Anomalous Behavior of Nuclear Spin-Lattice Relaxation Rates in $YBa_2Cu_3O_7$ below T_c

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The authors have measured the change in the anisotropy of the NMR spin-lattice relaxation rates for ^{63}Cu(2), ^{17}O(2,3), and ^{89}Y between the normal and superconducting states of $YBa_2Cu_3O_7$. These results cannot be explained by a straightforward extension to $T < T_c$ of current theories, such as the theory of Millis, Monien, and Pines of normal-state NMR relaxation.

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NMR measurements have shown that spin fluctuations in high-temperature superconductors have strong antiferromagnetic correlations with a characteristic correlation length ξ of several lattice constants. ξ varies with temperature in most of the normal state but has been assumed to be independent of temperature throughout the superconducting state. We have measured the anisotropy of the NMR spin-lattice relaxation rate W_1 in the normal and superconducting states of $YBa_2Cu_3O_7$ ($T_c = 93$ K) for the ^{63}Cu and ^{17}O nuclei in the planes [the Cu(2) and O(2,3) sites] and for the ^{89}Y nuclei. The ^{63}Cu anisotropy decreases dramatically upon entering the superconducting state. When combined with our measurements of the ^{17}O and ^{89}Y anisotropy at 100 and 77 K, we see that the change in the copper relaxation-rate ratio appears to require a modification of theories such as that by Millis, Monien, and Pines[1] (MMP) in which the temperature dependence of the NMR ratios comes only from the temperature dependence of the (assumed isotropic) antiferromagnetic correlation length. We describe four possible modifications.

The data presented below involve six samples. All samples but one exhibit 100% shielding fractions, and $T_c(H_0 = 0)$ was 93 K as measured by the change in coil inductance of a nuclear quadrupole resonance (NQR) coil and SQUID measurements.[2] Sample 1 was composed of ~ 50 single crystals whose c and a/b axes were optically aligned. Samples 2 and 3 were unaligned powder samples. Samples 4, 5, and 6 were aligned powder samples sealed in Stycast 1266 epoxy. Sample 6 was isotopically enriched (^{17}O) and exhibited a smaller shielding fraction (80%); however, all static and dynamic NMR properties agreed with previous measurements.[3,4]

Since ^{63}Cu and ^{17}O have spins of $I = \frac{3}{2}$ and $\frac{5}{2}$, respectively, their spin-lattice relaxation curves are multiexponential.[5] We report the rate $W_{1\alpha}$ ($\alpha = x,y,z$) utilized by MMP which is $\frac{3}{2}$ of the single-exponential relaxation rate which would occur in a strong magnetic field in the absence of electric quadrupole splittings. It is the temperature-dependent anisotropy of the quantities $W_{1\alpha}$ that we report. W_{1a} and W_{1b} for Cu(2) and Y are not experimentally distinguishable. However, three different oxygen resonances are distinguishable. Following Takigawa *et al.*,[3] we define $^{17}W_{1a}$ and $^{17}W_{1b}$ to be the rates when the field is in the CuO_2 planes parallel and perpendicular, respectively, to the Cu-O-Cu bond axis.

The values of $W_{1\alpha}$ as measured by NMR for the Cu(2) site in single-crystal sample 1 and aligned-powder sample 4 are shown in Fig. 1, demonstrating that the measured $W_{1\alpha}$'s are sample independent. Note that for $T > 92$ K, $W_{1a}(T)$ and $W_{1c}(T)$ have the same temperature dependence, as is also shown in a plot of $W_{1a}(T)/W_{1c}(T)$, Fig. 1, inset. The NMR measurements were performed in a strong (8.1-T) field, which affects the transition temperature.[6] Since $T_c(H_0 = 0) = 93$ K for our samples, we expect that $T_c(\mathbf{H}_0 \| \mathbf{c}) = 88$ K at $H_0 = 8.1$ T, and $T_c(\mathbf{H}_0 \| \mathbf{a/b}) = 92$ K.[7] We use these values for T_c in our plots of quantities versus T/T_c.

In the normal state, $^{63}W_{1c}(T)$ has the same value at any given temperature T whether it is measured in NMR or NQR. We have made the same comparisons

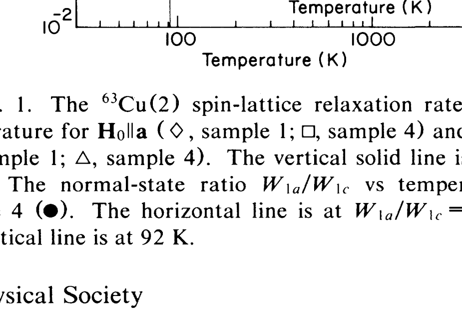

FIG. 1. The ^{63}Cu(2) spin-lattice relaxation rate $^{63}W_{1\alpha}$ vs temperature for $\mathbf{H}_0 \| \mathbf{a}$ (◇, sample 1; □, sample 4) and for $\mathbf{H}_0 \| \mathbf{c}$ (○, sample 1; △, sample 4). The vertical solid line is at 92 K. Inset: The normal-state ratio W_{1a}/W_{1c} vs temperature for sample 4 (●). The horizontal line is at $W_{1a}/W_{1c} = 3.73$, and the vertical line is at 92 K.

