Strong Dependence of the Superconducting Gap on Oxygen Doping from Tunneling Measurements on $Bi_2Sr_2CaCu_2O_{8-\delta}$

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(Received 20 August 1997)

Tunneling measurements are reported for break junctions on $Bi_2Sr_2CaCu_2O_{8-\delta}$ single crystals with various oxygen concentrations. Superconducting energy gaps Δ are observed in the underdoped samples which are considerably larger (~30%) than found in optimal doped crystals. The trend of decreasing Δ and $2\Delta/kT_c$ with increasing hole doping is continued into the overdoped region. Thus the superconducting gap and strong-coupling ratio change monotonically and dramatically over a narrow doping region where T_c exhibits a maximum. [S0031-9007(97)04904-1]

PACS numbers: 74.50.+r, 74.25.Dw, 74.62.Dh, 74.72.Hs

Tunneling spectroscopy and angle-resolved photoemission spectroscopy (ARPES) have emerged as powerful, complementary probes of the superconducting gap Δ in high-T_c superconductors (HTS). ARPES has made important contributions in $Bi_2Sr_2CaCu_2O_{8-\delta}$ (Bi2212), including strong support for d-wave symmetry of the gap and the evolution of the superconducting gap into a pseudogap which persists well above T_c for underdoped samples [1–3]. At present there is no generally accepted model for the ARPES spectral function $A(\mathbf{k}, E)$ in HTS, and this leads to uncertainty in the magnitudes of energy gaps, but also limits the ability to distinguish superconducting gaps from those arising from other electronic correlations such as charge density waves. It is therefore crucial to establish a correspondence to other traditional probes of superconductivity such as tunneling spectroscopy. We report here tunneling measurements in Bi2212 crystals using superconductor-insulator-superconductor (SIS) break junctions for which the peak in tunneling conductance is a direct measure of 2Δ. The Bi2212 crystals each have a $T_c = 95$ K at optimal doping and by changing the oxygen concentration they span a range from overdoped to moderately underdoped. We find a surprisingly strong, monotonic dependence of the superconducting energy gap and strong coupling ratio $2\Delta/kT_c$ on doping concentration. Furthermore, we find that the magnitude of Δ measured by tunneling agrees with the low-temperature peak position of $A(\mathbf{k}, E)$ measured in ARPES along the $(\pi, 0)$ momentum direction [1–3] and that the temperature and doping dependence of the tunneling spectra display the same trends as found in ARPES. Thus we confirm the superconducting origin of the gap in ARPES below T_c.

This work builds upon previous tunneling studies of Bi2212 in both the SIS and SIN (N: normal metal) configurations [4–10], but here we present a detailed, systematic examination of the doping dependence. The reproducibility of the SIS spectra indicates that the crystals have a homogeneous oxygen composition. In SIN tunneling the conductance at $T = 0$ K is proportional to $\Sigma A(\mathbf{k}, E)|T_{\mathbf{k}}|^2$ where the summation is over quasiparticle momentum $\mathbf{k}$. Assuming that the tunneling matrix element $T_{\mathbf{k}}$ varies only weakly with $\mathbf{k}$, it follows that tunneling probes the quasiparticle density of states (DOS), $\rho(E) = \Sigma A(\mathbf{k}, E)$ and this leads to a natural connection to ARPES [11]. A significant advantage of SIS junctions is that the measured results are insensitive to thermal broadening effects (Fermi factors) which play an important role in SIN junctions [5,6,8,9] for $T > 0$K. Consequently, they offer a more accurate measure of Δ and are a potentially more sensitive probe of the DOS above T_c. A key feature of SIS junctions is that they have the potential to display pair correlations through the Josephson effect [4,10]. For the range of doping in this study, all the SIS junctions displayed Josephson currents. In addition, each displayed similarly shaped quasiparticle conductance curves with gap features that disappeared near the measured bulk T_c. Thus it is clear that the superconducting gap in the DOS is being probed, a critical aspect in the comparison to the ARPES $A(\mathbf{k}, E)$ which probes the quasiparticles at a particular momentum. The dramatic change of Δ obtained from tunneling over this rather narrow doping range is unexpected based on specific heat measurements of $YBa_2Cu_3O_{7-\delta}$ [12] but as we will show is consistent with the low-temperature ARPES spectral functions measured along the $(\pi, 0)$ direction [1–3,13].

