RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Electron-tunneling studies of thin films of high-T_c superconducting La-Sr-Cu-O

M. Naito, D. P. E. Smith, M. D. Kirk, B. Oh, M. R. Hahn, K. Char, D. B. Mitzi, J. Z. Sun,
D. J. Webb,* M. R. Beasley, O. Fischer,† T. H. Geballe,*
R. H. Hammond, A. Kapitulnik, and C. F. Quate‡
Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 11 March 1987)

We report results of the study of electron tunneling into thin films of the new high-T_c superconductor La-Sr-Cu-O. Both sandwich-type tunneling with a Pb counterelectrode and point-contact tunneling have been successfully achieved. The results show exceptionally large energy gaps in these materials (roughly 20, 30, and possibly even 60 mV), larger than previously obtained on bulk sintered powders. We interpret these results as due to large anisotropy in this material or due to the presence of a very high-T_c layer near the surface of the films. The method of preparation of this new superconductor in thin film form is also discussed.

The discovery of very high superconducting transition temperatures in various metallic oxides with the perovskite structure[1,2] has raised many fundamental questions about the nature of the superconductivity in this class of materials. These questions include the origins of the high T_c's, whether a new mechanism of superconductivity is present, and whether the BCS theory, including its extensions to strong coupling, can describe the superconductivity in these materials. As is well known, one of the best probes of the microscopic nature of superconductivity is electron tunneling.[3] Tunneling provides a direct measure of the superconducting energy gap Δ and the single-particle density of states $N_s(E)$. By determining the ratio $2\Delta/kT_c$, tunneling data provide a gauge of the coupling strength of the interactions leading to the superconductivity in the material. Alternatively, if a value of $2\Delta/kT_c$ is assumed (e.g., from the BCS theory), tunneling can be used as a material diagnostic to determine the T_c of minority superconducting phases in an inhomogeneous material. For truly high-quality tunneling data, the spectral density of the interaction leading to superconductivity can be deduced from a detailed quantitative analysis of the tunneling I-V characteristic, at least within the conventional strong coupling theory of superconductivity.[3]

In this paper, we report the results of a study of electron tunneling into thin films of the high-T_c superconductor La-Sr-Cr-O. Both point-contact and conventional sandwich-type tunneling were successfully achieved. These combined results provide the most complete picture of the tunneling properties of this superconductor that has appeared to date. Moreover, to our knowledge, they represent the first tunneling study of La-Sr-Cu-O in thin film form. While the observed I-V characteristics are not yet ideal, they provide evidence for very large superconducting energy gaps in these materials. The observed gap values (roughly 20, 30, and possibly even 60 mV) are considerably larger than those reported previously for La-Sr-Cu-O.[4-8] Interestingly, the largest gaps are found in junctions with the most ideal tunneling I-V characteristics.

Taken at face value, these very large gaps (relative to the measured T_c) suggest either extremely strong coupling superconductivity or the existence of material with much higher T_c in particular regions near the surface. The results are in marked contrast to far-infrared absorption studies on La-Sr-Cu-O, which yield significantly smaller energy gaps and imply weaker coupling.[9-11] In this regard, it may be important to note that tunneling is a much more surface sensitive probe than far-infrared absorption, which senses the properties of the materials to a depth given by the far-infrared skin depth of the material.

The method of preparation of our La-Sr-Cu-O thin films will be reported in detail in a later publication. In brief, the La-Sr-Cu-O films were deposited onto room-temperature sapphire (Al_2O_3) substrates from multiple sources (La_2O_3, Sr, and Cu) in the presence of an oxygen flow (1×10^{-4} Torr). The evaporation rates were set and then carefully controlled to obtain films with the nominal composition $(La_{1-x}Sr_x)_2CuO_{4-y}$ with x near 0.1. The actual compositions of the films were determined by microprobe and Rutherford backscattering analysis. As deposited, the films were insulators with a transparent yellow color. X-ray diffraction studies showed that they are highly disordered or amoprhous. After heat treatment in oxygen, the films became dark brown and polycrystalline with the K_2NiF_4 structure. With an optimal heat treatment they could be made superconducting with sharp onset transition temperatures above 30 K, but true zero resistance at somewhat lower temperatures, around 15 K. In Fig. 1 we show the resistive transitions of the samples for which tunneling data are given below. Well away from the compositions shown, the samples were insulating. The foot in the resistive transition seen in most of these samples is reminiscent of behavior commonly observed in granular superconductors. X-ray diffraction and transmission electron microscope studies of a superconducting film prepared similarly to those discussed here show that these films are textured and comprised of 1–2-μm regions of small grains (about 100-Å across), all with the c axis lying in the plane of the film and well oriented in a single direction within each region. Thus, the tunneling is predominantly in a direction that we presume to be the strongly superconducting direction of this anisotropic material.