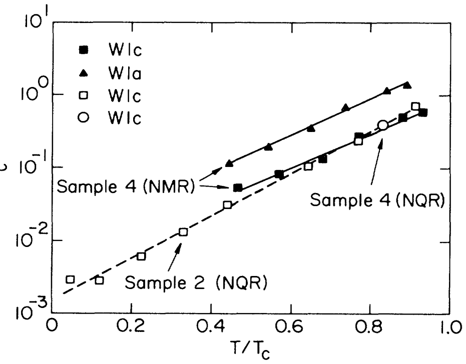

FIG. 2. The ^{63}Cu(2) relaxation rate $^{63}W_{1\alpha}$ divided by T/T_c vs T/T_c. The lines through the data reveal the exponential dependence of this quantity.

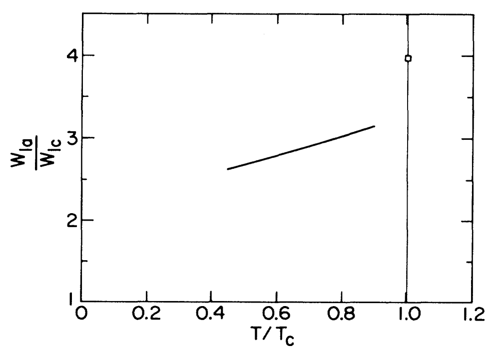

FIG. 3. $^{63}W_{1a}/^{63}W_{1c}$ vs T/T_c, where we have used the functional forms fitting the data for sample 4 in Fig. 2. The solid line is the range of our data. The square at $T/T_c=1$ would be the ratio at this point (3.98) if the $W_{1\alpha}$'s were continuous across the transition.

for the superconducting state for samples 4 and 6. We find for the superconducting state $W_{1c}(T)$ (NMR) does not equal $W_{1c}(T)$ (NQR). Within experimental error, this difference is removed if we assume $W_{1\alpha}$ is a function of the reduced temperature $\theta=T/T_c$ and calculate the field dependence of T_c. Thus at 77 K we find for the two samples $W_{1c}(\text{NQR})=0.33\pm0.02$ and 0.29 ±0.02 ms^{-1} for samples 4 and 6, respectively, while $W_{1c}(\text{NMR})=0.44\pm0.02$ and 0.44 ± 0.01 ms^{-1}, but the W_{1c}(NMR) if scaled to the same θ as for NQR are 0.29 ± 0.01 and 0.29 ± 0.01 ms^{-1}.

We have found that the character of the superconducting-state data is best revealed in a plot of $\ln[W_{1\alpha}(\theta)/\theta]$ vs θ (Fig. 2). It displays a straight-line fit to the superconducting-state data which agrees well with the values of $W_{1\alpha}(T)$ over *5 orders of magnitude.* This fit is

$$W_{1\alpha}/\theta=Ae^{B\theta},\quad \theta=T/T_c(\mathrm{H}_0)\,. \tag{1}$$

This form, with different values of A and B, fits all the data of which we are aware within experimental error, including the planar copper relaxation rate in $YBa_2Cu_3O_{6.52}$, 2:2:2:3 compounds, and $La_{2-x}Sr_xCuO_4$ as well as the relaxation rate at the O(2,3), Cu(1), and Y sites in $YBa_2Cu_3O_7$.[4,8-13] We have no explanation for why this form describes the superconducting-state data so well. It may have no fundamental significance.

The most dramatic feature of the superconducting-state data is seen in Fig. 3: We plot $^{63}W_{1a}(\theta)/^{63}W_{1c}(\theta)$ vs θ, using the phenomenological forms for $^{63}W_{1\alpha}(\theta)$ obtained in Fig. 2. The ^{63}Cu(2) nuclear relaxation-rate anisotropy ratio $^{63}W_{1a}/^{63}W_{1c}$, which was so far independent of temperature in the normal state, undergoes a rapid change just below T_c. $W_{1a}(\theta)/W_{1c}(\theta)$ decreases from 3.73 above T_c to 2.6 at $\theta=0.45$. Over half of this change occurs in the region $0.8<\theta<1$.

