Knight shift can also be determined from the central line spectrum shown in Fig. 5(a). It is easily seen that the resonance field for the central transition in the presence of both the second-order quadrupolar shift and the anisotropic Knight shift takes three extreme values when the external field is rotated in the ab plane. Accordingly, the spectrum shows three singularities as identified in the figure. The principal values of the Knight shift deduced from the central line spectra agree quite well with those determined from the satellite spectra above 80 K. At lower temperatures two principal values of the Knight shift cannot be determined separately from the central line spectra because the singularities for $\theta=0°$ and $\theta=90°$ are not well resolved.

The T dependences of the three principal values of the Knight shift tensor at the O(2,3) sites (denoted as ^{17}K) are shown in Fig. 6. $K_{\parallel}(K_{\perp})$ represents the components along (perpendicular to) the Cu—O bond axis. The O(2) and the O(3) sites are not distinguished in any of the NMR spectra, indicating that the EFT and K tensors are almost identical for these sites except for the interchange of the a and b axes. In deducing the Knight-shift values, a correction has been made of the first- and second-order quadrupolar effects. The values of EFG components $[(\nu_{\parallel},\nu_{\perp},\nu_c)=(0.905,\ -0.557,\ -0.347)$ MHz at 160 K] are only slightly different from those in the $y\simeq 0$ material and T independent within 2% in the measured range.

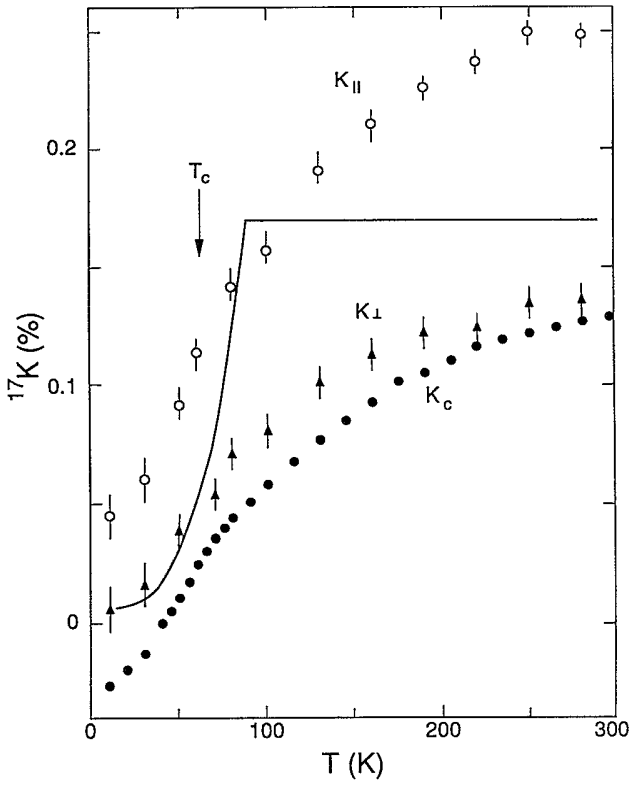

FIG. 6. Temperature dependences of the principal components of the Knight shift at the O(2,3) sites (^{17}K). $K_{\parallel}$ ($K_{\perp}$) represents the component along (perpendicular to) the Cu—O bond axis. The solid line is the data of $K_{\perp}$ in the $y\simeq 0$ material (taken from Ref. 28).

All components of the O(2,3) Knight shift decrease with decreasing temperature in the normal state in a way similar to that observed for K_{ab} at the Cu(2) sites, but different from the results in the $y\simeq 0$ material.[6,28,29] The central line O(2,3) spectra at several different temperatures are shown in Fig. 7. It should be emphasized that the temperature variation of the resonance field is much larger than the line width in each spectrum. This fact provides strong evidence that the observed T dependence of the Knight shift is an intrinsic property of a fairly homogeneous system and not much affected by disorder.

C. Discussion

The hyperfine interaction at the ligand nuclei has been extensively studied in various magnetic materials.[30] The hyperfine interaction at the O(2,3) sites in the $y\simeq 0$ material was discussed in Refs. 6 and 29. The spin Knight shift at the oxygen sites is mainly due to the spin density on the $2p$ and $2s$ states. The hyperfine field from the $2p$ states is mainly the spin dipolar field, which is purely anisotropic, i.e., whose orientational average is zero. On the other hand, the hyperfine field from the $2s$ states is the isotropic contact field. Therefore, if we define the axial Knight shift as

$$^{17}K_{\rm ax}=(K_{\parallel}-K_{\perp})/3\ , \tag{4}$$

the spin part of $^{17}K_{\rm ax}$ couples exclusively to the $2p$ states,[17] $^{17}K_{\rm ax,spin}=A_p\chi_p$, where A_p is the dipolar coupling constant for the $2p$ states and χ_p is the partial spin sus-

