Spin susceptibility in superconducting $YBa_2Cu_3O_7$ from ^{63}Cu Knight shift

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(Received 11 January 1989)

The ^{63}Cu Knight shift in $YBa_2Cu_3O_7$ has been measured at both Cu(1) (chain) and Cu(2) (plane) sites, using a uniaxially aligned powder. The isotropic part of the spin Knight shift (K_s) was found to be positive for both sites, suggesting large transferred hyperfine fields from oxygen p states. The Knight shifts at both sites show significant change below T_c, indicating important roles of both the planes and chains in the superconductivity. Despite the uncertainty in the diamagnetic screening, the axial part of K_s at Cu(2) sites is found to show linear-T behavior at low temperatures.

The measurement of the Knight shift in the high-T_c copper oxide superconductors is expected to provide valuable microscopic information because (1) it gives site specific information and (2) it is essentially the only method by which one can measure the spin susceptibility in the superconducting state.[1] In this Rapid Communication, we report the measurement of the Cu Knight shift (K) at both Cu(1) (chain) and Cu(2) (plane) sites in a $YBa_2Cu_3O_7$ powder sample, where the c axis of each grain has been aligned by a magnetic field.[2]

The NMR experiments were carried out with a standard pulsed spectrometer. ^{63}Cu NMR spectra were obtained by integrating the spin-echo intensity while sweeping the magnetic field. A sintered pellet of $YBa_2Cu_3O_7$, made by standard ceramic techniques, was ground into fine powder with grain size less than 20 μm. The magnetic susceptibility showed the superconducting transition at $T_c = 92$ K with almost complete flux exclusion. The powder was then mixed with epoxy (Stycast 1266) with a low packing fraction (~ 0.1), and cured in a magnetic field of 4.2 T. Good alignment of the c axis to the field direction ($\pm 3°$) and random orientation of the a and b

axes in the plane perpendicular to the field were confirmed by both x-ray diffraction and ^{63}Cu NMR spectra. ^{63}Cu NMR spectra taken with the magnetic field parallel to the c axis ($H \| \hat{c}$) at 100 K are in close agreement with those shown by Pennington *et al.* from single crystals.[3] The ^{63}Cu NMR spectra are reported in a separate paper,[4] where the procedure for obtaining the values of the Knight shift from the spectra is described in detail.

In Fig. 1 we show the temperature dependence of the Knight shift (K) for various field directions, deduced from NMR spectra taken at 85 MHz (~ 74 kOe). The Knight shift at Cu(2) sites was found to be axially symmetric about the c axis. The values of K at Cu(1) sites for $H \| \hat{a}$ and $H \| \hat{b}$ are deduced from the position of the edges in the powder pattern of the Cu(1) spectra with $H \perp \hat{c}$.[4] The solid dots in Fig. 1 show the data obtained by assuming that the magnetic field inside the grain is the same as the applied field. Below T_c, the NMR spectra were taken in the mixed state, where the vortex lattice produces a distribution of local fields whose centroid is given by $B = H + 4\pi M = H_0 + 4\pi M(1 - n)$. Here M is the volume magnetization, H_0 is the external field, and n is the
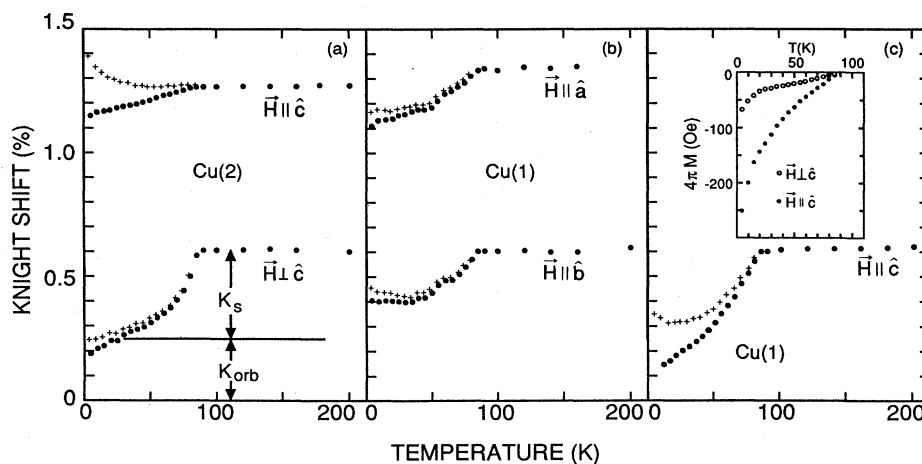

FIG. 1. The temperature dependence of the ^{63}Cu Knight shift. The crosses and filled circles are the results with and without the diamagnetic field correction ($\alpha_\| = 0.7$, $\alpha_\perp = 0.65$), respectively. The temperature dependences of the magnetization at the same field (74 kOe) are shown in the inset in (c).

