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Nuclear relaxation behavior of the superconducting cuprates: $Bi_2Sr_2CaCu_2O_8$

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Nuclear-magnetic-resonance data are presented and analyzed for the high-T_c compound $Bi_2Sr_2CaCu_2O_8$ for two oxygen doping levels. Both sample conditions lead to spin-gap behavior for the NMR shift, with a precursive downturn in the data at $T > T_c$. In addition, the relaxation times T_1 obey the relation $(T_1T)^{-1} \propto K^s(T)$ at low temperatures ($T \lesssim 100$ K), where $K^s(T)$ is the spin paramagnetic shift. This relation, which is also obeyed by other cuprate superconductors, is argued to be related to the spin-gap effects and thus incompatible with a Fermi-liquid approach to the understanding of these systems.

Some years ago BCS theory[1] identified the nuclear spin-lattice relaxation rate T_1^{-1} as a sensitive probe of the superconducting density of states and associated energy gap of ordinary superconductors.[2,3] From the BCS standpoint, however, T_1 measurements on the high-T_c cuprate superconductors[4-6] have been quite clearly anomalous from the outset and their implications for gap energies obscure. Not only is there no Hebel-Slichter "peak"[2] in the rate below T_c for the yttrium,[4] copper,[5,6] or oxygen[7] sites in $YBa_2Cu_3O_7$, but in addition T_1^{-1} exhibits a remarkably steep descent starting at T_c and typically extending over several orders of magnitude.[8] Moreover, the oxygen-deficient ($T_c \approx 60$ K) phase $YBa_2Cu_3O_{6.5-6.7}$ has been found to exhibit behavior that is sharply contrasting and even more puzzling. The normal-state spin paramagnetic shifts decline steadily below room temperature, the values at T_c being only 20%–25% of those at 300 K.[9,10] Both the shifts and relaxation rates of $^{17}O(2,3)$ and $^{63}Cu(2)$ traverse the vicinity of T_c in a smooth and nearly featureless decline toward zero.[11] Similar results have been reported for $YBa_2Cu_4O_8$,[12] verifying that this behavior is not the result of disorder. Combined with neutron-scattering data,[13] these results strongly indicate the formation of a spin gap in the excitation spectrum of these systems at low temperatures.[14,15]

We report in this paper a comprehensive NMR study of ^{63}Cu in crystals of $Bi_2Sr_2CaCu_2O_8$. The temperature dependences of the shift and relaxation rate in this system are intermediate in character between that of the 60 and 90 K phases of $YBa_2Cu_3O_7$, giving further confirmation that spin gap behavior is intrinsic to the superconducting cuprates. In addition, both $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ are found to exhibit a second effect which is emerging as a "signature" of these peculiar metals. For the planar ^{63}Cu spins, one finds that

$$(T_{1c}T)^{-1} \propto K_\perp^s(T) \qquad (1)$$

for $T \lesssim 100$ K, as opposed to Korringa-like[16] behavior, $(T_{1c}T)^{-1} \propto (K_\perp^s)^2$. Moreover, for nuclei such as ^{17}O in the CuO_2 planes, Eq. (1) is found to hold *for all temperatures up to 300* K. In Eq. (1), T_{1c} denotes the relaxation time with the field along the c axis and $K_\perp^s$ is the spin paramagnetic shift in the basal plane. After presenting the $Bi_2Sr_2CaCu_2O_8$ NMR data, we document the occurrence of behavior like Eq. (1) in other high-T_c systems and discuss some implications for the underlying physics. For the high-T_c cuprates studied to date, Eq. (1) is found to replace quite generally the sharply contrasting low-temperature shift and relaxation behaviors which characterize BCS theory.

