Cu Spin Dynamics and Superconducting Precursor Effects in Planes above T_c in $YBa_2Cu_3O_{6.7}$

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Spin dynamics at planar sites in oxygen-deficient $YBa_2Cu_3O_{6+x}$ have been investigated by nuclear spin-lattice relaxation measurements using $^{63,65}Cu$ nuclear quadrupole resonance and ^{89}Y NMR. A sharp decrease of ^{63}Cu nuclear relaxation below 100 K in $YBa_2Cu_3O_{6.7}$ suggests the possible onset of spin pairing in individual planes well above the transition to three-dimensional bulk superconductivity. Comparison of the relaxation rates for the 60-K superconductor $YBa_2Cu_3O_{6.7}$ with those of $YBa_2Cu_3O_{7.0}$ in the range 100–300 K shows that the planar Cu(2) spin dynamics are strongly affected by changes in carrier concentration.

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The remarkable sensitivity of its properties to changes in oxygen content is one of the essential characteristics of the high-T_c superconductor $YBa_2Cu_3O_{6+x}$. The system ranges from the antiferromagnetic insulator with an ordering temperature $T_N \sim 400$ K at low oxygen content ($x \lesssim 0.5$) to the superconducting phase with T_c exceeding 90 K close to the composition $YBa_2Cu_3O_{7.0}$. At intermediate compositions ($0.5 \lesssim x \lesssim 0.75$), samples annealed at relatively low temperatures exhibit a nearly constant T_c value of about 60 K.[1] Structural studies[2] have established that the vacancies introduced by removing oxygen from $YBa_2Cu_3O_{7.0}$ are primarily in the Cu-O linear chains and that the 60-K plateau is related to ordering of these vacancies.[3] Yet although the structural changes are confined to the chain layer, it is the *planes* which dominate both the antiferromagnetic[4] and superconducting[5] properties. The magnetic state and spin dynamics of the planar Cu in the superconducting range, their dependence on composition, and their relation to the value of T_c are of central importance for theory but remain poorly understood.

It is the purpose of this Letter to describe ^{63}Cu and ^{89}Y nuclear relaxation measurements which probe the spin dynamics of the planar sites in metallic $YBa_2Cu_3O_{6+x}$ samples of reduced oxygen content. We discuss two findings which may be of particular importance for an understanding of the mechanism of superconductivity in cuprate perovskites. First, and most remarkable in our view, we find that nuclear relaxation is strongly suppressed in the *normal state* of the 60-K superconductor $YBa_2Cu_3O_{6.7}$ as the temperature is reduced below about 100 K, exhibiting behavior resembling that associated with pair formation below T_c in the 90-K material $YBa_2Cu_3O_{7.0}$. This observation raises the possibility that the intrinsic pairing interaction in the planes is not greatly weakened in material of reduced oxygen content so that spin pairing and energy-gap formation take place in this material at temperatures well above the bulk superconducting transition at 60 K. Second, we find a dependence on oxygen composition of the ^{63}Cu relaxation rates at higher temperatures that shows the Cu(2) spin dynamics to be dominated by interactions with the charge carriers. There is little indication that Cu-Cu exchange interactions play a significant role.

The nuclear spin relaxation rates of $^{63,65}Cu$ in $YBa_2Cu_3O_{6+x}$ are proportional to the low-frequency spectrum of fluctuating local d-spin hyperfine fields[6] and offer a sensitive probe of Cu spin fluctuations. These can be studied separately and with relative ease for the Cu(1) (chain) and Cu(2) (plane) sites in $YBa_2Cu_3O_{7.0}$ where differing local environments lead to well-separated nuclear quadrupole resonance lines[7] for the two sites. The spectra develop additional complexity at lower oxygen content, but it is still possible to investigate the spin dynamics of different Cu sites. In this paper, we emphasize our study of a well-characterized sample of the 60-K superconductor $YBa_2Cu_3O_{6.7}$. As an aid to interpretation of the spectra, we have also investigated a sample of $YBa_2Cu_3O_{6.9}$.

Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) studies were carried out on powdered samples initially prepared as $YBa_2Cu_3O_{7.0}$ by standard solid-state reaction and oxygen anneal. We subsequently reduced the oxygen content by a low-temperature anneal in the presence of a Zr getter as described previously.[1] ac susceptibility measurements of the $YBa_2Cu_3O_{6.7}$ sample in ceramic form yielded a T_c value of 61 K and a Meissner effect[8] of essentially 100%. The paramagnetic susceptibility of this material shows no sign of a partial Meissner effect onset above T_c.[1] The onset of superconductivity in the powdered sample could be detected *in situ* during the NQR studies by a sharp change in the effective inductance of the tuned rf sample coil. With a sensitivity of a few percent, we found no evidence that any portion of the sample became superconducting above 61 K. Our previous studies[8] of the Cu(1) resonances in the present sample indicate that it is highly ordered, supporting structural models[9] in which the oxygen vacancies form so-called "empty chains" of twofold coordinated Cu(1) and intact chain segments of fourfold Cu(1). The $YBa_2Cu_3O_{6.9}$ sample is more disordered and exhibits a relatively broad superconducting transition ($\Delta T \sim 4$ K) in the neighborhood of 86 K.

The NQR spectra of our $YBa_2Cu_3O_{6.7}$ and

$YBa_2Cu_3O_{6.9}$ samples at 100 K are presented in Fig. 1 and compared with that of the fully oxygenated compound $YBa_2Cu_3O_{7.0}$. These spectra were obtained by quadrature detection and integration of the spin echoes to obtain the echo intensity as the frequency was scanned stepwise. The relatively simple and well-known[7] spectrum of $YBa_2Cu_3O_{7.0}$ [Fig. 1(a)] consists of two narrow ^{63}Cu lines at frequencies of 22.05 and 31.48 MHz. These are assigned,[10] respectively, to the Cu(1) chain and Cu(2) plane sites. The corresponding ^{65}Cu resonances occur at frequencies lower by a factor of 0.9254 in accord with the relative nuclear quadrupole moments of the two isotopes.

As the oxygen content is reduced, sharp new lines appear in the spectra [Figs. 1(b) and 1(c), solid points] due to a class of Cu site whose nuclear relaxation rates are more than 3 orders of magnitude lower than those of either site in $YBa_2Cu_3O_{7.0}$. Although their frequencies almost exactly match those of the Cu(2) sites in $YBa_2Cu_3O_{7.0}$, the slowly relaxing sites have been identified[8] as

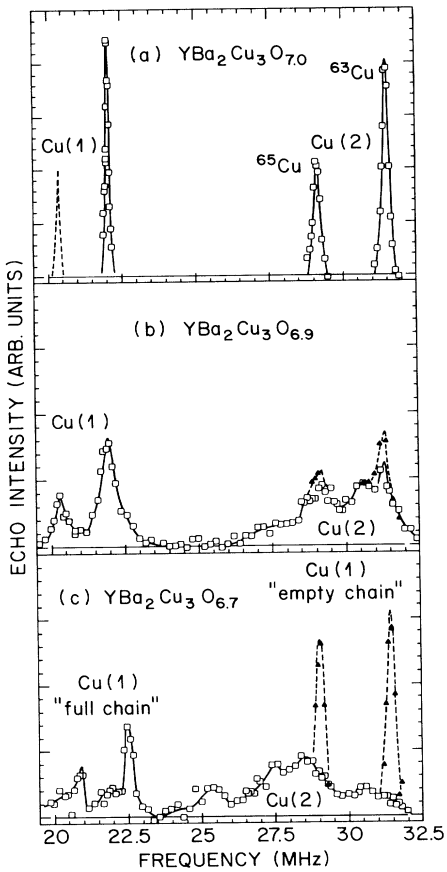

FIG. 1. $^{63,65}Cu$ NQR spin-echo spectra for $YBa_2Cu_3O_{6+x}$: (a) $YBa_2Cu_3O_{7.0}$; (b) $YBa_2Cu_3O_{6.9}$; (c) $YBa_2Cu_3O_{6.7}$. Open points denote spectra of rapidly relaxing sites ($T_1 < 1$ ms) obtained with pulse repetition frequency of 100 Hz; solid points denote lines observed for slowly relaxing Cu(1) empty chain sites using a pulse repetition frequency of 1 Hz.

Cu(1) sites in twofold oxygen coordination whose valence state is essentially Cu^+ (empty chain sites). The presence of these lines in the NQR spectrum and the inferred "full chain–empty chain" order agree with recent x-ray studies.[11]

The Cu(2) resonances of $YBa_2Cu_3O_{7.0}$ evolve into a complex of lines shifted to lower frequency [Figs. 1(b) and 1(c)]. The NMR spectrum of our $YBa_2Cu_3O_{6.7}$ sample shows that these sites provide a majority of the total Cu NMR intensity and, furthermore, that their electric-field-gradient tensors are nearly axial. Together with the emergence of the NQR lines from the Cu(2) resonance of $YBa_2Cu_3O_{7.0}$, the NMR observations show that the broad spectral features above 24 MHz in $YBa_2Cu_3O_{6.9}$ and $YBa_2Cu_3O_{6.7}$ originate from planar sites. The planar complex consists of several discrete NQR lines (31.3, 30.6, 28.6, and 27.5 MHz for ^{63}Cu). It is characteristic of these spectra and those obtained by other workers[12,13] that the frequencies remain nearly constant while the relative intensities change with composition. The structure in the spectra is thus due to variations of the Cu(2) environments corresponding to specific arrangements of full and empty chains in the neighboring Cu(1) layer and is not simply the result of large-scale compositional inhomogeneities in the samples. In the latter case, one would not expect to find correspondence in the frequencies among samples of different average composition and among samples prepared in different laboratories.

