NQR and NMR Studies of Spin Dynamics in High $T_c$ Superconducting Cuprates

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Recent NQR and NMR studies of Cu spin dynamics in metallic YBa$_2$Cu$_3$O$_{6+x}$, and other superconducting cuprates, are reviewed. The Cu nuclear relaxation rates are shown to be inconsistent with weak correlation (band) theory and the Korringa relation, but the Cu spins retain important characteristics of itinerancy. These include pairing of the Cu d-spins in the superconducting state and strong sensitivity of the Cu spin dynamics to changes in carrier concentration associated with variation of the oxygen content. Samples of reduced oxygen content ($T_c = 60$ K) are found to contain a high concentration of Cu$^{+2}$ Cu(1) sites associated with “full chain-empty chain” vacancy ordering. These samples also exhibit remarkable precursory suppression of planar Cu(2) nuclear relaxation above $T_c$.

Key words: NMR, NQR, Nuclear relaxation, Spin fluctuations, Superconductivity.

1. Introduction

Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) have emerged as key techniques for experimental study of high $T_c$ superconducting copper oxides. The reasons are directly related to the need to understand the Cu spin dynamics and their role in the mechanism of superconductivity in these materials. The magnetic phenomena are intimately connected with the unusual crystal structures of YBa$_2$Cu$_3$O$_{7-x}$, and other superconducting cuprates. Figure 1, illustrating the particular case of YBa$_2$Cu$_3$O$_{6+}$, shows the characteristic two-dimensional CuO planes in which the Cu electronic configuration is close to 3$d^9$. The d-hole occupies primarily a state with $d_{x^2-y^2}$ symmetry whose lobes are directed along the Cu–O bond direction. In YBa$_2$Cu$_3$O$_{6+}$, a fifth oxygen neighbor forms a bridge between the planar Cu(2) and Cu(1), a four-fold coordinated Cu site situated in one-dimensional CuO chains. The additional holes required by the average Cu valence (+2.333) do not occupy Cu d-states, but rather introduce holes in the oxygen p$_z$ orbitals directed along the Cu–O bond axis. The development of metallic (and superconducting) properties is associated with the presence of these extra holes.

Many key issues in the high $T_c$ cuprates revolve around the magnetic character of Cu, especially in the CuO planes, and the interactions between holes occupying Cu-d and O-p orbitals. Two extreme models can easily be formulated. In the case of strong electron-electron correlation energies and relatively weak Cu–O interactions the Cu-d states would be localized and carry a local spin moment while the metallic character is provided by itinerant O-p states. Indeed, in YBa$_2$Cu$_3$O$_{6+}$ for which the p-holes are absent, the d-states are localized in Cu$^{+2}$ ions and the compound is an antiferromagnetic insulator. The opposite limit, weak correlation and strong electron transfer, is the regime of conventional electron band theory. In this case, one does not distinguish between Cu and O holes which form a common, heavily hybridized p-d band.

The highly local nature of NQR and NMR experiments makes possible selective measurement of static and dynamic electron magnetism at distinct crystallographic sites in the structure. Thus, not only is it possible to probe the local properties of different elemental sites (Cu, O or Y), but one can selectively study, for example, Cu(1) or Cu(2) in YBa$_2$Cu$_3$O$_{6+}$. In each case, the local electronic magnetism couples to the nuclei via magnetic hyperfine interactions producing spin-lattice relaxation in NMR or NQR and resonance (Knight) shifts of NMR lines. In this paper we review the experimental situation for the system...
Fig. 1. Orthorhombic unit cell of YBa$_2$Cu$_3$O$_{7-0}$ showing local coordination of Cu atoms (cross-hatched). Small open circles denote O, shaded circles denote Ba, and large open circles at cell corners denote Y atoms.

YBa$_2$Cu$_3$O$_{6+x}$. It should come as no surprise that the experiments reveal that these materials are not well approximated by either extreme case described above. Rather, they fall into the fascinating, but difficult regime where competing electron correlation and transfer effects are of comparable importance.