The focus in this work was to examine the doping dependence of Δ for samples near the optimal T_c (measured with ac susceptibility) and the following crystals were studied in detail: underdoped (onset $T_c = 83$ K, transition tail ~15 K), optimally doped ($T_c = 95$ K, $\Delta T_c = 1$ K) and overdoped ($T_c = 82$ K, $\Delta T_c \sim 1$ K). We include the results for heavily overdoped crystals ($T_c = 62$ K)

0031-9007/98/80(1)/157(4)$15.00

[4,14] to show that the trend of decreasing Δ and $2\Delta/kTc$ continues with increasing hole concentration. Single crystals were grown using a floating zone process in a double-mirror image furnace NEC SC-M15HD modified with an external home-built control for very slow growth ~ 0.1 mm/h. Growth was carried out without solvent from high-density, carbonate-free, near-stoichiometric single-phase rods in flowing 20% oxygen. Doping level (i.e., the oxygen content) was changed by annealing optimally doped crystals in high purity flowing gases adjusted for different partial pressures of oxygen. Many break junctions were prepared on each crystal at 4.2 K using a point contact apparatus with a Au tip. Details of junction preparation are described elsewhere [4,5,14]. Scanning electron micrographs of the Au tip after one experiment revealed that a small (~ 100 μm) piece of the Bi2212 crystal was embedded, and this indicates that the SIS junction is formed in a cavity deep in the crystal minimizing the possibility of surface degradation and improving junction stability.

Figure 1 shows the measured tunneling current-voltage (I-V) curve for an SIS junction #1 on the underdoped Bi2212 crystal at 4.2 K. A hysteretic Josephson tunneling current is evident at zero bias and a well-defined quasiparticle current jump occurs at the superconducting gap voltage, $2\Delta/e \sim 90$ mV. The value of $I_c R_n$ product is in the range 15–25 mV, consistent with that found on low-resistance break junctions of overdoped Bi2212 [15]. Similar curves were found for the optimally doped and overdoped crystals.

Figure 2 shows the tunneling conductance data (dI/dV vs V) at 4.2 K for another SIS junction (#2) on the underdoped Bi2212 crystal where it is compared directly to similar curves on optimally doped and overdoped samples. In each case the data were normalized by a constant which was the conductance obtained at -200 mV bias. The Josephson effect, which shows up as a very large conductance peak near zero bias, has been removed for clarity. The shapes of the tunneling conductance curves are quite similar for these doping levels. In particular, each exhibit subgap conductance and pronounced dip features which occur at $\sim 3\Delta$. These features agree with previous break junction studies [4,7,10] and the subgap shape is consistent with a momentum-averaged, d-wave DOS [7,10]. The magnitude of the maximum superconducting gap value taken from the conductance peak position increases as follows: $2\Delta = 52$, 75, and 90 meV for the overdoped, optimally doped, and underdoped crystal, respectively. These results indicate that the superconducting gap changes monotonically and substantially with doping in a range where T_c exhibits a local maximum and changes by about 10%.

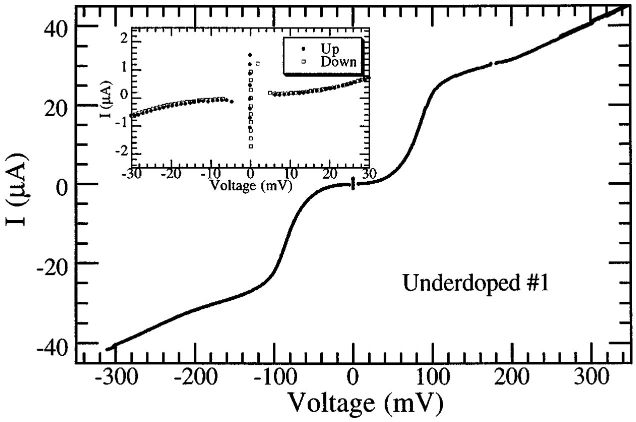

FIG. 1. Tunneling current vs voltage (I-V) characteristics for SIS break junction #1 at 4.2 K on an underdoped Bi 2212 with $T_c = 83$ K. Inset shows hysteretic I-V characteristics near zero bias indicative of a Josephson effect.