We turn now to consider the relaxation properties of the Cu(2) sites. In Fig. 2, we present experimental results for $(T_1T)^{-1}$ of ^{63}Cu for Cu(2) and ^{89}Y in $YBa_2Cu_3O_{6.7}$. The Cu(2) rates were measured in zero field by NQR at frequencies of 27.5 and 29.3 MHz,[14] while the ^{89}Y data were obtained by NMR in a field of 93.9 kG (19.6 MHz). For comparison we also show the behavior of the Cu(2) rates in $YBa_2Cu_3O_{7.0}$ [Fig. 2(a), dashed line] for which $(T_1T)^{-1}$ increases smoothly with decreasing temperature down to T_c, then drops precipitously on entering the superconducting state.[15,16] For $YBa_2Cu_3O_{6.7}$ above 100 K, the behavior of $(T_1T)^{-1}$ for the planar Cu(2) sites is strikingly different from that of $YBa_2Cu_3O_{7.0}$. Except for a weak maximum at ~ 110 K, $(T_1T)^{-1}$ is nearly constant from 100 to 300 K. The rates at 27.5 MHz are 20%–30% higher than at 29.3 MHz, while the temperature dependence of $(T_1T)^{-1}$ is only slightly stronger at this frequency. The value of $(T_1T)^{-1}$ for ^{89}Y increases strongly with temperature between 100 and 300 K,[17] quite unlike its behavior in $YBa_2Cu_3O_{7.0}$ where $(T_1T)^{-1}$ remains constant in this range.

We call particular attention to the data below 100 K where the value of $(T_1T)^{-1}$ for ^{63}Cu at 29.3 MHz drops sharply until, at T_c, it is only about $\frac{1}{3}$ the value at 100 K. The 27.5-MHz data also show a decrease in $(T_1T)^{-1}$ below a broader maximum at about 120 K. Relaxation rate measurements at 22.6 MHz for the full

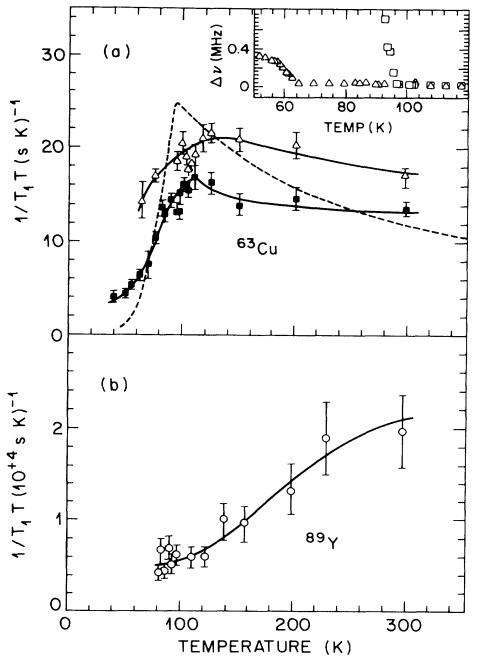

FIG. 2. (a) Nuclear spin-lattice relaxation rates $(T_1T)^{-1}$ for Cu(2) in $YBa_2Cu_3O_{6.7}$: Solid squares denote ^{63}Cu data obtained by NQR at 29.3 MHz; triangles denote ^{63}Cu data obtained by NQR at 27.5 MHz. Dashed line indicates behavior of ^{63}Cu rates for Cu(2) in $YBa_2Cu_3O_{7.0}$. Inset: Change in resonant frequency of tuned NQR rf coil vs temperature showing onset of superconductivity in powder samples of $YBa_2Cu_3O_{7.0}$ (squares) and $YBa_2Cu_3O_{6.7}$ (triangles) and the absence of effect above T_c in $YBa_2Cu_3O_{6.7}$. (b) $(T_1T)^{-1}$ for ^{89}Y obtained by NMR at 19.6 MHz.

chain Cu(1) sites[8] yield a roughly constant value of $(T_1T)^{-1}$ between 61 and 100 K indicating that the effect is limited to the planar sites. A sharp decrease in $(T_1T)^{-1}$ below 100 K is not evident in the ^{89}Y relaxation data [Fig. 2(b)], nor have we observed any anomalous behavior in the ^{89}Y Knight shift in this range. This raises the possibility that the effect seen for Cu(2) is suppressed when a magnetic field is applied.