To analyze the data, we utilized the theory of Millis, Monien, and Pines[1] which is representative of several theoretical approaches to relaxation in the normal state based on a one-component theory of CuO_2 planes.[14-17] MMP assume that the Cu(2) electron spins act much like ions with permanent spin magnetic moments, which couple to the nuclei with various hyperfine coupling constants. The system of electron spins, however, behaves like a so-called antiferromagnetic Fermi liquid. MMP define a correlation length ξ for the antiferromagnetic spin fluctuations.

Using this picture, MMP calculate the various relaxation rates $^{\eta}W_{1\alpha}$ ($\eta={}^{63}$Cu, ^{17}O, ^{89}Y; $\alpha=x,y,z$) using the parameters χ_0, Γ, β, and a, where χ_0 is the static spin susceptibility, Γ is the energy scale of the noninteracting electronic system, β measures the relative contribution of the antiferromagnetic enhancement, and a is the distance between nearest-neighbor Cu(2) atoms. MMP theory gives for the $^{\eta}W_{1\alpha}$'s

$$^{63}W_{1c}=A_0\{0.294+(\beta/\pi^2)[0.49(\xi/a)^2-0.62\ln(\xi/a)+0.0175]\}\,, \tag{2a}$$

$$^{63}W_{1a}=A_0\{0.722+(\beta/\pi^2)[1.83(\xi/a)^2-1.10\ln(\xi/a)-0.297]\}\,, \tag{2b}$$

$$^{17}W_{1c}=(C^2/8B^2)A_0\{1+(\beta/\pi^2)[0.39\ln(\xi/a)-0.17]\}\,, \tag{2c}$$

$$^{89}W_{1c}=(D^2/4B^2)A_0\{1+0.2(\beta/\pi^2)\}\,, \tag{2d}$$

where $A_0\equiv12\pi B^2k_BT\chi_0/\mu_B^2\hbar^2\Gamma$, and B, C, and D are hyperfine coupling constants. In the most general version of MMP, χ_0, Γ, and ξ/a are temperature dependent (β is independent of temperature). However, for our 90-K samples, only ξ/a is temperature dependent in the normal state.[1] MMP assume

$$[\xi(T)/a]^2=[\xi(0)/a]^2T_x/(T+T_x)\,, \tag{3}$$

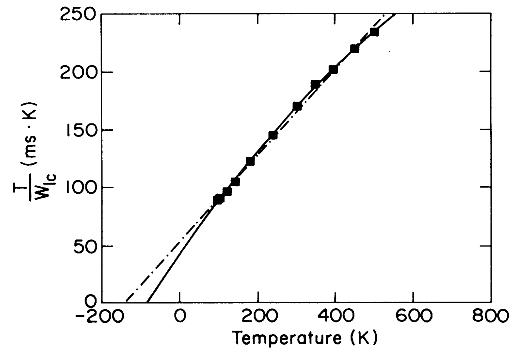

FIG. 4. Temperature divided by the relaxation rate $^{63}W_{1c}$ of sample 3 vs temperature. The dotted (solid) line is a linear (quadratic) fit to the data.

where $T_x \sim 120$ K. The dominant term for $^{63}W_{1\alpha}$ ($\alpha = x,y,z$) is proportional to ξ^2, so that

$$^{63}W_{1\alpha}/T \propto T_x/(T+T_x) \quad (4)$$

which is reminiscent of a Curie-Weiss law. This observation suggested to us that a plot of T/W_1 vs T should be a straight line with an intercept at $-T_x$. We see indeed from Fig. 4 that it is to a good approximation a straight line with an intercept at -144 K. A better fit can be achieved by adding a quadratic T dependence. This presumably results from use of the exact expression for $^{63}W_{1\alpha}$. For reduced oxygen samples χ_0 is found to be strongly temperature dependent.[18,19] Then $T\chi_0/^{63}W_{1\alpha}$ should approximate a straight line.

The MMP formulation assumes that χ_0/Γ and ξ are isotropic. The term χ_0/Γ plays the same role in the parallel and perpendicular relaxation rates for the Cu(2), the O(2,3), and the Y. Thus the ratio of any two relaxation rates removes the χ_0/Γ effect, and we are left with the effect of the temperature-dependent ξ/a alone. From the observation that $^{63}W_{1c}/^{17}W_{1c}$ is independent of temperature below about 120 K,[4] MMP conclude that ξ is independent of temperature below 120 K.[1] Then $^{63}W_{1a}/^{63}W_{1c}$ should be independent of temperature as well, in contrast to our result. Moreover, $^{63}W_{1c}/^{89}W_{1c}$ should also be independent of temperature below 120 K. However, we find experimentally (see Table I) that in going from 100 to 77 K this ratio changes from $(3.10\pm0.25)\times10^4$ to $(1.93\pm0.22)\times10^4$. *We thus find that a straightforward application of the MMP equations is not consistent with experiment below T_c.*

TABLE I. Relaxation rates and anisotropies in the normal and superconducting states.

