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Single Crystal NMR Studies of High Temperature Superconductors

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Abstract

The authors report Cu NMR studies in the normal state of a single crystal of the T_c = 90 K superconductor $YBa_2Cu_3O_{7-\delta}$. The authors have measured the magnetic shift tensor, the electric field gradient tensor, the nuclear spin-lattice relaxation rate tensor, and the time dependence and functional form of the transverse decay. From these data they obtain information about the charge state and magnetic state of the Cu atoms, and the existence and size of the electronic exchange coupling between spins of adjacent Cu atoms.

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I. Introduction

Conventional or pre-Bednorz-Müller superconductors are now thoroughly understood. Superconductivity arises because of an electron-electron coupling via the lattice distortion produced by the attraction between the negative charge of the electron and the positive charge of the lattice ion cores. J. R. Schrieffer has called this the "bedspring effect," after the tendency of the distortion of the bedsprings when one person is in a bed to cause a second occupant to roll into the depression. However, theorists generally agree that this interaction (also called the electron phonon mechanism) cannot account for the much higher transition temperatures, T_c, of the post Bednorz-Müller materials. In searching for mechanisms of superconductivity, observers have called attention to the fact that the high T_c materials (such as $La_{1.85}Ba_{.15}CuO_4$) are very similar to other materials (e.g. La_2CuO_4) which exhibit magnetism. Is it possible that magnetism plays a role in the high T_c materials which is analagous to the role that lattice distortions play in conventional superconductors? In trying to answer such questions, one soon realizes that the high T_c materials are both very complex and also little studied. Thus, one does not understand the normal state of these materials at all well. In such a case, it is natural to try to bring to bear the queen of the spectroscopies, magnetic resonance, and in particular nuclear magnetic resonance (NMR).

In applying NMR, two types of questions have been asked. The first type explores the properties of the normal state. For example, do the Cu atoms possess permanent electron spin magnetic moments? The second focuses on the properties of the superconducting state. Here one can ask to begin with whether or not a Bardeen-Cooper-Schrieffer (BCS)-like theory applies. If it does, there are detailed predictions about the temperature dependence of the spin-lattice relaxation and of the Knight shift as a function of the type of electron pairing. In a material such as the famous $T_c \approx 90$ K superconductor, $YBa_2Cu_3O_{7-\delta}$ (with $\delta << 1$), one can study Y, Cu, or O NMR in principle. In fact, NMR

can be used to observe Cu in the Cu-O planes (so-called Cu(2)) or in the Cu-O chains (so-called Cu(1)).

In this paper, we report Cu NMR studies in the normal state of a single crystal of the $T_c = 90$ K superconductor $YBa_2Cu_3O_{7-\delta}$.[1-3] We denote the crystal axes by a, b, and c (c is normal to the Cu-O planes, b lies along the direction of the Cu-O chains). For both plane Cu(Cu(2)) and chain Cu (Cu(1)), we measured the magnetic shift tensor $K_{\alpha\alpha}$ (α=a,b,c), the electric field gradient $\nu_{\alpha\alpha}$ where $\nu_{\alpha\alpha} = (eQ/2h)(\partial^2 V/\partial\alpha^2)$, the spin-lattice relaxation rate tensor $W_1)_{\alpha\alpha}$ (defined below), and the form and time dependence of the transverse decay of the spin-echo envelope. From these data we learn information about the charge state and the magnetic state of the Cu atoms, and the existence and size of the electronic exchange interaction between spins of adjacent Cu atoms.

II. Experimental

The data reported in this paper were all obtained on a 1.2 mg single crystal.[2,3] The insert in Fig. 2a shows the Meissner effect measurements of the sample,[3] which demonstrate the sharpness of the transition and thereby the homogeneity of the sample. It was mounted with its flat face against a planar surface of a Plexiglass plate, thereby aligning the c-axis perpendicular to the plane of the Plexiglass face. The a and b axes were oriented by use of polarized light. We then carried out experiments with the static field H_0 parallel to the a, b, and c axes. Since the crystals twin, when H_0 is parallel to the a-axis, it is also parallel to the b-axis. This is shown in Fig. 1 which shows the (+ 1/2, - 1/2) transition with H_0 parallel to the a-b direction. We see two resonance lines from the Cu(1) atoms corresponding to H_0 parallel to both the a and the b directions. For the planes, we see only a single line since the site possesses nearly axial symmetry about the c-axis.

The experiments were carried out in a field of 81.1 kG and at a temperature of 100 K. Line shapes were for the most part determined by plotting the area of the spin echo as a function of frequency. (However, in some cases the lines were narrow enough to observe using the Fourier transform of the second half of the echo.) Spin-lattice relaxation was

observed by the inversion-recovery method. The apparatus was a homemade NMR spectrometer.

Since the spins of ^{63}Cu and ^{65}Cu are both 3/2, in general the spin-lattice relaxation consists of a sum of three exponentials. For a magnetic relaxation mechanism arising from magnetic fields $h_\alpha(t)$ (α=a,b,c) which vary with the time, t, the three exponentials can be described in terms of a single (for each orientation of the static field) rate constant W_1 as 2/3 W_1, $2W_1$, $4W_1$. For an exponential correlation function with correlation time τ_0, one finds for H_0 along z:

$$W_1)_z = \frac{3}{2}\gamma_n^2 (\overline{h_x^2} + \overline{h_y^2})\tau_0. \qquad (1)$$

where the bar over h_x^2 and h_y^2 indicates a time average. For an inversion recovery sequence applied to the (1/2, -1/2) transition, the relaxation involves only the two exponentials 2/3 W_1 and $4W_1$. Figure 2a shows the recovery for the (1/2, -1/2) transition of the Cu(2) with H_0 parallel to the c axis. The theoretical curve is fitted by adjusting only the t=0 intercept and the time scale since the ratio of the exponentials is determined by the initial conditions. Figure 2b shows the recovery for the (1/2, 3/2) and (-1/2, -3/2) transitions. The theoretical curve is calculated, with only the t=0 intercept as an adjustable parameter, from the value of $W_1)_c$ deduced from fitting Fig. 2a, thereby showing that $W_1)_c$ is determined by a magnetic rather than electric quadrupolar mechanism, and is independent of frequency from 60 MHz to 124 MHz.

