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Nuclear magnetic resonance and nuclear quadrupole resonance study of copper in $Ba_2YCu_3O_{7-\delta}$

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Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies of copper nuclei are reported for high-quality single-phase powder samples of $Ba_2YCu_3O_{7-\delta}$. The high-field ^{63}Cu NMR spectrum shows well-defined axial symmetry for the chain-forming Cu(1) site and evidence of appreciable disorder in the Cu(2) planes. Spontaneous oxygen loss was found to degrade the sharp NMR spectrum of the Cu(1) site. Spin-lattice relaxation rates reveal strikingly different electron dynamics for the two sites. For neither site do the rates exhibit conventional Bardeen-Cooper-Schrieffer behavior near T_c.

In this paper we report studies of the nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) of ^{63}Cu and ^{65}Cu nuclei in the 90-K superconductor $Ba_2YCu_3O_{7-\delta}$.[1,2] Since copper-oxygen bonds provide the conducting links in this high-temperature superconductor, copper nuclear resonance provides a valuable microscopic probe for elucidating the underlying electronic properties. Our studies, carried out at temperatures ranging from 77 to 300 K, reveal unusual and unexpected features for these resonances. The crystal lattice contains two inequivalent sites for the copper ions. The crystalline environments of the two are superficially similar. Whereas they have comparable NQR frequencies, the NMR spectra are markedly different, suggesting a sharp distinction between local electronic properties for the two sites. Specifically, the Cu(2) site[3] exhibits a sharply modified NMR powder pattern, uncharacteristic of its nearly axial symmetry. We believe that this effect arises from disorder in the Cu(2) plane. Perhaps the most dramatic anomaly is found in the spin-lattice relaxation rates, which have been measured in zero field at the NQR frequencies. The two sites are found to have relaxation rates with markedly different temperature dependencies. Further, at $T \sim 100$ K, we find them to be ~ 20 times faster than an estimate of the presumably dominant rate contribution from orbital fluctuations. The behavior below T_c is not BCS-like, with an extremely sharp decrease in the rate and no peak.

High-quality single-phase material prepared by standard solid-state reaction techniques[2] was obtained from two sources at our laboratory. The pressed ceramic pellets were subsequently powdered for magnetic resonance studies. X-ray photographs taken before and after powdering gave identical results with sharp lines and strong orthorhombic splittings related to high oxygen content. These materials had T_c values above 90 K and were known to give near 100% magnetic-flux exclusion in tests at 77 K in ceramic form. Tests of flux exclusion conducted on the powder samples showed a strong effect which, however, could not be calibrated. Steps were taken to ensure that the copper NMR signals observed came only from the sample powder. The intensities were large enough to confirm that the signals came from throughout the volume of the particles, where rf penetration was excellent. The NMR samples were contained in unsealed, but tightly closed Teflon vials; the NQR sample was sealed in a quartz ampoule under 1 atm of O_2 gas.

NMR field spectra of both copper isotopes were recorded by measuring spin-echo amplitudes at fixed resonance frequency while scanning the magnetic field. A typical spectrum for a "fully oxygenated" powder sample at $T = 100$ K and $\nu = 81.44$ MHz is shown in Fig. 1 for ^{63}Cu. At this frequency the two isotopes are clearly separated, with the ^{65}Cu spectrum located just below the field range shown in Fig. 1. Each isotope exhibits a superposition of sharply contrasting powder patterns[4] for the two Cu sites in this structure.[3] In addition, we have observed first-order satellite peaks for one of the Cu sites at field values

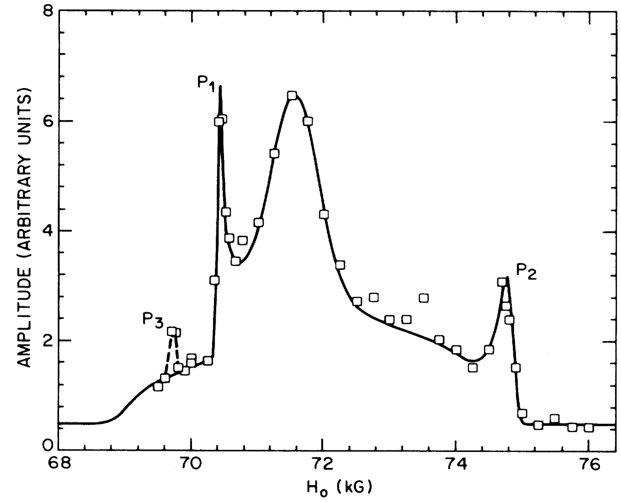

FIG. 1. NMR field spectrum of ^{63}Cu in $Ba_2YCu_3O_{7-\delta}$ taken at a frequency of 81.44 MHz and temperature 100 K. Peaks p_1 and p_2 are attributed to the Cu(1) site and the central peak to the Cu(2) site. Peak p_3 is as yet unidentified. The solid curve is a composite model fit, calculated as described in the text. The narrow peak at $H_0 \sim 73.5$ kG originates from ^{27}Al nuclei in ceramic materials in our NMR probe assembly.