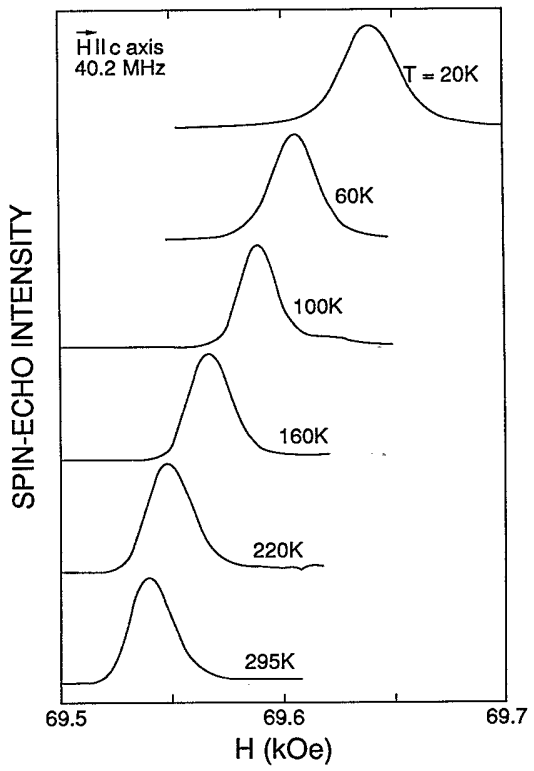

FIG. 7. ^{17}O NMR spectra of the O(2,3) center line with H∥c at several different temperatures.

ceptibility associated with the $2p$ states. Similarly the spin part of the isotropic Knight shift,

$$^{17}K_{\rm iso}=(K_{\parallel}+K_{\perp}+K_c)/3 \ , \tag{5}$$

is coupled mainly to the $2s$ states. Since the energy level of the $2s$ states is far from the Fermi level in this system, the spin density on the $2s$ states is produced only by the hybridization with neighboring Cu $3d$ states and/or O $2p$ states. The spin part of $^{17}K_{\rm ax}$ is positive in both $y\simeq 0$ and $y=0.37$ material. This indicates that the spin density at the O(2,3) sites resides on the $2p_\sigma$ orbital extending along the Cu—O bond axis.[6]

Since the spin part of $^{63}K_{ab}$ is exclusively coupled to χ_d, a comparison of the T dependence of the various Cu and O Knight-shift components will give direct information about the difference or similarity in the behaviors of χ_d and χ_p and an important clue to the problem of whether the single-spin or two-spin component model is appropriate.

Our major finding is that all components of the Cu and O Knight shifts show the same T dependence. More precisely, the following relations hold among $^{17}K_{\rm ax}$, $^{17}K_{\rm iso}$, $^{63}K_{ab}$ [K_{ab} at the Cu(2) sites] and $^{17}K_c$ for $T>60$ K (normal state):

$$\begin{aligned} ^{17}K_{\rm ax}(T)&=0.1886\ ^{17}K_c(T)+0.151\% \ , \\ ^{17}K_{\rm iso}(T)&=1.057\ ^{17}K_c(T)+0.039\% \ , \\ ^{63}K_{ab}(T)&=1.522\ ^{17}K_c(T)+0.32\% \ . \end{aligned} \tag{6}$$

These relations are demonstrated in Fig. 8, where these components are plotted with different scales and origins for the vertical axes. In this plot all the data in the normal state lie on a single curve. Systematic deviations from these relations are seen below 60 K, which is presumably due to the local field produced by diamagnetic supercurrents.

This plot strongly supports the view that the spin part of each component has the same T dependence. Indeed, values of the residual Knight shift at $T=0$ obtained from this plot, as described below, agree with the orbital Knight shift in the $y\simeq 0$ material. $^{17}K_{\rm ax}(0)$ is determined by extrapolating the data to $T=0$, assuming that the spin part becomes zero at $T=0$. This is justified because $K_{\rm ax}$ is the difference of two components, both with $\mathbf{H}\perp\mathbf{c}$, and the effect of the diamagnetic current will be canceled. Thus we obtain $^{17}K_{\rm ax}(0)=0.013\pm0.002\,\%$. The residual Knight shifts of other components were estimated from Eq. (5) and the value of $^{17}K_{\rm ax}(0)$: $^{17}K_c(0)=-0.014\pm0.01\,\%$, $^{17}K_{\rm iso}(0)=0.024\pm0.011\,\%$, $^{63}K_{ab}(0)=0.30\pm0.02\,\%$. These values are virtually unchanged from the orbital Knight shift in the $y\simeq 0$ material within the experimental error ($^{17}K_{\rm ax,orb}=0.013\pm0.004\,\%$, $^{17}K_{c,\rm orb}=0.02\pm0.03\,\%$, $^{17}K_{\rm iso,orb}=0.027\pm0.011\,\%$, $^{63}K_{ab,\rm orb}=0.28\pm0.02\,\%$ in the $y\simeq 0$ material[25,6]).

