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## Electron tunneling and the energy gap in  $Bi_2Sr_2CaCu_2O_x$

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Results of electron tunneling on single crystals of the  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>$  superconductor are reported. The junctions show a gap structure with  $\Delta \approx 25$  meV, whose temperature dependence exhibits a qualitatively Bardeen-Cooper-Schrieffer-like behavior with a gap-closing  $T_c \approx 81-85$  K. Comparisons of these tunneling spectra to those obtained on  $YBa_2Cu_3O_{7-x}$  are made. Evidence that  $2\Delta/kT_c \sim 7$  for both  $Bi_2Sr_2CaCu_2O_x$  and  $YBa_2Cu_3O_{7-x}$  is also discussed.

The measurement of the energy gap in the copper oxide family of high- $T_c$  superconductors has proven to be difficult and controversial. In  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>$ , optical measurements' of the gap have generally yielded a value  $2\Delta/kT_c \approx 4-7$ , while various tunneling measurements<sup>2-10</sup> have yielded wildly varying values of  $2\Delta/kT_c$  ranging from  $-4$  to as high as 20. In this Rapid Communication we report on tunneling measurements made on sandwichtype junctions formed on single crystals of  $Bi<sub>2</sub>Sr<sub>2</sub>$ - $CaCu<sub>2</sub>O<sub>x</sub>$  that show fairly clear gap structure around 25 meV at 4.2 K. Temperature dependence of the tunneling gap structure indicates a roughly Bardeen-Cooper-Schrieffer (BCS)-like gap closing around  $81-85$  K, giving  $2\Delta/kT_c \approx 7$ . Despite the nonideal characteristics seen in all reported tunneling spectra on  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>$  and  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>$ , features attributable to a gap are consistently seen at nearly the same energies in several tunneling experiments on ceramics, films, and single crystal. While several interpretations of the tunneling data have been offered, we will argue that, when the gap-opening  $T_c$ is known, the value of the coupling strength parameter  $2\Delta/kT_c$  is nearly the same for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> and  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>$  and significantly exceeds that for any conventional superconductor.

The  $Bi_2Sr_2CaCu_2O_x$  crystals used in this experiment were grown from a mix of oxide and carbonate powders melted at 950 $\degree$ C in air, and then slow cooled at 0.7 $\degree$ C/h to below 800 C. Many crystals with basal plane dimensions of several millimeters were obtained. Magnetic and resistive measurements showed a sharp  $(-1)$  K wide) superconducting transition just below 90 K. X-ray diffraction indicated that the samples were purely single phase, with the sharpness of the  $(00n)$  peaks being limited by instrumental resolution of the diffractometer. Tunnel junctions were formed by first cleaving an (001) face of a crystal, then evaporating a counterelectrode, usually of Pb or Nb. It is known that cleaving yields a surface good enough to allow scanning tunneling microscope imaging.<sup>11</sup> enough to allow scanning tunneling microscope imaging.<sup>11</sup> We believe a tunneling barrier formed from a reaction between counterelectrode and crystal; with an approximately 1-mm<sup>2</sup> junction area, the  $Bi_2Sr_2CaCu_2O_x/Pb$  junctions routinely had  $\geq 1$  k  $\Omega$  junction resistance, while the  $Bi_2Sr_2CaCu_2O_x/Nb$  junctions typically had  $\sim 1-10$   $\Omega$ resistances across the same areas, and a  $Bi<sub>2</sub>Sr<sub>2</sub>Ca Cu<sub>2</sub>O<sub>x</sub>/Au$  junction showed  $\sim 0.001 \Omega$  at low current

biases. Our best results were obtained using a Nb counterelectrode.

An I-V curve and the  $dV/dI$  for a  $Bi_2Sr_2CaCu_2O_x/Nb$ junction are shown in Fig. 1. For this sample the counterelectrode covered the thin  $(-100 \mu m)$  edges of the crystal, which form the (100) and (001) directions, as well as the (001) face of the crystal. Data for samples where only the (001) face was contacted are very similar. Clearly displayed are a large zero-bias conductance peak anomaly, sharp shoulders at  $\pm 25$  meV that we associate with the energy gap, and a flattening of  $dV/dI$  above 80 meV. While the spectrum shown is the clearest of our data, the shoulder at  $25 \pm 1$  meV was extremely reproducible from sample to sample while the flattening started between 70 to 110 meV, depending on the sample. Some  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>/Pb$  junctions also displayed very weak, broad gap structure between 25-30 meV and a flattening  $n \frac{dI}{dV}$  above 70 meV. In tunneling experiments on ceramic  $Bi_2Sr_2CaCu_2O_x$ , Ikuta *et al.* <sup>12</sup> have reported a quantitatively similar gap value and a vanishing of the gap around 85 K, though their temperature dependence seems to fit less well to the BCS curve.

