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Static and dynamic Cu NMR tensors of $YBa_2Cu_3O_{7-\delta}$

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The authors report single-crystal Cu NMR data for $YBa_2Cu_3O_{7-\delta}$ ($T_c=90$ K). The shift tensor $K_{\alpha\alpha}$ ($\alpha=a,b,c$), the electric-field-gradient tensor $\nu_{\alpha\alpha}$, and the spin-lattice-relaxation-rate tensor are reported for Cu atoms in the planes and chains. The authors show that a model in which both chain and plane Cu are approximated as Cu^{2+} ions with a net spin account for the field-gradient tensor and the shift tensor at both chain and plane sites, and for the relaxation rate at the plane sites.

Understanding the new high-T_c superconductors will require a clear understanding of their normal states. For example, many theories involve a role for magnetism in providing high transition temperatures. In that case, should one think of the Cu atoms as being part of an ordinary conduction band which gives rise to electrical conductivity, in which case the copper atoms would lack permanent magnetic moments, or should they be thought of as magnetic ions (as is the case in the insulating antiferromagnet $YBa_2Cu_3O_6$) with the electrical conduction largely provided by holes on the oxygens? Or should they be viewed as belonging at some in between state described by a fluctuation spectrum? We report Cu NMR studies of a single crystal of $YBa_2Cu_3O_{7-\delta}$ ($T_c=90$ K) which probe the character of the normal state. We have measured the principal components and orientations of the frequency shift and field gradient tensors as well as the relaxation rates at 100 K for both the chain [Cu(1)] and plane [Cu(2)] nuclei. We show that it is straightforward to explain our data by a model in which the Cu(2) and probably the Cu(1) atoms are magnetic with electronic states similar to those of Cu^{2+} ions with net spin. Thus, we are on the magnetic-ion end of the spectrum of possibilities.

While the Cu^{2+} magnetic-ion picture describes many features of the chain and plane Cu atoms, we caution the reader that we consider this picture to be established only as a first approximation since the O holes have not been directly included in the details.[1]

The crystal (mass 1.2 mg) was mounted with its c axis perpendicular to a flat plexiglass support. The a-b axes were then oriented with polarized light so that data could be collected with the static field H_0 parallel either to the c axis or to the a-b axis. (Twinning in the crystal prevents alignment along only the a or b axis.) Data were collected with the methods described earlier.[2] T_c is 90 K (see Fig. 1).

The $YBa_2Cu_3O_{7-\delta}$ crystal was prepared as described previously[3] except for two features. (1) We reduced the amount of Cu in the flux by using a Y:Ba:Cu molar ratio of 1:4:9 instead of 1:4:10. (2) In the oxidation procedure, carried out in flowing oxygen, the sample was kept at 600 °C for 1 h cooled to 400 °C in about 1 h, held at 400 °C for four days, and then cooled rapidly to room temperature.

Table I gives the magnetic shift and electric-field-gradient tensors and the spin-lattice relaxation rates. $K_{\alpha\alpha}$ ($\alpha=a,b,c$) is the magnetic shift tensor[2] (positive K corresponds to a shift to higher frequency at fixed field), and $\nu_{\alpha\alpha}$ is related to the electric-field-gradient component $\partial^2V/\partial\alpha^2$ by $\nu_{\alpha\alpha}=(eQ/2h)\partial^2V/\partial\alpha^2$, where e is the electron charge and Q is the nuclear quadrupole moment. The tensors were obtained by exact diagonalization of the 4×4 Hamiltonian matrix of each Cu atom with the three transition frequencies measured at a static field of 81.1 kG.

We measured the spin-lattice relaxation rate by observing the spin echo at a time τ after a 180° inversion pulse. For a spin-$\frac{3}{2}$ system, the size of the echo versus τ consists in general of a sum of three exponentials. We characterize this multiple exponential relaxation by a rate W_1 instead of $(1/T_1)$ customarily used when the relaxation is given by a single exponential. If we assume a magnetic relaxation mechanism independent of frequency, the reciprocals of the three time constants are given in terms of the fundamental rate W_1 as $2W_1/3$, $2W_1$, and $4W_1$. W_1 for Cu(1) and Cu(2) is given in Table I with H_0 oriented along the a, b, and c crystal axes. Figure 1(a) shows data for the Cu(2) $\frac{1}{2}\rightarrow(-\frac{1}{2})$ transition and a theoretical fit in which only one parameter W_1 is adjusted. Figure 1(b) shows that the *same* W_1 also fits the data for the $\frac{3}{3}\rightarrow\frac{1}{2}$ and $(-\frac{3}{2})\rightarrow(-\frac{1}{2})$ transitions, demonstrating convincingly that the relaxation is magnetic, and that W_1 is independent of frequency.[4]

