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Anisotropic nuclear relaxation in $YBa_2Cu_3O_7$

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Data are presented for the magnetic susceptibility of $YBa_2Cu_3O_7$ and for the anisotropy of the copper nuclear spin-lattice relaxation time T_1 in the normal state for planar [Cu(2)] sites in this system. Using the Cu NMR shift to partition the susceptibility and estimate the density of states, we analyze the conventional enhanced Korringa model of T_1 contributions, finding it incapable of accounting for the anisotropy of the observed relaxation times. A localized spin-fluctuation picture is also discussed briefly.

For many years the nuclear-spin-lattice relaxation process has helped to characterize the electron dynamics of complex metallic systems. For the case of transition metals, separate *s-p* and *d*-band contributions of both spin and orbital character have been identified.[1,2] The effects of electron-electron interactions have been incorporated into the theory.[3,4] One might have supposed that a substantial portion of that analysis would be applicable to the high-T_c oxides, in particular to the copper nuclei. However, nuclear relaxation results reported for $YBa_2Cu_3O_7$ (Refs. 5–9) reveal many surprising and anomalous features. Among them are (1) sharply contrasting temperature dependences for the two copper sites,[10] where in the normal state the Cu(1) (chain) nuclei exhibit a nuclear relaxation rate T_1^{-1} which varies roughly linearly with temperature T as predicted by the simple Korringa model,[2] while the Cu(2) (plane) relaxation process varies more gradually, approximately as $T^{1/2}$; (2) relaxation rates for both sites which are greatly enhanced over simple estimates[6] based on the band-theoretic density of states; (3) an extremely abrupt decrease in T_1^{-1} for the Cu(2) site for $T < T_c$, which is seemingly incompatible with the weak-coupling BSC theory[11] of T_1 behavior; and (4) strongly anisotropic relaxation rates for the Cu(2) site in the normal state, reported here for the first time.

In this Rapid Communication, our purpose is to report data on the T_1 anisotropy and inquire as to whether the conventional enhanced Korringa model[1–4] offers a straightforward explanation for the enhanced, anisotropic T_1 process found for the planar site. We also present an analysis in which the observed NMR shifts are used to partition the observed susceptibility and establish an upper limit on the Pauli paramagnetism and, thus, on the band density of states (exclusive of electron-phonon interaction). The latter is used to estimate the degree of T_1 enhancement. Our main finding is that the T_1 anisotropy cannot be explained with this formalism in terms of anisotropic hyperfine interactions alone.

Susceptibility measurements have been performed on high-quality single-phase ceramic samples of $YBa_2Cu_3O_7$, yielding data with very little of the spurious Curie-like term[12] commonly associated with this material. The temperature-independent component $\chi_0 = 2.7\times10^{-4}$ emu/mol formula unit (f.u.) is in very good agreement with data on the best of a series of samples analyzed by Junod *et al.*[13] In a scheme similar to that employed by the latter authors, we partition χ_0 into Van Vleck orbital, paramagnetic, and core diamagnetic contributions,

$$\chi_0 = \bar{\chi}_{vv} + \chi_p + \chi_{\rm core}\,, \tag{1}$$

where $\bar{\chi}_{vv}$ represents the powder average of the anisotropic $\chi_{vv}(\theta)$. In contrast with Ref. 13, however, we employ a relation between $\bar{\chi}_{vv}$ and χ_p derived from the observed copper NMR shifts to effect a separation of these two terms, meanwhile adopting the estimate $\chi_{\rm core} \sim -1.75\times10^{-4}$ emu/mol f.u.[13] We represent the powder average NMR shifts as $\bar{K} = \bar{K}_{vv} + K_{\rm cp}$, where $\bar{K}_{vv} = 2\mu_\beta\langle r^{-3}\rangle \times \bar{\chi}_{vv}/N_0$ and $K_{\rm cp} = \alpha_{\rm cp}\chi_p$. Here N_0 is Avogadro's number, and $\alpha_{\rm cp}$ is a coefficient proportional to the core-polarization hyperfine field. We estimate $\langle r^{-3}\rangle = 6$ a.u. for the Cu^{2+} ion from atomic calculations[14] (corrected for orbital reduction) and from EPR data[15] and take $\alpha_{\rm cp} = -23$ (emu/mol)$^{-1}$ from established systematics for $3d$ ions.[15,16] Since χ_0 represents the entire unit cell, we take for $\bar{K}$ the combined powder average shifts for the two Cu(2) sites ($\bar{K}_2 = 0.80\%$)[10] and the Cu(1) site ($K_1 = 0.83\%$).[17] Combining these elements gives the desired relation $135\bar{\chi}_{vv} - 23\chi_p = \bar{K}_1 + 2\bar{K}_2 = 0.0243$.

