

Tunneling measurement of the energy gaps in the superconductors Y-Ba-Cu-O and Tl-Ba-Ca-Cu-O

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Reported here are the results of point-contact electron-tunneling measurements in the high- T_c superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+8}$. The ratio $2\Delta/kT_c$ is 4.0–5.8 (probability maximum near 4.8) for Y-Ba-Cu-O and 4.6 for Tl-Ba-Ca-Cu-O. Both are consistent with strong-coupling superconductivity. The measurements at 600 different locations of the same sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ were performed. The energy distribution of energy gaps with the regularity of the ratio 1:3:5 reported by Kirk *et al.* have not been seen in our experiment.

Ever since the discovery of high-critical-temperature superconductivity in 1986, a series of physical phenomena and parameters have been investigated. One of those, the superconducting energy gap, is commonly of concern. According to the ordinary BCS theory there would be an energy gap of magnitude 2Δ in the density of state at the Fermi level E_F . BCS theory predicts that in the weak-coupling limit the ratio $2\Delta_0/kT_c$ is equal to 3.53. There have been many studies attempting to measure the energy gap in new high- T_c superconductors using a number of methods, especially two direct methods, infrared reflectance and electron tunneling. To date, the results of both infrared-reflectance measurement and electron-tunneling measurement have shown that the values of the energy-gap parameter Δ are in the range 2.5–50 meV (Refs. 1–8) for Y-Ba-Cu-O. Generally, the infrared measurement for Y-Ba-Cu-O showed a smaller energy gap than the tunneling measurement.^{1,4} Occasionally a large Δ was observed on the single-crystal sample.⁹ However, the results of the point-contact tunneling measurements and the sandwich tunneling measurements were also different.⁶ They also depend to a large extent on the surface situation of the samples. Since the sintered superconductors have serious inhomogeneity, it is significant to observe their point-contact tunneling characteristics statistically. In 1987, Edgar *et al.*⁸ first presented a histogram of gap parameters on the high- T_c superconductor Y-Ba-Cu-O with 29 data points. We considered, however, that much more data should be taken for statistical purposes.

We repeated the point-contact tunneling measurements for the high- T_c $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ sample, which had a superconducting critical temperature of approximately 92 K. They were performed at 600 different locations of the same sample. In this paper, we will present the results, including the values of $2\Delta/kT_c$ and a histogram of the energy distribution of the energy gaps, according to the assumption that their energy gaps exist, and have some discussions. We also present the result of the preliminary study of electron tunneling into the superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+8}$ using point-contact tunneling. Tl-Ba-Ca-Cu-O is a novel high- T_c superconductor

without any rare-earth elements.^{10,11} Its superconducting transition temperature is about 116 K. This will provide an extra material base for the study of the mechanism of high- T_c superconductivity.

Our experimental apparatus was a self-designed tunneling-separation-approaching unit, which could be used in a scanning tunneling microscope. During the measurements, this unit could be fully immersed either in liquid nitrogen or liquid helium. A sharpened tungsten tip was used as the probe. The tip radius was about 1000 Å. It was formed by using electrochemical etching. The tunneling separation between the probe and the sample was controlled electromagnetically. When the probe was touching the sample, a stable tunneling current could occur and was displayed on the oscilloscope. The samples were synthesized by a solid-state reaction. The surfaces of the samples were polished with sandpaper or scraped with a small scraping cutter, and then were cleaned. In order to determine the superconducting gap, the current-voltage characteristic and the derivative of the current-voltage characteristic were measured. All the measurements were performed at $T = 77$ K.

Figure 1 shows the typical curves of the current and the differential conductance as a function of the junction voltage for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ sample. There were no BCS-like peaks, which were reported in some papers previously.^{1–3} However, the dI/dV - V curve had the behavior of tunneling into a granular superconductor as suggested by Zeller and Giaever¹² and was like the curves obtained by Gijs *et al.* using a parallel tunneling junction.⁶ This shows that our sample is comprised of fine grains with a small intergrain capacitance.¹² A flat region near zero bias and both flanks with quadric dependence on the voltage were clearly observed in the Fig. 1(b) solid line. The dashed line also shown in Fig. 1(b) is the prediction of the Zeller-Giaever model with $\Delta_0 = 20$ meV.^{12,13} By comparison, we assigned the energy-gap parameter Δ at 77 K, which was half of the width between the two quadric flanks intersecting the nearly flat region, in the same way Gijs *et al.*⁶ did.

