RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Measurements of the superconducting gap of La-Sr-Cu-O with a scanning-tunneling microscope

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(Received 18 February 1987)

We report the first tunneling measurements made on the new high-transition-temperature perovskite superconductors. These were obtained using an ultrahigh-vacuum low-temperature scanning-tunneling microscope. The superconducting gap of a $La_{1.85}Sr_{0.15}CuO_{4-y}$ sample is 12 ± 3 mV, and the onset T_c is 40 K, from which $2\Delta/k_BT_c = 7 \pm 2$. The possibility that this surprisingly high ratio may be due to a mechanism other than superconductivity is discussed.

Since the first report of unexpectedly high transition temperatures by Bednorz and Müller,[1] the superconducting properties of perovskite-structure materials have been improving dramatically. Recent published reports[2-6] have placed the midpoint of the transition around 40 K, the transition width at 1-2 K, and the onset as high as 52 K.[3] Hence the tremendous interest in these compounds.

Tunneling is an important measurement that has not been reported so far for these superconductors. There are difficult technical problems involved in trying to make a conventional tunnel junction on these materials: the surfaces are rough[7] and may not be representative of the bulk of the sample, a suitable natural or artificial tunneling barrier is difficult to obtain, and the material is inhomogeneous. The scanning-tunneling microscope (STM) can get around these problems by using vacuum as a barrier and by probing properties on a scale smaller than the inhomogeneities. We have used a low-temperature STM to study $La_{1.85}Sr_{0.15}CuO_{4-y}$ samples and report here the first tunneling measurement of the superconducting gap for this class of materials.

$La_{1.85}Sr_{0.15}CuO_{4-y}$ samples were prepared as described previously,[5] cut into $1 \times 3 \times 12$ mm rectangles, and stored in air for a week before tunneling measurements were done on one of the cut faces. The resistive transition for this batch had an onset of 40 K, midpoint of 38.5 K, and width (10%-90%) of 1.1 K. A small piece was glued to a copper substrate with silver paint and loaded in the tunneling microscope through a load lock. The substrate is held in the microscope with pressure clips against a copper sample holder which has a calibrated thermometer. Temperatures will be given as measured by this thermometer; the sample may be at a higher temperature due to the fact that it is difficult to obtain good thermal contact in UHV. Thermal load is minimal, however, because the microscope is completely surrounded by concentric aluminum cylinders attached to liquid nitrogen and liquid helium dewars. The sample can be exchanged between the microscope and other surface analysis and preparation tools in the same ultrahigh vacuum chamber. This design is entirely different from our previous work;[8] a detailed description will be given elsewhere.[9]

The sample was loaded in the microscope at 77 K and was then cooled to 10-15 K. The tip was a Pt-Rh wire (0.76 mm diam), ground to a sharp point. The behavior of the tunneling current as the tip approaches the sample indicates that the tip is touching the surface. This is not surprising since we did not ion mill the surface prior to tunneling. It is therefore likely that we are tunneling through a layer of inhomogeneous insulating or semiconducting material, and not through vacuum. We are not likely to have a metallic point contact, however, because of the large resistance of our junction, typically 1 MΩ. Ion milling was not attempted because of the likely damage to the surface which cannot be annealed in vacuum due to loss of oxygen. Tunneling microscopy on this surface gives images showing sharp features extending over a few hundred angstroms in height. The size and irreproducibility of these features is another indication that the tip is touching the sample.

Figure 1 shows current-voltage (I-V) characteristics obtained at $T = 12$ and 77 K. The voltage was swept linearly in time by an oscillator at 2.5 Hz. While the curves at 12 K are not ideal superconductor-insulator-normal metal (SIN) I-V curves, it is reasonable to assume that the drop in slope at low bias is due to the superconducting gap of the sample. This is easier to see in dI/dV [Fig. 1(b)] and is supported by comparing with a similar curve taken at 77 K shown in the same figures. A rough estimate from these curves gives a superconducting gap of 10-15 meV; a more complete analysis is given below. The I-V curves in Fig. 1(a) were digitized from an enlarged photograph of an oscilloscope screen. The derivative was computed as a finite difference with a step of 2 mV, which enhances the noise introduced by the digitizing procedure.

