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^{63}Cu NMR shift and linewidth anomalies in the $T_c = 60$ K phase of Y-Ba-Cu-O

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^{63}Cu NMR shifts and spectra are presented for both Cu(1) and Cu(2) sites in a specimen of $YBa_2Cu_3O_{6.64}$ ($T_c \sim 60$ K). For **H** along the c axis, the Cu(2) shift is not distinguishable from that reported for $YBa_2Cu_3O_{7.0}$. For **H** in the a-b plane, the spin component of Cu(2) shift declines sharply as $T \to T_c$. The Cu(1) shift behaves similarly, showing also a dramatic broadening at low temperatures in clearly nonmetallic behavior. Combined with anomalous T_1 data reported earlier for the 60-K phase of $YBa_2Cu_3O_{6+x}$, these results are shown to be consistent with strong and monotonically increasing antiferromagnetic correlations as T is decreased.

The superconducting compounds $YBa_2Cu_3O_{6+x}$ divide roughly into a $T_c \sim 60$ K phase for $x = 0.5$–0.7 and the $T_c \sim 90$ K phase for x near 1.0.[1] Recent studies have revealed marked differences in the static and dynamic magnetic behavior of these major phases. For the 90-K phase the uniform susceptibility $\chi(T)$ is nearly temperature independent, whereas $\chi(T)$ for the 60-K material exhibits a decline at low temperatures that becomes progressively steeper as oxygen is removed.[2,3] Probed by means of the ^{89}Y NMR shift and relaxation process, this behavior for $\chi(T)$ appears consistent with a temperature-varying metallic density of states.[3,4] On the other hand, studies of the nuclear spin-lattice relaxation time (T_1) at Cu(2) sites[5–7] in 60-K-phase samples have revealed a more complex and anomalous temperature dependence than found for the ^{89}Y. One finds a broad maximum in $(T_1T)^{-1}$ near 150 K, descending sharply at lower T with only a rather minor feature at T_c. Both the susceptibility and nuclear relaxation results are suggestive of precursive superconducting pair formation at $T > T_c$.[5]

We report in this paper results from a study of Cu(1)- and Cu(2)-site NMR shifts in 60-K-phase samples for 10 K $\le T \le$ 300 K; we also discuss normal-state susceptibility data for one of the samples used. Our results confirm an earlier report of a strongly temperature-varying spin-paramagnetic NMR shift in the normal state with an anomalously small variation below T_c,[7] and reveal unexpected broadening of Cu(1) NMR lines setting in below 200 K. Previous studies[8] showed that chain segments from which oxygen has been removed are electronically and magnetically inert. The present work indicates that even filled chain segments in the 60-K phase deviate from normal-metallic behavior.

Specimens of composition (a) $YBa_2Cu_3O_{6.70}$ and (b) $YBa_2Cu_3O_{6.64}$, produced using the gettered annealing method,[9] were employed for shift and susceptibility measurements. Both have T_c's in the vicinity of 60 K and have been the subject of previous nuclear-resonance studies.[5,7,8] For the NMR work the sample materials were magnetically oriented and fixed in clear epoxy, giving a high degree of crystallite c-axis uniformity.