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demagnetizing factor of a grain. The resonance fields were determined from the peak of the spectra which may be shifted from B in a regular vortex lattice. This shift will also be roughly proportional to M,[1] and is certainly smaller than the width of the distribution.[5] This width was found to be about 60 Oe for $H \| \hat{c}$ and more than an order-of-magnitude smaller than this for $H \perp \hat{c}$ in a recent muon-spin-relaxation (μSR) experiment.[6] This is expected to be field independent for $H_{c1} \ll H \ll H_{c2}$ and much smaller than the difference between B and H_0, which we discuss below. The magnetic shift in the resonance frequency is then given by $\delta v = \gamma_N (KH_0 - 4\pi |M| a)$, where γ_N is the nuclear gyromagnetic ratio (1.1285 kHz/Oe) and a is the average of $1-n$ over all grains. Note that $a_{\|} + 2a_{\perp} = 2$.

The magnetization was measured up to 50 kOe (the maximum field of the magnetometer). The values of M at higher field were determined by extrapolation using the formula $M = a + b \ln H_0$.[7] The value of M at 74 kOe at which the NMR data were taken is reduced by 15% from the value at 50 kOe. The uncertainty in this extrapolation is less than the uncertainty in a, which we now discuss. In order to estimate a, we made use of the fact that the frequency shift due to the Knight shift and the diamagnetic M have different field dependences. First, $a_{\|}$ was estimated to be 0.75 ± 0.05 from the slope of the $\delta v / \gamma_N H_0$ vs $4\pi M / H_0$ plot at several values of $H_0 \| \hat{c}$ (50–80 kOe) at 7 K. Second, the difference in $\delta v / \gamma_N H_0$ at 56 and 74 kOe was plotted against the difference in $4\pi M / H_0$ at various temperatures. The slope of this plot gives $a_{\|} = 0.8 \pm 0.2$. Therefore, a reasonable range for the diamagnetic corrections are $a_{\|} \simeq 0.6$–0.8 and $a_{\perp} \simeq 0.6$–0.7. The values of the Knight shift below T_c were obtained after correcting for the diamagnetic field reduction with $a_{\|} = 0.7$ and $a_{\perp} = 0.65$, and are shown in Fig. 1 by crosses. This correction results in a substantial change in the temperature variation of the Knight shift for $H \| \hat{c}$ but it is small for $H \perp \hat{c}$ due to the small magnetization $(M_{\perp} \sim M_{\|}/5)$. We believe that the small upturn of the $H \| \hat{c}$ data below 15 K is spurious. All the NMR data were taken by sweeping the field from 10 kOe below the measuring range so that the results are independent of the starting field. We have made the same NMR and magnetization measurements on a different sample prepared similarly, which gave the same results.

The observed Knight shift is the sum of contributions from spin and orbital magnetic moments: $K = K_{orb} + K_s$, K_s being proportional to the spin susceptibility χ_s. Since K_{orb} is not affected by the superconducting transition, the temperature variation of K should be associated with the change of K_s. The results in Fig. 1 indicate that χ_s of both the Cu(2)-O planes and Cu(1)-O chains are significantly affected by the onset of superconductivity.

