

## Measurement of the energy gap in oxygen-annealed $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ high- $T_c$ superconductors by tunneling spectroscopy

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The superconducting energy gap has been determined in homogeneous, oxygen-annealed  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (BSCCO) single crystals by tunneling spectroscopy. Normal-metal-insulator-superconductor (NIS) point-contact tunneling measurements made on cleaved surfaces of these BSCCO crystals exhibit a well-defined gap with a low conductance,  $G(V)$ , within the gap region. The conductance and change of  $G(V)$  within the gap region differs from the behavior expected for either a gapless or BCS-like superconductor. Analysis of data from both NIS and superconductor-insulator-superconductor junctions provides a consistent scale for superconductivity with  $2\Delta \approx 6.8kT_c$ . In addition, since this gap structure is reproducible at different surface positions of these oxygen-annealed crystals we conclude that spatial variations in  $2\Delta$  and a high density of states within the gap are not intrinsic to the BSCCO system.

A detailed picture of the energy gap ( $2\Delta$ ) and low-energy excitations of the copper oxide superconductors is essential to understanding the mechanism of superconductivity in these materials. The BCS model of superconductivity predicts that there is a complete gap in the density of electronic states (no excitations within  $\pm\Delta$ ) as  $T \rightarrow 0$  and that the magnitude of  $2\Delta = 3.53kT_c$ .<sup>1</sup> For conventional superconductors these predictions have agreed well with tunneling and infrared spectroscopy measurements of the gap.<sup>2,3</sup> In the case of the copper oxide materials, however, the nature of the gap has been quite controversial.<sup>4-18</sup> Studies of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (BSCCO) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) single crystals have suggested values for  $2\Delta$  as large as  $12kT_c$ , although recent studies converge toward an energy scale of  $6-8kT_c$  for the excitations responsible for superconductivity.<sup>4,14-18</sup> The existence of excitations within the gap remains controversial.<sup>5-8</sup> For example, several tunneling studies of BSCCO crystals have reported low-energy excitations proportional to bias voltage ( $V$ ) within  $\pm\Delta$ .<sup>6,8</sup> Additionally, tunneling measurements made on BSCCO and YBCO single crystals often have exhibited large conductances at the Fermi level.<sup>6,7,10-13</sup> These results suggest, if they are indeed intrinsic, that the gap may vanish at points or along lines on the Fermi surface or that superconductivity is gapless. It thus remains essential to resolve the nature of these tunneling data.

It is likely that material inhomogeneities, such as oxygen nonstoichiometry, have been responsible for many of the apparently conflicting measurements of the energy gap by tunneling spectroscopy.<sup>6,11,12</sup> The very short coherence lengths of the copper oxide superconductors make tunneling measurements especially susceptible to local variations in the superconducting properties. Hence, in this Brief Report, we focus on investigations of BSCCO single crystals that have been carefully annealed in oxygen to produce homogeneous samples; we use a low-temperature scanning tunneling microscopy (STM)

to probe the low-energy excitations in these samples. Metal-insulator-superconductor (NIS) point-contact tunneling measurements made on cleaved surfaces of these BSCCO crystals exhibit a well-defined gap with a low conductance,  $G(V)$ , within the gap region. The conductance and change of  $G(V)$  within the gap region differ from the behavior expected for either a gapless or BCS-like superconductor. Analyses of the data from both NIS and superconductor-insulator-superconductor (SIS) junctions do, however, provide a consistent scale for superconductivity with  $2\Delta \approx 6.8kT_c$ . In addition, since this gap structure is reproducible at different surface positions of these oxygen-annealed crystals, we conclude that spatial variations in  $2\Delta$  and a high density of states within the gap are not intrinsic to the BSCCO system. Lastly, a reproducible linear background conductance was observed for both the NIS and SIS junctions.