The full NMR spectrum for Cu(1) and Cu(2) sites in sample (b) is shown in Fig. 1 for **H** along the c axis at a series of temperatures in the range 20 K $\le T \le$ 293 K. For this orientation, the Cu(1) line undergoes a second-order quadrupolar shift to lower fields. Although the Cu(1) nuclear-quadrupole-resonance (NQR) lines in this specimen are fairly sharp,[7] the corresponding NMR line has the appearance of an edge with a smear of intensity toward lower quadrupole couplings. Assuming the edge to correspond to the 22.6-MHz NQR peak, we calculate the quadrupolar shift to be[10] $K_q = 1.76\%$. The room-temperature magnetic shift value at the edge is thus $K_{1\mathrm{edge}} = 0.53\%$, and is only slightly smaller than the Cu(1)-site shift $K_{1c} = 0.58\%$ reported for $YBa_2Cu_3O_{7.0}$.[11] If we adopt the orbital shift value reported for the latter case[11] $K_{1c}^{\mathrm{orb}} = 0.25\%$, we find $K_{1c}^{s} = 0.28\%$ for the spin part. As the temperature is lowered, K_{1c}^{s} diminishes, at first by slight motion of the edge, then below 200 K by smearing of the line to higher field. By $T = 20$ K the Cu(1) line extends through the larger Cu(2) peak and may be as much as 1 kG wide. An accurate determination of its shift is not feasible, but the spin part (see Fig. 1) appears to have completely disappeared. This behavior obviously reflects disorder, but is clearly not that of a disordered metal, where the NMR linewidth would scale with the corresponding (diminishing) susceptibility. The broad line at low temperature evidently reflects the variety of magnetic ground states that various finite segments of the "filled" Cu(1) chain[8] can occupy.

The Cu(2) shifts are plotted versus temperature in Fig. 2. For **H** along the c axis, the shift K_{2c} is seen to be temperature independent in the normal state, with only a barely perceptible rise below T_c. This behavior, including the magnitude of the shift, is essentially indistinguishable from that of $YBa_2Cu_3O_{7.0}$.[11,12] From this we draw two important conclusions. First, the orbital shift (K_{2c}, $T \to 0$) is independent of oxygen composition in the metallic phase, implying that the Cu(2) ionic state and crystal-field splittings are also invariant. Second, the cancellation between local and transferred spin components of NMR shift at the Cu(2) site observed for the 90-K phase[12] carries over to the 60-K phase as well. This indicates that *the* Cu(2) *spin hyperfine coefficients are unchanged from those of the 90-K phase*, an observation which we use as a premise in interpreting these shift data below.

On the other hand, the Cu(2) a-b-plane shift data in

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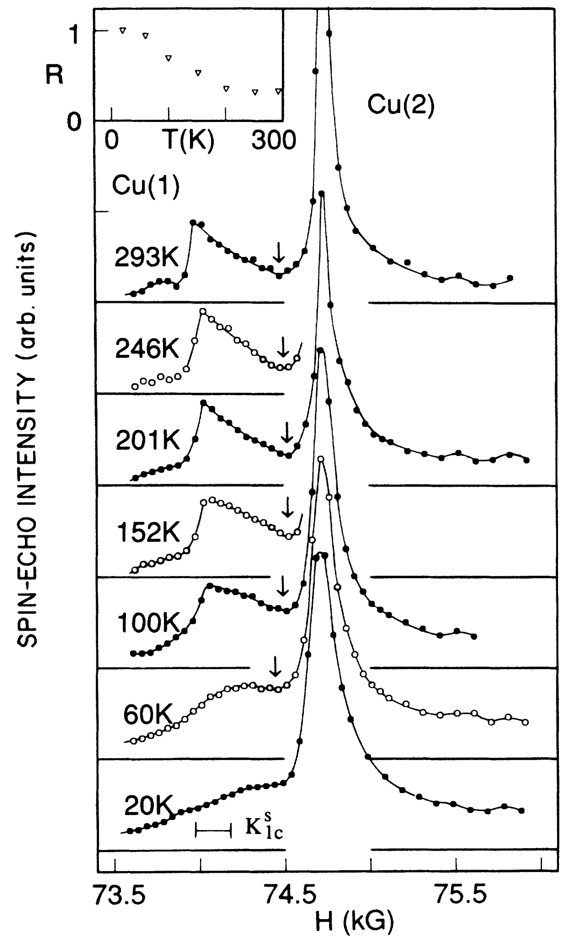

FIG. 1. ^{63}Cu nuclear spin-echo spectra ($\nu = 85.4$ MHz), taken with **H** along the c axis, for a sample of $YBa_2Cu_3O_{6.64}$ over the temperature range 20 K $\leq T \leq$ 293 K as shown. The ratio R of intensity at the position of the minimum between the peaks (arrows) to the Cu(1) peak amplitude is plotted in the inset to show the onset of broadening below 200 K.

