Evidence for Two Pairing Energies from Nuclear Spin-Lattice Relaxation in Superconducting $Ba_2YCu_3O_{7-\delta}$

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We report ^{63}Cu nuclear spin-lattice relaxation data for $Ba_2YCu_3O_{7-\delta}$ in the superconducting state obtained by nuclear quadrupole resonance in zero applied magnetic field. The temperature dependences of the relaxation rates reveal striking differences in the excitation spectra for quasiparticles on the chain-forming Cu(1) and planar Cu(2) lattice sites, corresponding to substantially different pairing energies for electrons on the planes and chains. Values of the gap ratio $2\Delta/kT_c$ of 8.3 and 2.4 are obtained for the Cu(1) and Cu(2) sites, respectively.

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Despite rapid recent progress in understanding the properties of the high-T_c superconductor $Ba_2YCu_3O_{7-\delta}$, there remain fundamental questions concerning the mechanism of superconductivity in this fascinating material. The validity of the BCS theory as a general framework for a microscopic description is still at issue, as are the respective roles of the planar [Cu(2)] and chain-forming [Cu(1)] Cu sites in the crystal structure. Nuclear spin-lattice relaxation offers a powerful local probe of the dynamics of excitations (quasiparticles) in the superconducting state and such measurements have yielded important insight into the microscopic properties of superconductors.[1] For example, the classic work of Hebel and Slichter[2] on Al provided one of the earliest confirmations of the BCS theory. In this Letter we present data for the spin-lattice relaxation rates of ^{63}Cu at the Cu(1) and Cu(2) sites in $Ba_2YCu_3O_{7-\delta}$ obtained by nuclear quadrupole resonance (NQR) in zero applied magnetic field. The NQR lines for the two Cu sites in $Ba_2YCu_3O_{7-\delta}$ are well separated[3] so that in addition to the obvious advantage of permitting study in the absence of an externally applied magnetic field, NQR permits separate relaxation measurements for the Cu(1) and Cu(2) sites. We have found strikingly different relaxation behavior for Cu(1) and Cu(2) in the superconducting state. The relaxation rates for the two sites are comparable just above T_c, but as the temperature is lowered below T_c, the rate for the Cu(2) sites decreases somewhat more slowly than the weak-coupling BCS prediction while for the Cu(1) sites, a much more rapid decrease occurs. This indicates a substantially larger energy for quasiparticle formation (pair breaking) on the chains. Neither site exhibits the peak in relaxation rate just below T_c which is characteristic of BCS superconductors having small or moderate anisotropy of the energy gap.[1,2] As we reported previously,[4] there are also differences in the normal state where relaxation at the Cu(2) sites approximates conventional Korringa behavior while that at the Cu(1) sites shows anomalously weak temperature dependence.

The samples used for these experiments were prepared by standard solid-state reaction in the form of pressed ceramic pellets. We subsequently powdered the pellets to improve penetration of the radio-frequency fields into the sample material. To prevent changes in sample characteristics due to oxygen loss or reaction with the ambient environment, the pellets were powdered in a dry oxygen atmosphere and sealed in quartz ampoules without further exposure. The ampoules contained roughly 1 atm of oxygen and about $\frac{1}{10}$ atm of helium gas, the latter to improve thermal contact during low-temperature measurements. Samples prepared and protected in this way yielded stable and reproducible results over the period of several weeks required to carry out the experiments. X-ray analysis showed that the samples consisted of high-quality single-phase material. An additional measure of sample quality was provided by the widths of the NQR lines, half widths at half height $\delta H \simeq 120$ kHz, which are the narrowest that have come to our attention.[3,5]

Relaxation times were measured at frequencies close to 22.0 and 31.5 MHz for the Cu(2) and Cu(1) sites, respectively, with small adjustments made for the temperature dependence of the NQR frequencies. To obtain the relaxation times, we measured the spin-echo amplitude as a function of the time delay between the first and second pulses of a three pulse π-$\frac{1}{2}\pi$-π sequence. Previous work[4] had shown that a single π pulse is sufficient to saturate or partially invert the spin polarization of the relatively narrow distribution of NQR frequencies. A regulated flowing–He-gas system provided the necessary variable sample temperatures which we measured with a calibrated gold-Chromel thermocouple.