The relations in Eq. (6) thus indicate that the spin part of all the Knight-shift components have a common T dependence,

$$K_i(T)=A_i\chi_{\rm spin}(T)+K_{i,\rm orb} \ . \tag{7}$$

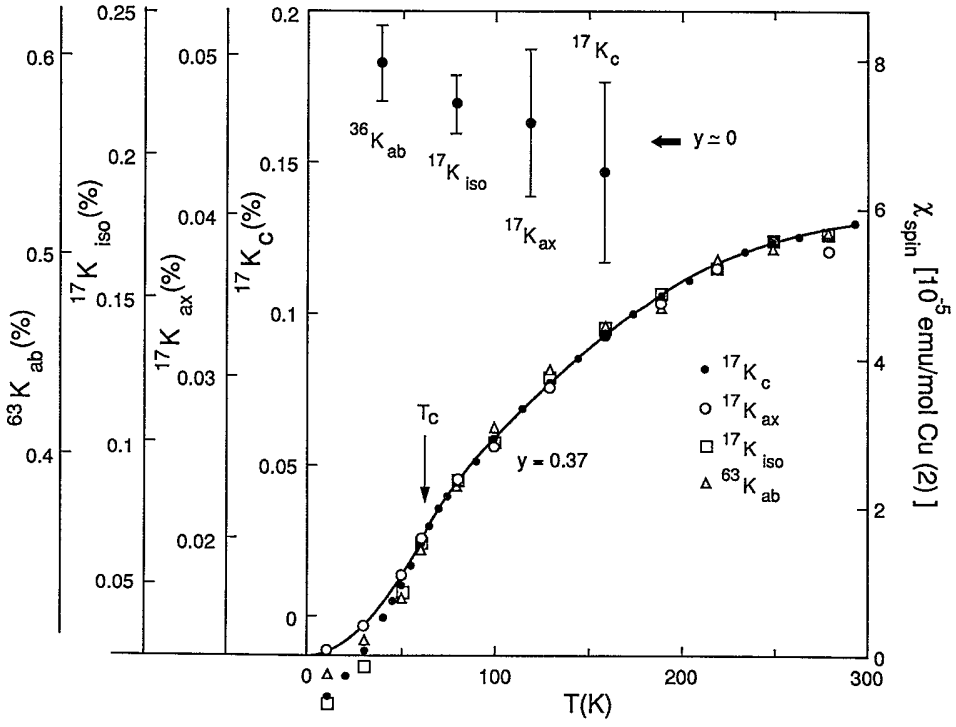

FIG. 8. Various components of the Cu and O Knight shift are plotted against temperature with different vertical scales and origins. The T-independent values of spin Knight shifts in the $y\simeq 0$ material (from Refs. 6 and 25) are also plotted with the same vertical scales.

These relations require that χ_d and χ_p have the same T dependence, supporting a single-spin component model where the spin densities on the Cu $3d$ and O $2p$ states behave as parts of a unique spin system. The various (T-independent) spin Knight-shift components in the $y \simeq 0$ material[6,25] are also plotted in Fig. 8, where all the data points are at the same vertical position within their error. This means that all the spin Knight-shift components change equally; therefore the ratio χ_d/χ_p does not change when the oxygen content is varied from $y=0.37$ to $y \simeq 0$.

These results are quite consistent with the ^{89}Y Knight-shift data by Alloul, Ohno, and Mendels[7] who observed that the ^{89}Y Knight shift has the same T and y (oxygen content) dependence as the bulk susceptibility. Since it is most likely that Y nuclei are dominantly coupled to the spin density on the O $2p$ states and the bulk susceptibility is dominated by Cu d spin, Alloul, Ohno, and Mendels have reached the same conclusion that χ_d/χ_p is independent of either temperature or oxygen content. In particular, their measurements cover a wide range of oxygen content ($0 \le y \le 0.6$). If χ_d/χ_p is strictly independent of y in the whole range extending to the insulating phase, which does not contain mobile O holes, the spin density on the oxygen sites must be entirely due to covalency effects that have been seen in typical magnetic insulators. This will then support the Zhang-Rice local singlet model[11] where the O-hole spin degrees of freedom are exhausted by the formation of a singlet and do not contribute to the susceptibility. It is therefore desirable to extend the direct Knight-shift measurements of χ_d and χ_p to the insulating phase.

