NMR measurement of the exchange coupling between Cu(2) atoms in $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K)

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The authors report the transverse NMR relaxation of chain [Cu(1)] and plane [Cu(2)] nuclei in a single crystal of $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K) in the normal state. They demonstrate the existence of a strong indirect spin-spin coupling between Cu(2) nuclei, and show that it can be explained using a model in which the Cu(2) atoms possess electronic magnetic moments which are exchange coupled to one another. In such a model, the strength of the coupling implies an effective electronic exchange coupling $J_{\rm eff} \approx 1100$ cm^{-1}.

Much attention has been paid to the role that localized electronic magnetic moments, and their coupling to one another, might play in the mechanism of high-temperature superconductivity, partly because of the known antiferromagnetic behavior of La_2CuO_{4-x} (Refs. 1-3) and $YBa_2Cu_3O_{6+x}$ (Refs. 4 and 5) with x near zero. Recently, it has been reported[6] that in the nonsuperconducting material $YBa_2Cu_3O_{6.0}$ there is an antiferromagnetic exchange coupling energy of $J \approx 950$ cm^{-1} between the Cu(2) electronic moments. We report NMR studies of the transverse relaxation of the Cu nuclei at both the plane [Cu(2)] and chain [Cu(1)] sites in a single crystal of $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K) in the normal state. We find that there is a spin-spin coupling between Cu(2) nuclei which is much stronger than the magnetic dipolar interaction. It can be understood in a model in which the Cu(2) atoms have permanent electronic-spin magnetic moments which are exchange coupled to one another and which are hyperfine coupled to the nuclei. The effective electronic exchange coupling constant, $J_{\rm eff}$, between Cu(2) atoms is $J_{\rm eff} \approx 1100$ cm^{-1}.

We have described the sample [a 1.2-mg single crystal of $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K)][7] and experimental methods earlier.[8] We measured the Cu transverse relaxation with the static field, H_0, along the crystal a, b, and c axes.

Ordinarily in NMR, the transverse relaxation arises from one or both of two mechanisms: (1) nuclear spin-spin coupling (via the magnetic dipolar[9] or indirect interaction[10,11]) 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 relaxation by Redfield theory.[12] We will denote this time constant as T_{2R}.

In our previous study,[7] we found that the spin-lattice relaxation times could be described in terms of fluctuating fields at the nuclei whose power spectrum was independent of frequency from 61 to 124 MHz. Applying Redfield theory to the data and assuming that the frequency independence extends to zero, we deduce the transverse relaxation times T_{2R} (first column of Table I).

Using spin echos, we measured the transverse relaxation for the various cases in Table I. In some cases, the relaxation is exponential, characterized by a time T_2 which, however, is significantly shorter than T_{2R} so that $S(t)$, the size of a spin echo at time t, may be written as $S(t) \propto \exp(-t/T_{2R})\exp(-t/T_2')$ where T_2' characterizes the additional relaxation. In other cases, we find that $S(t)$ consists of the product of an exponential with time constant T_{2R}, and a Gaussian, so that $S(t) \propto \exp(-t/T_{2R}) \times \exp\frac{1}{2}(-t/\tau)^2$, where τ characterizes the additional relaxation. T_2' and τ for both sites are also given in Table I.

We first consider the Cu(2) data. Figure 1 shows the transverse relaxation of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of the

TABLE I. Transverse relaxation measurements given in μsec.

Case	Redfield ^{63}Cu T_{2R}	^{63}Cu T_2'	^{65}Cu T_2'	$^{63}\tau$	$^{65}\tau$
Cu(2) $H_0 \| c$	190 ± 10	a	a	120 ± 7	147 ± 8
Cu(2) $H_0 \| a$	87 ± 5	550 ± 200	450 ± 300	b	b
Cu(1) $H_0 \| c$	440 ± 40	a	a	370 ± 20	300 ± 20
Cu(1) $H_0 \| a$	360 ± 30	700 ± 150	700 ± 200	b	b
Cu(1) $H_0 \| b$	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.