Solving the latter relation in conjunction with Eq. (1) leads to the results $\bar{\chi}_{vv} \geq 2.29\times10^{-4}$ emu/mol f.u. and $\chi_p \leq 2.16\times10^{-4}$ emu/mol f.u. The estimate of $\bar{\chi}_{vv}$ is considered a lower limit because the contribution from the open *p* shells on the O sites has been neglected. The consequent upper limit for χ_p is somewhat lower than given in Ref. 13. Interpreted as a Pauli susceptibility, it leads to an upper limit $\eta_T \leq 4.2\times10^{12}$ (erg f.u.)$^{-1}$ for the total density of electron states at the Fermi surface (FS). The band-structure value[18] is $\sim 6\times10^{12}$ (erg f.u.)$^{-1}$.

The anisotropy of T_1 was studied using the high-field NMR spectrum of the $m = \pm\frac{1}{2}$ transition of ^{63}Cu for a powdered sample of $YBa_2Cu_3O_7$. This sample had been used in a previous T_1 study[7] carried out in zero field by means of the nuclear quadrupole resonance (NQR) transition. In high-field NMR the powder pattern for the Cu(2) site presents the sharp extrema[10] characteristic of an axial electric field gradient tensor. The high- and low-field peaks at these extrema occur for crystallites which

have their c axis oriented at $\theta=42°$ and 90° relative to the applied magnetic field, respectively. By studying the spin-lattice relaxation rates at these peaks and combining the results with the NQR T_1 data,[7] we obtain relaxation behavior at $\theta=0°$, 42°, and 90°.

Spin-lattice relaxation data were taken by measuring the decay of the stimulated echo.[19] Since NMR and NQR studies measure different relaxation modes, the results are plotted in Fig. 1 as T_1^{-1} vs T, where T_1 is understood to be the "uniform" decay time corresponding to complete saturation of the NMR transitions.[20] A very substantial anisotropy in T_1 is revealed by these data with $T_1(0°)/T_1(90°)=3.4$. No variation of the temperature characteristic $T_1(T)$ with θ is resolved by these measurements.

Since the NMR measurements in Fig. 1 were performed at $\nu\sim 85$ MHz in a high field, whereas the NQR studies were done at $\nu=31.5$ MHz in zero field, spot checks were conducted at $\nu\sim 65$ MHz (Fig. 1, solid points) to test for (unexpected) field and/or frequency dependence to the T_1 process. None was found within the resolution of the measurements.

The spin-lattice relation rate can be expressed quite generally in terms of the dynamic susceptibility of the conduction electrons[3,21]

$$1/T_1=(\gamma^2 k_B T/g^2\mu_B^2)\sum_{\mathbf{q},i}(A_{i,\mathbf{q}}A_{i,-\mathbf{q}}+B_{i,\mathbf{q}}B_{i,-\mathbf{q}})\times\chi_i''(\mathbf{q},\omega_0)/\omega_0\,, \tag{2}$$

where $A_{i,\mathbf{q}}$ and $B_{i,\mathbf{q}}$ are suitably defined hyperfine field components acting at right angles in a plane perpendicular to the nuclear axis of spin quantization and i is summed over statistically independent hyperfine terms. $\chi_i(\mathbf{q},\omega_0)$ is explicitly assumed isotropic with i affixed to distinguish spin and orbital susceptibilities. The latter distinction is important, because electron-electron enhancement effects are different for these two cases. The sum on $\mathbf{q}$ is taken over vectors spanning the FS. The relevant hyperfine interactions for the Cu(2) site in $YBa_2Cu_3O_7$ are the d-spin dipolar and core-polarization terms and the orbital term. In a tight-binding picture appropriate to the Cu sites,[1] the field coefficients $A_{i,\mathbf{q}}B_{i,\mathbf{q}}$ in Eq. (2) becomes simply those for atomic orbitals and are effectively $\mathbf{q}$ independent. Dropping the subscripts $\mathbf{q}$ on A_i and B_i, Eq. (2) becomes

$$1/T_1=(\gamma^2 k_B T/g^2\mu_B^2)\sum_i(A_i^2+B_i^2)\sum_{\mathbf{q}}\chi_1''(\mathbf{q},\omega_0)/\omega_0$$
$$=(T_1^{-1})_{\rm dip}+(T_1^{-1})_{\rm cp}+(T_1^{-1})_{\rm orb} \tag{3}$$

for the three hyperfine interactions in an obvious notation. Note there is no interference term between the spin hyperfine processes in the presence of only Cu $3d$ orbitals.[1,2] The core polarization term is isotropic, so the observed T_1 anisotropy must arise from either the dipolar or orbital terms.