II. NQR and NMR Spectra: YBa$_2$Cu$_3$O$_{7-0}$

The unit cell of YBa$_2$Cu$_3$O$_{7-0}$ shown in Fig. 1 contains two Cu(2) sites in the CuO$_2$ planes and one Cu(1) site in the CuO chain. The local symmetry of each site is orthorhombic, but the Cu(2) sites are nearly tetragonal. The c-axis is parallel to the long axis of the unit cell. The electric field gradients (efg) at the two sites are quite different, and well-separated $^{63,65}$Cu NQR lines are observed as shown in Figure 2a. The $^{63}$Cu frequencies $v_{63}$ at 100 K are 22.05 MHz for Cu(1) and 31.48 MHz for Cu(2). The frequency ratio $v_{63}/v_{65}$ for the two Cu isotopes agree within experimental error with the ratio of the nuclear quadrupole moments for the isotopes. Thus there is no evidence of an internal magnetic field due to static magnetic order in this compound.

The $^{63,65}$Cu NMR spectrum of randomly oriented YBa$_2$Cu$_3$O$_{7-0}$ powders is very broad. At fixed frequency ~80 MHz, the central $\pm 1/2$ transition of the quadrupole-broadened powder pattern extends over about 5 kOe for each isotope. Fortunately, however, the total magnetic susceptibility of YBa$_2$Cu$_3$O$_{7-0}$ is sufficiently anisotropic that finely divided powders may easily be aligned with parallel c-axis in a magnetic field of a few tesla. In Fig. 3 we show some examples of $^{63}$Cu NMR lines obtained with oriented powders fixed in epoxy resin. The combination of NQR and NMR spectra such as those shown in Figs. 2a and 3 permits determination of the complete efg and Knight shift tensors for Cu(1) and Cu(2) in YBa$_2$Cu$_3$O$_{7-0}$ [1–3].

Far below the superconducting transition temperature, the spin susceptibility and the corresponding
susceptibility inferred from spin-lattice relaxation measurements.

III. Spin Dynamics in YBa$_2$Cu$_3$O$_{7.0}$: Nuclear Relaxation Rates

The spin-lattice relaxation rate can be expressed very generally in terms of the imaginary part of the generalized susceptibility $\chi''(q, \omega_0)$:

$$\nu^{-1}(T)\propto N_{\text{QR}} = \frac{3k_B}{\gamma_e^2 \hbar^2 \omega_0} \sum_q \left\{ [A_x + 2Bf_2(q)]^2 + [A_y + 2Bf_2(q)]^2 \right\} \chi''(q, \omega_0), \quad (1)$$

where $A_x$ and $A_y$ are the on-site hyperfine fields perpendicular to the axis of quantization, and $B$ is the isotropic Cu → Cu transferred hyperfine field. The form factor $f_2(q)$ for the transferred coupling is

$$f_2(q) = \cos(q_x a) + \cos(q_y b). \quad (2)$$

Its magnitude depends on the wave functions according to

$$B = \text{const} |\psi_{4s}(0)|^2 \langle 4s|3d\rangle^2 / \Delta E_2^2, \quad (3)$$

where $\Delta E_2$ is an appropriate excitation energy. The remaining symbols have the usual meanings. If the spins on oxygen neighbors fluctuate independently, that is if they do not form local singlets with the Cu d-spins, there will be an additional term due to the O → Cu transferred hyperfine field.

In ordinary metals, the hyperfine field is usually dominated by a single on-site contribution, and if electron-electron interactions are neglected, the susceptibility sum is given by

$$\sum_q \chi''_S(q, \omega_0) = \pi \chi''(0, 0) N(E_F) \hbar \omega_0. \quad (4)$$

The relaxation rate then takes the familiar form

$$\nu^{-1}(T)\propto \frac{3\pi k_B}{\hbar} \left\{ A_x^2 + A_y^2 \right\} N^2(E_F) \hbar \omega_0 \quad (5)$$

and is related to the Knight shift by the Korringa relation

$$\nu^{-1}(T)\propto \frac{(12\pi k_B/\hbar)(\gamma_e/\gamma_n)^2}{K^2}. \quad (6)$$

The validity of (5) and (6), with respect to both the value of $(T_1 T)^{-1}$ and constancy of $T_1 TK^2$ is therefore a direct test of the effects of electron correlation and exchange on the low frequency, non-uniform susceptibility. In the particular case of YBa$_2$Cu$_3$O$_{7.0}$, $K$ is independent of temperature in the normal state [6] so that if electron correlation effects are negligible, we
should expect to find \((T_i T)^{-1} \sim \text{constant}\) at the value given by (5) and (6).