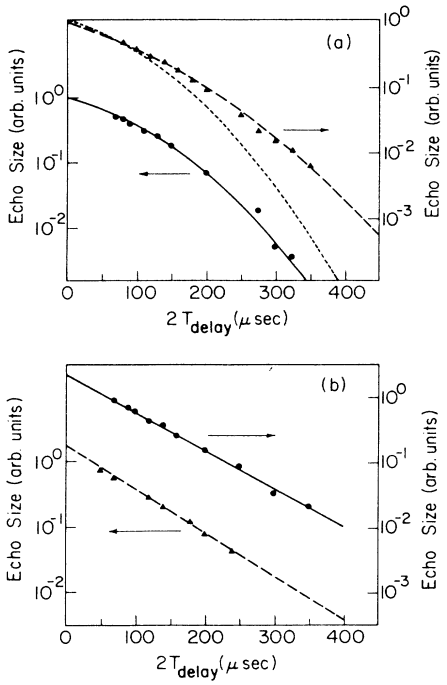

FIG. 1. The transverse NMR relaxation for both ^{63}Cu(2) (●) and ^{65}Cu(2) (▲) for (a) H_0 along c, and (b) H_0 along a. Plotted is the size of the spin echo vs $2T_{delay}$, where T_{delay} is the time between the 90° and 180° pulses. The solid (dashed) lines are fits to the ^{63}Cu (^{65}Cu) data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

^{63}Cu(2) and ^{65}Cu(2) nuclei for the two cases $\mathbf{H}_0\|c$ and $\mathbf{H}_0\|a$. When $\mathbf{H}_0\|c$, the ^{63}Cu(2) relaxation in excess of T_{2R} is Gaussian: $\tau_{63}=120\pm7$ μsec. When $\mathbf{H}_0\|a$, the additional relaxation is exponential: $T'_{2,63}=550\pm200$ μsec. We show shortly that the source of the Gaussian relaxation is a spin-spin coupling of like Cu nuclei, with a coupling strength much greater than that of the magnetic dipole interaction; the coupling is electron mediated.

We can derive an expression for the indirect nuclear coupling assuming the nuclear spin-spin coupling is the net effect of the hyperfine coupling between each Cu(2) nucleus and its electronic moment and an antiferromagnetic exchange coupling between the Cu(2) electronic moments. We write the Hamiltonian for the effective interaction between nuclei 1 and 2 as

$$\hat{\mathbf{H}}|_{1,2}=\sum_{\alpha=x,y,z}I_{1\alpha}A_{\alpha\alpha}S_{1\alpha}+\sum_{\substack{i,j\\i<j}}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+\sum_{\alpha'=x,y,z}I_{2\alpha'}A_{\alpha'\alpha'}S_{2\alpha'}, \quad (1)$$

where the $A_{\alpha\alpha}$'s express the anisotropic hyperfine coupling. Denoting the excited eigenstates of the exchange-coupled electron spins as $|n\rangle$, and the ground state as $|0\rangle$, we treat the electron-nuclear interaction in second-order perturbation theory to get an effective Hamiltonian involving only nuclear spin coordinates which replaces Eq. (1).[12,13] If α and α' are principal axes, as they will be for $\alpha=(a,b,c)$, one can show that

$$\hat{\mathbf{H}}_{\text{eff}}|_{1,2}=\hbar\sum_{\alpha=x,y,z}a_{\alpha\alpha,1,2}I_{1\alpha}I_{2\alpha}, \quad (2)$$

where

$$\hbar a_{\alpha\alpha,1,2}=A_{\alpha\alpha}^2\left(\sum_n\frac{\langle0|S_{1\alpha}|n\rangle\langle n|S_{2\alpha}|0\rangle}{E_0-E_n}+\text{c.c.}\right). \quad (3)$$

Evaluation of the sum requires a complete theory of the system of exchange-coupled Cu electron spins. The physical content of the expression can be found by considering an isolated pair of Cu atoms with antiferromagnetic exchange coupling for which $|0\rangle$ is the electronic singlet ground state and $|n\rangle$ are the excited triplet states. One finds

$$\hbar a_{\alpha\alpha,1,2}=\left(\frac{A_{\alpha\alpha}^2}{2J}\right). \quad (4)$$