III. Site Identification

Examination of the crystal structure shows that the Cu(2) atoms are at a site which is very nearly a four-fold axis about the c-direction. If one looks only at the nearest neighbor oxygens, the Cu(1) (chain) atoms have roughly a four-fold symmetry about the a-axis. The presence of six NMR lines found for each static field orientation shows that there are

two families of Cu NMR lines--one family for each of the two Cu sites. For each family of lines we use an exact computer diagonalization procedure to deduce the magnetic shift tensor, the electric field gradient tensor, and the spin-lattice relaxation rate tensor. The tensor components are given in Table I. One of these families of resonance lines has all three tensors axially symmetric about the c-direction and must therefore arise from the Cu(2) atoms. The other group of lines has a shift tensor which is axial about the a-axis, which is consistent with its arising from the Cu(1) atoms. Thus we assign the tensor components to the two Cu sites as indicated in the Table.

IV. The Cu Atom Electric Charge

Formal valence considerations suggest that the Cu(2) atoms are Cu^{2+} and the Cu(1) atoms are Cu^{3+}. However, since it is very costly in energy to convert a Cu^{2+} to a Cu^{3+}, one expects that the Cu(1) atoms may also be close to Cu^{2+}. It is known from the electron spin resonance studies of Bleaney, Bowers, and Pryce[4] that a single d-electron produces an electric field gradient of some 70 MHz at the Cu nucleus. Therefore, one might expect a substantial difference in the electronic contribution of the electric field gradient of Cu^{2+} compared to Cu^{3+}. We have found that we can fit our electric field gradient measurements quite well on the assumption that Cu(1) and Cu(2) are both Cu^{2+}. Frank Adrian[5] has independently come to the same conclusion in a thorough analysis based on our earlier data. Our analysis differs slightly from his. (For example, he assumes a value for the Sternheimer antishielding factor whereas we treat it as an unknown to be determined from fitting the data.) We assume that there is a hole in the Cu d-shell in the x^2-y^2 orbit for the Cu(2) and in the y^2-z^2 orbit for the Cu(1), where the x, y, z axes are parallel to the a, b, c axes respectively. Denoting its electric field gradient (properly oriented) as ν_{axial}, and denoting the Sternheimer factor for the Cu^{2+} ions as γ_S, we treat ν_{axial} and γ_S as unknowns. To achieve charge neutrality, we assign the hole which is removed from the Cu(1) atom in converting it from a formal valence of 3+ to an actual charge of 2+ equally to the four oxygen atoms adjacent to the Cu(1). Thus they each have a net charge of 5/3- and

the oxygens in the planes have a net charge of 2-. We then do a lattice sum to get the field gradient contributed by the ions. Combining the ionic contribution (multiplied by the unknown γ_S) with the Cu valence electron contribution ν_{axial}, we get the total field gradient tensor at both Cu sites. We now adjust the two unknowns ν_{axial} and γ_S to make the ν_{cc} of the chain and the ν_{cc} of the plane have the correct values. We then get for (ν_{aa}, ν_{bb}, ν_{cc}) the values (+13.1, +18.4, -31.5) MHz for the planes and (-17.6, +17.6, 0) MHz for the chains. These values are very close to the experimental values of Table I. For ν_{axial} we get 71.7 MHz, very close to the value for Cu^{2+} expected from ESR, and γ_S = 10.4, a reasonable value for Cu^{2+}. We therefore conclude that both Cu atoms are close to Cu^{2+}, with the d-shell hole in the x^2-y^2, and y^2-z^2 states for the Cu(2) and Cu(1) atoms respectively.

V. The Magnetic State of the Copper Atoms

To describe Cu metal, one uses band theory for the electrons. There are an equal number of electrons in the up-spin band states and the down-spin band states, so that individual Cu atoms lack a permanent spin magnetic moment. On the other hand, in insulators the Cu^{2+} ion has a net electron spin and associated magnetic moment. Such atoms have been studied extensively by electron spin resonance. In their classic paper on the theory of such ions, Bleaney, Bowers, and Pryce[4] outline the essential features. The Cu(1) and Cu(2) ions might be thought of in either of these two extremes (itinerant electrons in a band or localized electrons with a permanent magnetic moment). Or, one can consider the ions from the viewpoint of fluctuations, in which case the band model and permanent moment models correspond to the extremes of the fluctuation rate corresponding to fast and slow fluctuations respectively, with the possibility existing that the actual situation may lie somewhere in between. This approach has been developed extensively by Moriya.[6]

In discussing the permanent moment model, Bleaney et al. introduce the Hamiltonian describing the coupling of the nuclear spin components I_α (α=x,y,z) to the electron spin components S_α by

$$\hat{H} = \sum_{\alpha=x,y,z} I_\alpha A_{\alpha\alpha} S_\alpha \, . \tag{2}$$