The relations in Eq. (7) allow us to extract the unique T dependence of the spin susceptibility $\chi_{\rm spin}$ associated with the CuO_2 planes, as shown by the line in Fig. 8. The vertical scale for $\chi_{\rm spin}$ is estimated from Cu Knight-shift data,[22]

$$\chi_{\rm spin}=\chi_d/f_{\rm Cu}={}^{63}K_{ab,\rm spin}/f_{\rm Cu}(A_{ab}+4B)\ ,$$

where $f_{\rm Cu}$ is the fraction of the spin density on the Cu $3d$ states ($f_{\rm Cu} \simeq 0.7$).[28] The hyperfine coupling constants are estimated in Ref. 22 as $f_{\rm Cu}A_{ab}=34$ kOe/μ_B, $f_{\rm Cu}B=41$ kOe/μ_B. $\chi_{\rm spin}$ decreases strongly with decreasing temperature in a wide T range above T_c. This is in clear contrast to the Pauli-like, T-independent susceptibility in the $y \simeq 0$ material.

The anomalous T dependence of $\chi_{\rm spin}$ is quite unusual and could arise in several ways. One possibility is that the density of states decreases with decreasing temperature. Indeed, it has been suggested that strong antiferromagnetic correlations produce a pseudogap in the single-particle density of states[31] and the nuclear relaxation data suggest that AF correlations grow with decreasing temperature in this material, as we discuss below. The Fermi-liquid correction (Stoner factor) may also have a T dependence that suppresses the uniform ($q=0$) susceptibility as the AF correlations become stronger.[22,32] It may also be related to a general property of disordered quantum-spin systems. Recent studies of the quantum Heisenberg model show that short-range AF order produces a gap in the spin excitation spectrum,[33] which makes $\chi_{\rm spin}$ vanish at $T=0$.[34] Finally, short-range singlet correlations preceding the superconducting transition may also reduce $\chi_{\rm spin}$.

We would like to emphasize that a similar T dependence for $\chi_{\rm spin}$ has been observed in other high-T_c materials by means of Knight-shift measurements. For example, the planar oxygen Knight shift in $La_{1.85}Sr_{0.15}CuO_4$ (Kitaoka *et al.*[35]), the Cu Knight shifts in superoxygenated $La_2CuO_{4+\delta}$ (Hammel *et al.*[36]) and $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ (Reyes *et al.*[37]) show similar effects. The peculiar T dependence of $\chi_{\rm spin}$ thus seems to be a common feature of the "intermediate-T_c" materials. We have not tried to make a quantitative comparison between the Knight shift and the bulk susceptibility data in Fig. 1 because the latter contains a slight Curie-Weiss contribution, probably from an impurity phase, and we do not know the T dependence of the chain contribution to the susceptibility.

Recently, ^{17}O Knight-shift data in $YBa_2Cu_3O_{6.65}$ have been reported by Butaud *et al.*,[27] which are very different from our results. Particularly, they found a T-independent $^{17}K_{\rm ax}$ even though $^{17}K_{\rm iso}$ varies with temperature. This might be due to a difference in sample preparation. Indeed, their center line NMR spectra for $\mathbf{H}\perp\mathbf{c}$ do not show three well-resolved singularities as we have observed in the spectrum of Fig. 5(a).

IV. Cu AND O NUCLEAR RELAXATION RATES

The T dependence of $1/T_1T$ at the O(2,3) sites (denoted as $1/{}^{17}T_1T$) at 69 kOe with $\mathbf{H}\|\mathbf{c}$ is shown in Fig. 9. These measurements were made on the first high-field quadrupole satellite to ensure that only the signal from the O(2,3) sites was detected. These results are quite different from those reported by Butaud *et al.*[27] on $YBa_2Cu_3O_{6.65}$. Their data of $1/({}^{17}T_1T)$ show a weaker T dependence than our data above 100 K and have a hump below 100 K. In Fig. 10 we show the T dependence of $1/T_1T$ at the Cu(2) sites ($1/{}^{63}T_1T$) measured on the central transition line at 66 kOe with $\mathbf{H}\|\mathbf{c}$. Recovery of the nuclear magnetization after the saturating pulse is well fitted over two decades by the theoretical curve for a single value of $1/T_1$ above 60 K for both Cu and O. At lower temperatures the fitting becomes poor, indicating an inhomogeneous distribution of $1/T_1$. The data in Figs. 9 and 10 are obtained from reasonably good fits over 1.5 decades. The results in the $y \simeq 0$ material[38] are also shown in Figs. 9 and 10 for comparison.

The results in the $y \simeq 0$ material, particularly the different T dependence of $1/({}^{63}T_1T)$ and $1/({}^{17}T_1T)$, have been discussed by many authors in relation to possible short-range AF spin correlations in the CuO_2 planes.[19,20,38–41] Let us briefly review these arguments based on the single-spin component picture. Quite generally, $1/T_1T$ is expressed in terms of the dynamical spin susceptibility,

$$\frac{1}{T_1}=\frac{\gamma_n^2 k_B T}{2\mu_B^2}\sum_q |A_q|^2\frac{{\rm Im}\chi(q,\omega_0)}{\omega_0}\ ,$$