BSCCO single crystals were grown from CuO-rich melts as described previously.<sup>19</sup> The crystals obtained from the melt (as grown) were annealed in 12 atm  $\text{O}_2$  at  $540^\circ\text{C}$  for 18 h, and then equilibrated in 1 atm  $\text{O}_2$  at  $540^\circ\text{C}$  for 2 weeks. Diffraction measurements showed that no decomposition occurred under these annealing conditions. The transition widths determined by dc magnetization measurements for the as-grown and annealed samples were 10–15 and  $<5$  K, respectively. The tunneling measurements were carried out using a low-temperature STM. The NIS junctions were formed between a Pt-Ir tip and BSCCO sample, while the SIS junctions used a small BSCCO crystal glued to a Pt-Ir tip with silver epoxy. The BSCCO crystals were cleaved immediately prior to evacuating the STM chamber, which was filled with  $\approx 25$  mtorr of He during the measurements. Current ( $I$ ) versus voltage ( $V$ ) curves were acquired digitally at a constant tip-sample separation and numerically differentiated. All of the tunneling data reported were acquired at 4.2 K.

Typical  $I-V$  and  $dI/dV$  versus  $V$  curves obtained using

NIS junctions at 4.2 K are shown in Fig. 1. These results are representative of several hundred data sets obtained on the annealed BSCCO crystals. The tunnel-junction resistances in our experiments was varied from  $10^7$  to  $10^9 \Omega$ ; within this range, similar results were observed. Measurements of the current versus barrier thickness showed, however, that the tip was touching the sample surface in all of our experiments.<sup>20</sup> In this contact geometry, the tunneling measurements average both *a-b* and *c* directions.<sup>21,22</sup>

Qualitatively, the *I-V* curves exhibit a flat, low-current region about the Fermi level ( $E_f$ ,  $V=0$ ) and relatively sharp conductance onsets at  $\pm 25$  mV. These features are characteristic of a conventional superconducting energy gap. It is interesting that this well-developed gap structure is observed reproducibly over the surface of  $O_2$ -annealed BSCCO samples. In contrast, we observe a wide range of *I-V* behavior on as-grown BSCCO samples; these variations are similar to other reports.<sup>11</sup> It is thus possible that much of the uncertainty observed in previous work is due to oxygen nonstoichiometry. Below we confine our analysis solely to reproducible measurements obtained on oxygen-annealed BSCCO samples.

The conductance  $G(V) = dI/dV$  versus voltage curves provide essential insight into the nature of the superconducting gap in these materials [Figs. 1(b) and 1(d)]. First, the conductance within the gap is low. For the NIS junctions, we find that  $G(0)/G(150)$ , where  $G(150)$  is representative of the normal-state conductance, is be-

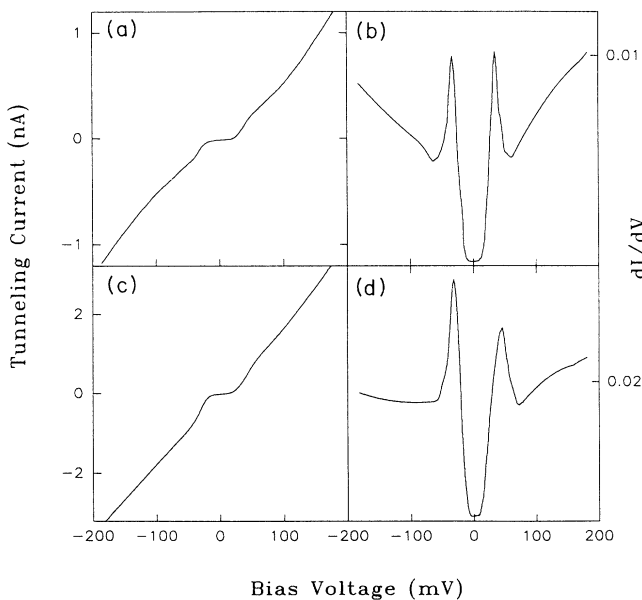


FIG. 1. (a), (c) Typical *I-V* curves obtained on oxygen-annealed BSCCO single crystals at 4.2 K. These NIS junctions were formed between a Pt-Ir tip and cleaved BSCCO crystal surfaces. (b), (d) Conductance ( $dI/dV$ ) vs voltage curves corresponding to the *I-V* data in (a) and (c), respectively. The curves exhibit well-developed gap structure and a linear background conductance for  $|V| > \pm \Delta$ . The conductances at  $V=0$  in (b) and (d) are 8% and 5%, respectively, of  $G(100)$ .