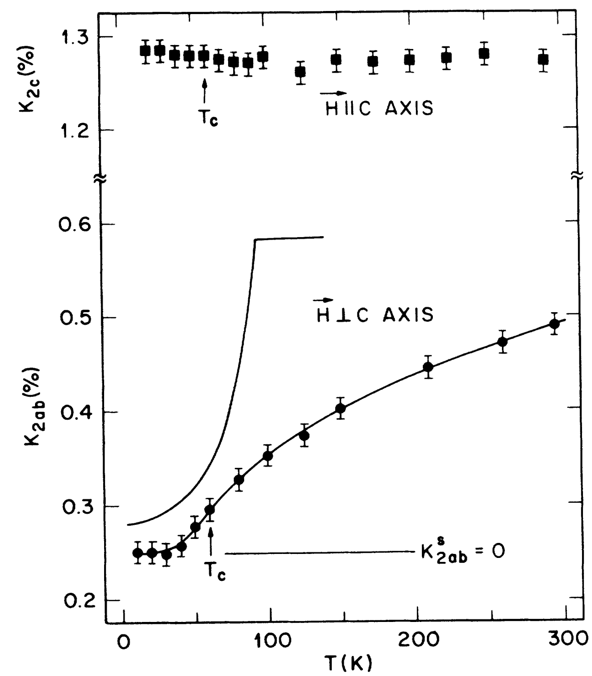

FIG. 2. Measured ^{63}Cu NMR shift values at the Cu(2) site are plotted vs temperature for **H** along the c axis (K_{2c}) and in the a-b plane ($K_{2a\text{-}b}$). The zero of spin-paramagnetic shift $K_{2a\text{-}b}$, i.e., the limiting $T \rightarrow 0$ value, is taken to be the orbital shift $K^{\text{orb}}_{2a\text{-}b} = 0.25\%$. These data have been corrected for temperature variation of the NQR frequency. The solid line shows Cu(2) shift vs T curve for 90-K material (Ref. 11).

Fig. 2 form a striking contrast with the corresponding $YBa_2Cu_3O_{7.0}$ data,[11] shown as a solid line. The present data were obtained by tracking the position of the main NMR peak [$\nu_{NQR} = 27.5$ MHz (Ref. 7)] as a function of temperature. After subtraction of the (temperature-dependent) second-order quadrupolar shift in a similar fashion to the Cu(1) case,[10] we obtain the magnetic shift $K_{2a\text{-}b}$ shown as circles in Fig. 2. A similar, but less accurate result is obtained by measuring the center of gravity of the NMR spectra.

The zero-temperature intercept of the $K_{2a\text{-}b}$ data, interpreted as the orbital shift, gives $K^{\text{orb}}_{2a\text{-}b} = 0.25\%$, only slightly smaller than the $YBa_2Cu_3O_{7.0}$ value shown by the solid line. We assume here, as have previous authors,[11–13] that *the spin components of the shift and susceptibility vanish as* $T \rightarrow 0$. We emphasize this point, because it leads to the unexpected conclusion that the planar spin susceptibility $\chi^{s}_{2}(T) \propto K_{2a\text{-}b}$ declines to $\sim 20\%$ of its room-temperature value as $T \rightarrow T_c$. This inference is further confirmed by the observation that the anisotropic part of the d-spin NMR shift ($\sim 0.05\%$) is an order of magnitude less at $T = 60$ K than it is for $YBa_2Cu_3O_{7.0}$.[11] This effect, which was foreshadowed by the ^{89}Y shift measurements reported for these materials,[3,4] has been attributed to the development of a pseudogap as a result of fermion scattering from antiferromagnetic fluctuations.[14]