Experimental values of \((T_i T)^{-1}\) obtained by NQR [7] for Cu(1) and Cu(2) are plotted versus temperature in Figure 4. Similar data may be obtained from NMR measurements on oriented powders [8]. It is immediately evident that the expected Korringa behavior \((T_i T)^{-1} = \text{constant}\) is not observed for either Cu site in the normal state. For Cu(1), \((T_i T)^{-1}\) increases slightly with increasing temperature while for Cu(2), \((T_i T)^{-1}\) decreases rapidly from its value at \(T_c\).

In addition to the anomalous temperature dependences of \((T_i T)^{-1}\) for Cu(1) and Cu(2), the magnitudes of the relaxation rates near \(T_c\) are enhanced relative to the predictions of the Korringa relation, (6). Taking the value \(K = 0.30\%\) for Cu(2) with the magnetic field perpendicular to the c-axis [3], we obtain \((T_i T)^{-1}\) \(\approx 1.8 (s K)^{-1}\). (In this calculation we introduce a factor \(1/4\) in the right-hand side of (6) to account for the fact that the transverse hyperfine field is dominated by the contributions from 4 near-neighbor Cu atoms [5] whose spins are assumed to be uncorrelated.) This corresponds to an enhancement at 100 K of about 14 with respect to the \(q = 0\) susceptibility represented by the Knight shift. The latter is, itself, modestly enhanced as we discuss shortly. The enhancement becomes progressively smaller at higher temperatures for Cu(2) while for Cu(1), for which the relaxation rate is comparable with Cu(2) at 100 K, there is no corresponding decrease in enhancement. Enhancements of more than an order of magnitude with respect to the non-interacting case are also inferred from band theory using (5) and calculated values [9] of \(N(E_F)\). Thus we can conclude that the relaxation behavior is inconsistent with the (band) model of strong electron transfer and weak correlation [10].

The nuclear relaxation rates have the further property of high anisotropy. Our measurements [8, 10] on oriented powders yield a value 3.6 for the ratio of the rates with the magnetic field perpendicular and parallel to the c-axis. This ratio can be understood using the analysis of Mila and Rice applied to the Knight shift data of Durand et al. [3].

As the temperature is lowered below \(T_c\), the rates for both Cu sites exhibit a sharp decrease, although the decrease is much more rapid for Cu(2) than for Cu(1). For neither site do the data show any indication of the so-called “coherence factor peak”, a sharp rise in relaxation rate just below \(T_c\) that is characteristic of BCS superconductors with s-wave pairing [11]. The rapid decrease of \((T_i T)^{-1}\) below \(T_c\) shows that gaps of some form, develop in the spin fluctuation spectra at each Cu site. But the exact nature of the gaps are still undetermined because it has not been possible to extract any simple temperature dependence for \((T_i T)^{-1}\).

At sufficiently low temperatures, the observed relaxation rate tends to a nearly constant value whereas theory predicts that the rate should go to zero at \(T = 0\). The background process is stronger for Cu(1) sites than for Cu(2) and may be due to extrinsic paramagnetic moments on or near the chains. But the background relaxation process and its temperature dependence at higher temperatures are not understood quantitatively and this has prevented determination of the intrinsic temperature dependence from the observed rates. Whatever the nature of the gaps in the spin fluctuation spectrum below \(T_c\), the effective gaps sensed at the Cu(1) sites is substantially different and effectively smaller than that measured at the Cu(2) sites.