tween 2% and 8%. These values can be compared to conductances of 30–50% that have been reported previously.<sup>7,10,11</sup> We do find, however, large conductances in tunneling measurements made on the as-grown BSCCO crystals. Since extrinsic effects such as sample inhomogeneity were not accounted for in the previous tunneling studies, we believe that these previous data are not necessarily indicative of *d*-wave pairing or gapless superconductivity. In our carefully annealed samples,  $G(V)$  is very low at  $V=0$ ; however, it is also important to consider the behavior of  $G(V)$  for  $V > 0$ . First, the increase in  $G(V)$  within the gap is not proportional to  $|V|$ . A linear increase in  $G(V)$  would be a clear signature for gapless superconductivity,<sup>8</sup> and thus we believe our results may argue against this possibility. We can also compare the conductance at  $V=0$  and  $\Delta/2$  predicted for the *s*-wave BCS gap with our data. We find that the increase in  $G(V)$  at  $V=\Delta/2$  is close to or slightly larger than the increase predicted by a thermally broadened (4.2 K) BCS gap expression [Figs. 1(b) and 1(d), respectively]. These results indicate a close analogy to a conventional BCS-like gap; however, we also find that the divergence at the gap edge differs from conventional behavior (see below).

Similar results have also been obtained from SIS junctions; representative *I-V* and  $G(V)$  curves are shown in Fig. 2. The *I-V* curves exhibit a flat, low-current region about  $V=0$  and pronounced conductance onsets at ca.  $\pm 50$  mV. The near-zero-current region about  $E_f$  detected in the SIS measurements is approximately 2 times larger than in the NIS data. This observation is consistent with the measurement of  $2\Delta$  and  $4\Delta$  in the NIS and SIS junctions, respectively, and indicates that other effects such as the Coulomb blockade do not contribute significantly to our data. The  $G(V)$  curves from the SIS junctions also exhibit a low conductance at  $E_f$  ( $\approx 4\%$ ). The background conductance within the gap increases more rapidly than found for the NIS junctions. The increase in conductance could be due to either poor junction quality or gapless superconductivity. We believe that poor SIS-junction quality is probably the major fac-

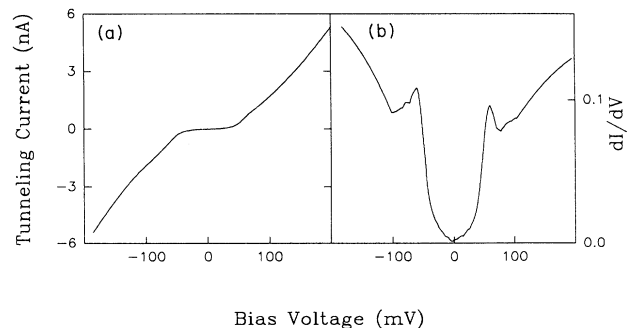


FIG. 2. (a) Representative *I-V* curve obtained for a SIS junction formed between two oxygen-annealed BSCCO crystals at 4.2 K. The junction geometry averages the *c* and *a-b* directions. (b) Conductance vs voltage curve corresponding to the data in (a). The conductance at  $V=0$  is 4% of  $G(100)$ . The gap structure observed in the SIS junctions exhibits greater broadening than the data obtained from the NIS junctions.

tor leading to the increase in  $G(V)$  within the gap; however, we do not have sufficient experimental evidence at this time to resolve the observed differences in the gap excitations for the NIS and SIS junctions. Regardless of the origin of the excitations observed in the gap of these SIS junctions, these data confirm the magnitude of  $2\Delta$  for the oxygen-annealed BSCCO crystals and thus provide a consistent and reproducible energy scale for superconductivity.

In addition, we have further analyzed the reproducible gap structure observed in our NIS measurements to assign quantitatively a value to  $2\Delta$  and to probe the energy dependence of the density of states. The experimental data was fit to a modified BCS model for the density of states (DOS):

