NMR Studies of Spin Excitations in Superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$ Single Crystals

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(Received 18 April 1994)

The oxygen NMR shift and the Cu nuclear spin-lattice relaxation rate ($1/T_1$) were measured in $Bi_{2.1}Sr_{1.9}Ca_{0.9}Cu_{2.1}O_{8+\delta}$ single crystals. While both the shift and $1/T_1T$ decrease sharply near T_c, $1/T_1T$ becomes nearly constant at low temperatures, indicating a gapless superconducting state with finite density of states at the Fermi level. From the oxygen shift data, the residual spin susceptibility at $T = 0$ is estimated to be 10% of the value at room temperature. Our results are most consistent with a d-wave pairing model with strong (resonant) impurity scattering.

PACS numbers: 74.72.Hs, 74.25.Nf, 76.60.Cq, 76.60.Es

The spin excitation spectrum in a superconductor reflects the symmetry and magnitude of the superconducting gap, which is an important current issue for high T_c cuprates. Several unusual features of spin excitations in Y-Ba-Cu-O systems have been clarified by NMR experiments. Among these, the nonmonotonic temperature (T) dependence of the Cu nuclear relaxation rate anisotropy [1,2] and the nearly T-independent Cu spin-spin relaxation rate [3] are best explained by a gap with $d_{x^2-y^2}$ symmetry [4–7], although some features are also explained by a nodeless but highly anisotropic gap [8]. In this paper we report the oxygen NMR shift and the Cu nuclear spin-lattice relaxation rate ($1/T_1$) in $Bi_{2.1}Sr_{1.9}Ca_{0.9}Cu_{2.1}O_{8+\delta}$ (BSCCO) single crystals. While both the shift and $1/T_1T$ decrease steeply near T_c, $1/T_1T$ becomes nearly constant at low temperatures, indicating a gapless superconducting state with finite density of states at the Fermi level. Similar observations have also been recently reported by Ishida *et al.* [9]. Combined with the shift data, the residual spin susceptibility at $T = 0$ is estimated to be 10% of the value at room temperature. The most consistent account of our results is given by an impure d-wave model with strong (resonant) impurity scattering.

BSCCO crystals were prepared by a directional solidification technique [10]. To measure ^{17}O NMR, two crystals, 1 (8 mg) and 2 (15 mg), were annealed in O_2 gas enriched with 45% ^{17}O at 600 °C for a week and at 550 °C for 20 h, resulting in a superconducting transition at $T_c = 85$ K with a 1 K magnetic transition width. The long annealing time, necessary to achieve significant isotope exchange, makes the crystal surface slightly cloudy. The original color was restored by cleaving the surface layer. Since the Cu relaxation rates measured on these crystals and a third crystal (3), annealed for only 20 h at 550 °C with no surface degradation, are nearly identical, we believe that the NMR data were not affected by the surface degradation. In order to estimate the amount of possible magnetic impurities, the magnetic susceptibility in the normal state was measured with a SQUID magnetometer on a collection of crystals (105 mg total weight) taken from the same batch as crystal 2 and annealed in oxygen to yield the same $T_c = 85$ K. The magnetic field of 5 T was applied perpendicular to the c axis to avoid a contribution from superconducting fluctuations. No trace of magnetic impurities was detected. The oxygen NMR spectra were obtained as Fourier transforms of the spin-echo signal. The best data were obtained on crystal 2, but 1 gave similar results. We measured $1/T_1$ at the ^{63}Cu sites by an inversion recovery method on the central ($I_z = -1/2 \leftrightarrow 1/2$) line of the quadrupole split spectrum in a magnetic field of 8 T.

We found two quadruple split sets of ^{17}O NMR lines, while there are three oxygen sites in the unit cell. For one set of lines, both the magnetic shift and the electric field gradient (EFG) tensors have the largest component in the a-b plane. This is assigned to the sites in the CuO_2 layers [O(1) sites]. [The value of the quadrupole coupling constants, $\nu_\alpha = (3/20)eQV_{\alpha\alpha}$, are -0.39 MHz for $\alpha = c$ and 1.14 or -0.75 MHz for $\alpha = a$ or b, where Q is the nuclear quadrupole moment and $V_{\alpha\alpha}$ is the EFG tensor.] The other set shows symmetric EFG around the c axis ($\nu_\alpha = 0.80$ MHz) with a narrow (5 kHz FWHM above T_c) central line and well resolved (40 kHz FWHM) satellite lines. This resonance presumably comes from the sites in SrO layer [O(2) sites], since the signal from BiO layers is more likely to be missing due to structural disorder in the BiO layers [11,12].