	$T=100$ K	$T=77.5$ K
$^{63}W_{1c}$ (ms^{-1})	1.07 ± 0.02	0.44 ± 0.02
$^{17}W_{1c}$ (ms^{-1})	0.056 ± 0.003	0.022 ± 0.002
$^{89}W_{1c}$ (s^{-1})	0.035 ± 0.003	0.023 ± 0.002
$^{63}W_{1a}$ (ms^{-1})	4.0 ± 0.1	1.00 ± 0.045
$^{17}W_{1a}$ (ms^{-1})	0.033 ± 0.003	0.013 ± 0.002
$^{89}W_{1a}$ (s^{-1})	0.041 ± 0.003	0.021 ± 0.002
$^{63}W_{1a}/^{63}W_{1c}$	3.74 ± 0.12	2.27 ± 0.15
$^{63}W_{1c}/^{17}W_{1c}$	19.2 ± 1.1	19.8 ± 1.8
$^{63}W_{1c}/^{89}W_{1c}$	$(3.10\pm0.25)\times10^4$	$(1.93\pm0.22)\times10^4$

TABLE II. Change in correlation length for $T<T_c$ for hypothesis (a).

$\xi_\parallel(T/T_c)/a$	T/T_c	$\Delta\xi_\parallel/a$ (%)
2.7	1.0[a]	−0
2.33	0.85	−14
2.21	0.65	−18
2.10	0.45	−22

[a]This assumes $\xi_\perp/a=2.7$ for all T/T_c, and $\beta=\pi^2$.

It is therefore necessary to generalize the MMP model. We consider four possible generalizations: (a) breaking the spin-rotation invariance of $\chi''(\mathbf{q},\omega)$ below T_c by introducing an anisotropic correlation length ξ_α and prefactor $(\chi_0/\Gamma)_\alpha$. MMP have pointed out to us that this hypothesis is consistent with some BCS spin-triplet Cooper-pairing states,[20] while the observed isotropy of the ^{17}O(2,3) Knight shifts[21] and the magnitudes of the ^{63}Cu(2) Knight shifts[22] are strong evidence for a spin-singlet pairing state. Nevertheless, they note that an anisotropy in $\chi''(\mathbf{q},\omega)$ which is much larger at $\mathbf{q}=(\pi/a,\pi/a)$ than near $\mathbf{q}=0$ might be possible in principle. Using this hypothesis, Eq. (2), and the parameter values $\beta=\pi^2$ and $\xi_\parallel(T=100\text{ K})/a=\xi_\perp(T=100\text{ K})/a=2.7$, we find that we can fit $^{63}W_{1a}/^{63}W_{1c}$, $^{63}W_{1a}/^{17}W_{1a}$, and $^{63}W_{1c}/^{17}W_{1c}$ in the superconducting state if we take χ_0/Γ to be isotropic, $\xi_\perp/a$ to be temperature independent, and $\xi_\parallel/a$ to vary from 2.7 at T_c to 2.1 at $T/T_c=0.45$ (see Table II). We are unable to explain the superconducting-state values of $^{63}W_{1a}/^{89}W_{1a}$ and $^{63}W_{1c}/^{89}W_{1c}$, unless we allow for the development of interplane spin correlations. (b) MMP have proposed another explanation, retaining isotropy in spin space but permitting the parameters β [which measures the relative contribution of large-q versus small-q spin fluctuations in $\chi''(\mathbf{q},\omega)$] and ξ/a to become temperature dependent.[23] Detailed calculations unfortunately show that one cannot account for the ratio $^{63}W_{1a}/^{63}W_{1c}$ while also accounting for $^{63}W_{1c}/^{17}W_{1c}$. (c) MMP suggest that a third possibility is that the MMP model must be extended to include an orbital relaxation mechanism which is anisotropic and has a different temperature dependence for $T<T_c$ than the spin-relaxation mechanism.[23] This hypothesis would also require the development of interplane spin correlations (to explain the change in $^{63}W_{1c}/^{89}W_{1c}$). (d) Finally, we consider the possibility of additional magnetic-field effects. For example, in V_3Sn, W_1 is found to have a field dependence which is much greater than that resulting from a mere correction for the magnetic-field dependence of T_c.[24] For our data (as remarked above)

W_{1c} in zero field and in an 8.1-T field scales as a simple function of $T/T_c(\mathbf{H})$. We have also measured W_{1a} at 77 K in a weak magnetic field (0.446 T) and find that W_{1a} likewise scales with $T/T_c(\mathbf{H})$. Thus, at 77 K there is no evidence for any additional magnetic-field effects.

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