If the ground state corresponds to a hole in the $d(x^2-y^2)$ state, if the energy $E_{x^2-y^2}$ is taken as zero, if E_{xy}, E_{xz}, E_{yz}, $E_{3z^2-r^2}$ are the energies of the other d-states, and if we assume axial symmetry about the z axis, the expressions of Bleaney et al. reduce to

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

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

where γ_e and γ_n are the electron and nuclear gyromagnetic ratios respectively, λ is the spin-orbit coupling parameter (-828.2 cm^{-1} in the free ion typically reduced to -710 cm^{-1} in a solid corresponding to $\langle 1/r^3 \rangle$, the average of $1/r^3$, being 6.3 a.u.), and κ describes the effect of core polarization (κ is typically between .25 and .32). McMahan, Martin, and Satpathy[7] have recently estimated E_{xy} = 2.0 eV, with $E_{xz} = E_{yz}$ = 2.2 eV. These make $|\lambda/E_{xy}| = 4.4\ 10^{-2}$. To appreciate the size of the $A_{\alpha\alpha}$'s it is useful to note that $\gamma_e \hbar \langle 1/r^3 \rangle$ for $\langle 1/r^3 \rangle$ = 6.3 a.u., a typical value, has the value 790 kG, a very large magnetic field.

If we consider the electron spin to be time dependent with components $S_\alpha(t)$ (α =x,y,z) the Cu nucleus experiences a time dependent magnetic field $h_\alpha(t)$ given by

$$h_\alpha(t) = - \frac{A_{\alpha\alpha} S_\alpha(t)}{\gamma_n \hbar} \, . \tag{4}$$

One then has that

$$\overline{h_\alpha^2}(t) = \frac{A_{\alpha\alpha}^2}{\gamma_n^2 \hbar^2} \overline{S_\alpha^2}$$

$$= \frac{A_{\alpha\alpha}^2}{\gamma_n^2 \hbar^2} \frac{1}{4} \qquad (5)$$

where the bar stands for an average over time. Thus one finds that

$$\overline{h_x^2} = \overline{h_y^2} = \overline{h_z^2} \left(\frac{A_{xx}}{A_{zz}}\right)^2 . \qquad (6)$$

If, then, the fluctuation of S_α in time gives rise to the spin lattice relaxation, we can utilize Eq. (6) to express the anisotropy in $W_1)_\alpha$ using Eq. (1). Or, one can use the three $W_1)_\alpha$'s of each site to derive the following ratios:

for the planes:

$$\sqrt{\frac{\overline{h_c^2}}{\overline{h_a^2}}} = 2.8 \pm 0.2 \qquad (7a)$$

for the chains:

$$\sqrt{\frac{\overline{h_a^2}}{\overline{h_c^2}}} \cong 0.7 \qquad (7b)$$

Utilizing the results of Eq. 7 in Eq. 6 then gives us the ratio of $|A_{xx}|$ to $|A_{zz}|$. If one assumes κ, and neglects the energy difference between E_{xy}, E_{xz}, and E_{yz}, one can then calculate the ratio of λ to E_{xy}, or if one assumes E_{xy} (for example, taking the 2.0 eV value of McMahan *et al.*), one can calculate κ. We have done the latter (E_{xy} = 2.0 eV) for the planes and find $\kappa = 0.21$, a reasonable value.

The orbital contribution to the shift tensor, $K^L_{\alpha\alpha}$ (i.e. the chemical shift) is

$$K^L_{\alpha\alpha} = 4\beta^2\left\langle\frac{1}{r^3}\right\rangle \sum_n \frac{|\langle 0|L_\alpha|n\rangle|^2}{E_n - E_0} \tag{8a}$$

$$= 2\left\langle\frac{1}{r^3}\right\rangle K^L_{\alpha\alpha} \tag{8b}$$

where $K^L_{\alpha\alpha}$ is the α component of the orbital contribution of the atom to the magnetic susceptibility. Likewise there is a spin contribution to the shift tensor.

Since the quantum thermodynamic average value of S_α, $\langle S_\alpha\rangle$ is related to the quantum thermodynamic average of the electron spin magnetic moment, $\langle\mu_\alpha\rangle$ by

$$\langle\mu_\alpha\rangle = -\gamma_e\hbar\langle S_\alpha\rangle$$

$$= \chi^S_{\alpha\alpha} H_0 \tag{9}$$

we can use Eq. 4 to write the spin contribution to the nuclear shift tensor

$$K^S_{\alpha\alpha} = \frac{\langle h\alpha\rangle}{H_0} = -\frac{A_{\alpha\alpha}}{\gamma_e\gamma_n\hbar^2}\frac{\langle S_\alpha\rangle}{H_0}$$

$$= \frac{A_{\alpha\alpha}}{\gamma_e\gamma_n\hbar^2}\chi^S_{\alpha\alpha}\,. \tag{10}$$

If we then assume that $\chi^S_{\alpha\alpha}$ (1) and $\chi^S_{\alpha\alpha}$ (2) are both isotropic and refer to Eq. (3) and Eq. (7a), we continue our analysis of the planes getting

$$K^S_{cc} = -2.8\, K^S_{aa} \tag{11}$$

for the planes. Assuming that $E_{xz} = E_{yz} = 2.2$ eV, $E_{xy} = 2.0$ eV, we get

$$K^L_{cc} = 4.4\, K^L_{aa}\,. \tag{12}$$

Then since

$$\begin{aligned} K_{cc} &= K^S_{cc} + K^L_{cc} \\ K_{aa} &= K^S_{aa} + K^L_{aa} \end{aligned} \tag{13}$$

we can then use the experimental values of $K_{\alpha\alpha}$ together with Eqs.(11), (12), and (13) to decompose the shift tensor. We find for the planes

$$\begin{aligned} K^L_{aa} &= 0.41\% \quad K^L_{cc} = 1.79\% \\ K^S_{aa} &= 0.19\% \quad K^S_{cc} = -0.52\%\,. \end{aligned} \tag{14}$$