A surprising feature of the results is that the isotropic part of K, defined as $K_{iso} = (K^{(a)} + K^{(b)} + K^{(c)})/3$, decreases below T_c at both sites. This implies a positive isotropic part of the spin Knight shift $K_{s,iso}$, since χ_s can never increase below T_c. This is in contrast to what would be expected for the hyperfine field from unfilled d shells, which gives an isotropic core polarization field with a negative value of about -120 kOe/μ_B.[8,9] The positive values

of $K_{s,iso}$ must be attributed to a contact interaction with unpaired spins, and is most probably associated with p orbitals of neighboring oxygen atoms which have finite overlap with the Cu nuclei. The anisotropic part of K at Cu(2) sites is defined at $K_{ax}(2) = [K^{(c)}(2) - K^{(a,b)}(2)]/3$. $K_{ax}(2)$ increases below T_c, indicating negative $K_{s,ax}(2)$ in the normal state. This is consistent with that expected for the dipolar field from a spin in the Cu $d(x^2 - y^2)$ state.[4] Thus, we conclude that both the Cu d and O p states contribute to K_s at Cu(2) sites. For Cu(1) sites, a nearly isotropic decrease of the Knight shift below T_c suggests that Cu d spins have a small contribution to K_s.

Further analysis of K_s requires that we make an assumption which will allow us to determine K_{orb} and K_s separately. It is known that $K_s = 0$ at $T = 0$ if the pairing is singlet and the effect of spin-orbit scattering is negligible. In the case of triplet pairing, K_s does not change much from the normal-state value when the field direction is in a plane perpendicular to the "d vector,"[10] which is likely to be pinned by the low-symmetry crystal field. Experimentally, K changes substantially for all cases except for $H \| \hat{c}$ at Cu(2) sites. This leads us to conclude that triplet pairing is unlikely, but cannot be ruled out completely. If the pairing is singlet, K_s at $T = 0$ becomes an appreciable fraction of its value above T_c only if the spin-flip rate $1/\tau_{so}$ due to the spin-orbit scattering is comparable to $\Delta/\hbar$, where Δ is the superconducting gap.[11] For example, $K_s(T = 0)$ for ^{51}V in $V_3 X$ class intermetallic compounds has been estimated to be about 25% of its normal-state value.[12] Although it is not easy to estimate $\hbar/\tau_{so}\Delta$ in $YBa_2Cu_3O_7$, we expect a much smaller value compared with other transition-metal compound superconductors because of a large Δ, assuming τ_{so} is similar to other $3d$ compounds. We will assume that the effect of the spin-orbit scattering is small so that $K_s(T = 0) = 0$ in the following discussion. We emphasize that conclusions drawn below do not crucially depend on this assumption.

We have estimated the values of K_{orb} by extrapolation of $K(T)$ to zero temperature [see Fig. 1(a)]. Normal-state values of K_{orb} and K_s deduced in this way are shown in Table I. An interesting problem arises from the comparison of the present data with the anisotropy of the Cu(2) nuclear relaxation rate $(1/T_1)$.[13-15] Pennington et al.[13] reported that $1/T_1$ of Cu(2) at 100 K for $H \perp \hat{c}$ is 4.5 times larger than that for $H \| \hat{c}$. If we assume an anisotropic hyperfine coupling to a single isotropic spin system, the observed anisotropy of $1/T_1$ would predict $|K_s^{(c)}(2)/K_s^{(a,b)}(2)| = 2.8$, which is clearly inconsistent with our result, $|K_s^{(c)}(2)/K_s^{(a,b)}(2)| = 0.22 \pm 0.2$. How-

TABLE I. Orbital and spin parts of the Knight shift (%) in the normal state.

| | Cu(1) | | Cu(2) | |
	K_{orb}	K_s	K_{orb}	K_s
$H \| \hat{c}$	0.31 ± 0.08	0.29 ± 0.08	1.35 ± 0.08	-0.08 ± 0.08
$H \| \hat{a}$	1.18 ± 0.02	0.16 ± 0.02		
			0.24 ± 0.02	0.37 ± 0.02
$H \| \hat{b}$	0.43 ± 0.02	0.18 ± 0.02		

ever, the anisotropy of $1/T_1$ was shown to be consistent with what would be expected from the hyperfine coupling to the Cu $d(x^2-y^2)$ state.[13] Since it is unlikely that the static or dynamical spin susceptibility is highly anisotropic, the most probable cause of this discrepancy is that the Cu(2) nuclei are coupled to two types of electron spins, one residing in the $d(x^2-y^2)$ state and the other associated with oxygen holes. The ratio of the two contributions must be different for $1/T_1$ and K_s. Such a clear discrepancy between the anisotropy of $1/T_1$ and K_s is not observed at Cu(1) sites, if the possible errors in the diamagnetic correction and the values of $K_s(T=0)$ are taken into account.