In fact, one has difficulties in getting reproducible current-voltage and conductance-voltage characteristics

from each measurement on the same sample. We measured 600 differential-conductance-voltage curves at different locations of the same sample $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ randomly in order to obtain the statistical data. There were no observable tunneling currents at about 5% of the locations. A variety of differential-conductance characteristics were observed. We present some types of curves in Fig. 2. However, neither a flat region nor flanks, which looked like a superconducting energy gap in curves C, D, and E, were observed. About 45% of the differential-conductance-voltage characteristics were similar to curves C, D, or E. We selected the remaining curves, which were remarkably similar to curves A and B, and made a histogram, shown in Fig. 3, with those data about energy-gap parameters. The values of the energy-gap parameters Δ had a large range, but there were no obviously regular energy distribution according to the ratio 1:3:5 reported by Kirk and co-workers.³ For the granular superconductor, the initial tunneling junction was a superconductor-insulator-normal-metal (SIN) tunneling junction which was formed by superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, nonconducting oxides on the surface of the sample, and the tungsten probe. If the second and third tunneling junctions could be formed by the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -intergrain-insulator-super-

conductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (SIS), the energy distribution of the energy gap would follow the ratio 1:3:5 roughly. However, some grains of the sample near the surface were not superconductive. The direct evidence was that there was neither tunneling current at 5% of the locations nor any observable data about the superconducting energy gaps at 45% of the locations. Moreover, the differential-conductance-voltage characteristics observed at room temperature were all similar to curve C, D, or E in Fig. 2, but not one was similar to curves A and/or B in Fig. 2. On the other hand, some grains of the sample were metallic. It seemed that our data were related to the case of a single SIN tunneling junction, a SIN-SIN junction, a SIN-SIS junction, or others. As a result, the first three peaks in histogram represented the energy-gap parameter, $\Delta=16-23$ meV, and the ratio $2\Delta/kT_c=4.0-5.8$. The maximum of probabilities in the distribution of the energy-gap parameters corresponds to $\Delta=19$ meV and $2\Delta/kT_c=4.8$. The quantitative difference may result from the anisotropic nature of the material. The different orientation of the Cu-O plane in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can cause a change in the gap values. Kirtley *et al.* have demonstrated this using the tunneling tip either parallel or perpendicular to the Cu-O planes.¹

Figure 4 shows the typical differential-conductance

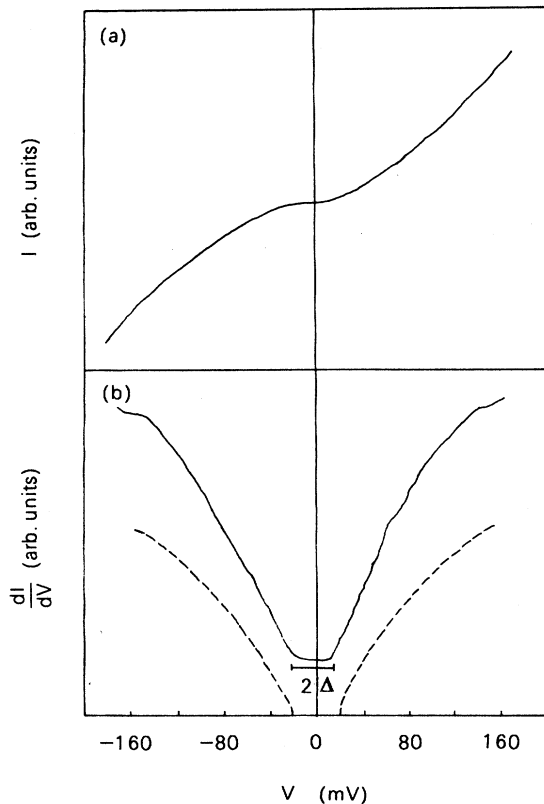


FIG. 1. The typical I - V and dI/dV - V curves for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The solid line is the experiment and the dashed line is the prediction by the Zeller-Giaever model with $\Delta_0=20$ meV.

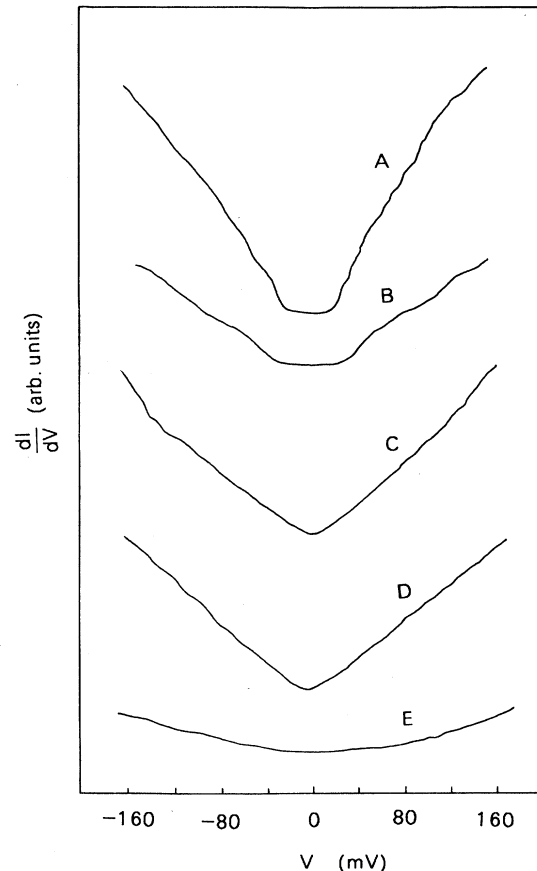


FIG. 2. Some types of differential-conductance-voltage characteristics for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 77 K.