$$N_S = \text{Re}\{(eV - i\Gamma)/[(eV - i\Gamma)^2 - \Delta^2]^{1/2}\},$$

where we take  $\Gamma$  to be a phenomenological parameter to account for broadening. A typical fit using this model is shown in Fig. 3. We find that the experimental data is well fit for  $|V| < \Delta/2$ , but that the experimental conductance peaks are broadened significantly compared to the model DOS. Similar fits have also been obtained for other  $G(V)$  data with  $\Gamma = 1-3$  meV; this broadening energy is greater than the thermal energy (0.36 meV). We believe that one should not, however, place too much significance on  $\Gamma$  since sample quality may still be limiting.<sup>23</sup> Nevertheless, there are several important points of this analysis. First, the well-defined gap in the NIS data can be fit at low energies using a conventional model, although the broadening needed for a best fit is greater than expected for only thermal effects. Second, the magnitudes of  $2\Delta$  and  $4\Delta$  extracted from our fits to the NIS and SIS data,  $50 \pm 5$  and  $98 \pm 5$  mV, respectively, show that the energy scale for superconductivity is  $\approx 6.8kT_c$ . The magnitude of  $2\Delta$  extracted from this analysis is thus consistent with high-resolution electron-energy-loss and photoemission spectroscopy measurements on BSCCO crystals.<sup>14-18</sup> Last, it is important to note that the divergence in the experimental data at the gap edge is weak in comparison to the behavior expected for a  $s$ -wave BCS superconductor. This deviation from conventional behavior may be a signature of  $d$ -wave pairing or gapless superconductivity, although we believe that additional studies will be needed to confirm the intrinsic nature of the divergence.

In conclusion, we have investigated the nature of the

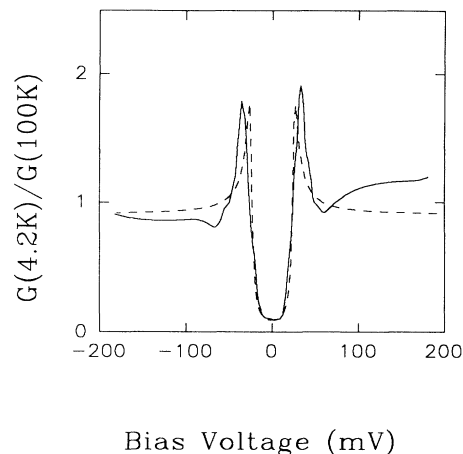


FIG. 3. Conductance determined at 4.2 K normalized by the conductance at 100 K,  $G(4.2 \text{ K}/G(100 \text{ K}))$ , vs voltage for an average NIS junction (solid line). The dashed line corresponds to a fit of this experimental data to model density of states,  $N_S = \text{Re}\{(eV - i\Gamma)/[(eV - i\Gamma)^2 - \Delta^2]^{1/2}\}$ . This simple model for the superconducting state fits the gap structure well, although the experimental conductance peaks are significantly broader than model fit. The values of  $\Delta$  and  $\Gamma$  extracted from the model fit are 25 and 3 meV, respectively.

superconducting energy gap in homogeneous, oxygen-annealed BSCCO single crystals by tunneling spectroscopy. We have shown that a well-developed gap structure is observed in  $I$ - $V$  and  $dI/dV$  data obtained on these high-quality single crystals in contrast to previous measurements. The low conductance and change of  $G(V)$  observed within the gap region differs from the behavior expected for either a gapless or BCS-like superconductor and thus may indicate  $d$ -wave pairing. Analysis of data from both NIS and SIS junctions provides a consistent scale for superconductivity with  $2\Delta \approx 6.8kT_c$ . In addition, we have found that the gap structure is reproducible at different surface positions for these oxygen-annealed crystals, and thus we conclude that spatial variations in  $2\Delta$  and a high density of states within the gap are not intrinsic to the BSCCO system.

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- <sup>20</sup>The current exhibits a weak, nonexponential dependence on the tip-sample separation. These results are characteristic of tip-sample contact in the STM experiment. We have not obtained clear evidence for vacuum tunneling in our measurements made at 4.2 K.
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- <sup>22</sup>The oxygen-annealed crystals also exhibited disorder in the BiO layer structure [Z. Zhang and C. M. Lieber (unpublished)]. Tip-surface contact and local disorder provide scattering channels for  $k_{\parallel}$  or  $a$ - $b$  tunneling.
- <sup>23</sup>The transition widths ( $\Delta T_c$ ) determined magnetically for the oxygen-annealed BSCCO crystals is 5 K. Although this  $\Delta T_c$  is less than observed for the as grown crystals, it is significantly broader than found for the best YBCO samples ( $\Delta T_c < 1$  K). Thus the oxygen-annealed crystals could contain inhomogeneities that broaden the energy gap structure.