For the case that spins 1 and 2 are nearest neighbors, we define a quantity J_{eff} by the equation

$$\frac{1}{2J_{\text{eff}}}=\sum_n\frac{\langle0|S_{1\alpha}|n\rangle\langle n|S_{2\alpha}|0\rangle}{E_0-E_n}+\text{c.c.} \quad (5)$$

giving $\hbar a_{\alpha\alpha,1,2}=A_{\alpha\alpha}^2/2J_{\text{eff}}$. Since one expects the states $|n\rangle$ to be something like spin waves,[13] we expect J_{eff} to be somewhat less than J. If spins 1 and 2 are more distant neighbors $a_{\alpha\alpha,1,2}$ will in general be smaller. We will for simplicity keep only nearest-neighbor nuclear spin-spin coupling omitting the subscripts i,j from the $a_{\alpha\alpha}$'s.

We have deduced $A_{\alpha\alpha}$ for the Cu(2) from measurements of the spin-lattice relaxation, and shift tensors in our previous studies. We found $A_{cc}=-118\times10^{-4}$ and $A_{aa}=A_{bb}=37\times10^{-4}$ cm^{-1}. These values are typical for the Cu^{2+} ion.[14] In the presence of a strong H_0 parallel to c, since $A_{cc}^2\gg A_{aa}^2,A_{bb}^2$, we can keep only terms involving a_{cc} in the total nuclear Hamiltonian for i and j nearest neighbors:

$$\hat{\mathbf{H}}=-\gamma_n\hbar H_0\sum_i I_{iz}+\hbar a_{cc}\sum_{\substack{i,j\\i<j}}I_{iz}I_{jz}. \quad (6)$$

This Hamiltonian can be solved exactly[9] since the individual I_{zi}'s commute with it. Consider an experiment in which we are tuned to the $+\frac{1}{2}\rightarrow-\frac{1}{2}$ transition and the neighboring plane Cu is the same isotope. Following a $\pi/2$ pulse, a nucleus coupled to one spin-$\frac{3}{2}$ neighbor would have a free-induction decay given by $\cos(at/2)+\cos(3at/2)$. However, the spin-echo envelope will be given by $1+\cos(at/2)$ were t is the time at which the spin echo forms. Extending this result to four spin-$\frac{3}{2}$ neighbors and including coupling to unlike isotopes, the resulting echo decay is

$$A+B\cos\left(\frac{a}{2}t\right)+C\cos(at)+D\cos\left(\frac{3a}{2}t\right)+E\cos(2at), \quad (7)$$

where A, B, C, D, and E depend on the isotopic abundance of the observed nucleus since the time-dependent terms

arise solely from coupling between identical isotopes. For short times this decay can be approximated by a Gaussian whose τ is related to the coefficient of the t^2 term in the series expansion of the decay. For ^{63}Cu we get $(1/\tau)^2 = 0.346 a_{cc}^2$ or

$$a_{cc} = \frac{1}{\hbar}\left(\frac{A_{cc}^2}{2J_{\text{eff}}}\right) = 1.70\frac{1}{\tau} . \tag{8}$$

Using $\tau = 117$ μsec from the spin-echo experiment, we see that $a_{cc} = 14.5\times10^3$ rad/sec. There is also a direct magnetic dipolar interaction between the Cu(2) of like isotopes for which the coefficient of $I_{iz}I_{jz}$ is 1.0×10^3 rad/sec, much less than the measured a_{cc}. Correcting the measured a_{cc} for the dipolar coupling and using A_{cc} from our previous study, we find $J_{\text{eff}} \approx 1100$ cm^{-1}.

A detailed examination of the isotopic dependence of Eq. (7) gives

$$\frac{\tau_{65}}{\tau_{63}} = \frac{\gamma_{63}^2\sqrt{P_{63}}}{\gamma_{65}^2\sqrt{P_{65}}} , \tag{9}$$

where P_{63} and P_{65} are the isotopic abundances of ^{63}Cu and ^{65}Cu, respectively. The resulting scaling, $\tau_{65} = 1.30\tau_{63}$, is shown to fit the data in Fig. 1(a).