It is important to recognize that the strong decrease in $(T_1T)^{-1}$ is characteristic of the majority of Cu(2) sites in the sample and that this effect is not what would be observed if portions of the sample had bulk superconducting transitions between 61 and 90 K. Because of intensity loss due to the decreasing penetration length and the rapid decrease in relaxation rates characteristic of 90-K superconducting material below T_c, the resonance experiments would actually be biased toward detection of *normal* portions of an inhomogeneous sample. Signal strengths indicate that the majority of Cu and Y nuclei contribute to the observed spectrum and we found only the expected smooth increase in signal intensity with decreasing temperature until reaching T_c. The rf susceptibility properties of the powder sample [inset of Fig. 2(a)] show no evidence of bulk superconductivity above the temperature of the Meissner effect onset.[18] Similarly, neither our data, the susceptibility data,[1] nor any other measurements indicate the presence of a *magnetic* transition that might lead to a reduction of $(T_1T)^{-1}$ below 100 K.

These decreases in $(T_1T)^{-1}$ for Cu(2) are remarkable because they closely mimic the rapid decrease in $(T_1T)^{-1}$ observed *in the same temperature range* in the $T_c=90$ K material [Fig. 2(a)] but here the effect occurs in a sample for which $T_c=61$ K.[19] Meanwhile, there is no noticeable feature in the $(T_1T)^{-1}$ curve at the actual 61-K bulk superconducting transition temperature of the $YBa_2Cu_3O_{6.7}$ sample. This behavior is, to our knowledge, unprecedented in nonmagnetic, metallic systems (superconducting or not) for which there is no crystallographic or other phase transition.

A possible explanation for the strong precursor to superconductivity, in the $T_c=61$ K material, is that pair formation and an energy gap begin to develop in the planes in the range 90–110 K followed by a transition to bulk three-dimensional superconductivity at 61 K. If this is the case, one might expect to find indications in other measured properties. There are, in fact, subtle hints of gaplike features in optical data obtained well above T_c in material of reduced oxygen content.[20] There are also indications that the paramagnetic susceptibility is suppressed below ~ 100 K in this composition range, although analysis of the susceptibility is complicated by the frequent presence of a small Curie term of extrinsic origin.[21] The optical and susceptibility data are suggestive, but they remain ambiguous as indicators of pair formation above T_c.

Finally, we return briefly to the ^{63}Cu relaxation results above 100 K to point out the implication of these data that the Cu(2) spin dynamics are strongly influenced by interactions with the charge carriers above the onset of pair formation. We note, in particular, that the composition dependence is not what one expects for a system of Cu^{2+} local moments whose spin dynamics are governed by antiferromagnetic Cu-Cu exchange couplings, partially frustrated by carriers (holes) on the planar oxygen sites.[22] At temperatures sufficiently high that the local moment spins are completely uncorrelated ($T \gtrsim J/k_B \sim 1000$ K), the relaxation rate has no explicit temperature dependence and is given by

$$1/T_1 = (1/4\hbar^2)(A_x^2 + A_y^2)\tau, \qquad (1)$$

where A_x and A_y are the transverse components of the magnetic hyperfine coupling and the correlation time τ is determined by the exchange coupling J, i.e., $\tau = (\sqrt{\pi}/4)\hbar/J$ for fourfold Cu-Cu coordination.[23] With $J \sim 0.1$ eV,[24] this expression yields the correct order of magnitude for the relaxation rate. But at lower oxygen content the aforementioned frustration effect should be diminished yielding a stronger effective exchange coupling and, by Eq. (1), a *lower* relaxation rate. In fact, the observed rates tend to *higher* values for $YBa_2Cu_3O_{6.7}$

than for $YBa_2Cu_3O_{7.0}$. The data imply that the correlation time τ becomes longer in oxygen-deficient material as expected if the local Cu spin hyperfine field is modulated by lower concentrations of mobile carriers.