We also used a personal computer to digitize and average 128 I-V curves each at $T = 12$ and 77 K. In this case the finite-difference derivative, Fig. 2(a), shows much less noise than the previous figure, even though the finite difference step is smaller (0.7 mV). The depth of the gap structure is, on the other hand, reduced from before, while the size of the gap is approximately the same. This is due to changes in junction quality as a function of time. The parabolic background in both curves may be due to tunneling through material with a low effective barrier height. We see this background quite consistently at all

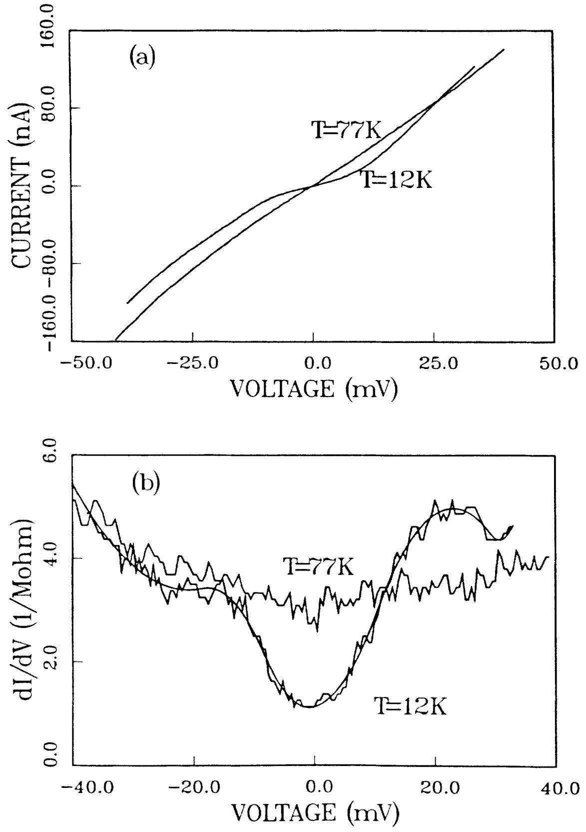

FIG. 1. (a) Current-voltage characteristics between tip and sample (x axis is tip voltage with respect to sample) at $T=12$ and 77 K. (b) Numerical derivative of (a). The smooth solid line is a spline fit.

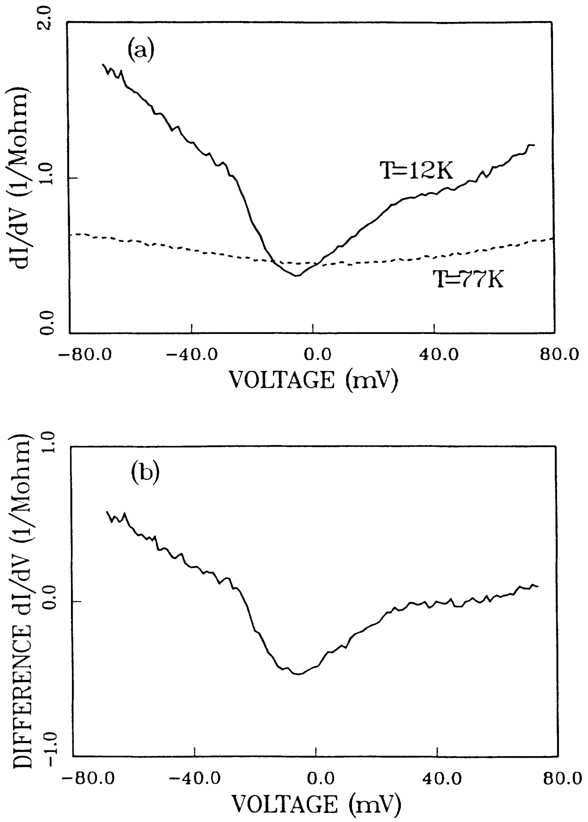

FIG. 2. (a) Numerical derivative of the average of 128 I-V curves at $T=12$ and 77 K digitized by a computer. (b) Difference between the two curves in (a).

temperatures between 10 and 77 K. An empirical method to take out this background is to subtract the $T=77$ K curve (scaled times 1.9 to match the high bias conductance) from the $T=12$ K curve in Fig. 2(a); the result is shown in Fig. 2(b). Using a simple model with a square barrier[10] we obtain a good fit to this background with a barrier height and thickness of 0.6 eV and 0.48 nm, respectively. It must be noted, however, that these parameters are dependent on the junction area, which has been very roughly estimated as $(0.2\ \mu m)^2$. Interestingly, as the junction area is reduced, the solutions to the nonlinear equations[10] give a fairly constant barrier thickness and a barrier height that goes to zero as the area approaches $(170\ nm)^2$, with no solutions for smaller areas.