Our results for the relaxation rates $1/T_1$ are summarized in Fig. 1 showing the temperature dependence of the rates for Cu(1) and Cu(2) in the normal and superconducting states. This plot shows the nearly Korringa-type behavior ($1/T_1 \propto T$) at Cu(2) and the anomalously weak temperature dependence of the Cu(1) rate in the normal state as well as a more rapid decrease in the rates

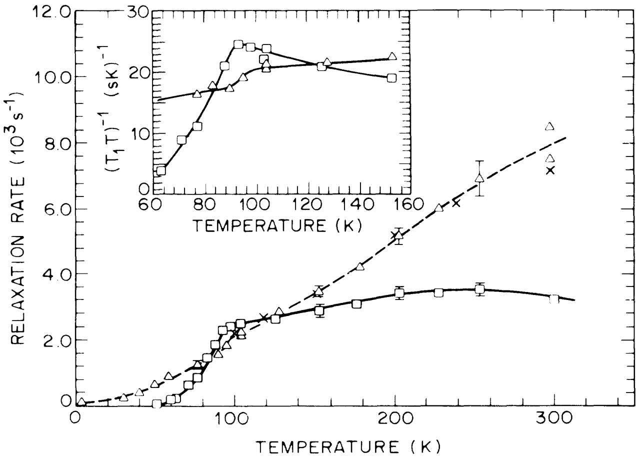

FIG. 1. Nuclear spin-lattice relaxation rates $1/T_1$ vs temperature of ^{63}Cu for chain-forming Cu(1) (squares) and planar Cu(2) (triangles) sites in $Ba_2YCu_3O_{7-\delta}$. Crosses denote relaxation rates of ^{89}Y measured by Markert *et al.* (Ref. 6), normalized to the present Cu(2) data just above T_c. Inset: Relaxation rates/temperature vs temperature for Cu(1) and Cu(2) in the region of the superconducting transition.

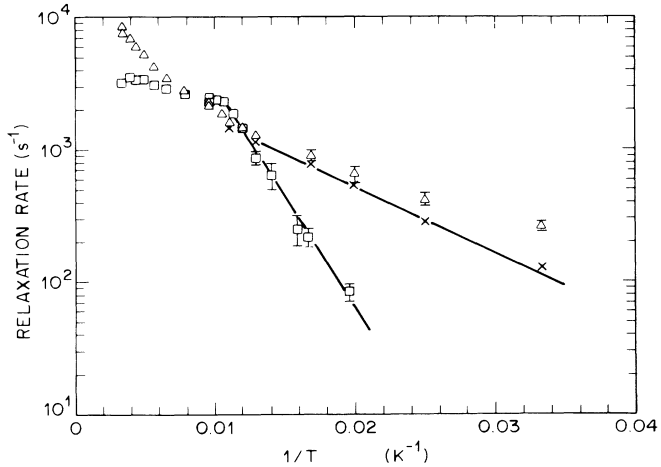

FIG. 2. Semilogarithmic plot of relaxation rate $1/T_1$ vs inverse temperature for Cu(1) (squares) and Cu(2) (triangles) sites in $Ba_2YCu_3O_{7-\delta}$. Crosses denote Cu(2) data after correction for temperature-independent background as described in text.

for both sites below T_c. Also shown in this figure are the ^{89}Y data of Markert *et al.*,[6] normalized to our Cu(2) data near T_c. Since the Y site is intimately associated with that of Cu(2) in the crystal structure of $Ba_2YCu_3O_{7-\delta}$, the essentially identical temperature dependences of the Y and Cu(2) rates in the normal state are strong evidence for associating the 22-MHz NQR line with Cu(2).[7] The inset presents our data near T_c plotted as $1/T_1T$ vs T and shows more clearly that the rates for both sites are affected by the superconducting transition, although the effect is obviously much stronger for the Cu(1) sites. It is evident that there is no sign of the so-called "coherence factor" peak[1] in the relaxation rates for either site just below T_c. At the lowest temperature, 4.2 K, the Cu(2) data reach an unexpectedly large limiting value, $(1/T_1)_0 = 133 \pm 20\ s^{-1}$.