K_s at Cu(2) sites is then expressed as

$$K_s^{(a)}(2)=A^{(a)}\chi_{s,d}+B\chi_{s,h} \quad (a=a,b,c),\tag{1}$$

where $\chi_{s,d}$ and $\chi_{s,h}$ are the susceptibilities of Cu d spins and oxygen holes, respectively. Since the transferred hyperfine field B is expected to be isotropic, only Cu(2) d spins will contribute to $K_{s,ax}(2)$. In contrast to the dominant contributions of d spins to $1/T_1$, both kinds of spins contribute significantly to $K_s(2)$. This can be understood if $\chi_{s,d}(q)$ is significantly enhanced at large wave vector q by antiferromagnetic spin fluctuations which do not affect the uniform ($q=0$) component of susceptibility.

We now discuss the temperature dependence of K_s at both Cu sites. It is very striking that $K_{s,iso}$ and $K_{s,ax}$ at Cu(2) sites show significantly different temperature dependences, despite the uncertainty of the diamagnetic corrections, as shown in Fig. 2(a). This fact supports the inference of two distinct contributions to K_s, where $\chi_{s,d}$ and $\chi_{s,h}$ have different temperature dependences. We note that the spin-orbit scattering would not alter the temperature dependence of K_s significantly,[11] particularly for $t=T/T_c \lesssim 0.5$ where Δ, as well as τ_{so}, are independent of temperature. A very interesting feature of these data is that $K_{s,ax}(2)$, which is proportional to $\chi_{s,d}$, is proportional to temperature for $t=T/T_c \lesssim 0.5$. This is inconsistent with conventional isotropic pairing for which the spin susceptibility has an exponential temperature dependence. This may be associated with anitotropic pairing where the gap vanishes along lines on the Fermi surface so that the density of quasiparticle states is proportional to energy for small excitation energy. Such an anisotropic gap is realized, for example, in d-wave pairing, as proposed by several authors.[16–18]

The isotropic part $K_{s,iso}(2)$, on the other hand, does not show linear-T behavior and the temperature dependence is more similar to K_s at Cu(1) sites. As shown in Fig. 2(b), the temperature dependences of $K_s(1)$ along the three principal axes are roughly the same. They follow a Yosida function[19] for isotropic pairing with a gap $\Delta \simeq 1.9k_BT_c$, which is close to the BCS value. Thus the results for Cu(1) are consistent with conventional isotropic pairing with a gap comparable to the BCS value, although there must be a large overlap of the unfilled O p orbital at the Cu(1) nuclei in order to explain positive $K_{s,iso}$.

Two possible hole states could contribute to $\chi_{s,h}$ in Eq. (1). The first is a linear combination of the p_x or p_y states of oxygen atoms in the Cu(2) plane which hybridizes with the Cu $d(x^2-y^2)$ state. In this case, we are led to a pic-
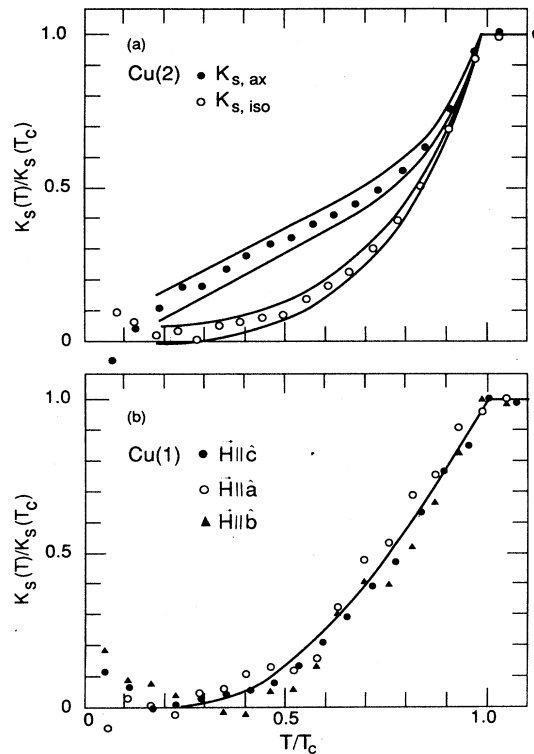