We do not show I-V curves at intermediate temperatures due to the fact that a temperature excursion between our lowest temperature and T_c, which may be locally as high as 40 K, causes enough thermal drift that the tip may move with respect to the sample. We have therefore not attempted to measure the local T_c by looking for the onset of gap opening. Nevertheless, the data shown here are representative of a large collection obtained at both temperatures and on various locations on the sample, ranging from a few tens of nm apart (obtained with the microscope scanner) to tenths of mm (by repositioning the sample). The superconducting properties at $T=12$ K seem inhomogeneous since we observe a variety of curves going from fully normal (zero gap) to the ones shown in these figures.

We now discuss two alternative explanations for the nonideal shape of dI/dV. The first is that the sample is at a higher temperature than its holder. Figure 3 shows a fit of the SIN tunneling theory[11] (solid curve) to the positive bias portion of Fig. 1(b), with $T=55$ K and $\Delta(T=55\ K)=12$ mV. This would imply that $T_c > 55$ K and $\Delta(T=0) \geqq 12$ mV. The discrepancy between the holder temperature (12 K) and the temperature obtained from the fit is too large for this to be a viable explanation. The second alternative is that the sample is inhomogeneous and the electrons are tunneling into several grains which have a distribution of T_c's and corresponding Δ's. This is consistent with the known structure of this material. The dotted curve in Fig. 3 is obtained assuming $T=12$ K and adding contributions from grains with gaps (relative contribution in parenthesis) of 15 meV (42%), 9 mV (16%), and 1 mV (42%). Adding a larger number of contributions would naturally give a better fit; the fit shown illustrates the method. We believe this to be the most appropriate model for our data, judging from the reasonable fit to the data and the consistency of this simple model with the small amount of structural information available

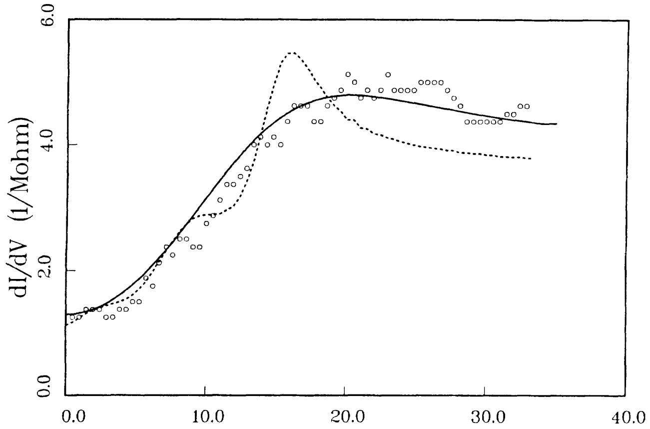

FIG. 3. Fits to the data of Fig. 1(b) (circles) from a model assuming $T=55$ K and $\Delta=12$ mV (solid line), and a model assuming $T=12$ K and a distribution of gaps (dotted line) as described in the text.

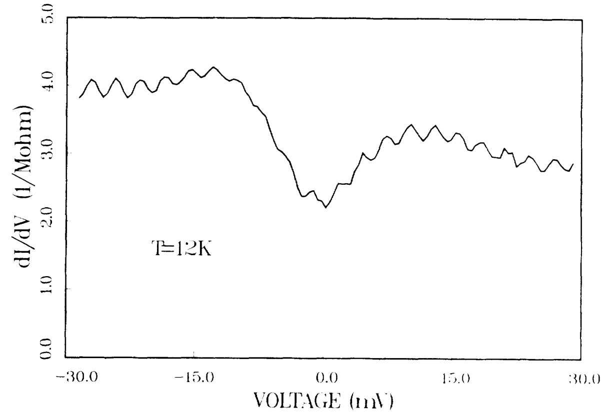

FIG. 4. Data taken as in Fig. 2(a) on the fresh surface of a sample broken *in situ* at low temperature. The gap is of the same size while the parabolic background is absent.

on this material. Taking the highest gap (15 meV) and the onset of the resistive transition (40 K) we get $2\Delta/k_BT_c=8.7$. This may be artificially high since a broad shoulder in the resistivity data indicates that there may be a few grains with T_c up to 45 K. Furthermore, the fact that the tip is touching the surface may result in high localized pressures which may increase T_c (Refs. 2 and 3) (and Δ) in the vicinity of the tip. Recent far-infrared reflectivity measurements by Sulewski *et al.*[12] give $2\Delta/k_BT_c=1.6$–2.7, well below our results and also below that predicted by Bardeen-Cooper-Schrieffer theory. We believe that differences in samples and sample homogeneity[13] can explain this discrepancy, especially since our measurement is highly localized.