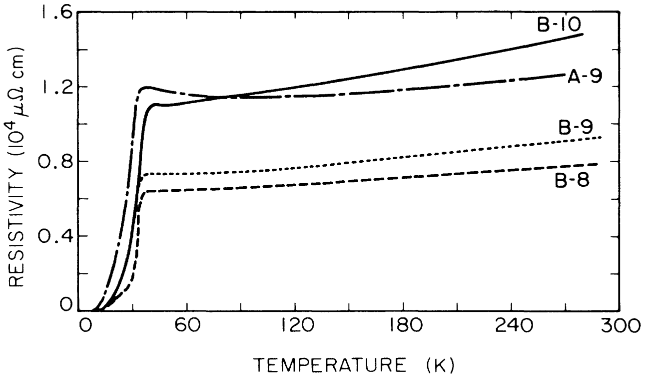

FIG. 1. Resistance vs temperature curves for samples similar to those used in Figs. 2 and 3.

The sandwich-type tunnel junctions were obtained by forming a small window (100×100 μm^1 or 200×200 μm^2) using a photoresist and then depositing a Pb counterelectrode. No special cleaning or other surface preparations were used to form the tunnel barrier. The surface of La-Sr-Cu-O in contact with the Pb appears to form a natural tunnel barrier. Tunnel junctions on the low-T_c perovskite superconductor Ba(Pb-Bi)O$_3$ using the native surface have been reported previously.[12] The junctions we fabricated have very high resistances (typically MΩ) and must be measured with properly buffered electronics.

The point-contact tunneling was done using a cryogenic scanning tunneling microscope.[13] An electrochemically etched tungsten wire was used as the probe. The tip radius was less than 1000 Å. Stable tunneling current could only be obtained when the tungsten probe was touching the sample. The tunneling most likely occurred through the native barrier. No continuous scanning was possible under these conditions, although several spots on the same sample could be studied by retracting and moving the tip to a new spot on the surface. Points within a 1×1-μm^2 window could be sampled.

The observed differential tunneling conductances dI/dV as a function of bias voltage for some of our junctions are shown in Figs. 2 and 3. Figure 2 shows the results obtained at 1.8 K with sandwich-type junctions with the compositions indicated. Series of samples with various compositions are obtained in a single evaporation run by depositing the films on substrates (numbered 1 to 10) arranged in a linear array along the phase-spread direction of the multiple sources. For the particular deposition shown here, the best superconducting transitions were obtained for samples A-8, -9, and -10 and their companions B-8, -9, and -10, which were in adjacent rows of samples deposited in the same evaporation run. In the case of sample B-9, the results from two junctions on the same film are shown for comparison. The results for two junctions formed at different times on sample A-9 are also shown. The lower of the two is the best sandwich-type tunnel junction characteristic we have obtained to date and shows evidence of a very large energy gap. Comparison of data for this sample to the BCS zero-temperature expression for the density of states using an energy gap of 31 mV shows that the characteristic is clearly broadened as compared with the BCS prediction.

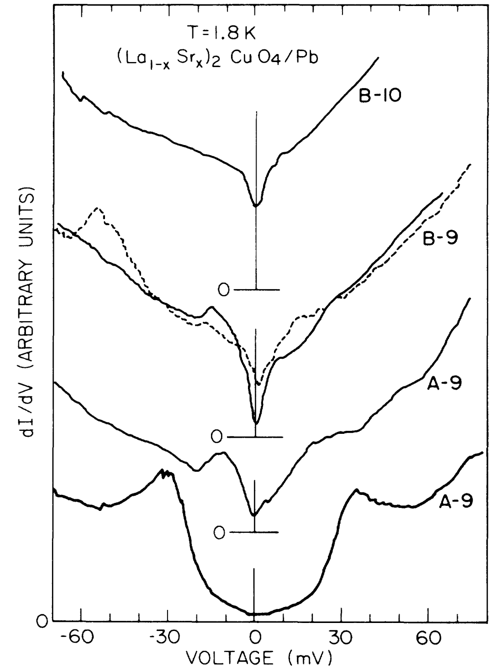

FIG. 2. Tunnel junction conductances for conventional sandwich-type junctions.