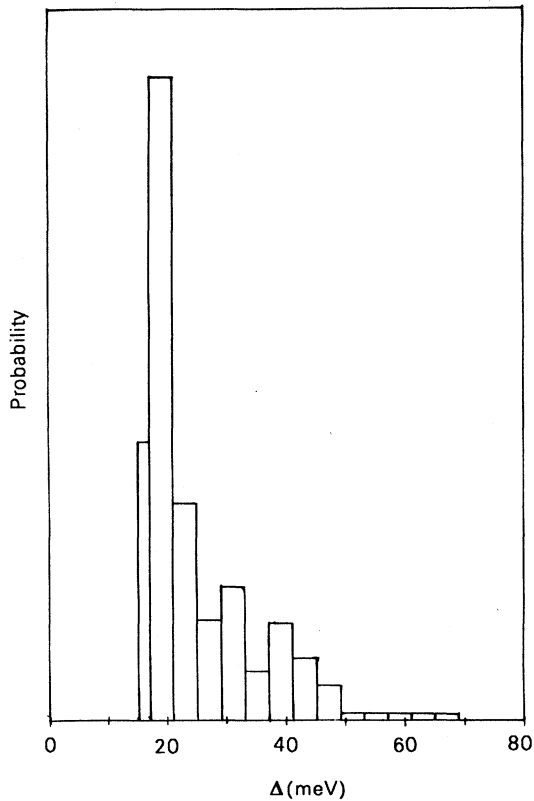


FIG. 3. The histogram showing the distribution of the energy gap parameter Δ .

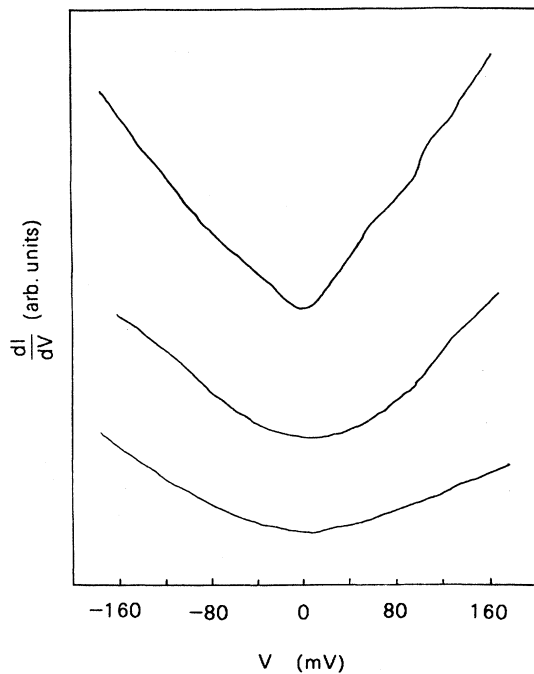


FIG. 4. The typical dI/dV - V curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at room temperature.

characteristics which represent a large number of curves observed from different locations of the sample at room temperature. Obviously, there is a barrier that has been formed between the probe and the semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Usually, the current-versus-voltage characteristic of a Schottky barrier has strong asymmetry. Here, the nearly symmetric behavior observed was possibly caused by the parallel and series connection of different junctions near the surface of the sample due to the grainy structure and the impurity. The rather thick interface layer may give rise to the current-voltage characteristic tending to symmetry.¹⁴ The derivative of the differential conductance changes with the increase of the bias. We could not find out the derivative maximum of the differential conductance from the curves in Fig. 4 or the curves *C*, *D*, *E* in Fig. 2 as well as we could from the curves *A* or *B* in Fig. 2.