Given the foregoing experimental facts of nuclear relaxation in the normal and superconducting states of \(\text{YBa}_2\text{Cu}_3\text{O}_7\), we now discuss the significance of the relaxation enhancement and its temperature dependence. We emphasize first that the “ordinary”, static, uniform spin susceptibility \(\chi_s(0, 0)\) is enhanced only modestly. Electronic band structure calculations [9] yield a value \(N(E_F) \sim 2.8 (\text{eV spin formula unit})^{-1}\).
for the total electronic density of states. This corresponds to a spin susceptibility \( \chi_s'(0,0)_\text{ba} \sim 1.8 \times 10^{-4} \) emu (mole formula unit)\(^{-1} \). From their analysis of the observed susceptibilities and Knight shifts, Mila and Rice [5] determine an "experimental" value \( \chi_s'(0,0) = 0.25 \times 10^{-4} \) emu (mole formula unit)\(^{-1} \) so that the enhancement \( \chi'_s(0,0)_{\text{expt}}/\chi_s'(0,0)_\text{ba} \sim 1.8 \). In contrast, the integrated dynamic susceptibility \( \Sigma \chi'_s(q, \omega_0) \) is enhanced by more than an order of magnitude relative to the non-interacting model. Reconciliation of these observations requires that additional enhancement of \( \chi'_s(q, \omega_0) \) occur at non-zero \( q \)-values of the form a peak around some value \( q = Q_0 \). In turn, this implies the presence of antiferromagnetic fluctuations of mean wave-vector \( \sim Q_0 \).

Enhancement of the low frequency, non-uniform susceptibility at the Cu sites by antiferromagnetic fluctuations would appear to conflict with recent relaxation data [12, 13] for \( ^{89}\text{Y} \) and for \( ^{17}\text{O} \) at the planar O(2) and O(3) sites. (It is argued that \( ^{89}\text{Y} \) essentially probes the electronic states on O(2) and O(3) [12].) For these nuclei the relaxation is only weakly enhanced and the temperature dependence is governed by the Korringa behavior \((T/T_\text{K})^{-1} = \text{const} \). One interpretation of the different spin dynamics at O and Cu relaxation might be based on a model of extreme correlation in which the two sites probe distinct systems of electrons – nearly localized d-spins at Cu and itinerant, weakly interacting p-electrons on the O. However, when the expected strong p-d hybridization is taken into account, it is not at all clear how the two groups of electrons could retain their individual dynamics. Further, the suppression of Cu relaxation observed below \( T_c \) (Fig. 4) shows that the Cu spins are intimately involved with the superconducting condensed state. Takigawa et al. [13] and Shastry [14] have recently suggested an alternative explanation that is closer in spirit to a highly correlated, but still single-band description of the electron system. These authors have emphasized the role of the form factor for the Cu \( \rightarrow \) O transferred hyperfine field given by

\[
f_1(q) = 1 + \cos(q_x a) + \cos(q_y a) + \cos(q_z a).
\] (7)

The essential point is that the oxygen form factor vanishes around the wave vector \((\pi/a, \pi/b)\) where a peak in \( \chi''_s(q, \omega_0) \) might be expected for antiferromagnetic spin fluctuations that are commensurate or nearly commensurate with the lattice. In contrast, the Cu form factor given by (2) is \( \sim 2 \) near these \( q \)-values. Thus, the distinction between Cu and O nuclear relaxation measurements is that they probe different regions of \( q \)-space rather than different points in real space as in a two-band model. In particular, the Cu relaxation is sensitive to antiferromagnetic fluctuations while the O relaxation is sensitive mainly to regions of low \( q \)-values where, as we have already seen, the susceptibility enhancement is small.

The foregoing interpretation of the nuclear relaxation rates for Cu and O in the normal state leads to a further conclusion concerning spin excitations in the superconducting state. Below \( T_c \), the relaxation rates for both Cu and O decrease rapidly with decreasing temperature and, remarkably, the temperature dependence is the same for the two nuclei [13]. In terms of the one band model, this means that \( \chi'_s(q, \omega_0) \) is suppressed uniformly at all \( q \)-values. The Cu relaxation rate is much more strongly enhanced at \( T_c \) than the O rate so that enhancement of the Cu rate must be preserved in the superconducting state, i.e. the dynamic susceptibility of quasiparticles excited in the superconducting state is essentially that characteristic of the normal state electrons at \( T_c \). We believe that this experimental observation is inconsistent with suggestions [15] that the rapid decrease of \((1/T)(\omega_0)\) is due, in part, to collapse of the enhancement as the superconducting gap develops.

