Theory of Nuclear Spin-Spin Coupling in $YBa_2Cu_3O_{7-\delta}$

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The indirect nuclear spin-spin coupling between Cu nuclei in the CuO_2 planes of $YBa_2Cu_3O_{7-\delta}$, deduced from ^{63}Cu transverse relaxation, is shown to yield information about the wave-vector dependence of the real part of the planar-Cu static electron-spin susceptibility. The coupling is evaluated with no adjustable parameters using the antiferromagnetic Fermi-liquid theory of Millis, Monien, and Pines, providing a new test of that model. At 100 K, the theoretical relaxation time is 190 ± 75 μsec versus the experimental 130 ± 10 μsec.

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NMR has proven to be a valuable tool for the study of both the normal and the superconducting states of $YBa_2Cu_3O_{7-\delta}$, especially through studies of the Knight shift and spin-lattice relaxation.[1] We analyze another aspect of its use in dealing with a crucial issue concerning the appropriate description of the CuO_2 planes. Measurements[2] of transverse relaxation of the ^{63}Cu nuclei in the planes have shown that there is a nuclear spin-spin coupling an order of magnitude larger than would be expected from conventional nuclear dipolar coupling, requiring that there be an additional nuclear spin-spin coupling mechanism. Such an additional nuclear spin-spin coupling is well known in molecules (the so-called J coupling seen in high-resolution NMR) and solids (for example, the RKKY coupling of metals) where it arises from the hyperfine coupling of the nuclear spins to the electron spins of the valence electrons.[3] The strength of the coupling is calculated using perturbation theory in which the valence electrons are described by molecular or band wave functions, respectively. A major issue for high-temperature superconductors is finding the proper description of the valence electrons. One model which has been very successful in understanding the Knight shift and spin-lattice relaxation is to represent the electrons of the CuO_2 planes as an antiferromagnetic Fermi liquid. Using the Millis, Monien, and Pines formulation of this model,[4] we calculate the extra nuclear-nuclear coupling as a test of that description of the CuO_2 planes. While introducing no adjustable parameters, we find a theoretical transverse relaxation time of 190 ± 75 μsec compared to the experimental 130 ± 10 μsec.[2]

There are two broad classes of theories of the CuO_2 planes: the "one-component" and "two-component" pictures. In the two-component picture one thinks of two separate systems; a set of Cu^{2+} ions, and a conduction band made up of holes in oxygen p orbitals. Recent experimental and theoretical advances, however, favor the one-component picture. The key insight for this description, given by Hammel *et al.*[5] and developed by Shastry,[6] is that one may obtain differing spin-lattice relaxations for ^{17}O and ^{63}Cu by invoking a spin-wave-vector-dependent hyperfine coupling of each nuclear species to temperature-dependent antiferromagnetic fluctuations. Bulut *et al.*,[7] Mila and Rice,[8] Millis, Monien, and Pines (MMP),[4] and Lu *et al.*[9] have each presented theoretical descriptions of the NMR Knight shifts and spin-lattice relaxation which incorporate this feature. Experiments by Takigawa *et al.*[10] have lent strong support to the one-component theories by showing that for the CuO_2 planes the Knight shifts of ^{63}Cu and ^{17}O are accurately proportional to each other as a function of temperature in $YBa_2Cu_3O_{6.63}$, and Monien, Pines, and Takigawa[11] have shown that they can give a detailed account of the normal-state NMR data for the Knight shift and spin-lattice relaxation for ^{63}Cu, ^{17}O, and ^{89}Y in both the O_7 and the $O_{6.63}$ material.

In this paper, we calculate the indirect nuclear spin-spin coupling between Cu(2) nuclei in the planes, which was measured recently by Pennington *et al.*[2] from studies of the amplitude of the spin-echo signal as a function of pulse spacing and from ^{63}Cu-^{65}Cu spin-echo double resonance. Expressing the dependence of the complex electron-spin susceptibility on wave vector $\mathbf{q}$ and angular frequency ω as $\chi(\mathbf{q},\omega)$, we show that the strength of the coupling is determined by $\chi'(\mathbf{q},0)$, the real part of the wavelength-dependent Cu(2) static electron-spin susceptibility. The previous analyses[4,7-9] involve nuclear-spin-lattice relaxation [related to $\chi''(\mathbf{q},\omega_n)$, the imaginary part of the electron-spin susceptibility at the nuclear Larmor frequency ω_n] and the Knight shift [related to $\chi'(0,0)$]. Thus, our calculation provides an independent test of the form of the $\chi(\mathbf{q},\omega)$. Since we apply our calculation to the MMP theory, we test both their form of $\chi'(\mathbf{q},\omega)$ as well as the numerical values of the parameters they deduce.