The NMR shift in cuprates has been measured mostly on oriented powders [13,14] and is subject to large uncertainty below T_c due to uncertainty in the local magnetic field caused by diamagnetic currents. In our case of a thin BSCCO crystal in a magnetic field parallel to the CuO_2 layers, however, effects of the diamagnetic currents turned out to be negligible at the O(1) sites. The oxygen NMR spectra of the central lines were taken with the magnetic field (8.0 T above 75 K, 5.4 T below 80 K) along the (110) direction and are shown in Fig. 1. We found that the rf-pulse width that maximizes the spin-echo signal is different for the two sites, and T_1 is much longer for the O(2) sites. Therefore, an appropriate pulse condition can be set to optimize the intensity of one site relative to the other. The spectra in Figs. 1(a) and 1(b) were taken to optimize the intensity from the O(1) and [O(2)] sites. It is clearly seen that the O(1) line shifts

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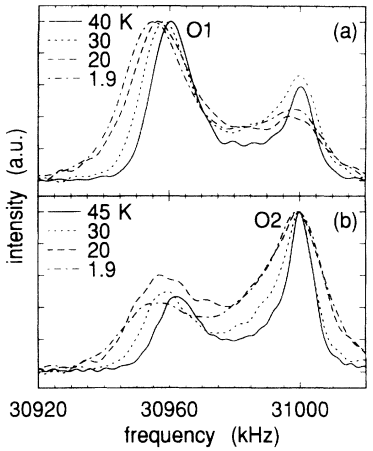

FIG. 1. Oxygen NMR spectra of the central lines from crystal 2 in a magnetic field (5.4 T) along (110) at different temperatures. Different pulse conditions were used to emphasize the signal from the O(1) sites (a) and the O(2) sites (b).

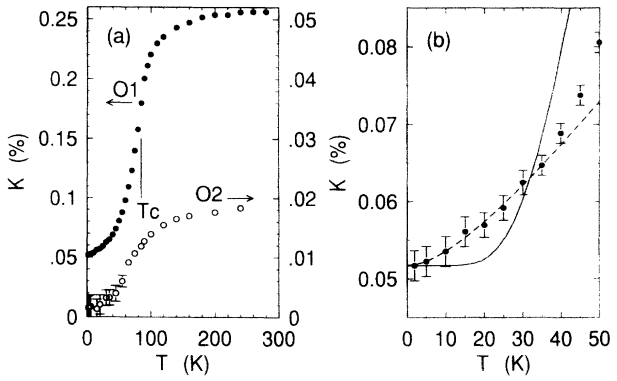

FIG. 2. (a) Temperature dependence of the oxygen magnetic shift (K) along (110) direction for crystal 2. Note different scales for O(1) and O(2) sites. (b) Low temperature data at the O(1) sites. The solid line is the result of the weak coupling BCS model and the dashed line is the fit of the impure d-wave expression.

to lower frequency with decreasing temperature while the O(2) line shows only broadening without appreciable change in the peak position.

The magnetic shift (K) was obtained from the peak position after correcting for the calculated quadrupole shift and is shown in Fig. 2(a). Generally, K is a sum of two terms, the spin shift and the orbital shift. The spin shift (K_{spin}) arises from the hyperfine coupling to conduction electron spins, and only this term varies with temperature. Although K at the O(1) sites starts to decrease near 220 K, it decreases most steeply near T_c, consistent with the rapid reduction of density of states due to an opening of a superconducting gap. The O(2) sites show a similar T dependence but overall variation is much smaller. The total change of K below T_c is 0.01% at the O(2) sites, while it is 0.12% at the O(1) sites. Thus, even if some fraction of the change of K at the O(2) sites is due to diamagnetic currents, it is negligible for O(1) sites, since the magnetic field from diamagnetic currents should be the same for both sites. In particular, K at the O(2) sites is nearly constant below 40 K, ensuring that the change of K at O(1) sites in this T range is solely due to variation of the spin susceptibility. A striking feature of the low-T data at the O(1) sites shown in Fig. 2(b) is the substantial variation even below 30 K. This is not expected for a clean superconductor with an isotropic gap. For example, the solid line is the calculation [15] for the weak coupling BCS model, taking K above 240 K as the normal state shift and assuming that $K_{\text{spin}} = 0$ at $T = 0$. Such behavior suggests that the density of quasiparticle states has a substantial energy dependence over a small (a few meV) energy range.