In all cases, the overall (asymmetric) shape of the background conductance is very similar and signatures of a superconducting energy gap are evident around zero bias. By a signature of a superconducting energy gap we mean

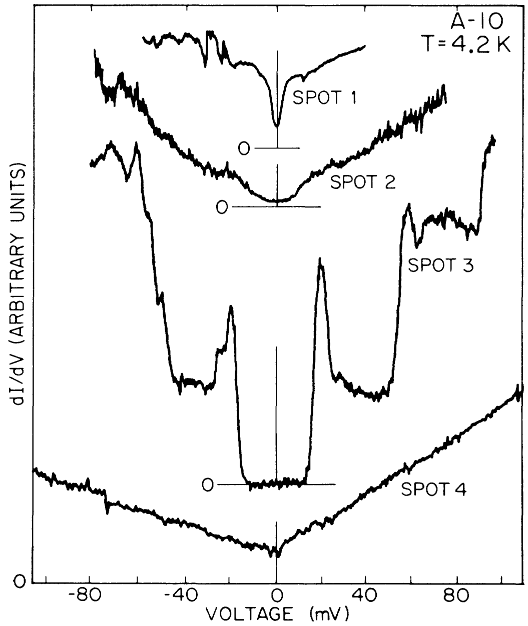

FIG. 3. Point-contact conductance results for four locations on sample A-10.

that there is a peak (or at least a distinct shoulder) in the differential conductance. As can be seen in the figure, the precise value of the dominant energy gap is very sensitive to composition and/or the exact surface condition. We estimate gap values in the range 5–30 mV depending on composition and, presumably, the surface condition. The gap observed on sample B-8 was essentially that of the Pb counter electrode, while it was clearly optimum for samples A- and B-9. By contrast, the resistively determined T_c varies very little. By the nature of sandwich-type tunneling, the data obtained represent an average over the area of the sample weighted by the local tunneling transmission of the barrier. In contrast, the point-contact tunneling data presented below detect local tunneling characteristics.

Figure 3 shows the tunneling conductance obtained by point-contact tunneling at 4.2 K on sample A-10 at four different locations on the film. The general similarity of these curves to those shown in Fig. 2 is reassuring. Clearly, however, the tunneling characteristic varies substantially over the surface of a given sample. The result obtained at location 3 is striking indeed, and represents the best tunneling characteristic we have obtained so far on La-Sr-Cu-O. Remarkably, it also apparently shows two clear BCS-like peaks in the density of states at 22 and 65 mV, with a suggestion of a possible third peak at 90 mV. The I-V characteristic obtained at location 3 is shown in Fig. 4. It is remarkable to note that below the gap voltage, the curve shows zero current to an accuracy of 10^{-12} A. Location 4 in Fig. 3 is only 100 Å away, but shows no evidence of a superconducting energy gap. Nevertheless, it clearly shows the asymmetric barrier common to all the tunneling results.

An unambiguous interpretation of these data is not possible at the present time. The nature of the observed tunneling barrier is completely unknown, although overall it is very reliable. Since very few shorted junctions were observed and the barrier was always observed to be asymmetric, we suggest that the barrier is likely a Schottky barrier of some kind. Presumably it is a layer of La-Sr-Cu-O with an oxygen content deviating from that necessary to achieve metallic (and superconducting) behavior. As a result, the oxygen content of the region of the superconductor being probed in tunneling measurements is likewise not entirely clear. The possibility that some of the structure observed in Figs. 2 and 3 is due to a small band-gap semiconducting form of La-Sr-Cu-O at some locations on the surface cannot be entirely ruled out, although we feel it is unlikely that this is the source of all the observed structure. We believe that the density of states of the superconductor is indeed being observed. The superconducting energy gaps deduced from these data are the largest yet observed in this material. Given the particular texture of our films, it seems probable that we are sensing the behavior along the direction most favorable for superconductivity, i.e., along what is believed to be the highly conducting direction of this anisotropic (layered) material.[14] This would explain why the gaps observed here are systematically larger than those reported previously from point-contact tunneling on randomly oriented sintered powders. Alternatively, it is possible that because of a varying oxygen content near the surface of the films, we are sensing a very high-T_c layer near the surface at which the oxygen content is optimized. In either case, the data suggest remarkable superconducting behavior in the La-Sr-Cu-O system. Either these materials are extremely strong-coupled superconductors with $2\Delta/kT_c$ in the range 8 to 18, or much higher T_c's are still possible within this material system.