where

$$A_q = \sum_i A_i \exp(iqr_i) \ . \tag{8}$$

In Eq. (8), γ_n is the nuclear gyromagnetic ratio; A_i is the hyperfine coupling between the nuclear spin and the electron spin at site r_i. ω_0 is the nuclear Larmor frequency, which is much smaller than the characteristic energy of the electronic spin system. Since $\mathrm{Im}\chi(q,\omega)/\omega$ in the paramagnetic state typically has a Lorentzian frequency dependence with width Γ_q,

$$\mathrm{Im}\chi(q,\omega_0)/\omega_0 = \pi\chi(q)/\Gamma_q \ , \tag{9}$$

where $\chi(q)$ is the static wave-vector dependent susceptibility. For a Fermi-liquid without strong magnetic correlations, both $\chi(q)$ and Γ_q are only weakly q dependent and are given by the density of states ρ_0. Therefore

$$\sum_q \mathrm{Im}\chi(q,\omega_0)/\omega_0 \simeq \pi\mu_B^2\rho_0^2 \simeq \pi\chi_{\mathrm{spin}}^2/\mu_B^2 \ .$$

For noninteracting electrons and a local and isotropic hyperfine interaction (i.e., q independent and isotropic A_q), we have a universal relation between $1/(T_1T)$ and the spin Knight-shift (Korringa relation),

$$\frac{1}{T_1TK_{\mathrm{spin}}^2} = \frac{\pi h\gamma_n^2 k_B}{\mu_B^2} \equiv S \ . \tag{10}$$

If the system has short-range AF correlations, $\chi(q)$ and $1/\Gamma_q$ will have a peak at $q = Q = (\pi,\pi)$. This makes $\sum_q \mathrm{Im}\chi(q,\omega_0)/\omega_0$ much larger than $\pi\chi_{\mathrm{spin}}^2/\mu_B^2$ or equivalently, this leads to a large enhancement of $1/(T_1TK_{\mathrm{spin}}^2)$ over the Korringa value S. This is indeed observed experimentally at the Cu(2) sites.[38,42,43] These AF correlations are not seen by the oxygen nuclei because an oxygen nuclear spin is coupled to the two nearest-neighbor Cu spins, resulting in a hyperfine coupling $A_q = A[1+\exp(iq_x a)]$, which goes to zero at $q = Q$. Thus the oxygen relaxation is dominated by spin fluctuations in a broad q region around the zone center ($q = 0$) and shows a normal Korringa behavior, in agreement with experiment.[38]

Millis, Monien, and Pines have developed a phenomenological model that embodies the above picture and gives a quantitative account of the relaxation behavior at various sites in the $y \simeq 0$ material.[19] They assume the dynamical susceptibility consisting of two parts

$$\frac{\mathrm{Im}\chi(q,\omega_0)}{\omega_0} = \frac{\pi\chi(0)}{\Gamma} + \frac{\pi\chi_{\mathrm{AF}}(q)}{\Gamma_{\mathrm{AF},q}} \ , \tag{11}$$

where the first term is the Fermi-liquid-like q-independent contribution from the entire q space and the second term is the contribution from AF spin fluctuations. Based on the mean-field expression for $\chi(q,\omega)$, the second term can be expressed in terms of the AF correla-

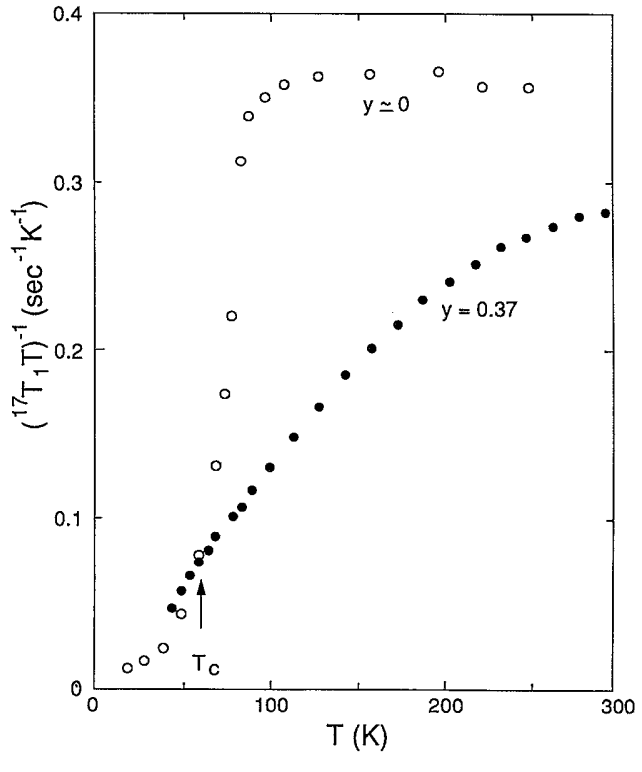

FIG. 9. Temperature dependence of $1/(T_1T)$ at the O(2,3) sites measured on the first high-field satellite with H||c at 69 kOe. The results in the $y \simeq 0$ material in Ref. 38 are also shown by open circles.