The zero-bias conductance peak anomaly occurred in all good  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>/Nb$  junctions, but not in any  $Bi_2Sr_2CaCu_2O_x/Pb$  junctions. We can only remark that the anomaly was probably not a Josephson-type effect, as it showed no magnetic field dependence in either the low-



FIG. 1. I-V and  $dV/dI$  curves taken from a Bi<sub>2</sub>Sr<sub>2</sub>Ca- $Cu<sub>2</sub>O<sub>x</sub>/Nb$  junction.

field regime (0-10 6) or the medium-field regime (0.03-6 kG). The anomaly was also seen to diminish continuously and vanish with the gap above 80 K.

The temperature dependence of the gap structure, normalized to its low-temperature value, is shown in Fig. 2, where a BCS weak-coupling curve fitted to a  $T_c$  of 85 K is shown for reference. Figure 3 shows some data on how the conductance  $dI/dV$  varies with temperature in a  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>/Nb$  junction. Clearly a subgap region fills in as temperature increases towards  $T_c$ , while the higher-bias portion ( $> 30$  meV) is nearly independent of temperature as long as  $T < T_c$ . This general behavior has been observed before in  $YBa_2Cu_3O_{7-x}$  junctions.<sup>8</sup> Above  $T_c$  the junction conductance suddenly decreases. We believe that this conductance decrease arises from a contact resistance introduced in the junction region by the relatively high resistivity of  $Bi_2Sr_2CaCu_2O_x$  in its normal state.<sup>13</sup> This was not observed in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> junctions since  $R_{\text{junction}} \gg R_{\text{contact}}$  in that case.<sup>8</sup> Also in contrast to most YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-<sub>x</sub> tunneling results, we note that the background conductance of the  $Bi_2Sr_2CaCu_2O_x$  junctions is less linear and tends to flatten out at higher biases, whereas the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-<sub>x</sub> background conductance has been seen to be linear out to at least 500 meV.

From the temperature dependence of the gap, the  $T_c$  of the cleaved  $Bi_2Sr_2CaCu_2O_x$  crystal surface participating in the tunneling seems to be within a few degrees of the bulk  $T_c$ . A construction used commonly to infer gaps from nonideal tunneling spectra on standard BCS superconductors is to find where the extrapolated background conductance,  $dI/dV$ , intersects the actual conductance in the gap region. From the data of Fig. 3, this gives about 24.5 meV which, after subtracting off  $1.5$  meV for the Nb gap, yields  $2\Delta/kT_c = 6.3$ . While reasonable for BCS superconductors, such a construction is not valid in all cases, for instance that of large-gap anistropies where the largest gap could be best inferred from the conductance maximum. In such a case the largest gap which can be inferred from the data in Fig. 3 is about 24.5 meV, accounting for the Nb gap, yielding  $2\Delta/kT_c = 6.7$ . However one wishes to infer the gap value, the important qualitative



FIG. 2. Gap structure as a function of temperature, normalized to unity at 4.2 K. The solid curve is a BCS weak-coupling theory curve fitted to a  $T_c$  of 85 K. Numbers here are derived from the data in Fig. 3.



FIG. 3. Tunneling spectra  $dI/dV$  at various temperatures. The subgap region fills in as T increases towards  $T_c \approx 85$  K. The lowest temperature represented is 4.2 K, with curves taken at roughly 10 K intervals up through  $T_c$  also shown.

conclusion is that  $2\Delta/kT_c$ , as measured by tunneling, is significantly larger than the BCS weak-coupling limit of 3.52. A recent point-contact tunneling result by Kirk et 3.52. A recent point-contact tunneling result by Kirk *et*  $nl$ .<sup>11</sup> on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub> thin films showed sharp gap structure at 50-54 meV at 4.2 K. However, whether this gap should be interpreted as  $\Delta$  or a multiple of  $\Delta$  is not clear as the tunneling mechanism (i.e., tungsten to  $Bi_2Sr_2CaCu_2O_x$  or intergrain  $Bi_2Sr_2CaCu_2O_x$ ) is not known and no measurement of the temperature dependence was possible. We note that interpreting the point contact result as  $2\Delta$  yields excellent quantitative agreement with the data presented here.

Using sandwich junctions on  $YBa_2Cu_3O_{7-x}$  both Iguchi et al.<sup>3</sup> on bulk ceramic samples and Lee et al.<sup>8</sup> on thin films reported observation of a broad 20 meV gaplike structure that closed around 60-70 K rather than the bulk 90 K  $T_c$ , leading to a value in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> of  $2\Delta/kT_c$  – 7, consistent with the results on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub> presented here. The degradation in  $T_c$  presumably was due to oxygen deficiency near the surface, indicating the the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-<sub>x</sub> surface degrades more readily than the  $Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>$  surface. Tunneling experiments by Edgar, Adkins, and Chandler<sup>9</sup> and Sera, Shamoto, and Sato<sup>10</sup> on bulk ceramic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-<sub>x</sub> also display structure near 20 meV at 4.2 K interpreted as due to a gap. These researchers claim a gap-opening  $T_c$  of 80-90 K, which would lead to a value of  $2\Delta/kT_c \sim 4$  or 5. To infer this gap-opening  $T_c$ , however, both groups relied on normalizing their data to a model-dependent, numerically fitted normal-state density of states, whereas we have chosen simply to track a clear structure in the conductance curves as temperature is changed. It should be cautioned that the 20 meV structures seen in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>$ 