The dominant nuclear relaxation mechanism in superconductors involves nuclear spin flips induced by unpaired excitations (quasiparticles) and is proportional to the density of such excitations. For a BCS superconductor with energy gap $2\Delta \simeq 3.5\ kT_c$, the temperature dependence of the rate well below T_c is given by $1/T_1 \propto \exp(-\Delta/kT)$. To compare our results with the expected BCS behavior we present a semilogarithmic plot, $\log_{10}(1/T_1)$ vs $1/T$, in Fig. 2. The Cu(1) data are consistent with an activation energy $\Delta = 32.8 \pm 0.8$ meV, or a ratio $2\Delta/kT_c = 8.3$ for $T_c = 92$ K. The rate for Cu(2) exhibits some deviation from activated temperature dependence at 30 K and below. However, if we assume a constant background rate equal to the measured rate at 4.2 K as discussed below, an exponential temperature dependence is recovered. Thus, the rates for the Cu(2) sites in the superconducting state can be represented by the sum of a constant term, $(1/T_1)_0$, and an exponentially activated term with $\Delta = 9.6 \pm 0.2$ meV. This value of Δ corresponds to $2\Delta/kT_c = 2.4$.

In discussing the nuclear relaxation data, we now consider in turn the following features of the experimental results: the apparent presence of a relative large "background" rate for the Cu(2) sites at 4.2 K, the absence of the BCS peak for both sites just below T_c, and the significance of dramatically different temperature dependences for the relaxation rates at the two sites.

A possible explanation for residual relaxation at Cu(2) at 4.2 K would be the presence of a small amount of normal material associated with a second, nonsuperconducting phase. We believe this not to be the case for two reasons. First, the value of $1/T_1T$ is roughly 50% *higher* than measured in the normal state of $Ba_2YCu_3O_{7-\delta}$ just above T_c, yet the most likely nonsuperconducting phase is oxygen-deficient $Ba_2YCu_3O_{7-\delta}$ with $\delta > 0.5$, a semiconductor for which very low relaxation rates can be expected.[8] Second, the NQR frequency is extremely sensitive to local structure as exemplified by the nearly 50% difference in frequencies for Cu(1) and Cu(2). Since the relaxation is measured at the frequency of the Cu(2) NQR, the local environment of Cu in the impurity phase would have to be essentially identical to that of Cu(2) in $Ba_2YCu_3O_{7-\delta}$, a highly improbable coincidence.

It is much more likely, in our view, that the background relaxation is due to interactions of Cu nuclei with localized magnetic moments coupling preferentially to Cu(2) in superconducting $Ba_2YCu_3O_{7-\delta}$. The presence of moments in samples of this compound is strongly suggested by observation[9] of a Curie-Weiss term in the magnetic susceptibility, but their specific location has not been determined. The situation of local moments in or near the Cu(2) planes is consistent, however, with our previous finding[4] of appreciable disorder in the planes, inferred from high-field NMR spectra for the two sites in the normal state. Possible sources of moments coupling to Cu(2) include divalent copper associated with disorder in the Cu(2) planes and antisite defects in which Cu is located on the Y lattice. Relaxation of nuclei by fixed paramagnetic impurities is frequently only weakly dependent on temperature. On this basis, we have assumed a temperature-independent background in our analysis of the data.