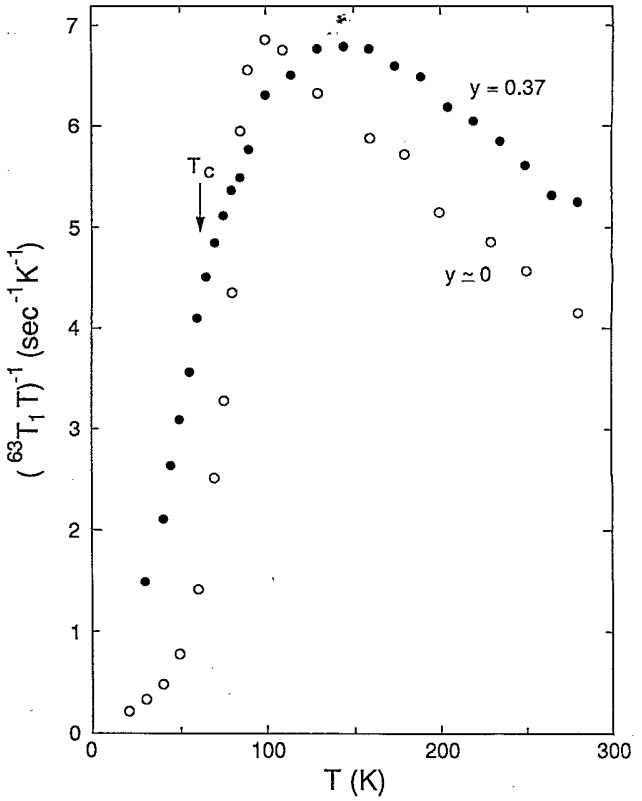

FIG. 10. Temperature dependence of $1/(T_1T)$ at the Cu(2) site measured on the central line with H||c AT 66 kOe. The results in the $y \simeq 0$ material in Ref. 38 are also shown by open circles.

tion length ξ through the following relationship:

$$\chi_{AF}(q)=\chi(0)f_q(\xi)\,,$$
$$\Gamma_{AF,q}=\Gamma/f_q(\xi)\,, \tag{12}$$
$$f_q(\xi)=\frac{(\xi/\xi_0)^2}{[1+(\mathbf{q}-\mathbf{Q})^2\xi^2]}\,.$$

Thus the AF correlation length ξ determines the width of the peak of $\chi_{AF}(q)$ and $1/\Gamma_{AF,q}$ around Q, and another parameter ξ_0 determines the height of the peak relative to $\chi(0)$. Millis, Monien, and Pines[19] have shown that this model explains the magnitude and the T dependence of the relaxation rates at the Cu, O, and Y sites in the $y\simeq 0$ material by assuming a T dependence of ξ given by

$$\xi(T)^2=\xi(0)^2T_x/(T+T_x)$$

and typical values of the parameters $\xi(0)/a=3.4$, $(a/\xi_0)^4=10$, and $T_x=120$ K, where a is the lattice constant.

We now discuss the results in the $y=0.37$ material based on a similar picture. We first look at the oxygen results. $1/(^{17}T_1T)$ shows a monotonic decrease with decreasing temperature in a wide T range in the normal state. We found that the T dependence of $1/(^{17}T_1T)$ is almost the same as that of the spin susceptibility as shown in Fig. 11:

$$1/(^{17}T_1T)\propto\chi(0)\,. \tag{13}$$

Because of the hyperfine form factor, $1/(^{17}T_1T)$ is determined by the spin fluctuations with wave vector away from Q. We therefore expect from Eq. (11),

$$\frac{1}{^{17}T_1T}\propto\sum_{q\sim 0}\frac{\mathrm{Im}\chi(q,\omega_0)}{\omega_0}\simeq\frac{\pi\chi(0)}{\Gamma}\,. \tag{14}$$

Equations (13) and (14) require that Γ is almost T independent in this material even though χ_{spin} has a strong T dependence. The similar value of $(^{17}T_1TK_{c,spin})^{-1}$ in the $y\simeq 0$ material indicates that Γ does not much depend on the hole concentration either. Γ is estimated to be about 0.5 eV in Ref. 19. This result contradicts the argument of Alloul, Ohno, and Mendels.[7] They found that $1/(T_1T)$ at the Y sites is proportional to the square of K_{spin}. Since the hyperfine coupling at the Y sites also filters out AF spin fluctuations, one would expect a behavior at the Y site similar to that at the O sites. We find, however, that this discrepancy is resolved simply by taking the ^{89}Y chemical shift ($^{89}K_0$) to be 170 ppm instead of the 300 ppm given by Alloul, Ohno, and Mendels. A more detailed analysis of the Y relaxation data in Ref. 22, which takes a weak T dependence of Γ into account, shows $^{89}K_0\sim 200$ ppm. By plotting our data of χ_{spin} (Fig. 8) against the Y Knight shift by Alloul, Ohno, and Mendels for the $y=0.37$ material (same oxygen content), we also find that $^{89}K_0\sim 200$ ppm. A similar conclusion has been reached by Walstedt *et al.*[15]