To gain insight into the doping dependence of the maximum superconducting gap, we have plotted Δ vs hole concentration p in Fig. 3. Here p has been obtained from the empirical relation $T_c/T_{c,\max} = 1 - 82.6(p - 0.16)^2$ which is satisfied for a number of HTS [16] and we use $T_{c,\max} = 95$ K. To further establish the doping dependence we also include Δ values obtained from other SIS junctions on Bi2212 [4,7,10] as well as some ARPES measurements [1,2,13] of the $(\pi, 0)$ gap (the d-wave maximum) for the same region of doping. For temperatures far below T_c, the ARPES spectral function is sharp [1,2,3,13] over this doping range and we use the peak position to estimate Δ. Error bars indicate the range of Δ values observed for each crystal. We have also included some preliminary SIS tunneling gap values for a $T_c = 77$ K underdoped Bi2212 which show an increase to $2\Delta = 100$ meV for four junctions, in agreement with ARPES gap values (peak position) on similar crystals [3,13]. The plot shows good overall agreement among the SIS tunneling and ARPES data for this region of doping and demonstrates a remarkable dependence of Δ

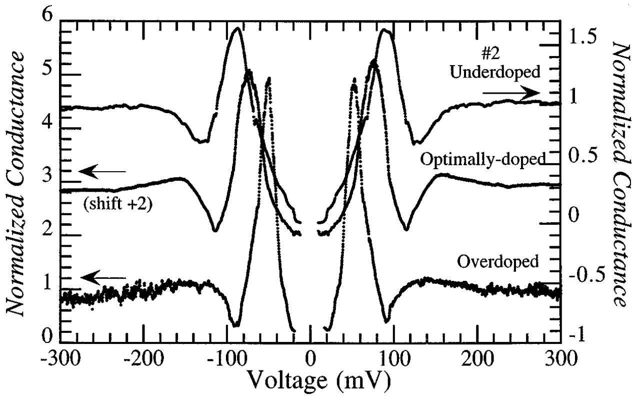

FIG. 2. Comparison of SIS tunneling conductance curves at 4.2 K for Bi2212 single crystals with different oxygen concentrations. Each curve has been normalized by its conductance value at -200 mV and the zero-bias conductance peak from the Josephson current has been removed. For clarity, the spectra for the optimally doped Bi2212 has been shifted vertically by 2 units. Using peak position as a superconducting gap value, 2Δ is 90, 75, and 52 meV for underdoped, optimally doped, and overdoped Bi2212, respectively.

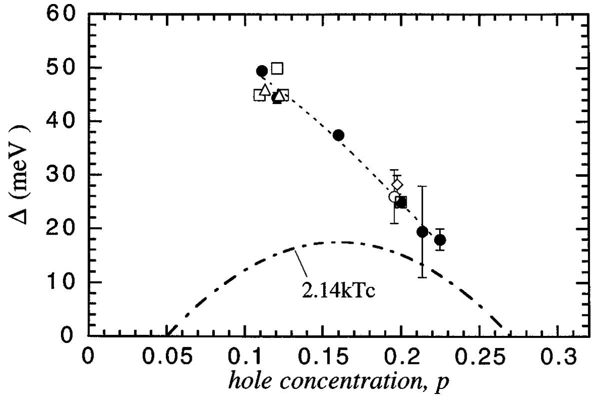

FIG. 3. Plot of the low temperature superconducting gap Δ vs hole concentration p. Filled circles are the measured Δ by SIS junctions in this work. For comparison, Δ obtained from other experiments have also been plotted: Ref. [7] (open diamond) and Ref. [10] (open circle) from SIS tunneling; Refs. [1,2] (open triangle) and Ref. [13] (open square) from ARPES. For ARPES results the spectral weight peak position has been chosen as estimate of Δ. The dashed line is $\Delta_{\rm MF} = 2.14kT_c$ from the BCS mean-field d-wave prediction.

on p. This result is quite different from that found in specific heat studies of $\rm YBa_2Cu_3O_{7-\delta}$ [12] and earlier scanning tunneling microscope (STM) measurements on Bi2212 [17] which indicated a weak dependence on hole doping of the superconducting gap. On the overdoped side the result is consistent with more recent STM studies of Bi2212 [4,9]. Of particular note is the fact that Δ continues to increase in the underdoped region as T_c decreases.