We have also observed the behavior of electron tunneling into the superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. Here, we present the I - V curve and the associated dI/dV - V curve in Fig. 5. The Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O systems are both novel superconductors without any rare-earth elements and have superconductivity up to 120 K (Ref. 11) and 114 K (Ref. 15), respectively. To our knowledge the reports about energy gaps of high-temperature superconductivity in a rare-earth-free system

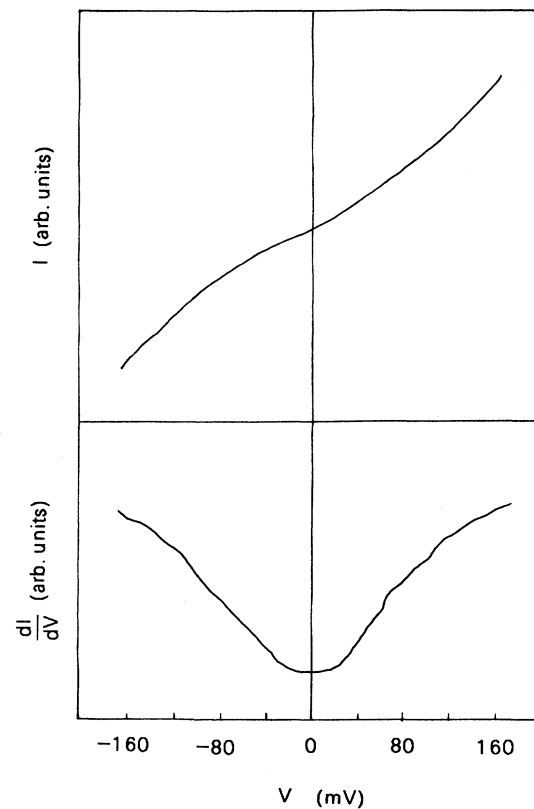


FIG. 5. The current-voltage and differential-conductance-voltage characteristics for superconducting $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$.

were seldom seen, especially for Tl-Ba-Ca-Cu-O. Our experimental results indicated that an energy gap was also possessed in the rare-earth-free superconducting $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. The gap parameter Δ was about 23 meV, and the value of $2\Delta/kT_c$ was about 4.6. The data at different locations of the sample $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ were relatively more concentrative than the sample $\text{YBa}_2\text{Cu}_3\text{O}_{7+\delta}$. Perhaps the homogeneity of the polycrystalline $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ sample was better than the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample.

In summary, the high- T_c superconductors Y-Ba-Cu-O and Tl-Ba-Ca-Cu-O have been studied with point-contact tunneling measurements. The results for the

ratio $2\Delta/kT_c$ were 4.0–5.8 and 4.6 in Y-Ba-Cu-O and Tl-Ba-Ca-Cu-O, respectively. The results show that the two superconductors are both of strong-coupling despite containing rare-earth and rare-earth-free metallic oxide. It seems that the appearance of Zeller-Giaever tunneling is irrelevant to the junction geometry of the sandwich-type⁶ or the point-contact-type but is dependent on the properties of the material and the quality of the surface.

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- ¹J. R. Kirtley, R. T. Collins, Z. Shlesinger, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, *Phys. Rev. B* **35**, 8846 (1987).
- ²M. F. Crommie, L. C. Bourne, A. Zettl, M. L. Cohen, and A. Stacy, *Phys. Rev. B* **35**, 8853 (1987).
- ³M. D. Kirk, D. P. E. Smith, D. B. Mitzi, J. Z. Sun, D. J. Webb, K. Char, M. R. Hahn, M. Naito, B. Oh, M. R. Beasley, T. H. Geballe, R. H. Hammond, A. Kapitulnik, and C. F. Quate, *Phys. Rev. B* **35**, 8850 (1987).
- ⁴S. Sugai *et al.*, *Physica B+C* **148**, 282 (1987).
- ⁵H. F. C. Hoevers and P. J. M. Van Bentum, *Physica C* **152**, 105 (1988).
- ⁶M. A. M. Gijs, J. W. C. de Vries, and G. M. Stollman, *Phys. Rev. B* **37**, 9837 (1988).
- ⁷M. C. Gallagher, J. G. Adler, J. Jung, and J. P. Franck, *Phys. Rev. B* **37**, 7846 (1988).
- ⁸A. Edgar, C. J. Adkins, and S. J. Chandler, *J. Phys. C* **20**, L1009 (1987).
- ⁹Z. Schlesinger, R. T. Collins, D. L. Kaiser, and F. Holtzberg, *Phys. Rev. Lett.* **59**, 1958 (1987).
- ¹⁰Z. Z. Sheng and A. M. Herman, *Nature* **332**, 55 (1988).
- ¹¹R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadjidakos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. El Ali, and A. M. Hermann, *Phys. Rev. Lett.* **60**, 1657 (1988).
- ¹²H. R. Zeller and I. Giaever, *Phys. Rev.* **181**, 789 (1969).
- ¹³J. R. Kirtley, C. C. Tsuei, Sung I. Park, C. C. Chi, J. Rozen, and M. W. Shafer, *Phys. Rev. B* **35**, 7216 (1987).
- ¹⁴H. C. Card and E. H. Rhoderick, *J. Phys. D* **4**, 1602 (1971).
- ¹⁵C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, I. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue, *Phys. Rev. Lett.* **60**, 941 (1988).