We first consider the spin hyperfine terms in Eq. (3), where the anisotropy is caused by the dipolar interaction. Band theory[18] places d holes at the Cu(2) site primarily in the x^2-y^2 orbital. Ignoring for the moment any admixture of orbital character other than this, a tight-binding model of the dipolar hyperfine coupling then gives, for

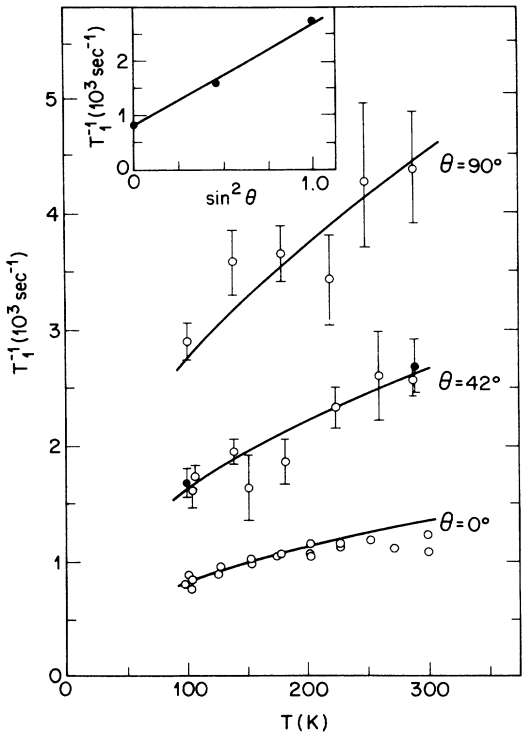

FIG. 1. ^{63}Cu nuclear relaxation rate data for the Cu(2) site at temperatures $100\le T\le 300$ K for three different angles θ between the spin quantization axis and the crystalline c axis in $YBa_2Cu_3O_7$. The rates plotted are for the uniform relaxation mode. The $\theta=0$ data are from Ref. 7. The inset shows the variation of T_1^{-1} with $\sin^2\theta$ at $T=100$ K, in good accord with Eq. (5).

such a d hole,

$$H_{\rm dip}=-\gamma\hbar H_{\rm dip}(I_xS_x+I_yS_y-2I_zS_z)\,, \tag{4}$$

where $H_{\rm dip}=2/7\mu_B\langle r^{-3}\rangle$, the average $\langle\,\rangle$ being taken over the relevant $3d$ radial function. In Eq. (4) the z axis is to be identified with the crystalline c axis. Thus, the c-axis dipolar fluctuation amplitude is twice the in-plane value. Neglecting correlations between components of $\mathbf{S}$, Eqs. (3) and (4) lead to an anisotropic relaxation process

$$T_1(\theta)^{-1}=R_\parallel\cos^2\theta+R_\perp\sin^2\theta\,, \tag{5}$$

where θ is the angle between the nuclear-spin axis of quantization and the crystalline c axis, and the coefficients $R_{\parallel,\perp}$ are functions of temperature. For purely dipolar coupling $R_\perp/R_\parallel=\frac{5}{2}$, i.e., less than the observed ratio. Moreover, inclusion of the isotropic core-polarization term, which is of comparable magnitude, degrades the predicted anisotropy further. We conclude that the spin hyperfine terms in Eq. (3) are incapable of explaining the observed relaxation anisotropy shown in Fig. 1.

We next turn to the orbital term in Eq. (3). This term can, at least in principle, account for the T_1 anisotropy as we shall see below. Because the orbital term is frequently predominant, we consider it here in some detail. For the

cubic case[2] this term is given by

$$(T_1^{-1})_{\rm orb} = \frac{8\pi\hbar}{3}(\gamma H_{\rm orb}\eta_d)^2 k_B T f(2-\tfrac{5}{3}f), \qquad (6)$$

where $H_{\rm orb}=2\mu_B\langle r^{-3}\rangle$ is the orbital hyperfine field, f is the fraction of T_{2g} character in the Cu $3d$ bands at the FS, and η_d is the relevant density of states. Since the predominant $3d$ orbital at the FS (i.e., x^2-y^2) has E_g symmetry, f is at most a few percent and is difficult to determine from band calculations with any accuracy. Thus $(T_1^{-1})_{\rm orb}$ is in any case a small fraction of its peak value, which occurs for $f=0.6$. Any known enhancement effects for the orbital rate are represented by a modified value for η_d.