These values of $K^L_{\alpha\alpha}$, if combined with $\langle 1/r^3\rangle = 6.3$ a.u. in Eq. (8b) give $E_{xy} = 2.0$ eV, just what McMahon *et al.* estimated it to be. Thus, we see that we can account for the data in the planes with very reasonable values of κ, $\langle 1/r^3\rangle$, λ and E_{xy} within the

permanent electron spin moment model. Consequently we conclude that the Cu atoms in the planes are at or near the permanent moment end of the fluctuation spectrum.

For the chains, the same model would predict a $W_1)_{\alpha\alpha}$ anisotropy which would be very similar to that for the planes, except that the a-axis would be the axis of symmetry. Clearly we have a problem since the chain $W_1)_{\alpha\alpha}$'s much more isotropic, but even worse the axial component of W_1 is bigger than the perpendicular component!

One then wonders if the Cu(1)'s also have permanent electron spin magnetic moments (or more precisely are close to the permanent moment moment end of the fluctuation spectrum). There are two things which make us think they probably do. The first is the very great similarity of the axial and perpendicular components of the shift tensor, which reflect the electronic structure of the Cu(1) and Cu(2) atoms. The second is that the existence of the permanent moment arises fundamentally because of the relative size of certain matrix elements involving Cu^{2+} ions and oxygens. It is hard then to see why the Cu(2) would meet the magnetic criteria whereas the Cu(1) would not.

In all the above considerations we have neglected any explicit role of holes on the oxygens. (They might have an implicit role in determining the $\chi^S_{\alpha\alpha}(1)$ and $\chi^S_{\alpha\alpha}(2)$ through Cu-spin-oxygen spin exchange coupling).

M. Takigawa, P. C. Hammel, R. H. Heffner, and Z. Fisk[8] have measured Knight shifts of both Cu(1) and Cu(2) using aligned powders. Their results for temperatures below T_c lead them to different values of the shift tensors. Mila and Rice,[9] in analyzing the data of Takigawa *et al.* have concluded that there is an additional hyperfine interaction which should be included which couples the nuclear spin of one Cu atom with the electron spin of a neighboring copper atom. This process is called a transferred hyperfine interaction. The theory for it was developed in detail by Huang, Orbach, Simanek, Owen, and Taylor.[10] The mechanism by which this coupling occurs may be viewed in a slightly simplified manner as an interplay between the processes which produce the exchange coupling between the Cu electron spins (the super exchange process of P. W. Anderson[11])

and the necessity of orthogonalizing the wave functions of orbitals on the Cu atoms with those on the 0 atoms if one wishes to use an orthogonal basis set. Owen and Taylor[12] used ENDOR to demonstrate and measure the transfer coupling in Fe:La AlO_3 between Fe^{3+} and Al^{3+} through the intervening O^{2-} as 1.1 X 10^{-4} cm^{-1}.

These sorts of considerations lead to refinements of the numbers for the individual contributions to the shift tensor,[13] but they do not change the essential conclusion that the Cu(2) atoms act very much like atoms possessing permanent electron spin moments. Thus, we conclude that in a fluctuation picture one must be close to the permanent moment end of the spectrum.

If one now takes the parameters we deduced, one knows $\overline{h_x^2}$, $\overline{h_y^2}$, and $\overline{h_z^2}$ for the planes and can therefore calculate the τ_0. We find it to be 2.3 X 10^{-15} sec which corresponds to an energy ($\hbar/\tau_0$) of 2320 cm^{-1}. This energy is of the order of the exchange energy, J, which we have measured between adjacent Cu atoms[2] (see next section) or the value deduced by Lyons, Fleury, Schneemeyer, and Waszczak[14] from light scattering experiments for crystals with $\delta \approx 1$. Thus τ_0 is of the order of the precession period of one electron in the exchange field of its neighbors. However, that numerical similarity depends on the details of the analysis and, as is shown by Monien, Pines, and Slichter, is not as close when one performs an analysis which includes a transferred hyperfine interaction.

VI. The Exchange Coupling Between Electron Spins of Neighboring Cu Atoms

The existence of antiferromagnetism for $YBa_2Cu_3O_{7-\delta}$ for $\delta = 1$, as well as for La_2CuO_4 show that in these materials not only do the Cu atoms possess permanent electron spin moments, but also that they are coupled together with an exchange constant, J. of the order of 1000 cm^{-1}. In their light scattering experiments, Lyons *et al.*[14] observe a splitting which they attribute to exchange, confirming this size for J. However, in a sequence of crystals with progressively higher oxygen content, the splitting disappears and is gone for $\delta \approx 0$, the 90 K material. The question then arises whether or not the coupling has gone to

zero. We now turn to some experiments which reveal that the coupling is still present when the oxygen content produces a 90 K crystal.