We next discuss the Cu results. The present data of $1/(^{63}T_1T)$ are in good agreement with the NQR results by Yasuoka, Imai, and Shimizu.[18] A similar NQR result was also reported by Warren *et al.*[17] A striking feature is a broad peak in $1/(^{63}T_1T)$ around 150 K. Reduction of $1/(^{63}T_1T)$ below 150 K, a temperature well above T_c,

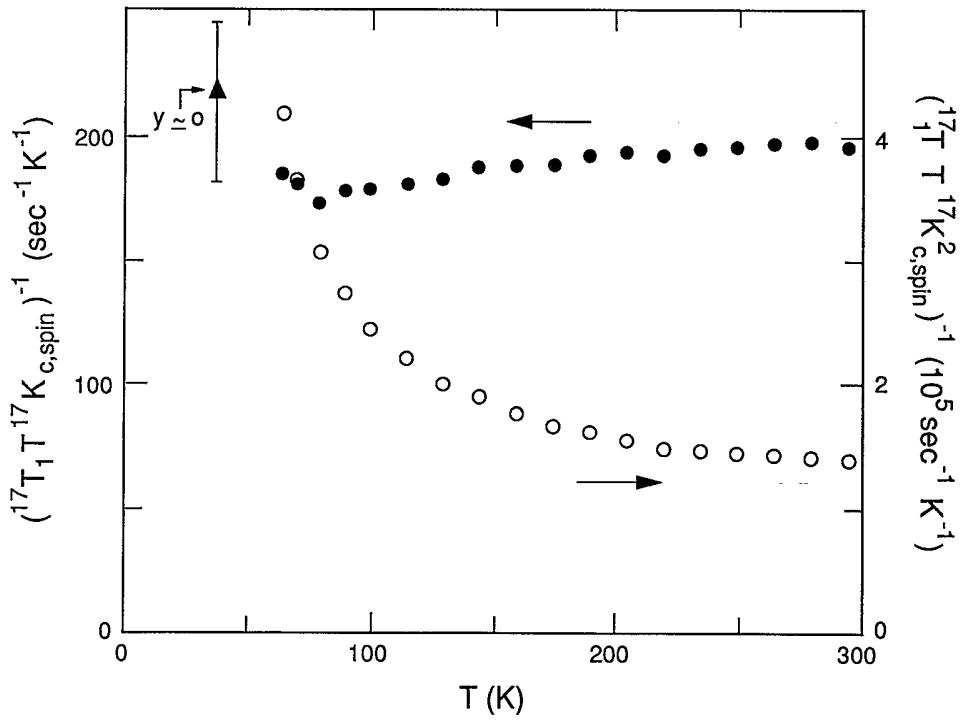

FIG. 11. $1/(T_1T)$ at the O(2,3) sites divided by $^{17}K_{c,spin}$ ($^{17}K^2_{c,spin}$) is plotted against temperature by solid dots (open circles). The (T-independent) value of $1/(T_1T^{17}K_{c,spin})$ in the $y\simeq 0$ material is also shown.

is a novel feature not seen in the $y \simeq 0$ material. Warren *et al.*[17] discussed this as possible evidence for a superconducting precursor effect. Yasuoka, Imai, and Shimizu[18] suggested a gap opening in the spin excitation spectrum at this temperature. Although we do not have a definite explanation for this behavior, we would like to show that this result can be understood based on a model of AF correlations similar to that proposed to explain results in $y \simeq 0$ material.

In the presence of the strong AF correlations, $1/(^{63}T_1T)$ is dominated by spin fluctuations near $Q=(\pi,\pi)$. We take the same form of $\mathrm{Im}\chi(q,\omega_0)$ as Eqs. (11) and (12). We should emphasize that by this we have assumed the following two points: (1) Both the static susceptibility $\chi(q)$ and the inverse energy width $1/\Gamma_q$ can be factorized into the product of an unenhanced part and the AF enhancement factor $f_q(\xi)$, and (2) the unenhanced static susceptibility near Q has the same T dependence as the uniform ($q=0$) spin susceptibility $\chi(0)$. The second assumption is not trivial. However, this may be justified to some extent by the good proportionality between χ_{spin} and $1/(^{17}T_1T)$ (Fig. 11). Since the latter has contributions from rather broad q space, we may conclude that the T dependence of χ_{spin} is not restricted to $q=0$. We then obtain the following expressions for the Cu relaxation rate,

$$\frac{1}{^{63}T_1T} \propto \frac{\chi(0)}{\Gamma}\langle 1+[f_q(\xi)]^2\rangle \ , \tag{15}$$

where $\langle\ \rangle$ means the average over the q space including the region near Q. By comparing Eqs. (14) and (15) we obtain