We now present the relaxation data in terms of a model in which the nucleus is acted on by a magnetic field $h_\alpha(t)$ ($\alpha=a,b,c$), with a, b, and c components that fluctuate in time.[5] Assuming an exponential correlation function with correlation time τ_0, one can derive an expression for W_1 when the static field lies along the c direction, $W_{1c}=\frac{3}{2}\gamma_n^2[(\overline{h_a^2})+(\overline{h_b^2})]\tau_0$ where $\overline{h_\alpha^2}$ is the mean-square value of $h_\alpha(t)$ and γ_n the nuclear gyromagnetic ratio. Since similar expressions hold for W_{1a} and W_{1b}, one can determine from W_{1a}, W_{1b}, and W_{1c} the three quantities $\overline{h_a^2}\tau_0$, $\overline{h_b^2}\tau_0$, and $\overline{h_c^2}\tau_0$. For the planes we find for $\frac{3}{2}\gamma_n^2\overline{h_\alpha^2}\tau_0$ ($\alpha=a,b,c$, respectively) 0.53 ± 0.05, 0.53 ± 0.05, and 4.2 ± 0.3 msec^{-1}, and for the chains 0.3 ± 0.16, 0.5 ± 0.13, and 0.6 ± 0.08 msec^{-1}, giving the following for

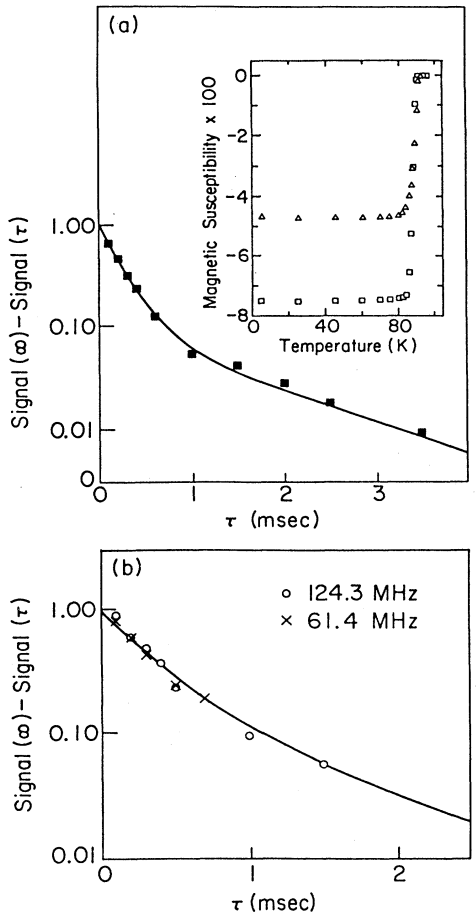

FIG. 1. (a) Inset: The magnetic susceptibility of the crystal vs temperature showing a sharp superconducting transition at 90 K and a complete Meissner effect, $H=16$ Oe$\perp c$ axis (△, field cooled; □, zero-field cooled). Main figure: The spin-lattice relaxation of the ^{63}Cu(2) nuclei for the transitions (a) $\frac{1}{2}\rightarrow(-\frac{1}{2})$, (b) $\frac{3}{2}\rightarrow\frac{1}{2}$ and $(-\frac{3}{2})\rightarrow(-\frac{1}{2})$. The points are the data plotted as the $\log_{10}$ [signal (∞) − signal (τ)], where τ is the time after an inversion pulse. The solid line in (a) is a theoretical fit to the data assuming a magnetic relaxation mechanism independent of frequency (see text) where the fundamental rate W_1 has been adjusted to yield the best agreement with the data ($W_1=1.05$ msec^{-1}). The solid line in (b) is the theoretical prediction for these transitions with the same W_1 as deduced in (a).

the two sites.

$$\text{Planes: } (\overline{h_c^2}/\overline{h_a^2})^{1/2}=2.8\pm0.2\,. \tag{1a}$$

$$\text{Chains: } (\overline{h_a^2}/\overline{h_b^2})^{1/2}\cong0.7\,. \tag{1b}$$