Further evidence that the gap structure seen in Figs. 1 and 2 is not due to a surface layer is shown in Fig. 4. In this case we cooled a sample to 77 K and then broke it *in situ*. This is the best way to obtain a surface that is more representative of the bulk, especially since the low temperature should minimize the loss of oxygen. The tip was placed in the middle of the fresh surface. In contrast with the previous data, the sensitivity of the tunneling current to the distance from the surface was typical of vacuum tunneling, i.e., the surface was clean and there was no need to punch through an insulating layer as before. The main difference compared to the previous data is the absence of the parabolic background of dI/dV. It is therefore likely that the parabolic background in Figs. 1 and 2 and similar ones of other authors[14] is due to a contaminated, damaged, or nonstoichiometric surface layer. Furthermore, the gap structure is still present with roughly the same value. The additional smearing seen in this curve can be qualitatively understood in terms of the depairing caused by the high current densities present in vacuum tunneling, which are of the order of 10^6 A/cm^2. Finally, the structure with a period of 5.0 mV in Fig. 4 may not be due to noise, since the figure represents the average of 128 curves so that an external noise source would have to be synchronized with an accuracy of at least one part in 5000. Furthermore, this structure is not seen in any previous measurement.

Given that our I-V curves are not ideal, we must consider other mechanisms not necessarily involving superconductivity. Similar curves can be obtained, for example, by tunneling through a matrix of small insulated metallic grains which are on top of a metal electrode.[15] The "gap" in this case is the charging energy of the small particles. The data in Figs. 1 and 2 would require a particle size of the order of 2 nm and a size distribution smaller than 40%. While this tight distribution is unlikely, this explanation cannot be ruled out without more structural and tunneling information.

In summary, we have obtained the first tunneling measurement of the superconducting gap in the recently reported perovskite structures.

We are grateful to J. M. Rowell for starting this collaboration as well as for useful discussions and to J. C. Thompson for providing the Pt-Rh wire and daily encouragement. This work is supported by the Texas Advanced Technology Project and the National Science Foundation under Grant No. DMR-8553305, with matching funds from IBM, Bell Communications Research, Texas Instruments, Kodak, and Microelectronics and Computer Technology Corp. (MCC).

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

[2] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[3] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, and Z. J. Huang, Science **235**, 567 (1987).

[4] R. J. Cava, R. B. van Dover, B. Batlogg, and A. E. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[5] J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull,

and T. H. Geballe, Science (to be published).

[6] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. (to be published); H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *ibid.* (to be published).

[7] Several groups are currently making thin films with these compounds, which should have smooth surfaces. Unfortunately the superconducting properties of films are currently inferior to those of bulk samples.

[8] A. L. de Lozanne, S. A. Elrod, and C. F. Quate, Phys. Rev. Lett. **54**, 2433 (1985); S. A. Elrod, A. L. de Lozanne, and C. F. Quate, Appl. Phys. Lett. **45**, 1240 (1984).

[9] S. Pan, C. Snyder, and A. L. de Lozanne (unpublished).

[10] J. G. Simmons, J. Appl. Phys. **35**, 2655 (1964).

[11] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[12] P. E. Sulewski, A. J. Sievers, S. E. Russek, H. D. Hallen, D. K. Lathrop, and R. A. Buhrman, Phys. Rev. B **35**, 5330 (1987).

[13] Very recently, reflection FIR measurements have been done on a sample from a similar batch to ours, but with slightly lower Sr concentration [P. E. Sulewski, A. J. Sievers, R. A. Buhrman, J. M. Tarascon, and L. H. Greene, Phys. Rev. Lett (to be published)]. $2\Delta/k_BT_c$ is higher but still below our values. Similar results have been obtained with transmission FIR on samples made elsewhere [Z. Schlesinger, R. L. Greene, J. G. Bednorz, and K. A. Müller, Phys. Rev. B **35**, 5334 (1987)]. Inhomogeneities may therefore be playing an important role in the properties measured by the two techniques.

[14] T. Ekino, J. Akimitsu, M. Sato, and S. Hosoya, Solid State Commun. (to be published); J. Moreland, A. F. Clark, H. C. Ku, and R. N. Shelton, Cryogenics **27**, 227 (1987); M. E. Hawley, K. E. Gray, D. W. Capone II, and D. G. Hinks, following paper, Phys. Rev. B **35**, 7224 (1987).

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