The rapid decrease of the nuclear relaxation rate by more than 3 orders of magnitude[11] together with the reduction of the Knight shift[25] for Cu(2) below T_c in $YBa_2Cu_3O_{7.0}$ shows that the d electrons not only interact with the carriers, but that the d electrons are actually paired in the superconducing ground state. This is not only a significant physical finding *per se*, indicating that the d electrons have an appreciable degree of itinerant character, but also motivates our suggestion that the precursive reduction of the Cu(2) relaxation rate in $YBa_2Cu_3O_{6.7}$ is due to spin pairing. As a test of this idea, it is clear that Knight shift data for $YBa_2Cu_3O_{6.7}$ will be of great interest when they become available, especially if NMR studies of Cu(2) relaxation can establish that the precursor effect survives in a magnetic field.

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[1]R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature (London) **329**, 423 (1987); R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987).

[2]F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, Phys. Rev. B **35**, 8778 (1987); J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. V. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[3]C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, J. L. Hodeau, and M. Marezio, Phys. Rev. B **36**, 7118 (1987); D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, Phys. Rev. B **37**, 2317 (1988); R. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, and J. V. Waszczak, Phys. Rev. B **37**, 7920 (1988).

[4]J. M. Tranquada *et al.* Phys. Rev. Lett. **60**, 156 (1988).

[5]See, for example, J. R. Schrieffer, X.-G. Wen, and S.-C. Zhang, Physica (Amsterdam) **153-155C**, 21 (1988).

[6]R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, G. F. Brennert, G. P. Espinosa, R. J. Cava, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **38**, 9299 (1988).

[7]H. Lütgemeier and M. W. Pieper, Solid State Commun. **64**, 267 (1987).

[8]W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, R. J. Cava, B. Batlogg, and L. W. Rupp, Phys. Rev. B **39**, 831 (1989).

[9]J.-L. Hodeau, P. Bordet, J.-J. Capponi, C. Chaillout, and M. Marezio, Physica (Amsterdam) **153-155C**, 582 (1988).

[10]R. E. Walstedt, W. W. Warren, Jr., R. Tycko, R. F. Bell, G. F. Brennert, R. J. Cava, L. Schneemeyer, and J. Waszczak, Phys. Rev. B **38**, 9303 (1988).

[11]J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and Y. Xu, Phys Rev. B **38**, 8893 (1988).

[12]H. Yasuoka, T. Shimizu, T. Imai, S. Sasaki, Y. Ueda, and K. Kosuge, in Proceedings of the International Conference on Nuclear Methods in Magnetism, Munich, 1988 (to be published).

[13]A. J. Vega, W. E. Farneth, E. M. McCarron, and R. K. Bordia, Phys. Rev. B **39**, 2322 (1989).

[14]The frequency 29.3 MHz was chosen to obtain the maximum ^{63}Cu signal from the 28.6-MHz resonance while avoiding signals from the ^{65}Cu isotopic companions of the 30.6- and 31.3-MHz ^{63}Cu resonances.

[15]M. Mali, D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, and J. Hulliger, Phys. Lett. A **124**, 112 (1987).

[16]W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, Phys. Rev. Lett. **59**, 1860 (1987).

[17]The data are in reasonable agreement with recent measurements above 200 K by G. Balakrishnan, R. Dupree, I. Farnen, D. McK. Paul, and M. E. Smith, J. Phys. C **21**, L847 (1988).

[18]The apparent onset temperatures shown in the inset to Fig. 2 are roughly 3 K higher than the Meissner onsets due, we believe, to a systematic temperature error in our gas-flow temperature-control system.

[19]An indication that the effect persists in the presence of an applied field may be seen in ^{63}Cu relaxation data for oxygen-deficient single crystals obtained with NMR by M. Horvatic *et al.* (to be published).

[20]G. A. Thomas, J. Orenstein, D. H. Rapkine, M. Capizzi, A. J. Millis, R. N. Bhatt, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **61**, 1313 (1988); J. Orenstein and G. A. Thomas (unpublished).

[21]S. S. P. Parkin, E. M. Engler, V. Y. Lee, and R. B. Byers, Phys. Rev. B **37**, 131 (1988); D. C. Johnston, S. K. Sinha, A. J. Jacobson, and J. M. Newsam, Physica (Amsterdam) **153-155C**, 572 (1988).

[22]See, for example, R. J. Birgeneau, M. A. Kastner, and A. Aharony, Z. Phys. B **71**, 57 (1988).

[23]A. Narath, in *Hyperfine Interactions,* edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 287.

[24]G. Shirane *et al.*, Phys. Rev. Lett. **59**, 1613 (1987); K. B. Lyons *et al.*, Phys. Rev. Lett. **60**, 732 (1988).

[25]M. Takigawa, P. C. Hammel, R. H. Heffner, and Z. Fisk (unpublished).