We consider first the electric-field-gradient tensor. A formal valence description makes oxygens O^{2-}, the Cu in the plane Cu^{2+}, the Cu in the chain Cu^{3+}. However, it is very costly in energy to convert a Cu^{2+} to a Cu^{3+}. Thus, the formal valence picture may not be accurate. Bleaney and co-workers[6,7] show from electron-spin-resonance studies that a single hole in the d shell produces an axial electric-field gradient at the ^{63}Cu nucleus of some 70 MHz, the sign of which changes if the hole is in the x^2-y^2 as opposed to the $3z^2-r^2$ state. Thus the field gradient of a Cu^{3+} should differ from that of a Cu^{2+} by approximately 70 MHz, much larger than the measured difference of the Cu(1) and Cu(2) field gradients (assuming that they have the same sign). We therefore start with the hypothesis that the valence of the Cu(1) is close to that of the Cu(2); hence close to Cu^{2+}, to see if we can fit the data.

TABLE I. The shift, field-gradient, and relaxation tensors.

	Plane	Chain
K_{aa} (%)	0.59 ± 0.04	1.38 ± 0.07
K_{bb}	0.59 ± 0.04	0.55 ± 0.07
K_{cc}	1.267 ± 0.001	0.60 ± 0.04
ν_{aa} (MHz)[a]	$+15.94\pm0.05$[b]	-19.03 ± 0.07[a]
ν_{bb}	$+15.56\pm0.05$[b]	19.17 ± 0.07[a]
ν_{cc}	-31.50 ± 0.05	-0.16 ± 0.03
W_{1a} (msec^{-1})	4.7 ± 0.3	1.1 ± 0.1
W_{1b}	4.7 ± 0.3	0.9 ± 0.1
W_{1c}	1.05 ± 0.1	0.8 ± 0.1

[a]Since the experiment does not determine the sign of the field gradient, the values of ν_{aa} at either the chain or the plane sites could all be reversed.

[b]For the plane, ν_{aa} and ν_{bb} could be interchanged. For the chain, ν_{aa} and ν_{bb} were assigned by the symmetry of the shift tensors.

We can apply the Cu^{2+} model to calculate the electric-field-gradient tensor. In a recent calculation by Adrian our earlier data[2] is analyzed in a somewhat different manner, but he reaches essentially the same conclusion.[8] In addition, an experimental determination of the electric-field-gradient tensor with oriented powders has been published by Shimizu *et al.*[9] We add the axial field gradient ν_{axial} from the d-shell Cu hole to the field gradient of the other atoms in the lattice treated as point ions. We assume that the plane oxygens are O^{2-}, but that there is one extra hole per Cu residing on the chain and bridge oxygens making them each on average $O^{5/3-}$. We treat ν_{axial} and the Sternheimer factor γ_S as variables, adjusting them to give the correct values of ν_{cc} at both sites. We find $\nu_{\text{axial}}=71.7$ MHz, and $\gamma_S=10.40$, giving the following for $(\nu_{aa},\nu_{bb},\nu_{cc})$.

Chain: -17.6, $+17.6$, and 0 MHz.

Plane: $+13.1$, $+18.4$, and -31.5 MHz.

These values are remarkably close to those of Table I.[10] The value of γ_S is quite reasonable. The value of 71.73 MHz for ν_{axial} would make the radial average $\langle 1/r^3\rangle=6.6$ a.u., close to the value 6.30 a.u. quoted by Bleaney and co-workers[6,7] for Cu^{2+}. Note that the electric-field gradients not only show that all the Cu atoms are close to Cu^{2+} but also show that the hole in the Cu(2) [Cu(1)] d shell is in the x^2-y^2 [y^2-z^2] state, which gives the correct sign for the ν_{axial} contribution relative to the lattice contribution (whose sign is known). These results fit theoretical expectations.[11–13]

We have found that we can understand the shift and re-

laxation data of the Cu(2) in terms of a model where the Cu ions have valence Cu^{2+} and a net spin $\frac{1}{2}$. Calculations by McMahan, Martin, and Satpathy[11] support this limit and give the energies of a hole in the various d states as $E_{xy}=2.0$ eV, and $E_{xz}=E_{yz}=2.2$ eV, measured from the ground state $E_{x^2-y^2}$.