The existence of a non-zero J is revealed through measurements of the decay of the transverse nuclear magnetization. Consider a $\pi/2$-τ-π echo sequence in which we study the echo by varying τ. If we denote the size of a spin echo at time t ($=2\tau$) after the initial $\pi/2$ pulse as S(t), in general S(t) falls off with t, perhaps with some oscillatory component. The functional form of S(t) and the time-scale on which it occurs are what we refer to when we speak of transverse relaxation. Ordinarily in NMR it arises from one or both of two mechanisms: (1) nuclear spin-spin coupling (via the magnetic dipolar or indirect interaction) or (2) spin-lattice relaxation. The first mechanism leads to relaxation curves which have a wide variety of time dependences for which in general it is not possible to find the exact theoretical form. Under certain circumstances the decay has a simple time dependence such as an exponential or a Gaussian. The second mechanism leads to an exponential decay with a time constant related to the spin-lattice relaxations by Redfield[15] theory. We will denote this time constant as T_{2R} (R for Redfield).

As we explain in Section II, we can understand the T_1 data in terms of fluctuating fields at the nuclei whose power spectrum is independent of frequency from at least 61 to 124 MHz. Applying Redfield theory to our T_1 data, we calculate the values T_{2R} shown in Table II for the Cu(1) and Cu(2) sites and for H_0 along the a, b, and c axes. These data are all for the (1/2, -1/2) transition.

Experimentally we find that in some cases the transverse relaxation is characterized by a single exponential time constant T_2 but the value of T_2 is considerably shorter than T_{2R}. Thus we might write

$$S(t) \propto e^{-t/T_{2R}} e^{-t/T_2'} \qquad (15a)$$

where T_2' characterizes the excess relaxation rate above that contributed by spin-lattice relaxation. In other cases we find that S(t) is a product of an exponential with the Redfield T_2 and a Gaussian

$$S(t) \propto e^{-t/T_{2R}}\ e^{-1/2(t/\tau)^2}\ . \tag{15b}$$

T_2' and τ are listed in Table II. Figure 2 shows these two functional forms.

Let us focus on the Cu(2) spins with H_0 parallel to c, for which there is a strong Gaussian component. Figures 2a shows the echo envelope for the ^{63}Cu and ^{65}Cu components together with an analysis of the data which utilizes a scaling procedure. The data are first fit by finding a τ which fits the ^{63}Cu data, τ_{63}. Then, we scale the T_{2R} for ^{65}Cu, and scale the ^{65}Cu τ, τ_{65}, using a ratio

$$\tau_{65} = \tau_{63}(\gamma_{63}/\gamma_{65})^2 \sqrt{(P_{63}/P_{65})} \tag{16}$$

where P_{63} and P_{65} are the isotopic abundances of the respective isotopes. This theoretical relationship results from an analysis we outline below, which shows that the nuclear spin-spin coupling is an order of magnitude larger than the direct nuclear magnetic dipolar coupling. In fact, we believe the coupling is indirect, going via the exchange coupling between the Cu(2) electron spins of adjacent Cu atoms.[16-18]

To describe the coupling between a pair of nuclear spins 1 and 2, we take a Hamiltonian

$$\hat{H}_{12} = \sum_{\alpha=x,y,z} I_{1\alpha}A_{\alpha\alpha}S_{1\alpha} + \sum_{\substack{i,j \\ i<j}} J_{ij}\ \vec{S}_i \cdot \vec{S}_j + \sum_{\alpha} I_{2\alpha}A_{\alpha\alpha}S_{2\alpha} \tag{17}$$

where the $A_{\alpha\alpha}$'s express the anisotropic hyperfine coupling. We can eliminate the term involving J_{ij} by a second order perturbation calculation which gives an effective nuclear spin-spin coupling $\hat{H}_{eff}$:

$$\hat{H}_{eff} = \sum_{a=x,y,z} a_{\alpha\alpha 1,2}\, I_{1\alpha}\, I_{2\alpha} \tag{18}$$

with

$$\hbar a_{\alpha\alpha 1,2} = A_{\alpha\alpha}^2 \left\{ \sum_n \frac{(0|S_{1\alpha}|n)(n|S_{2\alpha}|0)}{E_0 - E_n} + c.c \right\} . \tag{19}$$

For a pair of atoms only this gives

$$\hbar a_{\alpha\alpha 1,2} = \frac{A_{\alpha\alpha}^2}{2J} \tag{20}$$

so we define an effective J, J_{eff} by the relation

$$\frac{1}{2J_{eff}} = \sum_n \frac{\langle 0|S_{1\alpha}|n\rangle\langle n|S_{2\alpha}|0\rangle}{E_0 - E_n} + c.c. . \tag{21}$$

In Section V, we found for values of the parameters in planes which make

$$A_{cc} = -\,118 \times 10^{-4}\ cm^{-1}$$

$$A_{aa} = A_{bb} = +\,37 \times 10^{-4}\ cm^{-1} . \tag{22}$$

These are highly anisotropic so that with H_0 parallel to c we can write the nuclear Hamiltonian in the presence of a static field as

$$\hat{H} = -\gamma_n \hbar H_0 \sum_i I_{iz} + \hbar a_{cc} \sum_{\substack{i,j \\ i<j}} I_{iz} I_{jz} \, . \tag{23}$$

This Hamiltonian can be solved exactly. For a nucleus with four neighbors the echo envelope S(t) obeys the relation

$$S(t) = A + B\cos(\tfrac{at}{2}) + C\cos(at) + D\cos(\tfrac{3a}{2}t) + E\cos(2at) \tag{24}$$

where $a = a_{cc}$. The coefficients A,B,C,D,E depend on the isotopic abundance of the nucleus under observation. For short enough times, this curve is indistinguishable from a Gaussian whose τ is related to the t^2 term in a series expansion of the decay. As a result we find

$$a_{cc} = \frac{1}{\hbar}\frac{A_{cc}^2}{2J_{eff}} = \frac{1.70}{\tau} \, . \tag{25}$$

From the measured T_1 and our value of A_{cc}^2 we get

$$J_{eff} = 1100 \text{ cm}^{-1} \, . \tag{26}$$

Clearly the value of J_{eff} varies if one changes the assumed value of A_{cc}, but the general size of J_{eff} will still be of the order of magnitude of the value of Eq. 26.