We now use the Cu(2) shift data ($K^{s}_{2a\text{-}b}$) from Fig. 2 to discuss and analyze relaxation data for both ^{63}Cu(2) (Refs. 5-7) and Y (Refs. 3 and 4) in the 60-K phase. One measure of correlation effects in Fermi liquids is the Korringa ratio $T_1(\text{Korringa})/T_1$, where

$$T_1(\text{Korringa})^{-1} = 4\pi k_B T \gamma_n^2 K_s^2 / (N_s \gamma_e^2 \hbar)$$

is the relaxation rate corresponding to spin hyperfine shift K_s for the case of noninteracting fermions.[15] The factor N_s is placed in the denominator to account for multiple sources of hyperfine fluctuations.[16] The ^{63}Cu(2) relaxation in these materials is enhanced preferentially over that of the ^{17}O(2,3) and ^{89}Y nuclei. That observation suggests the occurrence of an antiferromagnetic fluctuation peak[17,18] in the dynamic susceptibility $\chi''(\mathbf{q},\omega)$.[19] Recent model calculations based on this assumption[20,21] have yielded quantitative simulations of T_1 behavior for ^{63}Cu(2), ^{17}O(2,3), and ^{89}Y nuclei in the 90-K phase using a single dynamic susceptibility. At low frequencies the mean-field models give $\chi''(\mathbf{q},\omega) \propto \omega \chi^{s}_{0} F(\mathbf{q})$, where χ^{s}_{0} is the uniform spin susceptibility and $F(\mathbf{q})$ models the q-dependent (antiferromagnetic) enhancement effect. Thus,[19]

$$(T_1 T)^{-1} \propto \chi^{s}_{0} \sum_{\mathbf{q}} A(\mathbf{q})^2 F(\mathbf{q}) , \qquad (1)$$

where $A(\mathbf{q})$ is the q-dependent hyperfine coupling.[20-22]

In applying Eq. (1) to the 60-K phase, we point out that χ_0^s is thereby constrained to take on a strong temperature dependence which is inconsistent with mean-field theory behavior. With that caveat in mind, we use Eq. (1) to isolate the behavior of the antiferromagnetic fluctuations by forming a quantity proportional to $(T_1 T \chi_0^s)^{-1}$. To that end we define a modified Korringa ratio (MKR) $[T_1(\text{Korringa})/T_1][K^s(T)/K^s(300\text{ K})]$, which has the desired property and is also independent of hyperfine coupling parameters. Values of the MKR are plotted in Fig. 3 for ^{63}Cu(2) (solid circles) using T_1 data from Ref. 7 (Fig. 3, inset). For comparison we plot $T_1(\text{Korringa})/T_1(T)$ for ^{63}Cu(2) in 90-K material,[23] assuming $K_{2a\text{-}b}^s = 0.30\%$ (Ref. 11) independent of temperature. The 90-K material shows enhancements ~ 10 which increase monotonically with decreasing T, while enhancement for the 60-K phase grows with a similar power of temperature ($\sim T^{-1/3}$) but is a factor of 4–5 greater. These results appear to reflect antiferromagnetic correlations between Cu(2) spins which grow stronger as the composition nears that of the insulating phase. Most importantly, the mean-field model [Eq. (1)] succeeds in separating the peculiar shift behavior from that of the antiferromagnetic fluctuations.

As a control for this procedure, we plot the MKR for ^{89}Y in $YBa_2Cu_3O_{6.63}$ in Fig. 3 using NMR data from Ref. 3 (solid squares). The spin-paramagnetic shift component is obtained from the data of Ref. 3 as follows. By plotting measured ^{89}Y shifts against the Cu(2) shifts in Fig. 2 and extrapolating to zero copper (spin) shift, we find $K_0^Y \sim 175$ ppm for the zero of ^{89}Y spin-paramagnetic shifts.[4] As we see from Fig. 3, the MKR for the ^{89}Y nuclei shows background enhancement, but little variation with temperature, in accord with the antiferromagnetic fluctuation-model results.[20,21,24] A similar result is found using ^{17}O(2,3) NMR data for the 60-K phase.[25] The ^{89}Y and ^{17}O nuclei do not respond to the antiferromagnetic fluctuations, because their form factors $A(\mathbf{q})$ vanish at $\mathbf{q} = (\pi,\pi)$.[20-22] For comparison with the ^{89}Y data we also show in Fig. 3 the Korringa ratio for ^{89}Y NMR data on 90-K material[4] (open squares), using the chemical shift determined as described above, as well as for ^{17}O(2,3) using new T_1 data with the isotropic spin-paramagnetic shift given in Ref. 13 (triangles). These results confirm that the ^{89}Y and ^{17}O(2,3) nuclei in either phase are little affected by the growing fluctuation peak involving the Cu(2) spins, evidently for the reasons given above.