Another important observation on the superconducting density of state (DOS) is provided from $1/T_1$. We have measured $1/T_1$ at Cu sites on three crystals at high field (8 T) and a powder sample at zero field using nuclear quadrupole resonance (NQR). Because of the weak signal intensity, the NQR measurements were limited to temperatures below 20 K. The recovery of nuclear magnetization after the inversion pulse does not follow the time dependence expected for a single $1/T_1$ value, indicating some distribution of $1/T_1$. Instead, the data were well fitted with a sum of two components with the values of $1/T_1$ different by about an order of magnitude. The weight of the smaller $1/T_1$ component is less than 10% of the weight of the larger $1/T_1$ component. $1/T_1T$ for the larger $1/T_1$ component is plotted in Fig. 3. The smaller $1/T_1$, although determined with poor accuracy, shows similar T dependence. The relative weight of two components does not depend on temperature below 100 K and is roughly the same for all samples.

Although $1/T_1T$ decreases most steeply near T_c, it shows a peak at a significantly higher temperature, a feature observed also by other groups [9,16]. The most remarkable feature is the weak T dependence of $1/T_1T$ at low temperatures and the tendency to saturate at a finite value at $T = 0$. (In contrast to Ishida *et al.*, who found $1/T_1T$ = const below 10 K [9], $1/T_1T$ in our data keeps

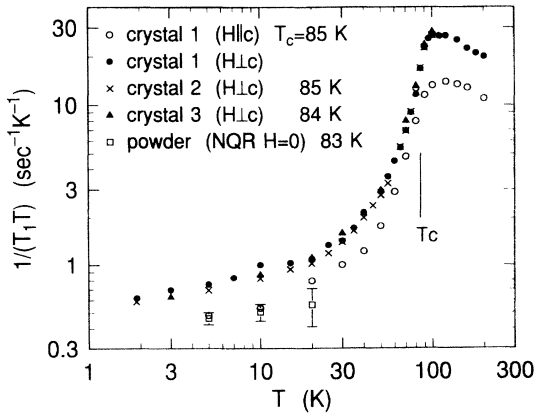

FIG. 3. Temperature dependence of $1/T_1T$ at the Cu sites. Only the results for the larger $1/T_1$ component are shown. The vertical bar indicates T_c of the crystal 1 and 2.

changing slightly down to 1.9 K.) A similar behavior has been seen in Zn-doped $YBa_2Cu_3O_7$ [17] but not in undoped $YBa_2Cu_3O_7$. We can rule out the possibility that either vortex motion [18] or fast relaxation at a normal vortex core is responsible for the nearly constant $1/T_1T$ at low T, since essentially the same result was obtained at zero magnetic field (NQR) and at high field along the c axis below 20 K. Note that any enhancement of $1/T_1$ by vortices should be weaker for the field perpendicular to the c axis. Relaxation due to dilute magnetic impurities should be unimportant since it would result in additional (sample dependent) distribution of $1/T_1$ at low T, which was not observed [19]. The nearly constant $1/T_1T$ then implies a finite DOS at the Fermi level, i.e., a gapless superconducting state.