As an independent check of the theory which leads to Eq. 24, we have performed a spin echo double resonance[2,15] to measure directly the spin-spin coupling between a ^{63}Cu and a ^{65}Cu. We observe the ^{65}Cu echo, while flipping the ^{63}Cu nuclei using the pulse

sequence shown in the inset in Fig. 3. One can show that the decay of the SEDOR will also approximate a Gaussian with a τ value, τ_{SEDOR}, given by

$$\tau_{SEDOR} = (\gamma_{63}/\gamma_{65})\tau_{63} \tag{27}$$

where τ_{63} is the spin-echo value listed in Table II. We find experimentally that τ_{SEDOR} = 130 μsec, whereas its theoretical value using Eq. 27 and the measure τ_{63} is 112 μsec, confirming the correctness of the analysis.

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Table I. The Shift, Field Gradient, and Relaxation Tensors

	Plane	Chain
K_{aa} (%)	.59±.04	1.38±.07
K_{bb}	.59±.04	.55±.07
K_{cc}	1.267±.001	.60±.04
ν_{aa} (MHz)*	+15.94±.05**	-19.03±.07*
ν_{bb}	+15.56±.05**	19.17±.07*
ν_{cc}	-31.50±.05	-0.16±.03
$W_1)_a$ (ms^{-1})	4.7±.3	1.1±.1
$W_1)_b$	4.7±.3	.9±.1
$W_1)_c$	1.05±.1	0.8±.1

*Since the experiment does not determine the sign of the field gradient, the values of $\nu_{\alpha\alpha}$ at either the chain or the plane sites could all be reversed.

**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.

Table II: The Spin-Spin Relaxation Tensors

case	Redfield ^{63}Cu T_{2R}	^{63}Cu T_2'	^{65}Cu T_2'	$^{63}\tau$	$^{65}\tau$
Cu(2) H0 ‖ c	190±10	a	a	120±7	147±8
Cu(2) H0 ‖ a	87±5	550±200	450±300	b	b
Cu(1) H0 ‖ c	440±40	a	a	370±20	300±20
Cu(1) H0 ‖ a	360±30	700±150	700±200	b	b
Cu(1) H0 ‖ b	410±40	a	...	290±20	...

a In these cases the additional relaxation is Gaussian so no T_2' is needed.

b In these cases the additional relaxation is exponential so no τ is needed.

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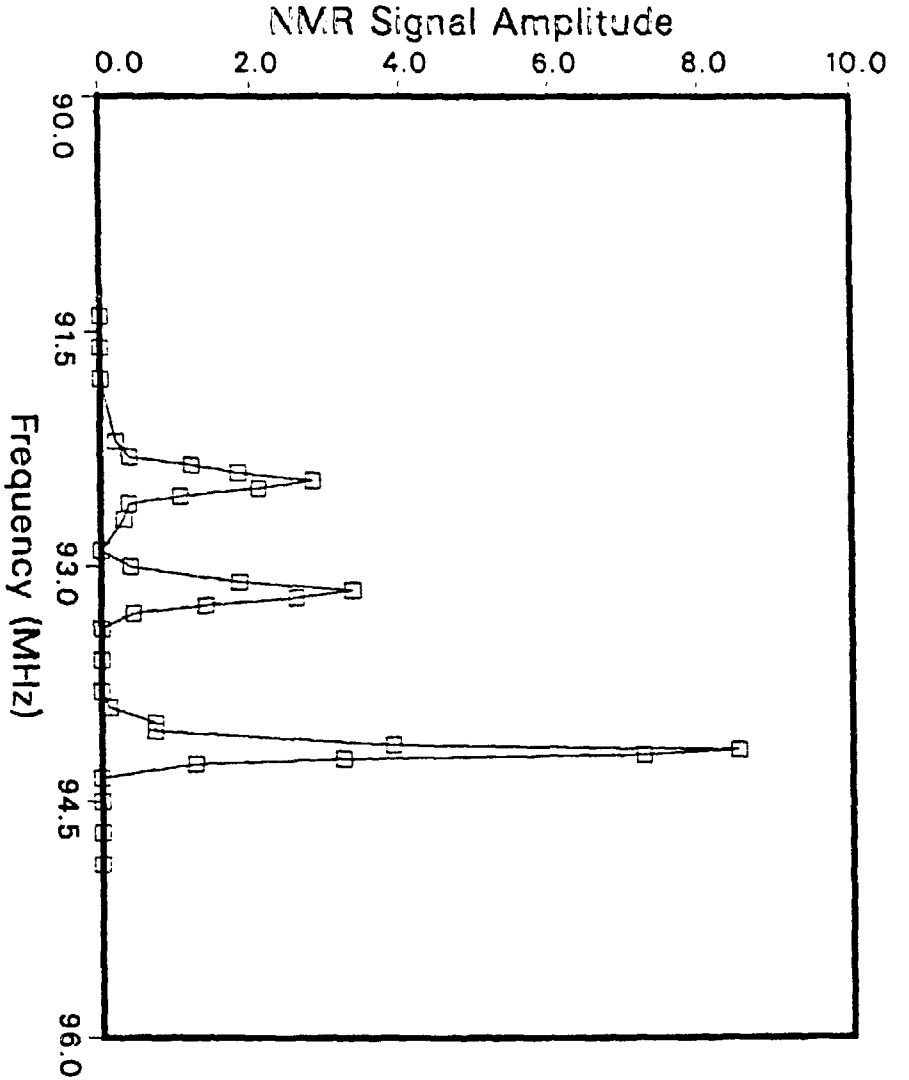
Figure Captions