above and below the range shown in Fig. 1, for a total spectral range of over 60 kG.

The issue of site identification is critical for understanding the implications of these results. One site presents the two peaks (p_1 and p_2) of a wide but sharply defined $\pm\frac{1}{2}$ transition powder pattern characteristic of a nearly axial electric field gradient.[4] We associate this structure with the lower-intensity (^{63}Cu) NQR peak at 31.49 MHz (Ref. 5) and thus with the chain-forming Cu(1) site.[3] As we discuss shortly, this assignment is confirmed by the observed temperature dependence of the spin-lattice relaxation. The Cu(2) site, associated with the higher-intensity ^{63}Cu NQR peak at 22.0 MHz,[5] evidently yields the broad central feature in the spectrum.[6] This site exhibits a strong deviation from the expected nearly axial form shown by Cu(1). We attribute this deviation to disorder in the Cu(2)-O(2)-O(3) plane. A detailed fit to the Cu(2) NMR spectrum was not attempted.

In fitting to the data of Fig. 1, we develop separate models for the Cu(1) and Cu(2) site intensities and superimpose the results. The central [Cu(2)] feature appears to be a narrow peak on a broad base that terminates abruptly at ± 2 or 3 kG from the center. We model this intensity with two Gaussians, one representing the peak and a wider one with truncated wings for the base. The position of the central peak corresponds to a shift $K \sim 0.7\%$, but it must be noted that shift anisotropies and the second-order quadrupolar shift[4] could alter this estimate substantially.

The Cu(1) powder pattern is fitted with an exactly calculated quadrupolar field spectrum, where the quadrupolar splitting parameter ν_Q was taken from NQR measurements.[5] The character of the powder pattern is modified, we believe, by the presence of anisotropies in both the shift and T_2. The shift anisotropy results in a peak separation $[H(p_2)-H(p_1)]$ nearly 1 kG less than the purely quadrupolar value. We take the total shift to be of the form

$$K = K_i + K_a \cos^2\theta \ , \tag{1}$$

where K_a is an orbital term[7] and θ is the polar angle between the magnetic field H_0 and the a axis of the crystal. Consideration of d-orbital symmetries determined by band-structure calculations[8] leads to an estimate of orbital shift structure in which the $\cos^2\theta$ term dominates. The K_i term is a combination of both orbital and d-spin contributions. Indeed, the negative d-spin part is dominant, giving $K_i = -0.44\%$ for the calculated fit. Note that p_2 is shifted to lower field by the K_a term while p_1 is unaffected. The fitted value of K_a is 2.6%.

Measurements of T_2 yielded different values for each of the peaks in Fig. 1. Most striking is the contrast between p_1 and p_2, where T_2 for p_2 is $\sim 40\%$ shorter than for p_1. Since the spin-echo spectra are taken with pulse spacings comparable to T_2, relative peak intensities are strongly affected by this. The NQR T_1 measurements reported below suggest that T_2 is dominated by spin-lattice contributions. For the fit to Fig. 1 we take

$$1/T_2(\theta) = 5.2\times10^3 + R\cos^2\theta \, \mathrm{sec}^{-1} \ , \tag{2}$$

where the first term is the decay rate for p_1, and we adjust $R(=5.6\times10^3\ \mathrm{sec}^{-1})$ to give the greatly diminished intensity observed for p_2. Equation (2) is then found to be in good agreement with the measured T_2 value for p_2. The fitted curve so calculated yields a Cu(2) site intensity $\sim 50\%$ greater than that for Cu(1), i.e., less than the expected ratio of 2. This observation, combined with the smeared character of the Cu(2) NMR line noted above, suggests the possibility that localized magnetic moments associated with disorder occur on a minor fraction of the Cu(2) sites. A Curie-like term makes a substantial contribution to the measured susceptibility.[9] Sites with local moments would be broadened and/or relaxed out of the NMR spectrum, and sites neighboring local moments would undergo broadening. In NQR the broadening effects would be greatly diminished.