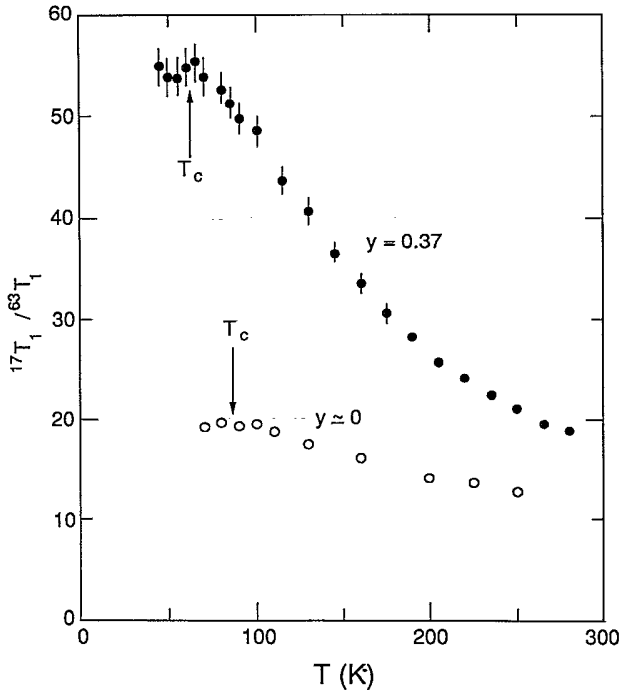

FIG. 12. The ratio of $1/^{63}T_1$ to $1/^{17}T_1$ is plotted against temperature (solid dots). The results in the $y \simeq 0$ material (from Ref. 38) are also shown by open circles.

$$^{17}T_1/^{63}T_1 \propto \langle 1+[f_q(\xi)]^2\rangle \ ,$$

with a proportionality constant determined by the gyromagnetic ratio and the hyperfine coupling of the Cu and the O nuclear spins. For large ξ the leading term of $\langle [f_q(\xi)]^2\rangle$ is ξ^2.[19] Therefore, this ratio of two relaxation rates $^{17}T_1/^{63}T_1$ gives a good measure of the AF correlations.

This ratio is plotted in Fig. 12 as a function of temperature together with the result for the $y \simeq 0$ material. $^{17}T_1/^{63}T_1$ in the $y=0.37$ material is much larger than that in the $y \simeq 0$ material, indicating stronger AF correlations in the $y=0,37$ material. This is reasonable, since the more oxygen defficient system is closer to the AF phase. The ratio $^{17}T_1/^{63}T_1$ in $y=0.37$ material increases smoothly with decreasing temperature, and no anomaly is seen around 150 K, where $1/(^{63}T_1T)$ has a peak. This T dependence of $^{17}T_1/^{63}T_1$ is understood quite naturally as resulting from the growth of AF correlations with decreasing temperature. This suggests a possibility that the peak in $1/(^{63}T_1T)$ is a combined effect of the T dependence of χ_{spin} and the development of AF correlations and may not require a spin gap opening around 150 K. It is interesting to see that $^{17}T_1/^{63}T_1$ saturates at a temperature slightly above T_c, around 110 K for $y \simeq 0$ and 70 K for $y=0.37$, indicating that AF correlations cease to grow before the system becomes superconducting.

V. CONCLUDING REMARKS

The Cu and O Knight shifts in the $y=0.37$ material ($T_c=60$-K phase) show a strong T dependence in contrast to the observation in the $y \simeq 0$ material ($T_c=90$-K phase). The T dependence of the various spin Knight-shift components are found to be identical, strongly supporting the view that there is only one spin component in a unit cell of the CuO_2 planes. This spin degree of freedom could be associated either with the strongly hybridized Cu-O antibonding band, as appeared in the band calculation, or with the Cu d spin as a consequence of the Zhang-Rice singlet formation. Further experiments will be necessary to distinguish these situations.

The spin susceptibility deduced from the Knight shift decreases with decreasing temperature, and its value at T_c is only about 30% of the value at 300 K. Although we do not have a microscopic explanation for this behavior, this appears to be a rather common feature for many high-T_c oxides.

The nuclear relaxation rates at the Cu and O sites in the $y=0.37$ material also show behaviors that contrast sharply with the $y \simeq 0$ material. The T dependence of the oxygen relaxation rate indicates that the energy scale of spin fluctuations Γ_q away from $Q=(\pi,\pi)$ is nearly independent of temperature and oxygen content. The Cu relaxation results are understood based on a picture of short-range AF correlations, provided that the unenhanced susceptibility has the same T dependence everywhere in q space. Therefore, the difference between the $y \simeq 0$ and the $y=0.37$ materials may be attributed to the increased AF correlation length and the T dependence of the spin susceptibility.

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