A peak in the nuclear relaxation rate just below T_c is predicted by the BCS theory as a consequence of a singularity in the theoretical density of states at the gap edge.[10] Even in the best BCS superconductors, anisotropy of the gap smears the singularity so that a finite peak in the rate is observed. Numerical calculations[1,11,12] have shown how the size and shape of the peak are affected by varying degrees of anisotropy, but such studies yield, at most, a range of weak temperature dependence just below T_c. There is no evidence that a highly anisotropic, nonzero gap can lead to the rapidly-decreasing relaxation rates we have observed, most notably for Cu(1). Pair breaking by paramagnetic impurities can also eliminate the BCS peak, but the transition temperature is strongly suppressed and the temperature dependence below T_c is weakened relative to the normal BCS behavior.[13] We cannot exclude the possibility of some pair breaking at the Cu(2) sites, particularly in view of the apparent presence of moments in or near the planes and the low activation energy for these sites. However, studies of rare-earth substitution have shown that large moments on the Y sites have essentially no effect on the superconducting transition while magnetic impurities on the Ba sites, closer to the planes, completely suppress superconductivity.[14] Furthermore, pair breaking seems incompatible with the strong temperature dependence found for Cu(1).

A relaxation peak is not expected for true gapless superconductivity, say by non-s-wave pairing, for which the superconducting density of states $N_s(E)$ decreases monotonically to zero. A linear variation $N_s(E) \propto E$ leads to a T^3 power-law dependence for $1/T_1$. Such behavior has been observed, for example, in the heavy-fermion superconductor UBe_{13}.[15] Exploring an alternative to the exponentially activated temperature dependence described above, we have found that our data are also consistent with power-law dependences of the form $1/T_1 \propto T^n$, after subtraction of $(1/T_1)_0$ for the Cu(2) rates. The exponents obtained by power-law fits are $n = 5.5 \pm 0.5$ for Cu(1) and $n = 2.4 \pm 0.2$ for Cu(2). This representation might be construed as appropriate for the Cu(2) relaxation, implying a somewhat nonlinear variation of $N_s(E)$ but it does not explain the large exponent required for a power-law representation of the rate for Cu(1). Moreover, recent tunneling studies provide strong evidence for a nonzero (s wave) gap in $Ba_2YCu_3O_{7-\delta}$.[16]

Finally, we consider what we view as the central implication of these experiments, the simultaneous existence of distinct excitation spectra for quasiparticles interacting with the two Cu sites in the crystal. If we accept the presence of a vanishingly small density of states at low energies, as indicated by tunneling studies,[16] we are led to the novel concept of different energies for pair formation and quasiparticle excitations associated with the two sites. This local distinction is easily seen by NQR relaxation, whereas nonlocal spectroscopies such as tunneling and infrared do not easily distinguish between sites. The situation is reminiscent of that of the quasi one-dimensional Bechgaard salts such as $(TMTSF)_2X$ (TMSF is tetramethyltetraselenafulvalene), where tunneling measurements show that the pair-breaking range of weak energy on the chains is substantially larger than that associated with the three-dimensional ordering temperature.[17] In such systems, superconducting order may persist in the chains up to a much higher one-dimensional ordering temperature. The present situation, unlike the quasi one-dimensional metals, involves coexisting one- and two-dimensional conductors which interact in a still poorly understood way to cause "three-dimensional ordering" at $T \simeq 90$ K.

In the context of interacting chains and planes, it is significant that the observed ordering temperature is intermediate between those that can be inferred from the "local gaps" on the two sites. If we assume standard weak-coupling BCS gap ratios, $2\Delta/kT_c \simeq 4$, the nuclear relaxation activation energies correspond to transition temperatures of roughly 60 to 200 K, respectively, for the planes and chains. The lower temperature, 60 K, is close to the value of T_c found[18] for the oxygen-deficient phase with $\delta \simeq 0.3$. The chains in this phase contain a large number of partially ordered vacancies while the planes apparently remain intact. With respect to the higher pairing energy on the chains, it is difficult to suppress the speculation that one-dimensional superconducting order may be responsible for the persistent reports[19] of intermittent superconductivity in this class of materials at temperatures near and exceeding 200 K.

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