The powdered samples used in our NMR study were found to gradually lose oxygen content when stored at room temperature and possibly to undergo other chemical changes as well. These effects led to degradation of the peaks in the Cu(1) NMR spectrum, as illustrated by the data in Figs. 2(a) and 2(b). Here we show the ^{63}Cu spectrum of a sample after 10–12 days of storage at room temperature in a reasonably dry N_2 atmosphere, having looked very much like that of Fig. 1 at the outset. The dashed line in Fig. 2(a) shows the original relative ampli-

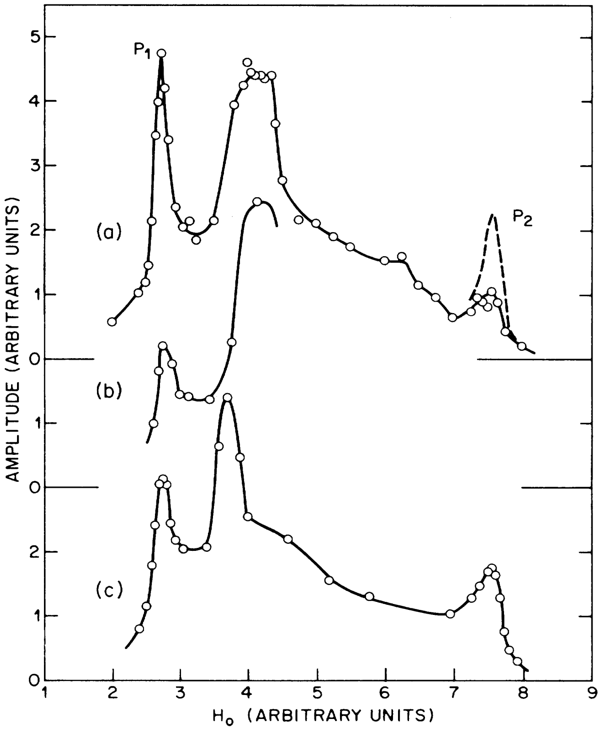

FIG. 2. The ^{63}Cu NMR spectrum taken at frequencies in the vicinity of 80 MHz and temperature 100 K is shown for a powder sample at various stages of chemical change resulting from storage in an unsealed Teflon vial at room temperature. (a) Spectrum obtained after about 20 days of storage; the original spectrum was very similar, with peak p_2 shown as a dashed line. (b) Several days later peak p_1 has also lost intensity. (c) Overnight annealing in O_2 gas at 500 °C partially restores p_1 and p_2.

tude of p_2 to the central peak from incomplete initial data. We find that the Cu(1) p_2 peak degrades most rapidly. Several days later, p_1 was also found to have lost intensity, as can be seen in the partial spectrum of Fig. 2(b). The central peak is not much affected. The original NMR peaks can be partially restored by heat treatment at 500 °C overnight in a pure O_2 atmosphere. This is shown in Fig. 2(c) where p_1 and p_2 are seen to have regained over half of their original intensity. The Cu(1) peak appears to have narrowed and shifted to lower field. We believe that the observed changes in the spectra are due, at least in part, to depletion of oxygen from the O(4) site neighboring Cu(1).

The superconductivity of the powdered sample used for the data in Fig. 2 was monitored by checking the degree of magnetic-flux exclusion at 77 K before and after oxygen loss. At the time the data of Fig. 2(a) were taken, the flux exclusion had diminished by ~25% from its original value. Reoxygenation as described above did not, however, restore the flux exclusion appreciably from this diminished value. This observation also suggests that additional damage to the crystal structure beyond simple oxygen loss may have occurred while the sample was at room temperature.

We have measured NQR spin-lattice relaxation times for both sites at temperatures above and below T_c. Results for ^{63}Cu on the Cu(1) site are shown in Fig. 3 in the form of $1/T_1$ vs T. These data are anamalous in several ways. First, the temperature dependence in the normal state is very flat with an apparent maximum just below room temperature, as opposed to the expected Korringa behavior ($1/T_1 \propto T$) for a metallic system. In contrast, data for the Cu(2) site (not shown) exhibit nearly Korringa-like behavior above T_c. Indeed, they mirror very closely the normal-state T_1 behavior reported for ^{89}Y in this compound by Markert *et al.*[10] Because of the proximity of Y to Cu(2), this connection is strong evidence in favor of our identification of the Cu(2) site with the 22.0 MHz NQR line[5] as mentioned earlier. Both sites give anomalously high relaxation rates. These rates are approximately equal at $T \sim 110$ K, where they exceed by more than an order of magnitude a realistic estimate $(T_1T)^{-1} \sim 1\ (\text{sec K})^{-1}$ of the presumably dominant orbital contribution[11] to the relaxation. Comparison of T_1 values for the two isotopes of copper under otherwise identical conditions confirms that the relaxation is magnetic in character.[12]