Thin platelets of $Bi_2Sr_2CaCu_2O_8$ were synthesized by a directional solidification technique as described in previous papers.[17] These platelets were stacked in a small rectangular box so as to form an NMR sample with a common c axis. The material on which NMR shift and relaxation data were taken was investigated in two different states of oxygen doping. The sample was first studied "as grown" with $T_c \approx 90$ K, then a second time, after an overnight anneal at $T = 550\,^\circ$C under an applied pressure of 12 atm of O_2. The latter treatment increases the (Hall effect) carrier concentration by $\sim 50\%$. As a consequence, T_c drops to 77 K,[17] thus penetrating a doping regime where T_c *decreases* with carrier density.

The NMR spectra were first taken with the field along the c axis so as to diminish the line-broadening effect of the broad distribution of electrical-field gradients (EFG's). The corresponding line profiles are ~ 200 G wide at $\nu = 88$ MHz, easily narrow enough for accurate shift measurements. We also note that there is only one copper site in this structure, greatly simplifying the interpretation of the results. Shift data taken at temperatures $20\text{ K} \leq T \leq 300$ K are shown in Fig. 1(a) for both doping conditions described above. These c-axis data exhibit a very substantial temperature dependence, in contrast with the Cu(2) sites in $YBa_2Cu_3O_7$, for which the c-axis hyperfine coefficient is accidentally very small.[18] The zero-temperature intercept of the shift is identified as the orbital component $K_c^{orb} \approx 1.22\%$. This value is quite close to that of $YBa_2Cu_3O_7$ (1.27%),[19] suggesting that the Cu^{2+} crystal-field parameters of these systems are nearly the same.[20] The temperature-dependent portion of K_c is attributed to the spin paramagnetic term, $K_c^s(T)$

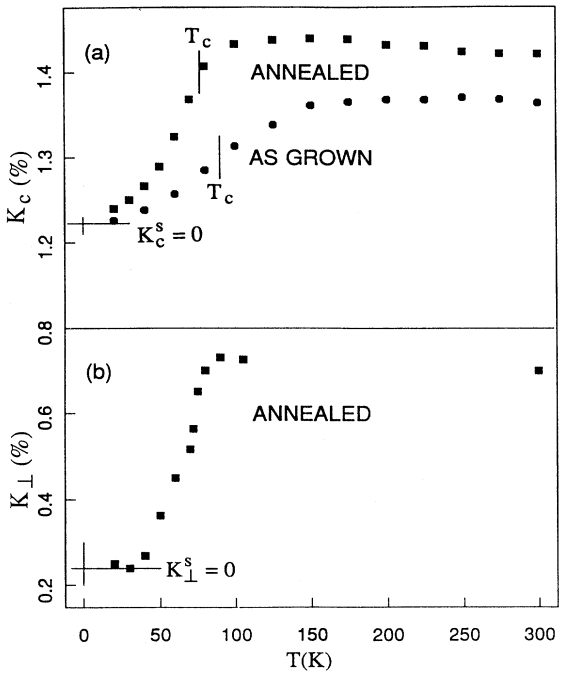

FIG. 1. (a) ^{63}Cu NMR shifts are plotted vs temperature T for both doping levels studied, with field $H \sim 7.6$ T oriented along the c axis. Values of T_c in low field (Ref. 17) are indicated. The estimated extrapolation point for these two curves at $T=0$ K, i.e., $K_c^{orb} \approx 1.227\%$, is also shown. (b) Shift values with field-oriented $\perp c$ axis are shown for the annealed case only. The estimated extrapolation to $T=0$, K, i.e., $K_\perp^{orb} \approx 0.24\%$ (marked $K_\perp^s = 0$), is indicated.