Fig 1. The (1/2, –1/2) transitions for ^{63}Cu with the static field H_0 along the a axis. Owing to the twinning, the field is also along the b axis. The intensity of the NMR signal (integral of the echo amplitude) is plotted versus the NMR frequency. The left hand line is from the chains, with H_0 along the a axis, the middle line is from chains, with H_0 along the b axis. The right hand line is from the planes. It consists of a single line despite the crystal twinning showing that the plane site has axial symmetry about the c axis. The data are taken for a spin echo pulse spacing of 55 μsec.

Fig. 2. (a) inset: The magnetic susceptibility of the crystal vs. temperature showing a sharp superconducting transition at 90K and a complete Meissner effect, H = 16 Oe ⊥ c-axis (Δ: field cooled, □: zero-field-cooled). Main figure: The spin-lattice relaxation of the $^{63}Cu(2)$ nuclei for the transitions (a) 1/2, -1/2 (b) 3/2, 1/2 and -3/2, -1/2. The points are the data plotted as the Log [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 using the same W_1 as deduced in (a).

Fig. 3. The transverse NMR relaxation for both $^{63}Cu(2)$ (○) and $^{65}Cu(2)$ (▲) for (a) H_0 along c, and (b) H_0 along a. Plotted is the size of the spin echo vs. $2T_{delay}$ is the time between the 90° and 180° pulses. The solid (dashed) lines are fits to the ^{63}Cu (^{65}Cu) data using the parameters given in Table II. The time constants used in (b) are related by $T_{2,65} = (\gamma_{63}/\gamma_{65})^2 T_{2,63}$. The τ's used in (a) are related by $\tau_{65} = (\gamma_{63}/\gamma_{65})^2 (P_{63}/P_{65})^{1/2} t_{63}$. For comparison, the dotted line in (a) is an attempt to fit the ^{65}Cu data by the scaling $\tau_{65} = (\gamma_{63}/\gamma_{65})\tau_{63}$.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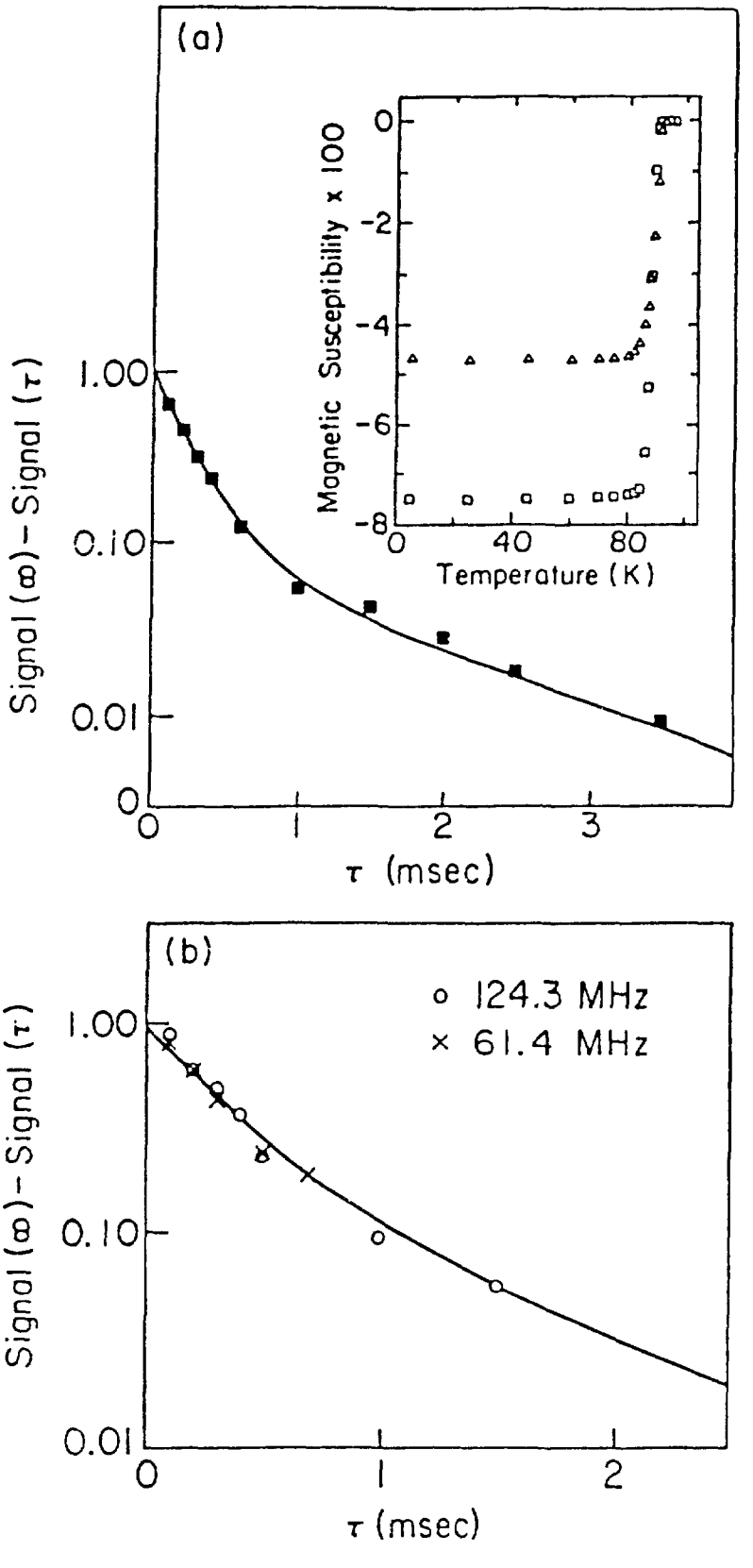
Frequency (MHz)