The dashed line of Fig 3 is a plot of $2.14kT_c$ vs p using the empirical relation above, but the prefactor of T_c rescales the plot to indicate how a mean-field, BCS d-wave gap maximum, $\Delta_{\rm MF}$ would behave with doping [1,18]. The plot of Fig. 3 is similar to one found in Ref. [1] using the midpoint of the ARPES leading edge which was argued to scale with Δ. But we emphasize here that accurate magnitudes of the superconducting gap are presented which allow a quantitative analysis. For example, Δ values as high as 50 meV are found and there is a startling increase in the strong-coupling ratio as doping is decreased from the overdoped regime. For the limits of the doping region studied, $2\Delta/kT_c$ changes from a value ~6 for overdoped Bi2212 with $T_c = 62$ K to values approaching ~14 in the underdoped region. It appears that the trend for overdoping is to approach the BCS mean-field gap value. Such a rapid variation in $2\Delta/kT_c$ with doping puts important constraints on the potential pairing mechanisms being considered for high-temperature superconductors.

The temperature dependence of the tunneling conductance was measured, and some of the observed results for junction #2 on the 83 K underdoped crystal are shown in Fig. 4(a) for selected temperatures. For temperatures between 4.2 and 25 K there is little change in the tunneling data. For T close to the measured bulk T_c, the conductance data broaden considerably, and at $T = 82$ K the superconducting gap structure has all but disappeared and there remains only a weak depression of the conductance at zero bias. We emphasize that Fermi factors are playing virtually no role in the smearing out of the superconducting gap structure. This has been verified by using

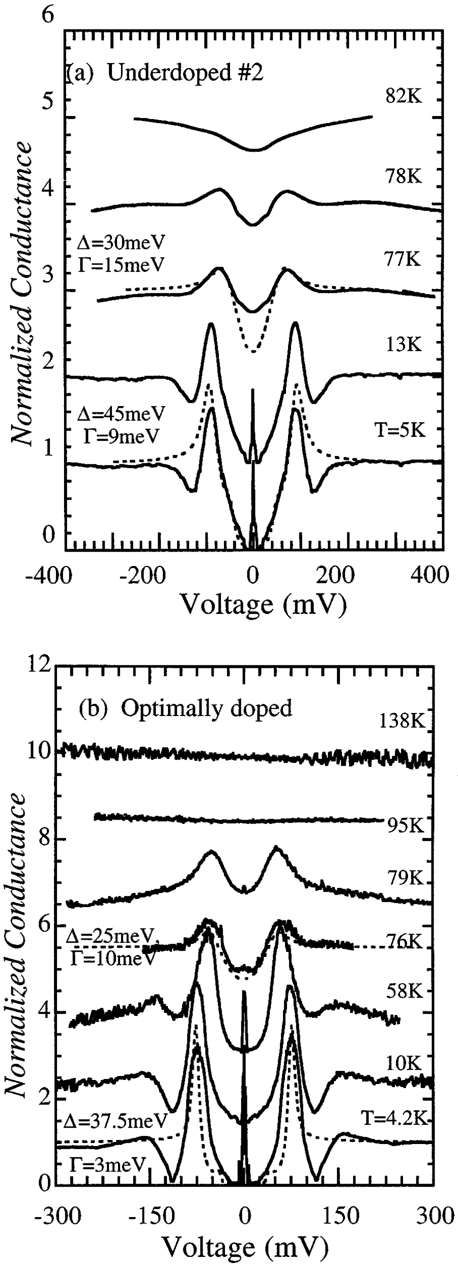

FIG. 4. (a) Temperature dependence of tunneling conductance on an underdoped Bi2212 SIS junction. The dashed line shows the SIS fit with $\Delta = 45$ meV, $\Gamma = 9$ meV and $\Delta = 30$ meV, $\Gamma = 15$ meV for the tunneling conductance at 5 and 77 K, respectively. (b) Temperature dependence of tunneling conductance on an optimally doped Bi2212 SIS junction. The dashed line shows the SIS fit with $\Delta = 37.5$ meV, $\Gamma = 3$ meV and $\Delta = 25$ meV and $\Gamma = 10$ meV for the tunneling conductance at 4.2 and 76 K, respectively. For clarity, each conductance in both graphs has been normalized by a constant value and (except for the lowest temperatures curve) is offset vertically.