We expect the electron spins of neighboring Cu atoms to be strongly exchange coupled to each other and to holes on the O atoms. Thus, the orientation of an individual Cu electron spin fluctuates rapidly, contributing to the Cu nuclear relaxation.

We expect two contributions to the shift, one from the electron orbital moment (the chemical shift) and one from the electron spin (the Knight shift in metals).[5] By use of β for the Bohr magneton, the orbital contribution $K^L_{\alpha\alpha}$ is given by[5]

$$K^L_{\alpha\alpha}=4\beta^2\left\langle\frac{1}{r^3}\right\rangle\sum_n\frac{|(0|L_\alpha|n)|^2}{E_n-E_0}$$
$$=2\left\langle\frac{1}{r^3}\right\rangle\chi^L_{\alpha\alpha},\quad \alpha=a,b,c, \tag{2}$$

where $\chi^L_{\alpha\alpha}$ is the orbital contribution to the magnetic susceptibility. If we take E_{xz} as 10% greater than E_{xy} (Ref. 11) and evaluate the matrix elements of L_α in Eq. (2), we get

$$K^L_{cc}/K^L_{aa}=4.4. \tag{3}$$

Writing the electron-spin contribution to the Hamiltonian[6,7]

$$\hat{H}=\sum_\alpha S_\alpha A_{\alpha\alpha} I_\alpha, \tag{4}$$

we get the spin contribution to the shifts as

$$K^S_{\alpha\alpha}=\frac{A_{\alpha\alpha}\chi^S_{\alpha\alpha}}{\gamma_e\gamma_n\hbar^2}, \tag{5}$$

where $\chi^S_{\alpha\alpha}$ is the spin susceptibility of the Cu atom defined by the relationship $\langle\mu^S_\alpha\rangle=\chi^S_{\alpha\alpha}H_0$ between the time-averaged electron-spin magnetic moment $\langle\mu^S_\alpha\rangle$ induced on the Cu atom and the applied field H_0 when acting along the α principal axis. Treating the Cu^{2+} as axially symmetric about the z axis, Bleaney, Bowers, and Pryce[6] get

$$\frac{A_{zz}}{\gamma_e\gamma_n\hbar^2}=\left[-\kappa-\frac{4}{7}-\lambda\left(\frac{6}{7}\frac{1}{E_{xz}}+\frac{8}{E_{xy}}\right)\right]\left\langle\frac{1}{r^3}\right\rangle, \tag{6a}$$

$$\frac{A_{xx}}{\gamma_e\gamma_n\hbar^2}=\left[-\kappa+\frac{2}{7}-\frac{11}{7}\frac{\lambda}{E_{xz}}\right]\left\langle\frac{1}{r^3}\right\rangle, \tag{6b}$$

where λ is the Cu spin-orbit coupling parameter ($\lambda=-828.7$ cm^{-1} for the free ion, typically reduced to a value ~ -710 cm^{-1} in solids), and κ is the core polarization coefficient typically 0.25–0.32. $\langle 1/r^3\rangle$ is typically 6.3 a.u., reduced from the value 7.5 a.u. for the free atom.[6] Using $E_{xy}\cong E_{xz}=E_{yz}=2.0$ eV and $\lambda=-710$ cm^{-1}, one finds $\lambda/E_{xy}=-4.4\times10^{-2}$. This gives

$$A_{zz}=(-\kappa-0.181)\gamma_e\gamma_n\hbar^2\left\langle\frac{1}{r^3}\right\rangle,$$
$$A_{xx}=(-\kappa+0.355)\gamma_e\gamma_n\hbar^2\left\langle\frac{1}{r^3}\right\rangle, \tag{7}$$

$\bar{K}$, the average shift over the a, b, and c directions, is positive. Equations (5) and (7) with reasonable κ's make the spin contribution negative. Therefore, in this model the experimental shifts cannot be solely from electron spin in an x^2-y^2 orbit. While Eq. (2) shows that the orbital contribution to $\bar{K}$ is positive, Eq. (3) shows that it is much more anisotropic than the 2 to 1 found experimentally. Thus in this model *both* an orbital and a spin shift are needed.