(a)
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2
3
τ (msec)
Magnetic Susceptibility x 100
0
-2
-4
-6
-8
0
40
80
Temperature (K)
(b)
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× 61.4 MHz
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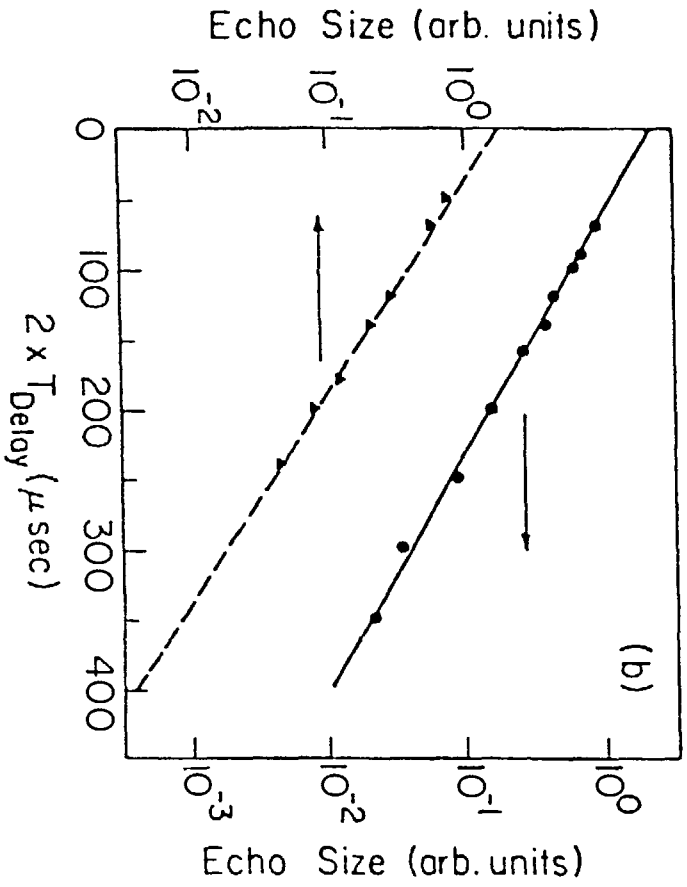
1
2
τ (msec)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200
300
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$2 \times T_{Delay}$ (μ sec)
(b)
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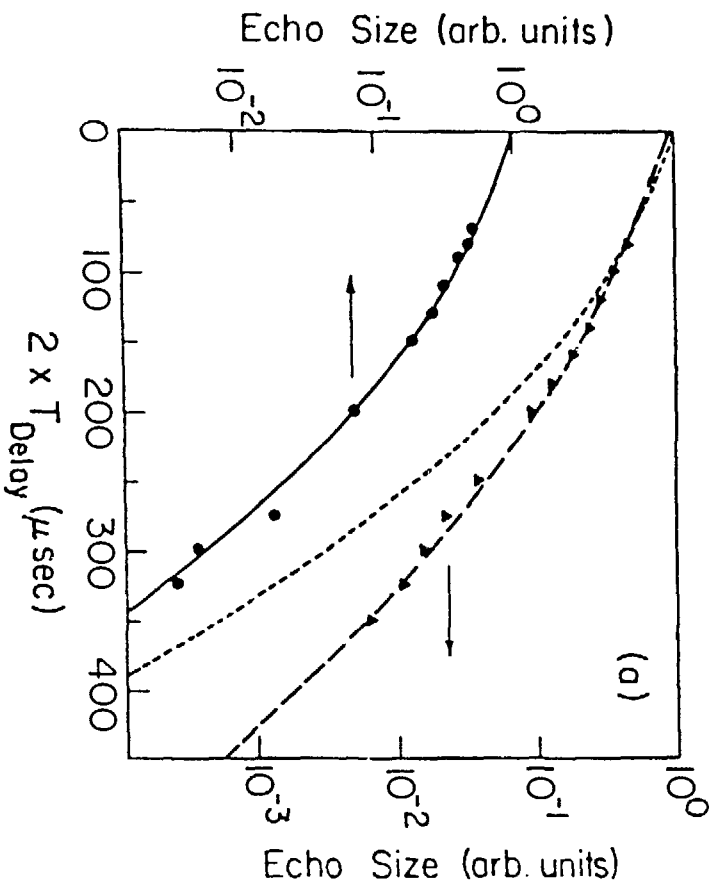
10^{-2}
10^{-1}
10^{0}
Echo Size (arb. units)


Echo Size (arb. units)
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10^{0}
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100
200
300
400
$2 \times T_{Delay}$ (μ sec)
(a)
10^{-3}
10^{-2}
10^{-1}
10^{0}
Echo Size (arb. units)