**IV. Effect of Oxygen Concentration**

One of the most important characteristics of the \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) system is the strong dependence of its electronic properties on oxygen concentration \((x)\). Whereas \( \text{YBa}_2\text{Cu}_3\text{O}_{7.0} \) is the well-known 90 K superconductor, \( \text{YBa}_2\text{Cu}_3\text{O}_{6.0} \) is an insulating antiferromagnet with a Neel temperature greater than 400 K. Structural studies have established that oxygen vacancies generated by reducing \( x \) are located primarily in the chains. The limiting case \( \text{YBa}_2\text{Cu}_3\text{O}_{6.0} \) corresponds to a complete absence of chain oxygens so that Cu(1) is two-fold coordinated with valence Cu\(^+\). As \( x \) decreases below \( x = 1 \), the carrier (hole) concentration decreases, but the quantitative relation between the concentrations of carriers and oxygen is not yet understood in detail. The value of \( T_c \) generally drops with decreasing \( x \), but in samples from which oxygen is removed at a relatively low temperature, a wide \( "T_c\) plateau" develops whereby \( T_c \) is essentially independent of concentration between \( x = 0.5 \) and \( x = 0.7 \) with a value \( \sim 60 \) K [16, 17]. The transition from metal to antiferromagnetic insulator occurs roughly in
the range $0.4 \leq x \leq 0.5$. Because the primary structural effects of varying oxygen concentration are confined to the chain layer and because the oxygen concentration can be very precisely controlled, variation of $x$ offers a powerful means to manipulate the electronic and magnetic properties of the planes while minimizing changes in their structure.

The effects of reduced oxygen concentration on the NQR spectrum of YBa$_2$Cu$_3$O$_{6+x}$ are illustrated in Figs. 2b and 2c. As $x$ decreases, the higher frequency Cu(2) resonance shifts to lower frequencies and broadens into a spectrum consisting of several discrete lines. By comparison, the Cu(1) resonance near 22 MHz develops only modest broadening and a small splitting ($\sim 600$ kHz). Most remarkable is the appearance of a new line whose frequency (31.4 MHz) is almost precisely the same as that of the Cu(2) resonance of YBa$_2$Cu$_3$O$_{6.0}$. We have concluded that this resonance arises from a distinct site (i.e. not Cu(2)) because its relaxation rate is reduced by about a factor 2000 below that characteristic of Cu(2) in YBa$_2$Cu$_3$O$_{7.0}$. The very low relaxation rate of this site is unlikely to be fully ordered and (ii) one does not know how the holes are distributed between the planes and the full chains.

The existence of two main classes of Cu(1) site (two-fold and four-fold oxygen coordination) implies corresponding classes of neighboring Cu(2) sites. This simple structural relationship is illustrated in Figure 5. Neglecting second and higher neighbor effects, we should then expect to find two Cu(2) NQR lines in a fully ordered sample. Unfortunately, the spectra of samples of reduced oxygen content become so broad (Figs. 2b and 2c) that the $^{63}$Cu resonance of one site can overlap the $^{65}$Cu resonance of another making it very difficult to analyze the spectra. To simplify the spectrum, we have therefore prepared a sample of YBa$_2$Cu$_3$O$_{6.64}$ enriched to nearly 100% $^{63}$Cu. As shown in Fig. 6, the Cu(2) spectrum does indeed consist of two dominant lines (27.5 MHz and 30.6 MHz at 100 K) with additional intensity forming a broader background centered at an intermediate frequency. Essentially the same frequencies have been reported by other workers [23] in samples of various concentrations. This suggests that the local environments of these sites are relatively insensitive to oxygen concentration. We speculate that the lower frequency line corresponds to Cu(2) neighbors of two-fold coordinated Cu(1). The lower frequency would be due, primarily, to the movement [24] of the bridging oxygen toward Cu(1) in two-fold coordination [25].