MMP describe the spin dynamics of the CuO_2 planes with a spin susceptibility $\chi(\mathbf{q},\omega)$ strongly peaked about the antiferromagnetic wave vector $\mathbf{Q}=(\pi,\pi)$ (where we have taken the lattice constant a to be 1). Spins reside on planar Cu atoms, and $\mathbf{q}$ takes on values in the first Brillouin zone of the two-dimensional lattice reciprocal to the lattice of planar Cu atomic sites. The antiferromagnetic enhancement of χ is given in a mean-field approach in terms of the complex susceptibility χ^0 of a noninteracting system. MMP relate the real and imaginary parts of χ^0 with the assumption of a characteristic energy scale Γ (which functions as an electron-spin-relaxation rate). For NMR, one takes the small-ω limit of $\chi(\mathbf{q},\omega)$. MMP then expand the exchange coupling about the zone corner $\mathbf{Q}=(\pi,\pi)$ in terms of an expansion parameter ξ, the correlation length of antiferromagnetic fluctuations. As MMP point out, one would expect the expansion about $\mathbf{Q}$ to be valid for small $\mathbf{q}-\mathbf{Q}$ only. For large values of ξ, χ is quite small for $\mathbf{q}$ near zero. It is likely, then, that another parameter is needed to describe the physics adequately and to represent χ over the whole Brillouin zone. MMP have added a $\mathbf{q}$-independent term to χ, giving (for low ω)

$$\chi'(\mathbf{q},\omega)=\chi_0\left[1+\frac{(\xi/\xi_0)^2}{1+(\mathbf{q}-\mathbf{Q})^2\xi^2}\right], \tag{1}$$

$$\chi''(\mathbf{q},\omega)=\frac{\pi\omega\chi_0}{\Gamma}\left[1+\frac{(\xi/\xi_0)^4}{[1+(\mathbf{q}-\mathbf{Q})^2\xi^2]^2}\right], \tag{2}$$

where $\chi_0=\chi^0(\omega=0)$. The parameter ξ_0 determines the ratio of the $\mathbf{q}$-dependent and $\mathbf{q}$-independent parts.

As we show below, the real part χ' results in a nuclear spin-spin coupling which can be observed in measurements of transverse (T_2) relaxation. The coupling may be understood as a process in which a nucleus at site 1 induces an electron-spin polarization via the electron-nucleus hyperfine coupling which extends spatially to the positions of nearby nuclei where those nuclear spins experience the polarization through their electron-nucleus hyperfine interaction. Note that all the nuclei within distance ξ are coupled. With the MMP estimates of ξ/a, there are on the order of 30 nuclei coupled together.

To calculate the strength of the nuclear spin-spin coupling one must determine the nuclear-electron hyperfine coupling. It is now widely agreed that the appropriate picture to describe the hyperfine coupling of the planar Cu nuclei with the electron-spin system is close to the limit of the Cu^{2+} ion, with a net electron-spin moment of $\frac{1}{2}$. The electron-nuclear Hamiltonian consists then of a sum of an on-site term of the nucleus at site k with the electron spin at site k (Ref. 12) and a coupling B (Ref. 8) of the nuclear spin to the nearest-neighbor electron spins k':

$$H_{e\text{-}n}=\sum_{\alpha,k}I_{\alpha k}A_{\alpha\alpha}S_{\alpha k}+B\sum_{k,k'}\mathbf{I}_k\cdot\mathbf{S}_{k'}, \tag{3}$$

where k' ranges over the nearest neighbors to nucleus k and $\alpha=x,y,z$. It is believed that as a result of detailed analysis of the NMR results good estimates of all of the coupling parameters are known.[4,8,11,13] Following MMP, we take for the hyperfine couplings the following values (where $^{63}\gamma$ is the gyromagnetic ratio of the ^{63}Cu nucleus): $B/^{63}\gamma=82$ kG, $A_{cc}/^{63}\gamma=-4B/^{63}\gamma=-328$ kG, and $A_{aa}/^{63}\gamma=69$ kG. They estimate the precision of these values to be better than 20%.