To discuss the anisotropy of $(T_1^{-1})_{\rm orb}$ we must generalize Eq. (6) to tetragonal symmetry. Considering the orbital hyperfine interaction

$$H_{\rm orb}=\gamma\hbar\mu_B \mathbf{L}\cdot\mathbf{I}/r^3, \qquad (7)$$

it is easy to show that the quantities $(R_\perp - R_\parallel/2)$ and $R_\parallel$ from Eq. (5) are proportional to the amount of xy and (yz,zx) Cu $3d$ character at the FS, respectively. The observed anisotropy would therefore correspond to a predominance of xy character within the T_{2g} portion of the density of states. To estimate $R_\perp$(orb) using Eq. (6) we assume an upper limit of $f=0.1$, with a correspondingly smaller value for $R_\parallel$ (orb).

The appropriate value of η_d in Eq. (6) is thought to be the "bare" density of states[2,22] at the Cu site, the upper limit of which we shall estimate from the upper limit η_T for the density of states derived from the uniform susceptibility using Eq. (1). For this purpose we partition η_T among the sites according to the results of band theory,[18] giving $\eta_d \le 3.5\times10^{11}$ (erg atom spin direction)$^{-1}$ for the Cu sites. Using $\langle r^{-3}\rangle=6$ a.u. as discussed earlier,[14,15] Eq. (6) gives $R_\perp$(orb) ≤ 70 sec^{-1} at $T=100$ K. This estimate falls short of the measured value in Fig. 1 by a factor $\sim$40. We are aware of no enhancement process by which this shortfall could be made up. In comparison, the estimate for the combined d-spin terms in Eq. (3) is $R_\perp(d\text{-spin})\sim 38$ sec^{-1} using the same values of f and η_d.

An alternative to the enhanced Korringa model for T_1 is suggested by theories of the copper-oxide systems in which the (planar) copper ions remain in a Cu^{2+} state while itinerant holes propagate on the oxygen lattice.[23–26] In this picture, the dynamics of the (localized) Cu(2) spin moments are generated by exchange couplings among themselves and with the itinerant oxygen holes. The relaxation of copper nuclei induced by these fluctuations will be very strong. In a localized Cu^{2+} picture for the ions at the Cu(2) sites[15] the hyperfine tensor includes crystal-field and spin-orbit coupling effects and is in general quite anisotropic. A detailed analysis along these lines goes beyond the scope of this article. As a limiting case we may examine the effects of extreme localization by taking $\sum_{\mathbf{q}}\chi''(\mathbf{q},\omega_0)/\omega_0 \sim 2\tau\chi_c(T)/(1+\omega_0^2\tau^2)$, where $\chi_c(T)$ is the Curie susceptibility of a localized moment and τ is its correlation time for orientational fluctuations. Anticipating $\omega_0\tau \ll 1$, substitution into Eq. (3) yields the estimate

$$R_\perp = \tfrac{2}{3}\gamma^2(A^2+B^2)S(S+1)\tau, \qquad (8)$$

where we assume for convenience that the (spin) hyperfine coupling is dominated by the large c-axis term $\gamma A I_z S_z$. Here $A=2\gamma(H_{\rm dip}-H_{\rm cp})$, where $H_{\rm cp}=-1.25\times10^5$ G is the core polarization field per Bohr magneton.[15] Taking $R_\perp=2.8\times10^3$ sec^{-1} (Fig. 1, $T=100$ K), Eq. (8) yields $\tau\sim10^{-15}$ sec. This rather short correlation time could be interpreted as the modulation lifetime associated with motion of the itinerant holes. It is, we note, substantially shorter than the spin lifetime $\tau_s \gtrsim 7\times10^{-15}$ sec implied by two-magnon Raman spectra reported for $YBa_2Cu_3O_6$,[27] as one might expect.

We point out, however, that this model of strongly localized Cu $3d$ electrons and O $2p$ holes is highly idealized. In particular, it cannot easily account for the superconductivity of the Cu electrons implied by the rapid loss of relaxation below T_c. A model calculation including strong correlations among itinerant Cu $3d$ electrons has been given by Koyama and Tachiki.[28] We remark that their theory appears to yield a relatively q-independent enhancement of the susceptibility, implying enhancement of *both* χ_p and T_1^{-1}, whereas only the latter is experimentally enhanced. The experiments interpreted according to Eq. (3) suggest strongly q-dependent enhancement.