FIG. 2. The temperature dependence of the spin Knight shift normalized to the normal-state values. (a) $K_s(2)$ can be decomposed into axial (filled circles) and isotropic (open circles) parts. The solid lines indicate the range of values obtained when the parameter α employed in the correction for the diamagnetic field is allowed to vary ($0.6 \leq \alpha_\perp \leq 0.7$, $0.6 \leq \alpha_\parallel \leq 0.8$). The solid line in (b) is the calculated curve for isotropic pairing (Ref. 19) with $\Delta_0 = 1.9kT_c$.

ture of the two coupled spin systems within the Cu(2)-O plane,[20] where the susceptibilities of the Cu d spins and the spins of oxygen holes have different temperature dependences. The second possibility is the p_z state of the O(4) site which is located between the Cu(1) and Cu(2) sites. Since the O(4) sites are located closer to Cu(1) sites than Cu(2) sites, holes in the Cu(1)-O(1,4) chain are presumably responsible for $\chi_{s,h}$. This case is not inconsistent with the single-band picture for the Cu(2)-O plane, as proposed by Zhang and Rice.[21]

In conclusion, the temperature dependence of the Cu Knight shift reveals the following features which are independent of diamagnetic or spin-orbit corrections: (1) $K_{s,iso}$ is positive for both sites, indicating significant contributions of the transferred hyperfine field from oxygen p states, and (2) a substantial gap appears on those parts of the Fermi surface originating both from the Cu(1)-O chains and the Cu(2)-O planes, indicating that not only Cu(2)-O planes but also Cu(1)-O chains play a significant role in the superconductivity. The rapid change of the Knight shift at T_c seems to rule out the existence of preformed singlet pairs in the normal state. Conclusions regarding the temperature dependence of K_s below T_c are,

of course, dependent upon the validity of the diamagnetic corrections. Our best effort to make these corrections leads to a temperature dependence of K_s at Cu(1) sites which is consistent with isotropic pairing. However, the linear-T behavior of the anisotropic Knight shift at Cu(2) sites below 0.5 T_c suggests anisotropic pairing in the Cu(2)-O plane.

[1] For a review, see D. E. MacLaughlin, Solid State Phys. **31**, 1 (1976).

[2] D. E. Farrell *et al.*, Phys. Rev. B **36**, 4025 (1987).

[3] C. H. Pennington *et al.*, Phys. Rev. B **37**, 7944 (1988).

[4] M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, and R. Schwarz, Phys. Rev. B **39**, 300 (1989).

[5] E. H. Brandt, Phys. Rev. B **37**, 2349 (1988).

[6] D. R. Harshman, L. F. Schneemeyer, J. V. Waszczak, G. Appeli, R. J. Cava, B. Batlogg, L. W. Rupp, E. J. Ansaldo, R. F. Kiefl, G. M. Luke, T. M. Riseman, and D. L. Williams, Phys. Rev. B **39**, 851 (1989).

[7] M. Tinkham, *Introduction to the Superconductivity* (McGraw Hill, New York, 1975).

[8] R. F. Watson and A. J. Freeman, *Hyperfine Interaction,* edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 53.

[9] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[10] A. J. Leggett, Rev. Mod. Phys. **47**, 331 (1975).

[11] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **42**, 1088 (1962) [Sov. Phys. JETP **15**, 752 (1962)].

[12] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Rev. Mod. Phys. **36**, 170 (1964).

[13] C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39**, 2902 (1989).

[14] R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, G. F. Brennert, G. P. Espinosa, R. J. Cava, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **38**, 9299 (1988).

[15] We have benefited from discussions with D. Pines, H. Monien, and T. M. Rice in developing the arguments below.

[16] C. Gros, R. Joynt, and T. M. Rice, Z. Phys. B **68**, 425 (1987).

[17] F. C. Zhang *et al.*, Supercond. Sci. Technol. **1**, 36 (1988).

[18] G. Kotliar and J. Liu, Phys. Rev. B **38**, 5142 (1988).

[19] K. Yosida, Phys. Rev. **110**, 769 (1958).

[20] V. J. Emery and G. Reiter (unpublished).

[21] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).