$= K_c(T) - K_c^{orb}$ in the usual fashion.[18] Noting that $K_c^s(T) = \alpha_c^s \chi_c^s(T)$, the temperature dependences of the shifts are found to resemble those of the corresponding susceptibilities as expected.[17]

The c-axis shift measurements in Fig. 1(a) display an interesting contrast in behavior between the two doping levels. The 12 atm annealed condition yields a nearly constant shift in the normal state, with a downturn just above T_c. This is reminiscent of $YBa_2Cu_3O_7$ with a very slight oxygen deficiency.[21] On the other hand, the shift for as-grown material shows a very pronounced decline well above T_c. This behavior is similar to, but not as extreme as that of the 60 K phase of $YBa_2Cu_3O_7$.[9] These behaviors suggest formation of a spin gap from causes unrelated to the superconductivity.[14,15] Other data on the cuprates also support such a picture. Tunneling data on oxygen-deficient $YBa_2Cu_3O_8$ (Ref. 22) exhibit a structureless energy gap larger than that of fully oxygenated material. The related $Bi_2Sr_2Ca_2Cu_3O_{10}$ system, which exhibits a spin gap effect similar to that of $Bi_2Sr_2CaCu_2O_8$,[23] shows a weak and greatly broadened specific heat peak at T_c (Ref. 24) in comparison with $YBa_2Cu_3O_7$.

We also report, in Fig. 1(b), shift measurements for the annealed sample with the field in the basal plane. The NMR line for this orientation is broader than for the c-axis case and undergoes a second-order quadrupolar shift.[25] As expected, the orbital ($T \rightarrow 0$) shift in this case is only $\sim \frac{1}{5}$ of K_c^{orb} (Refs. 18 and 20) [Fig. 1(a)], and the spin part $K_\perp^s$ is much larger than K_c^s [cf. $YBa_2Cu_3O_7$ (Ref. 18)]. There is some structure in $K_\perp^s(T)$ in the vicinity of T_c, but otherwise its temperature dependence follows closely that of $K_c^s(T)$.

Spin-lattice relaxation times T_1 have been measured on the ^{63}Cu nuclei in this compound for both doping levels, with the field directed along the c axis. The results are plotted as $(T_1T)^{-1}$ vs T in Fig. 2. For the as-grown sample condition, $(T_1T)^{-1}$ rises to a broad maximum as T is lowered, then descends through T_c with only a barely resolved change of slope. This result mirrors very closely the behavior of $YBa_2Cu_3O_{6.7}$.[10,11] The annealed sample condition yields similar behavior, but rolls off more abruptly below $T \approx 100$ K in correspondence with the shift behavior in Fig. 1. As with the shift, the relaxation behavior of $Bi_2Sr_2CaCu_2O_8$ at these two doping levels is intermediate between that of the 60 and 90 K phases of $YBa_2Cu_3O_7$ suggesting that there is a continuum of such behaviors available.[21]

Considering the T_1 data in terms of Eq. (1), we replot the shift data from Fig. 1(a) in Fig. 2, scaled to have the same amplitude. In both cases the shift and relaxation data are seen to follow Eq. (1) up to $T \sim 100$ K, above which they gradually diverge. In $YBa_2Cu_3O_7$, Eq. (1) also holds for the Cu(2) sites, again below $T \sim 100$ K.[26]