Since in our model the electron orbital moment does not fluctuate in time, we attribute the relaxation to fluctuations in the electron-spin orientation. From (4) we can write $h_\alpha(t)=-A_{\alpha\alpha}S_\alpha(t)/\gamma_n\hbar$ giving

$$\overline{h^2_\alpha}(t)=\left(\frac{A_{\alpha\alpha}}{\gamma_n\hbar}\right)^2\overline{S^2_\alpha}=\frac{A^2_{\alpha\alpha}}{\gamma_n^2\hbar^2}\left(\frac{1}{4}\right). \tag{8}$$

Taking $(\overline{h^2_c}/\overline{h^2_a})^{1/2}=|A_{zz}/A_{xx}|$ we use our measurements of $\overline{h^2_\alpha}\tau_0$ to conclude that $\kappa=0.214\pm0.009$, slightly below typical values.[7] We then find $|K^S_{cc}/K^S_{aa}|=(2.8\pm0.25)\chi^S_{cc}/\chi^S_{aa}$. Assuming that $\chi^S_{\alpha\alpha}$ is isotropic, we can then write

$$K^L_{cc}+K^S_{cc}=1.267\%=4.4K^L_{aa}-2.8K^S_{aa},$$
$$K^L_{aa}+K^S_{aa}=0.59\%, \tag{9}$$

to get

$$K^L_{aa}=0.41\%,\quad K^L_{cc}=1.79\%,$$
$$K^S_{aa}=0.19\%,\quad K^S_{cc}=-0.52\%. \tag{10}$$

Taking $\langle 1/r^3\rangle$ as 6.3 a.u., in Eq. (2), and K^L_{cc} above we get $E_{xy}=2.0$ eV in good agreement with the theoretical calculation of McMahan, Martin, and Satpathy.[11] Using (5), (7), and (10) we get $\chi^S=31.2\times10^{-29}$ emu/Cu. From (2) and (10) we find that the powder average of the orbital susceptibility $\langle\chi^L\rangle$ is $\langle\chi^L\rangle=10.2\times10^{-29}$ emu so that the total susceptibility per Cu(2) atom is 41.2×10^{-29} emu. Junod, Bezinge, and Muller[14] have measured the susceptibility of $YBa_2Cu_3O_{7-\delta}$. Correcting for core diamagnetism, they find χ of 27×10^{-29} emu/Cu, somewhat less than the 41.2×10^{-29} emu/Cu calculated above for the Cu(2). (Note in addition that their number may also include paramagnetism from O.)

Utilizing (7), (8), and the experimental value of $\frac{3}{2}\overline{h^2_a}$ we get $\tau_0=2.3\times10^{-15}$ sec which corresponds to an energy $\hbar/\tau_0$ of 2318 cm^{-1}. This energy is on the order of the exchange energy J of 1000 cm^{-1}, which we have measured by studying the transverse relaxation in our crystal[15] and which has been deduced by Lyons, Fleury, Schneemeyer, and Waszczak[16] from light-scattering experiments for crystals with $\delta\cong1$. τ_0 is therefore on the order of the precession period of an electron spin in the exchange field of a neighbor, perhaps, by coincidence. Two recent papers on $\delta\cong1$ material report the antiferromagnetic resonance of Cu(2) nuclei.[17]

For the Cu(1) atoms, the shift tensor is, apart from its orientation change, very similar to that of the Cu(2). The analysis of the planes shows that K is largely a chemical shift, implying that the structure of the ground and excited states of the Cu(1) and Cu(2) are very similar. We

therefore postulate that the Cu(1) are also Cu^{2+} ions with a net spin, the hole ground state being y^2-z^2. The fact that $K_{cc}/K_{aa}=2.4$ rather than 4.4 shows that there must be a spin contribution to the Cu(1) shift tensor (i.e., the shift is not solely an orbital effect). One would at first sight suppose the T_1 anisotropy of the Cu(1) would be similar to that of the Cu(2) with $|h_a/h_c| \approx 2.8$ instead of the $|h_a/h_c| \cong 0.7$ found experimentally. However, it is known that the Cu(1) T_1 has a very different temperature dependence than that of the Cu(2)'s,[18,19] implying a different mechanism. If that mechanism suppressed the relaxation by the Cu(1) electron spin (e.g., by shortening the correlation time τ_0), then we can still have a net Cu(1) electron spin. A candidate mechanism is the coupling of the Cu(1) nucleus to the spin of a hole on the bridge and chain oxygens via a transferred hyperfine coupling.

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[1]We have recently become aware of unpublished work by M. Takigawa, P. C. Hammel, R. H. Heffner, and Z. Fisk who have made NMR measurements of the Cu shifts in the 90-K material in the superconducting state. They believe aspects of their data show a direct O hole contribution.

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