We can also use the shift data of Fig. 2 to analyze the measured susceptibility into its component parts. The details of this analysis will be presented elsewhere. Our main finding is that the spin susceptibilities associated with the Cu(1) and Cu(2) sites have similar temperature dependences and magnitudes. This is the first experimental evidence on this point; it supports the assumption made by Mila and Rice in their hyperfine coupling analysis[12] (for 90-K phase $YBa_2Cu_3O_{6+x}$) that the spin susceptibilities on the two copper sites are the same. It should be emphasized that this conclusion depends on assuming the spin hyperfine coefficients for the 90-K phase[12] to be valid here.

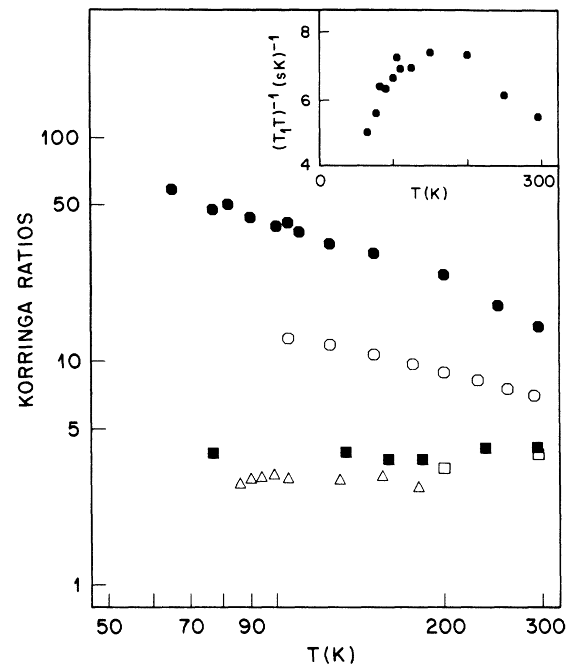

FIG. 3. MKR is plotted vs T for ^{63}Cu(2) (solid circles) and ^{89}Y (solid squares) for the 60-K phase. For comparison, the simple Korringa ratio is shown for ^{63}Cu(2) (circles), ^{89}Y (squares), and ^{17}O (triangles) in the 90-K phase. See text for definitions and sources of data. The inset shows the ^{63}Cu(2) T_1 data from Ref. 7 used for the corresponding MKR curve (solid circles).

In conclusion, the anomalous shift and relaxation behavior at planar sites in the 60-K phase of $YBa_2Cu_3O_{6+x}$ can be analyzed in terms of an antiferromagnetic fluctuation peak in the dynamic susceptibility. The corresponding correlation lengths[21] for antiferromagnetic short-range order are 5–6a for the 60-K phase samples as opposed to 2–3a for 90-K material. Recent neutron-scattering data[26] show antiferromagnetic correlations to be present in a sample with $T_c = 50$ K, giving at least qualitative support to this kind of model. Second, it must be emphasized that the temperature-varying spin susceptibility is not understood. This effect, and the absence of any prominent feature in the T_1 curve at T_c, strongly contrast with the behavior of the 90-K phase. These differences are accompanied by a similar contrast in specific-heat behavior, where the 60-K phase exhibits a specific-heat peak at T_c which is very small and difficult to resolve.[27]

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$$T_1^{-1} = (\gamma^2 k_B T / g^2 \mu_B^2) \sum_q A_{\mathbf{q}}^2 \chi''(\mathbf{q},\omega)/\omega ,$$

where $A_{\mathbf{q}}$ is the **q**-dependent hyperfine coupling parameter.
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