To calculate the planar-Cu nuclear spin-spin coupling, we express the electron spin $\mathbf{S}(\mathbf{r})$ and the resulting magnetic field $\mathbf{H}(\mathbf{r})$ acting on the electron spins as a result of the nuclear spins as a function of lattice site in terms of their Fourier transforms; for example,

$$\mathbf{S}(\mathbf{r})=\sum_{\text{1st BZ}}\mathbf{S}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}). \tag{4}$$

From Eq. (3), we see that nuclear spin $\mathbf{I}_1$ at the origin acting on the electron spin gives an effective magnetic field at site $\mathbf{r}$ with z component H_z:

$$H_z(\mathbf{r})=\left[-\frac{I_{1z}}{\gamma_e\hbar}\right]\left[A_{zz}\delta_{\mathbf{r},0}+B\sum_i\delta_{\mathbf{r},\mathbf{r}_i}\right], \tag{5}$$

where i is summed over nearest neighbors to the nucleus. We identify the Fourier transform $H_z(\mathbf{q})$:

$$H_z(\mathbf{q})=-[A_{zz}+2B(\cos q_x+\cos q_y)]I_{1z}/N\gamma_e\hbar, \tag{6}$$

where N is the number of Cu atoms per unit area in a plane. We then calculate the induced spin polarization using $S_z(\mathbf{q})=\chi'(\mathbf{q})H_z(\mathbf{q})$. We Fourier transform $S_z(\mathbf{q})$ to obtain $S_z(\mathbf{r})$ at $\mathbf{r}=(n_x,n_y)$, measured in lattice constants. The result is

$$S_z(n_x,n_y)=\left[\frac{1}{2\pi}\right]^2\left[-\frac{I_{1z}}{\gamma_e\hbar}\right]\chi_0\left[A_{zz}F(n_x,n_y)+B\sum F(n_x',n_y')\right], \tag{7}$$

where the sum is over (n_x',n_y'), the four Cu sites adjacent to (n_x,n_y), and $F(n_x,n_y)$ is

$$F(n_x,n_y)=4\xi^2\cos(n_x\pi)\cos(n_y\pi)\int_{0,0}^{\pi,\pi}dq_x\,dq_y\cos(q_xn_x)\cos(q_yn_y)\left[1+\frac{1/\xi_0^2}{1+q_x^2\xi^2+q_y^2\xi^2}\right].$$

We now have an expression for the electron polarization due to a nuclear spin $\mathbf{I}_1$ at the origin. Using Eq. (3) for the hyperfine coupling, we may express the interaction Hamiltonian H of nuclear spin $\mathbf{I}_2$ at position (n_x,n_y) with the electron-spin polarization cloud as

$$H=I_{2z}\left[A_{zz}S_z(n_x,n_y)+B\sum S_z(n_x',n_y')\right], \tag{8}$$

where again the sum is over the four sites (n_x',n_y') adjacent to (n_x,n_y). Equations (6)–(8) give the coupling between I_{1z} and I_{2z}. There are similar couplings between the other components, so that finally

$$H_{(1\text{-}2)}=\sum_{\alpha=x,y,z}a_{(1,2)\alpha}I_{1\alpha}I_{2\alpha}. \tag{9}$$

We have included additional coupling from the nuclear-spin dipole-dipole interaction. For nearest-neighbor spins dipole-dipole coupling is about 20% as large as the above mechanism; it then falls off rapidly as $1/r^3$.

The effects of the spin-spin coupling on the spin-echo size, measured as a function of the delay time between the 90° and 180° pulses, have been treated by Pennington *et al.* For the static field H_0 along z, a principal axis, it is appropriate to include only the secular part of Eq. (9). Typical theoretical and experimental values of $a_{(1,2)\alpha}$ in this material are highly anisotropic, with $a_{(1,2)c} \gg a_{(1,2)a} = a_{(1,2)b}$. For example, for typical input parameters the theoretical nearest-neighbor coupling a_c is 6000 rad/sec, with a_a only 500 rad/sec. It is then appropriate to neglect a_a

For H_0 parallel to the c axis, the nuclear-spin Hamiltonian becomes

$$H = \sum_i -\gamma_n H_0 I_{iz} + \sum_{i,j;i>j} a_{(i,j)z} I_{iz} I_{jz} . \quad (10)$$

Though in principle the form of the decay of the NMR spin-echo envelope resulting from Eq. (10) may be quite complex, in practice it is well approximated theoretically and experimentally by a Gaussian:

$$\text{signal}(t) = \exp(-t^2/2\tau^2) , \quad (11)$$

where t is 2 times the interval between the 90° and 180° pulses making up the spin-echo experiment. For the $YBa_2Cu_3O_7$ Cu $(\frac{1}{2}, -\frac{1}{2})$ transition with H_0 parallel to c, the experimental τ is 130 ± 10 μsec.

$$\frac{1}{\tau} = \sum_k \frac{1}{2} \left(\frac{a_{1k}}{2} \right)^2 \quad (12)$$

for the $(\frac{1}{2}, -\frac{1}{2})$ transition. We must additionally use a weighting factor equal to 0.69 to account for the natural abundance fraction of the ^{63}Cu isotope.