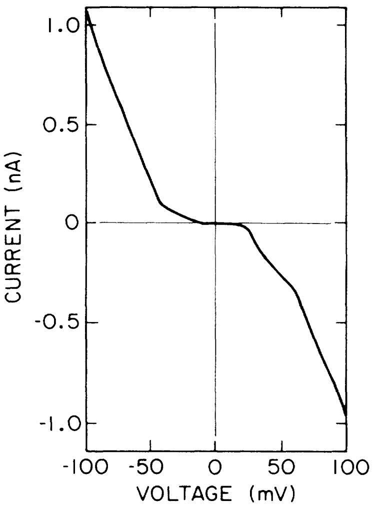

FIG. 4. I-V curve for location 3 in Fig. 3.

Finally, we turn to the multiple peaks in the density of states observed at location 3 of the point-contact tunneling data (Fig. 3). It is possible that two regions with different gaps—one very large indeed—are being observed. A more intriguing possibility is that some new features in the density of states of the superconductor are being detected, perhaps associated with the inferred extremely strong coupling or with as yet unrecognized effects. The possibility of charging effects of the grains[15] seems unlikely given the greater-than-micrometer sized distribution of grains which we observed using scanning and transmission electron microscopies.

We would like to acknowledge the Office of Naval Research, the Air Force Office of Scientific Research, and the National Science Foundation for supporting various participants in this work. The samples were characterized using the facilities of the Center for Materials Research at Stanford, supported in part by the National Science Foundation through the Materials Research Laboratories Program. D.B.M. was partially supported by AT&T, A.K. was partially supported by the Alfred P. Sloan Foundation.

---

[*] Also at the Center for Materials Research, Stanford University, Stanford, CA 94305.

[†] On leave from the Department de Physique de la Matiere Condensee, University of Geneva, Geneva, Switzerland.

[‡] Also at the Department of Electrical Engineering, Stanford University, Stanford, CA 94305.

[1] J. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987); P. H. Hor *et al.*, *ibid.* **58**, 911 (1987).

[3] See, e.g., E. L. Wolf, *Principles of Electron Tunneling Spectroscopy* (Oxford University Press, Cambridge, England, 1985).

[4] S. Pan, K. W. Ng, A. L. deLozanne, J. M. Tarascon, and L. H. Greene, Phys. Rev. B, this issue, **35**, 7220 (1987).

[5] J. R. Kirtley, C. C. Tsuei, S. I. Park, I. Sung, C. C. Chi, J. Rozen, and M. W. Shafer, this issue, Phys. Rev. B **35**, 7216 (1987).

[6] J. Moreland, A. F. Clark, H. C. Ku, and R. N. Shelton (unpublished).

[7] T. Ekino, J. Akimitsu, M. Sato, and S. Hosoya (unpublished).

[8] M. E. Hawley, K. E. Gray, D. W. Capone II, and D. G. Hinks, preceding paper, Phys. Rev. B **35**, 7224 (1987).

[9] Z. Schlesinger, R. L. Greene, J. G. Bednorz, and K. A. Müller, Phys. Rev. B **35**, 5334 (1987).

[10] P. E. Sulewski, A. J. Sievers, R. A. Buhrman, J. M. Tarascon, and L. H. Greene (unpublished).

[11] U. Walter, M. S. Sherwin, A. Stacy, P. L. Richards, and A. Zettl, Phys. Rev. B **35**, 5327 (1987).

[12] W. Reichardt, B. Batlogg, and J. P. Remika, in *Proceedings of the International Conference on Materials and Mechanisms of Superconductivity,* edited by K. A. Gschneidner, Jr. and E. L. Wolf (North-Holland, Amsterdam, 1985).

[13] D. P. E. Smith and G. Binnig, Rev. Sci. Instrum. **57**, 10, (1986).

[14] See, e.g., L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[15] I. Giaver and H. R. Zeller, Phys. Rev. Lett. **20**, 1504 (1968); Phys. Rev. **181**, 789 (1969).