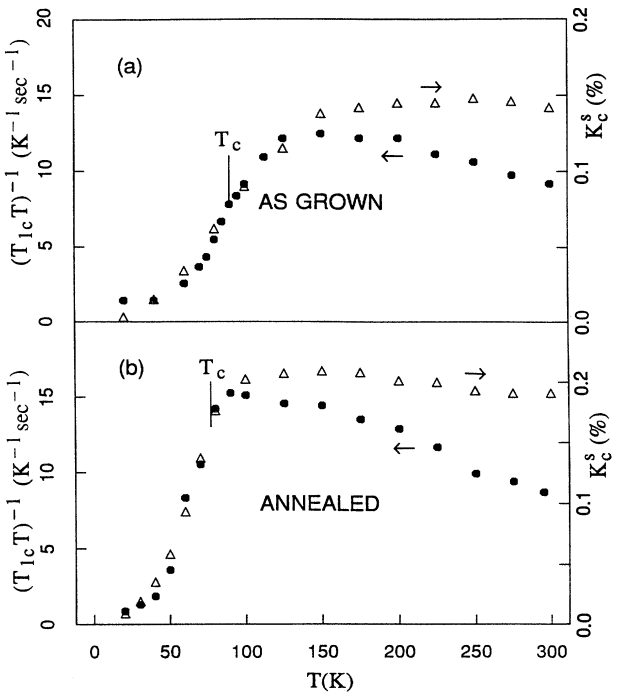

FIG. 2. Values of $(T_{1c}T)^{-1}$ for ^{63}Cu are plotted vs temperature T for both sample doping conditions (dots). These data were taken at a resonance frequency of 88 MHz. Values of T_c in low field (Ref. 17) are indicated. A barely resolved feature at T_c is visible for the as-grown sample. At the lowest temperatures the relaxation becomes noticeably nonexponential, indicating the presence of nonintrinsic contributions. Data for the shift values $K_c^s(T)$ taken from Fig. 1(a) are also plotted (triangles), scaled to coincide with the relaxation curves at low temperatures.

In contrast, NMR data for the ^{89}Y and planar ^{17}O in both phases of $YBa_2Cu_3O_7$ have been found to follow Eq. (1) over the entire range of temperatures studied.[10,26]

To discuss the relaxation data we employ a simple model form for the imaginary part of the dynamical susceptibility $\chi(\mathbf{q},\omega)$, i.e.,

$$[\chi''(\mathbf{q},\omega)/\omega]_{\omega\to 0}=\chi'(\mathbf{q},0)\tau(\mathbf{q})[1+P(\mathbf{q})]\,. \tag{2}$$

The relaxation rate is then given by

$$(T_1T)^{-1}=\frac{2\gamma^2k_B}{g_\perp^2\mu_B^2}\sum_{\mathbf{q}}A_\perp(\mathbf{q})^2[\chi''(\mathbf{q},\omega)/\omega]_{\omega\to 0}\,. \tag{3}$$

Equation (2) is similar to mean-field forms discussed in the literature,[27-29] where $P(\mathbf{q})$ represents the antiferromagnetic (AFM) fluctuation peak required to explain the observed distinction between the behavior of planar ^{63}Cu nuclei and that of the corresponding ^{17}O and (for $YBa_2Cu_3O_7$) ^{89}Y spins. The parameter $\tau(\mathbf{q})$ is defined by the linear region $\chi(\mathbf{q},\omega)\propto\omega$ as $\omega\to 0$. In using Eq. (2) to describe the behavior of a spin gap system, it is necessary to let $\chi'(\mathbf{q},0)$ and $\tau(\mathbf{q})$ be temperature-dependent parameters.

We first consider the case of ^{17}O and ^{89}Y in $YBa_2Cu_3O_7$, for which the form factors $A_\perp(\mathbf{q})^2$ vanish at the AFM wave vector $\mathbf{q}_{AFM}=(\pi/a,\pi/a)$.[30] This emphasizes small q values, where to a good approximation $P(\mathbf{q})$ can be neglected[28] and $\chi'(\mathbf{q},0)$ may be presumed to behave like the measured susceptibility $\chi^s(T)$. Substituting Eq. (2) into Eq. (3) and comparing with Eq. (1), we conclude that under these conditions $\tau(\mathbf{q})$ is independent of temperature. Using ^{17}O T_1 data from $YBa_2Cu_3O_7$ in these equations, one may estimate $\tau(\mathbf{q}\approx 0)\sim 6\times 10^{-15}$ sec.[28,31] If we regard τ as an inverse bandwidth, then it is interesting to note that it is of the same order as $\hbar/J\approx 5\times 10^{-15}$ sec, where J is the AFM exchange constant in the insulating phase. Cluster simulations have predicted a low-lying band of width $\sim J$ in these systems.[32]