Since the finite DOS leads to finite spin susceptibility, the spin should not be zero at $T = 0$. The residual spin shaft at $T = 0$ may be estimated as follows. The spin shaft and the relaxation rate are both related to the DOS $N(\varepsilon)$ as $K_{\rm spin} \propto \int(-\partial f/\partial\varepsilon)N(\varepsilon)\,d\varepsilon$, $1/T_1T \propto \int(-\partial f/\partial\varepsilon)\{N(\varepsilon)\}^2\,d\varepsilon$, where $f(\varepsilon)$ is the Fermi function. Thus we expect approximately $K_{\rm spin} \propto 1/\sqrt{T_1T}$ [20], which is indeed observed below 35 K as shown in Fig. 4. The orbital shift is estimated to be $(0.030 \pm 0.002)\%$ by extrapolating the linear relation to $1/\sqrt{T_1T} = 0$. Then the spin shift at 1.9 K is 0.022%, which is about 10% of the spin shift at room temperature (0.23%). The spin susceptibility is expressed as $\chi_{\rm spin} = \chi_0/(1 + J\chi_0)$, where χ_0 is proportional to DOS. $J\chi_0$ may be either negative as in the Hubbard model [4] or positive as in the t-J [21] or the three band model [22]. In either case, the value of $|J\chi_0|$ is typically 0.5 above T_c and negligible at low temperatures. The above result then implies that the residual DOS at $T = 0$ is 6%–20% of the normal state DOS.

Let us now discuss possible origins of the gapless state. Since DOS at the Fermi level is zero for any pure superconducting states, the gapless behavior must be caused by disorder. For isotropic or anisotropic s-wave pairing, it is known that potential disorder is not strongly pair breaking [23,24] but magnetic scattering can lead to a gapless state [25]. A shown in Fig. 5, we found no trace of magnetic impurities in the magnetic susceptibility (χ). It follows that the same T dependence as the shift at the O(1) sites as expected (solid circles in the inset). If we assume, for example, 0.3%/Cu of spin 1/2 impurities and subtract the impurity Curie term, the resultant χ is clearly incompatible with the shift data (open circles in the inset). We estimate an upper limit of 0.1%/Cu spin 1/2 impurities, which then sets an upper limit for the scattering rate $1/\tau \leq 0.04T_c$ by assuming the s-wave unitarity limit and 1 state/eV Cu normal state DOS.

The pair breaking effect of magnetic impurities depends critically on scattering strength. The original Abrikosov-Gorkov theory [25], which used the Born (weak scattering) approximation, requires a large scattering rate $1/\tau \geq 0.46\Delta_0$ to reach the gapless state, where Δ_0 is the gap for the pure state. This value is orders of magnitude larger than our estimate. Also such a large $1/\tau$ is incompatible with the rapid reduction of K and $1/T_1T$ near T_c [26] and the typical resistivity of BSCCO [27] which extrapolates to a small residual value at $T = 0$.

The situation is quite different for resonant (strong) scattering, which allows the formation of an impurity band near the Fermi level by a small amount of impurities without affecting the major feature of DOS near the original gap [28–30]. Such effects are possible, however, only when the Kondo temperature of the impurities is comparable to T_c. In such a case, 10%–20% residual DOS requires that $n_i/(2\pi)^2N_0T_c = 0.01$–$0.1$, where n_i is the impurity concentration and N_0 is the normal state DOS [30]. For $N_0 = 1$ state/eV Cu, $n_i = 0.3\%$–3%, which appears to be still somewhat larger than our estimate. Also the significant T dependence of K at low T is

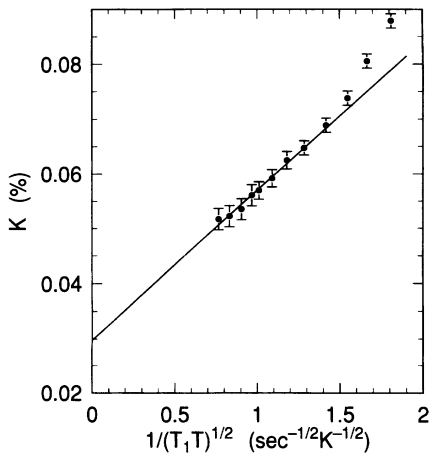

FIG. 4. Magnetic shift at the O(1) sites (K) is plotted against $\sqrt{T_1T}$ for crystal 2 with temperature as an implicit parameter.