In conclusion, the orbital hyperfine coupling is too small to account for the observed Cu nuclear relaxation rates in $YBa_2Cu_3O_7$. The spin fluctuation terms are more viable, because they undergo strong enhancement effects. The T_1 anisotropy is larger than we can account for with isotropic spin susceptibilities in Eq. (3). Thus, it remains to be resolved whether a new formulation of anisotropic hyperfine fluctuations in the presence of strong exchange and correlation effects will suffice to account for the present data or whether anisotropic dynamical susceptibilities will be required.

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[1] Y. Obata, J. Phys. Soc. Jpn. **18**, 1020 (1963).
[2] Y. Yafet and V. Jaccarino, Phys. Rev. **A133**, 1630 (1964).
[3] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[4] T. Moriya and K. Ueda, Solid State Commun. **15**, 169 (1974).
[5] M. Mali, D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, and J. Hulliger, Phys. Lett. **124**, 112 (1987).
[6] R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, G. F. Brennert, G. P. Espinosa, J. P. Remeika, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 5727 (1987).
[7] W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, Phys. Rev. Lett. **59**, 1860 (1987).
[8] Y. Kitaoka, S. Hiramatsu, T. Kondo, and K. Asayama, J. Phys. Soc. Jpn. **57**, 29 (1988).
[9] T. Imai, T. Shimizu, H. Yasuoka, Y. Ueda, and K. Kosuge, J. Phys. Soc. Jpn. **57**, 2280 (1988).
[10] It is to be noted that the assignment of nuclear resonance parameters to the two copper sites in this system is reversed from that employed in our previous publications. We refer

the reader to the following paper for a discussion of this point: R. E. Walstedt, W. W. Warren, Jr., R. Tycko, R. F. Bell, G. F. Brennert, R. J. Cava, L. Schneemeyer, and J. Waszczak, following paper, Phys. Rev. B **38**, 9294 (1988).

[11]L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1962).

[12]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy. S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[13]A. Junod, A. Bezinge, and J. Muller, Physica C **152**, 50 (1988).

[14]A. J. Freeman and R. E. Watson, in *Magnetism,* edited by G. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA.

[15]A. Abraham and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), Sec. 7.16.

[16]R. E. Walstedt, J. H. Wernick, and J. Jaccarino, Phys. Rev. **162**, 301 (1967).

[17]W. W. Warren, Jr., R. E. Walstedt, R. F. Bell, G. F. Brennert, R. J. Cava, G. P. Espinosa, and J. P. Remeika, Physica C **153–155**, 79 (1988).

[18]L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987); J. Yu, W. Massidda, A. J. Freeman, and D. D. Koeling, Phys. Lett. A **122**, 203 (1987).

[19]E. L. Hahn, Phys. Rev. **80**, 580 (1950). The stimulated echo offers favorable circumstances for reduction of noise and spurious background in the case, encountered here, of extremely short relaxation times [R. F. Bell and R. E. Walstedt (unpublished)].

[20]In magnetic hyperfine processes $W_{m+1,m} \propto |\langle m+1|I_x|m\rangle|^2$, leading for $I=\frac{3}{2}$ (i.e., ^{63}Cu and ^{65}Cu nuclei) to three exponential decay modes for spin relaxation with rates T_1^{-1}, $3T_1^{-1}$, and $6T_1^{-1}$. In NQR the "odd" mode $3T_1^{-1}$ is exclusively observed, whereas saturation of the $m=\pm\frac{1}{2}$ transition in NMR leads to a combination of the "even" modes T_1^{-1} and $6T_1^{-1}$, typically dominated by the latter decay rate.

[21]In Eq. (2) we have generalized Moriya's stated result to account for multiple, anisotropic hyperfine processes in accord with the formulations in Refs. 1 and 2.

[22]This result was proved by L. P. Kadanoff for the highly localize Fermi contact interaction [Phys. Rev. **132**, 2073 (1963)]. In the tight-binding limit the core-polarization (Ref. 2) and orbital [Eq. (6)] terms are also local, i.e., intra-atomic in character, suggesting that Kadanoff's argument will also go through in those cases without severe correction.

[23]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[24]Y. Guo, J.-M. Langlois, and W. A. Goddard III, Science **239**, 896 (1988).

[25]R. J. Birgeneau, M. A. Kastner, and A. Aharony, Z. Phys. B **71**, 57 (1988).

[26]H. Kamimura, S. Matsuno, and R. Saito, Solid State Commun. (to be published).

[27]K. B. Lyons, P. A. Fleury, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **60**, 732 (1988).

[28]T. Koyama and M. Tachiki (unpublished).