a simple model for SIS junctions [11] which assumes that $I(V) \sim \int dE \rho(E) \rho(E - eV)[f(E) - f(E - eV)]$ where the superconducting DOS is a smeared BCS expression given by $\rho(E) = \mathrm{Re}[E - i\Gamma]/[(E - i\Gamma)^2 - \Delta^2]^{1/2}$ and $f(E)$ is the Fermi function. Here Γ is a measure of the quasiparticle scattering rate [19]. Although $\rho(E)$ with a finite Γ is at best a crude estimate of the momentum averaged DOS for a d-wave gap the model demonstrates that $f(E)$ has little effect on the conductance (especially near the peak) in going from 5 to 82 K.

The model curves [dashed lines in Fig. 4(a)] indicate that a reasonable fit of the T = 5 K data is achieved with $\Delta = 45$ meV and $\Gamma = 9$ meV, except for the obvious discrepancies occurring near the dips at $eV = 3\Delta$. The dip features appear to be a strong-coupling effect, and they continue to scale with Δ over the entire range of doping studied [4,5,14]. The shape of the subgap conductance implies that all $\mathbf{k}$ values of the d-wave gap $\Delta(\mathbf{k})$ are contributing to the tunnel current [7,10] and thus the conductance peak is a measure of the maximum of the d-wave gap. The fit at 77 K leads to values, $\Delta = 30$ meV and $\Gamma = 15$ meV. The large increase in Γ/Δ from 5 to 77 K suggests that an intrinsic quasiparticle damping is responsible for smearing out the gap structure and this makes it difficult to interpret the data at 82 K. It is not clear whether superconductivity has been destroyed at 82 K or whether the scattering rate is so large as to smear out a finite superconducting gap structure in the DOS. The weak depression of the conductance near zero bias could also be an indication of a remaining pseudogap in the DOS [1–3] but measurements above the bulk T_c were not obtained and thus no conclusions can be drawn. ARPES measurements of underdoped Bi2212 with similar T_c values [3,13] indicate the rapid growth of a quasiparticle damping rate as T_c is approached from below and furthermore, that the momentum averaged DOS in the pseudogap regime would not necessarily reveal a well-defined energy gap. Thus our observations at $T = 82$ K are not surprising.

Temperature-dependent conductance curves are shown for the optimally doped sample in Fig. 4(b). Model fits [dashed lines in Fig. 4(b)] give $\Delta = 37.5$ meV, $\Gamma = 3$ meV at 4.2 K and $\Delta = 25$ meV, $\Gamma = 10$ meV at 76 K. Again there is the rapid growth of a scattering rate as T_c is approached and at $T = T_c$ the superconducting gap has disappeared. There is no indication of a pseudogap above T_c for optimally doped crystals.

In summary, we have obtained SIS tunnel junctions on Bi2212 crystals with various oxygen concentrations, including the first results in the underdoped regime. Detailed analyses of the tunneling spectra, including the temperature dependence, indicate that for all doping levels we are directly measuring the superconducting energy gap. Assuming d-wave symmetry, the parameter plotted in Fig. 3 is the maximum superconducting gap Δ which compares well with the low-temperature spectral weight peak position found in ARPES at the $(\pi, 0)$ point. Values of Δ as large as 50 meV and $2\Delta/kT_c \sim 14$ are found for underdoped samples. The rapid, monotonic change of Δ and $2\Delta/kTc$ with doping and the concomitant decrease of T_c with underdoping is highly unusual and puts severe constraints on any theoretical model of the pairing interaction. The connection of these results to ARPES data indicates that, for the doping levels examined here, the energy gaps found in ARPES below T_c are the superconducting gaps and therefore do not arise from some other electronic correlations.

This work was partially supported by U.S. DOE-BES Contract No. W-31-109-ENG-38, and the NSF-STCS Contract No. DMR 91-20000. The authors would like to thank Mike Norman, Ji Ung Lee, and Lutfi Ozyuzer for valuable discussions.

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