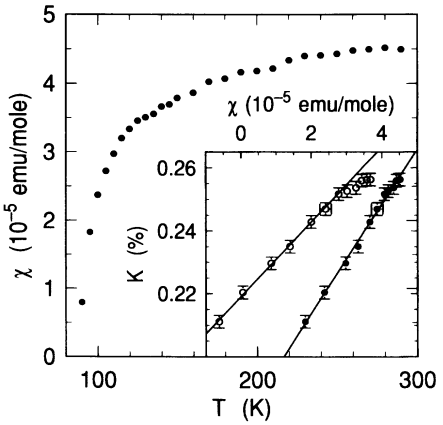

FIG. 5. Temperature dependence of the magnetic susceptibility (χ) measured using a SQUID magnetometer. In the inset, the magnetic shift (K) at the O(1) sites is plotted against χ with (open circles) or without (solid circles) subtracting an arbitrarily chosen Curie term corresponding to 0.3%/Cu spin 1/2 impurities. Note the deviation from linearity by subtracting a Curie term.

incompatible with this picture is the original gap is isotropic. We cannot rule out, however, the possibility that a highly anisotropic s-wave state is made gapless by a small amount of resonant magnetic impurities.

If the pairing state has d-wave symmetry, nonmagnetic impurities have the same pair breaking effect as the magnetic impurities and $N(0)$ becomes finite with any amount of impurities. However, the quantitative aspect depends on the strength of the scattering. In the Born approximation [31,32], a large scattering rate $1/\tau \sim T_c$ is required to yield 10% residual DOS, again inconsistent with the present results.

If the impurities cause resonant scattering, the low energy DOS is significantly modified by a small amount of impurities [24,33]. For the $d_{x^2-y^2}$ pairing state in two dimensions, the residual DOS is given as $N(0)/N_0 = k(1/\tau\Delta_0)^{1/2}$ in the unitarity limit, where k is a constant of order unity, $1/\tau = n_i/\pi N_0$, and Δ_0 is the maximum gap. Then a small scattering rate of $1/\tau\Delta_0 \sim 10^{-2}$, corresponding to an impurity concentration of order 10^{-3}, results in 10% residual DOS. Since only the low energy DOS is modified by impurities, we expect a crossover to the pure d-wave behavior at higher temperatures. Hirschfeld and Goldenfeld [33] studied such crossover in T dependence of the penetration depth, which should be applicable to spin susceptibility as well. We found that their form $K_0 + \alpha T^2/(T + T^*)$, which interpolates the T^2 behavior at low T and the T-linear behavior at high T, fits the low-T shift data below 35 K quite well [the dashed line in Fig. 2(b)]. The crossover temperature is given as $T^* = 0.83(\Delta_0/\tau)^{1/2}$. If we take $\Delta_0 = 20$ meV [34], the fitted value $T^* = 25 \pm 15$ K leads to the scattering rate $1/\tau\Delta_0 = 0.017$, consistent with the above estimation. By extrapolating the T-linear behavior at high T to $T = 0$, the same fit yields $\alpha T^* = (0.016 \pm 0.01)$ for the residual spin shift, also in agreement with the previous estimation. Thus the $d_{x^2-y^2}$ state with resonant impurity scattering gives a semiquantitative account of the observed behavior. While the origin of such resonant scattering in BSCCO is not yet clear, it should be noted that BSCCO has two types of intrinsic disorder. First is the cation nonstoichiometry resulting from the random substitution of Bi/Cu for the Sr/Ca sites or vacancies in Sr/Ca sites. Second is the structural disorder in the BiO layers associated with the incommensurate structural distortion and excess oxygen in the BiO layers [11,12].

In conclusion, our measurements of oxygen NMR shift and Cu nuclear relaxation rate revealed a gapless superconducting state in nominally pure BSCCO crystals and finite spin susceptibility at $T = 0$, which is about 10% of the value at room temperature. Such a gapless behavior at low T and the rapid reduction of the shift and $1/T_1T$ near T_c can be explained only by strong (resonant) impurity scattering. Our results are most consistent with an impure d-wave pairing state, although we cannot rule out the possibility of an anisotropic s-wave state with a small amount of resonant magnetic impurities.

We would like to thank D. Pines, A. J. Millis, S. Chakravarty, P. Littlewood, and D. J. Scalapino for helpful discussions. We thank T. McGuire for assistance in susceptibility measurements.

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