Spin dynamics at the Cu(2) planar sites are significantly affected by changes in oxygen concentration. In Fig. 7 we present data for $(T_e/T)^{-1}$ measured for the two dominant Cu(2) NQR lines in YBa$_2$Cu$_3$O$_{6.64}$...
and compare them with the corresponding rates measured in $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$. Both the magnitudes and the temperature dependences are affected. At the higher temperatures, $(T_1 T)^{-1}$ is increased relative to $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$. We have found from Knight shift measurements [26] that the spin component of the Knight shift is reduced so that we can conclude that the enhancement of $\chi_s(q, \omega_0)$ is increased in samples of lower oxygen content. This can be viewed as a slowing down of the fluctuating local hyperfine field in material that is closer to the antiferromagnetic phase, and it shows that the Cu spin dynamics are affected significantly by the presence of holes on the neighboring oxygen sites. This observation does not support the suggestion [27] that the Cu spin dynamics are governed by a Cu–Cu superexchange interaction ($J$) which is essentially unchanged from the insulating antiferromagnet to the 90 K superconductor. Since the relaxation rate in such a picture depends inversely on $J$, the present data would imply an even higher value of $J$ in the superconductor than in the insulator, unless there are compensating changes in the hyperfine couplings.

Finally we call attention to the remarkable pre-cursive behavior occurring well above $T_c$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$ [28]. Between 100 K and 200 K, the temperature dependence of $(T_1 T)^{-1}$ begins to weaken and the rates drop sharply as the temperature decreases below about 100 K. Careful investigation of the Meissner effect and rf shielding properties of our samples reveals no evidence of macroscopic superconductivity above 60 K. Although further work is required to achieve a complete understanding of the relaxation behavior, the data suggest the possibility that Cu spins begin to pair well above $T_c$ due to local superconducting fluctuations. As we have shown, the full chain-empty chain ordering creates regions that locally resemble the structure of the 90 K superconductor. Because the superconducting coherence length is comparable with the lattice constant and hence with the scale of the structural modulations, it is possible that the system begins to develop local pairing below 100 K.

V. Summary

The nuclear relaxation data reveal that the Cu spin dynamics in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ are profoundly influenced by both electron correlation and electron transfer effects. The experiments lead to a description of the magnetic behavior in terms of a band of delocalized, but highly correlated Cu-d–O-p electronic states. The generalized q-dependent susceptibility is enhanced at finite $q$-values by antiferromagnetic fluctuations, but for high oxygen concentrations the system shows no
sign of magnetic order and, presumably, the fluctuations have a relatively short correlation length. Below $T_c$, the susceptibility is uniformly suppressed at all $q$-values as the concentration of excited quasiparticles decreases.

When oxygen is removed from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the vacancies in the chain layer arrange so as to generate a high concentration of two-fold coordinated Cu$^+$ Cu(1) sites. The presence of these lower valence states tends to maintain a higher carrier concentration on the remaining sites and in the planes. The spin dynamics at the Cu(2) planar sites are affected significantly by the change in oxygen content, showing that the Cu-Cu superexchange interaction of the insulating antiferromagnet is increasingly irrelevant as $x \to 1$. Rather, the presence of carriers tends to increase the rate of spin fluctuation on the Cu sites due to the combined effects of d-electron itinerancy and d-p exchange interactions. At lower temperatures, but well above $T_c$, nuclear relaxation at Cu(2) is strongly inhibited in the 60 K superconductor. This suggests the development of spin-paired singlet states, possibly due to local superconducting fluctuations.

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[4] An exception to this is the so-called "planar state" for which the susceptibility retains its normal-state value below $T_c$ for some orientations and is reduced, but non-vanishing in others. See, for example, S. E. Barrett, D. J. Durand, C. H. Pennington, C. P. Slichter, T. A. Friedman, J. P. Rice, and D. M. Ginsberg (to be published) and A. J. Leggett, Rev. Mod. Phys. 47, 331 (1975).