The input parameters needed for our calculation are the hyperfine couplings A_{aa}, A_{cc}, and B, the susceptibility χ_0, the coherence length ξ, and the parameter ξ_0. MMP introduce the dimensionless parameter $\beta = (a/\xi_0)^4$ which they pick as π^2. These values, together with the Knight shift of Barrett *et al.*,[14] give $\chi(\mathbf{q}=0, \omega=0)$ equal to 7.56×10^{-9} unit of electron spin per gauss. MMP find for the remaining parameter ξ approximately 2.5 lattice constants.

In order to give a flavor of the nature of the nuclear spin-spin coupling we show in Fig. 1 the coupling strengths a_{cc} between near-neighbor nuclei, using a coherence length $\xi = 3a$. As expected the coupling falls off at the distance of a coherence length. Finally, in Fig. 2 is calculated the Gaussian time constant τ for a range of ξ, with the experimental result $\tau = 130 \pm 10$ μsec shown for comparison. If we take the value of $\xi/a = 2.5$ given by MMP, in which case we have *no adjustable parameters,* then the calculated value of τ is 190 ± 75 μsec with the precision determined by the precision of 20% in hyperfine coupling constraints. Thus, one finds excellent agreement between theory and experiment. To a good approximation, the graph gives $\tau \propto a/\xi$.

Barrett and Martindale in our laboratory are measuring the temperature dependence of τ to check the temperature dependence of ξ. In addition, our calculations show that the indirect ^{17}O-^{17}O coupling is smaller than the straight dipolar coupling, and that the ^{63}Cu-^{17}O coupling is comparable to the ^{17}O-^{17}O straight dipolar coupling, and thus these indirect couplings will not be easily observed.

We have shown that the MMP theory for $YBa_2Cu_3O_7$ predicts a strong indirect Cu nuclear spin-spin coupling

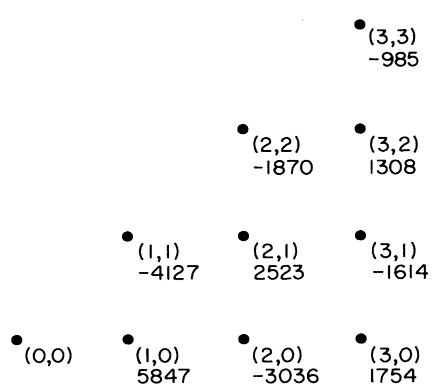

FIG. 1. The coupling strength $a_{(1,2)c}$ in rad/sec between a nucleus 1 at the origin (0,0) and a nucleus 2 at position (n_x, n_y), demonstrating the antiferromagnetic nature of the coupling at nearest-neighbor positions (positive $a_{(1,2)c}$), and the range of the coupling.

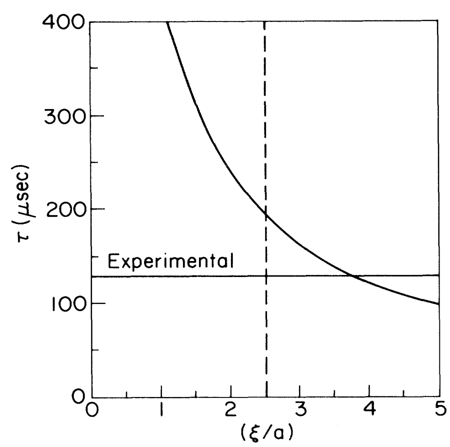

FIG. 2. The spin-spin coupling parameter τ vs the ratio of the coherence length ξ to the lattice constant a. The experimental value of τ (130 μsec) is shown (horizontal solid line), and the MMP best value for ξ/a (2.5) is indicated by the vertical dashed line.

with a strong anisotropy. Since the spin-spin coupling tests the form of $\chi'(\mathbf{q},0)$, whereas previous tests have involved nuclear-spin-lattice relaxation [which tests $\lim\chi''(\mathbf{q},\omega)/\omega$ at low ω] and Knight shifts [dependent on $\chi'(0,0)$], the agreement that is achieved with experiment may be viewed as an independent verification of the general correctness of the MMP picture.

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