In contrast with the foregoing result, neutron data for $\chi''(\mathbf{q}_{AFM},\omega)$ (Ref. 13) lead to the conclusion that $\tau(\mathbf{q}_{AFM})$ vanishes as $T\to 0$ in a fashion similar to $\chi^s(T)$. This follows because the Kramers-Kronig relation, $\chi'(0)=\pi^{-1}\int d\omega\chi''(\omega)/\omega$, shows that $\chi'(\mathbf{q}_{AFM},0)$ in Eq. (2) remains finite, while $[\chi''(\mathbf{q}_{AFM},\omega)/\omega]_{\omega\to 0}$ vanishes as $T\to 0$.[13] Since the T_1 process of the ^{63}Cu is dominated by the AFM fluctuations, the origin of behavior like Eq. (1) for that site is therefore different in essential detail from that of the ^{17}O. Not surprisingly, then, discussion of the spin gap effect on T_1 in terms of a simple model susceptibility[29] reveals underlying complexities. Let us finally note that the divergence of $K^s(T)$ and $(T_1T)^{-1}$ above $T\approx 100$ K for ^{63}Cu (Fig. 2) is presumably attributable to the gradual decay of AFM correlations [$P(\mathbf{q})$ in Eq. (2)] at higher temperatures, an effect which has been discussed extensively in the literature.[27-29] The decay of $P(\mathbf{q})$ does not alter the shift, which therefore remains above the relaxation curve.

It is interesting at this point to inquire also as to how Eq. (1) might arise in a traditional electron-gas picture, under conditions of a rapidly varying $\chi^s(T)$. If we presume this temperature variation to stem from a gapped density of states $n(E)$, then Eq. (1) requires $\langle n(E)\rangle \propto\langle n(E)^2\rangle$, where $\langle\cdots\rangle$ denotes a thermal average and where we have neglected any possible coherence factor effects.[32] The latter relation would hold, for example, with a constant density of states having a simple gap near E_F.[33] We do not propose this as a serious model, but only note that one cannot easily rule out a more conventional approach on the basis of Eq. (1) alone.

Viewed in a broader context, however,[15] the spin gap effects discussed earlier appear to represent a separation of charge and spin channels which is not Fermi liquid-like in character. The absence of significant features in the NMR data at T_c in many of these systems suggests a link between the spin gap behavior and Eq. (1). This correspondence also calls into question the ability of Fermi-liquid-type models to account for the nuclear relaxation behavior in any broad sense for the cuprate materials. Up to now, several theory papers have addressed the question of the missing BCS peak in these systems,[34-37] finding at least qualitative agreement through a variety of mechanisms. Based on the present work, we suggest that an important test for any theory is to see whether the results satisfy Eq. (1). The marginal Fermi-liquid picture does so at least in part.[35]

The question of the superconducting energy gap vis-à-vis the low temperature T_1 and shift data remains an open one. As the carrier concentration is diminished (as in, e.g., $YBa_2Cu_3O_{6.7}$ (Refs. 9 and 10) or as-grown $Bi_2Sr_2CaCu_2O_8$ [Fig. 2(a)]), the spin gap effect becomes predominant, with little expected relevance to a superconducting gap. On the other hand, for $YBa_2Cu_3O_7$ the spin gap effect is weak, and one feels on purely intuitive grounds that the parallel decline of $K^s(T)$ and $(T_1T)^{-1}$ below T_c (Ref. 26) is in some sense a measure of the superconducting gap. As many authors have noted, a Yosida function[38] fit to these data implies a substantially larger gap than the value $2\Delta=3.5k_BT_c$ provided by weak-coupling BCS theory. Other experimental probes have given similar indications.[39]

In summary, we have presented comprehensive NMR shift and relaxation data on ^{63}Cu in crystals of $Bi_2Sr_2CaCu_2O_8$. The data exhibit a spin gap effect at both doping levels tested. These and comparable data on $YBa_2Cu_3O_7$ are found to follow Eq. (1) below $T\sim 100$ K. Combined with the absence of significant features in the data at T_c, these observations suggest a separation of charge and spin-related phenomena in these systems.

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