While this isotope comparison for H_0 along c is strong evidence that the Cu(2) Gaussian decay is due to a spin-spin coupling between identical isotopes, we have performed an experiment that independently measures the nuclear spin-spin coupling, a spin-echo double resonance (SEDOR). The pulse sequence is shown in the inset to Fig. 2. We look for an effect on the size of the ^{65}Cu(2) spin echo as a result of the inversion of the ^{63}Cu(2) nuclei at a time T_{flip}. One can show that the decay of the ^{65}Cu(2) echo size with $2T_{\text{flip}}$ will be a Gaussian with $\tau_{\text{SEDOR}} = (\gamma_{63}/\gamma_{65})\tau_{63}$, where τ_{63} is the ^{63}Cu(2) spin-echo time constant. Figure 2 shows the size of the ^{65}Cu(2) spin echo versus T_{flip} fit with a Gaussian with $\tau_{\text{SEDOR}} = 130$ μsec, in reasonable agreement with the expected τ (derived from the ^{63}Cu spin-echo decay) of 112 μsec. This experiment convincingly shows that the Gaussian component of the spin-echo envelope arises solely from the spin-spin coupling of the $+\frac{1}{2} \rightarrow -\frac{1}{2}$ transition between identical spins in identical environments, and thus confirms the correctness of the detailed analysis on which we base our measurement of J_{eff}.

Next consider the decay of the ^{63}Cu(2) nuclei when H_0 is along the a axis. Defining z as the direction of H_0 and x as lying along the c axis, the secular part of $\hat{\mathbf{H}}_{\text{eff}}|_{1,2}$ can be written as

$$\hat{\mathbf{H}}_{\text{eff}}|_{1,2} = \hbar[a_{aa}I_{1z}I_{2z} + \tfrac{1}{4}(a_{aa}+a_{cc})(I_1^+I_2^- + I_1^-I_2^+)] . \tag{10}$$

Recognizing that $a_{cc} \gg a_{aa}$, we see that the second term, which leads to mutual spin flips, is much larger than the first term, which leads to a static frequency splitting. In this limit, the transverse relaxation will be exponential with T_2 being determined by the size of the frequency jumps, and the jumping rate leading to the relationship

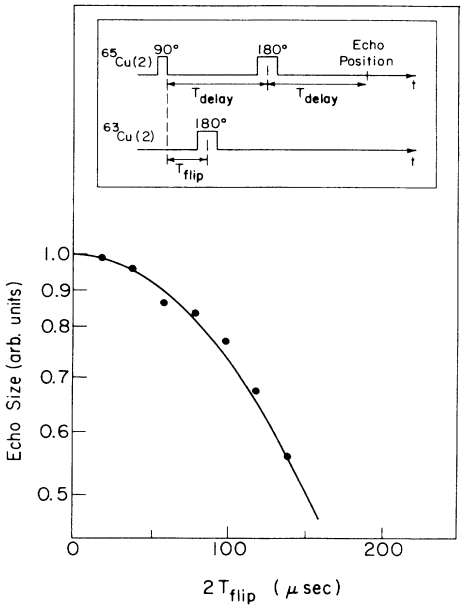

FIG. 2. The ^{63}Cu(2)-^{65}Cu(2) SEDOR (spin-echo double-resonance) pulse sequence (inset) and data (main figure). Plotted is the echo size vs $2T_{\text{flip}}$. The solid line is a Gaussian with $\tau_{\text{SEDOR}} = 130$ μsec.

$T_{2,65} = (\gamma_{63}/\gamma_{65})^2 T_{2,63}$. This scaling is shown to work in Fig. 1(b).

This localized moment model describes the Cu(2) data very well with reasonable values for A_{aa}'s and J_{eff}. An explanation within a band-structure model would require a bandwidth of 1000 cm^{-1}.

We are able to understand the Cu(2) data completely because the form of the transverse relaxation can be calculated in the two limiting cases: (1) Gaussian relaxation in the static limit where mutual spin flips are negligible (when $\mathbf{H}_0 \| c$), or (2) exponential relaxation in the motionally narrowed limit where mutual spin flips dominate (when $\mathbf{H}_0 \| a$). We know that the Cu(1) relaxation for $\mathbf{H}_0 \| c$ is not described by either limit because though the decay is Gaussian, indicating absence of motional narrowing, the isotope dependence is $\tau_{65} = (\gamma_{63}/\gamma_{65})^2\tau_{63}$, not that of Eq. (9). In this case, there is no exact solution of the relaxation process, so we do not know whether or not an indirect nuclear spin-spin coupling is present.

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