The behavior of T_1 in the vicinity of T_c and below is also surprising. The Cu(1) site relaxation in Fig. 3 shows no peak at T_c and falls away extremely rapidly for $T < T_c$. The Cu(2) site (as well as the ^{89}Y)[10] behaves in a similar fashion. This is in sharp contrast with behavior found, e.g., for ^{27}Al in aluminum metal.[13] It remains to be seen whether the asymptotic behavior of T_1 as $T \rightarrow 0$ reflects the superconducting energy gap according to the BCS picture or not. Furthermore, because of the highly anisotropic nature of the crystal structure as well as the possibility of non *s*-state pairing, it is by no means clear that the behavior of conventional superconductors is to be expected here.

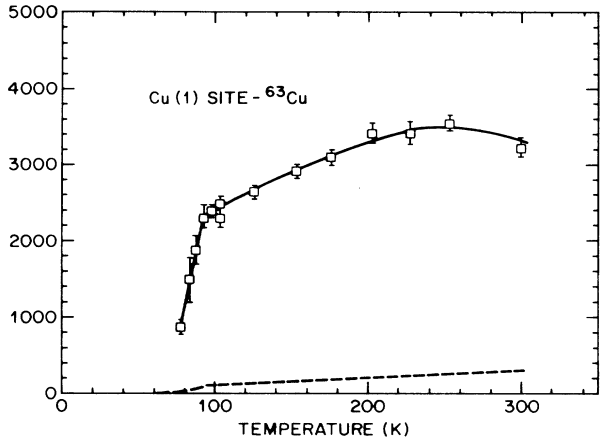

FIG. 3. The ^{63}Cu spin-lattice relaxation rate $1/T_1$ for the Cu(1) site is plotted versus T. The rate shows a sharp drop for $T < T_c$ and enhanced non-Korringa behavior in the normal state. The dashed line shows the estimated orbital relaxation rate (Ref. 11) obtained from the band-structure Cu(1) density of states (Ref. 8) and an orbital hyperfine field corresponding to $\langle r^{-3} \rangle = 4.5$ a.u.

In summary, these results point up in a unique way the contrasting behavior of the two copper sites in this structure. The clear evidence for static disorder in the Cu(2) planes while the Cu(1) sites retain cleanly axial symmetry is not foreshadowed by other experimental data that we are aware of. The strong T_1 enhancement is suggestive of correlation effects. Moreover, the contrasting temperature dependences of T_1 values for the Cu(1) and Cu(2) sites show a startling distinction between the electron dynamics of chainlike and planar regions of the crystal. Finally, the behavior of T_1 in the vicinity of T_c is clearly at variance with the BCS behavior found in conventional superconductors.

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[4] For a general discussion of the quadrupolar-broadened NMR powder patterns reported here, see the article by M. H. Cohen

and F. Reif, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 321.

[5] At 100 K, one set of NQR frequencies for ^{63}Cu and ^{65}Cu was found to be 31.49 and 29.14 MHz, respectively, in excellent agreement with the expected ratio $Q_{63}/Q_{65}=1.081$ [see, for example, G. A. Fuller and V. W. Cohen, Nucl. Data Tables **A5**, 433 (1969)]. The ^{63}Cu NQR frequency declines to 31.15 MHz at 297 K. The frequency for a second ^{63}Cu line was measured to be 22.05 MHz at 100 K. These frequencies agree with those given in recent reports by Lutgemeier and Pieper [Solid State Commun. (to be published)] and Furo *et al.* (unpublished). Half width at half height for these lines is ~150 kHz and varies somewhat among samples.

[6] However, at higher temperatures this central peak splits into two parts, showing conclusively that it is a broadened quadrupolar powder pattern. At room temperature, the splitting of these peaks is ~350 G.

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[12] For magnetic relaxation processes the rate $1/T_1$ is proportional to the square of the gyromagnetic ratio γ. Thus, $T_1(63)/T_1(65)=(\gamma_{65}/\gamma_{63})^2=1.148$.

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