Group	Material	Δ	$T_c$ (gap)	$\frac{2\Delta}{\Delta}$ $kT_c$	Method
Edgar <i>et al</i> .ª	$YBa2$	20	$-90$	$4 - 5$	P
Sera <i>et al</i> . <sup>b</sup>	$YBa2Cu3O7-x$	20	$-90$	$4 - 5$	P
Iguchi et al. <sup>c</sup>	$YBa2$	20, 40, 60	$60 - 70$	7.1	S
Lee et al. <sup>d</sup>	$YBa2Cu3O7-x$	$-20,40$	60	7.5	S
Tsai <i>et al</i> .º	$YBa2Cu3O7-x$	20	77	6	B
Tsai <i>et al</i> .º	$YBa2Cu3O7-x$	10	40	5.9	B
Bulaevskii <i>et al</i> . <sup>1</sup>	$Er-Ba-Cu-O$	36	90	10	P
Iguchi et al. <sup>c</sup>	$Er-Ba-Cu-O$	20, 40, 100	$60 - 70$	7.1	S
Lee <i>et al</i> . <sup>d</sup>	$Bi2Sr2CaCu2Ox$	24	83	6.7	S
<sup>a</sup> Reference 10.	$d$ Reference 8.				

TABLE I. Gap voltage and gap-opening  $T_c$  measurements from seven different experiments. Where multiple gap structure is reported, the smallest gap is used for a given  $T_c$  in determining  $2\Delta/kT_c$ . Methods used are S (sandwich junction),  $P$  (point contact), and  $B$  (break junction).

Reference 10.

**b** Reference 11.

Reference 6.

<sup>c</sup> Reference 3.

Reference 7.

have all been very broad, hence the value of  $\Delta$  obtained is quite sensitive to the construction used to infer a gap value.

The accumulating experience from tunneling studies of the cuprate superconductors clearly demonstrates the need to determine the  $T_c$  of the material under study directly from tunneling measurements. The  $T_c$  of the surface layer of these materials, particularly  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>$ , can be strongly depressed. Use of the resistive or bulk transition temperature in determining  $2\Delta/kT_c$  is not justified a priori in tunneling experiments. Restricting attention to tunneling studies where gap-closing  $T_c$  data are also available leads to a much clearer picture of tunneling results. For example, Table I shows a compilation of some of the available data. With the exceptions of Edgar et al.<sup>9</sup> and Sera et al.<sup>10</sup> on the low side and Bulaevskii et  $al.$ <sup>7</sup> on the high side, we see that much of the data indicate a value of  $2\Delta/kT_c$  – 6 to 7 for both YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (and its rare-earth variants) and  $Bi_2Sr_2CaCu_2O_x$ . We believe that this value, indicative of very strong coupling in the framework of conventional superconductivity theory, is

- <sup>1</sup>See, for example: Z. Schlesinger *et al.*, Phys. Rev. Lett. 59, 1958 (1987); S. L. Cooper et al., Phys. Rev. B 37, 5920 (1988).
- <sup>2</sup>J. R. Kirtley et al., Phys. Rev. B 35, 8846 (1987).
- <sup>3</sup>I. Iguchi et al., Physica B 148, 322 (1987).
- <sup>4</sup>D. P. E. Smith et al., Phys. Rev. B 35, 8850 (1987).
- $5J.$  Moreland *et al.*, Phys. Rev. B 35, 8856 (1987).
- $6J. S.$  Tsai et al. (unpublished).
- ${}^{7}L$ . N. Bulaevski et al. (unpublished).
- $8$ Mark Lee et al., Solid State Commun. (to be published).

about the correct value, at least in the ab plane directions, for the family of superconducting copper oxides.

In summary, we have presented electron tunneling data on single crystals of  $Bi_2Sr_2CaCu_2O_x$  which show a gap of  $\approx$  25 meV at 4.2 K. Temperature dependence of the gap indicates a qualitatively BCS-like gap closing around 81-85 K, yielding a value for  $2\Delta/kT_c$  – 7. Comparison of this data with earlier tunneling experiments on  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>$  and its related "1:2:3" materials where both a gap structure and a gap-opening  $T_c$  were established suggests that  $2\Delta/kT_c$  – 7, distinctly larger than the BCS value, is a common number for the cuprate superconductors.

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<sup>9</sup>A. Edgar, C. J. Adkins, and S. J. Chandler, J. Phys. C 20, L1009 (1987).

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- <sup>12</sup>Hiroshi Ikuta et al., Jpn. J. Appl. Phys. **27**, L1038 (1988).
- $3$ We thank R. C. Dynes for pointing out the problems of contact resistance in tunnel junctions with high normal-state resistance electrodes.