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Point-contact electron tunneling into the high-T_c superconductor Y-Ba-Cu-O

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We report results of a study of electron tunneling into bulk samples of the new high-T_c superconductor Y-Ba-Cu-O using point-contact tunneling. Based on a superconductive tunneling interpretation, the results show exceptionally large energy gaps in these materials (roughly $2\Delta=100$ meV), implying $2\Delta/k_BT_c\sim13$. Similar values were found previously by us for La-Sr-Cu-O. We also see structure in the I-V curves similar to that seen in La-Sr-Cu-O. On the basis of the asymmetries observed in the I-V characteristics, we believe that the natural tunneling barrier on this material is of the Schottky type.

The existence of very high transition-temperature superconductors among metallic oxides with the perovskite structure[1-3] has stimulated much interest in the nature of the superconductivity in these remarkable materials. As is well known, one of the most effective probes of superconductivity at the microscopic level is electron tunneling.[4] Already, several preliminary studies of the superconductor La-Sr-Cu-O ($T_c=35$ K) have been reported. These include tunneling using point contacts[5-10] and sandwich-type junctions with Pb counterelectrodes.[5] Very large energy gaps and values of $2\Delta/k_BT_c$ are generally observed.

In this Rapid Communication, we report the results of a study of electron tunneling into sintered powders of the superconductor Y-Ba-Cu-O ($T_c=90$ K) using point-contact tunneling. As in La-Sr-Cu-O, based on a superconductive tunneling interpretation of the data, we find evidence for very large energy gaps and a value of $2\Delta/k_BT_c$ roughly equal to 13. We also see evidence in this material for structure in the differential conductance dI/dV that is remarkably similar to that seen previously in La-Sr-Cu-O.[5] Such strong structure is not seen in the tunneling conductance of conventional lower T_c superconductors. We also find that in most cases the tunnel barrier exhibits electrical characteristics suggestive of the behavior seen previously in superconductive tunneling studies using Schottky barriers.[11-13] Similar characteristics were present in the case of La-Sr-Cu-O. This suggests that Schottky-barrier formation may be a general feature of the surface of the perovskite superconductors under certain preparation techniques. This may be of considerable practical utility in tunneling studies and applications.

Our Y-Ba-Cu-O samples of nominal composition $Y_{0.5}Ba_{0.5}CuO_y$ were prepared from mixtures of high-purity Y_2O_3, $BaCO_3$, and Cu-O powders. The powders were premixed in water and subsequently heated to 100 °C to evaporate the solvent. The samples were further heated in Pt crucibles for 6 h in air at 1000 °C. After this first firing, the samples were porous and black in color. The samples were then ground and cold pressed to form disks about 1 cm in diameter and 0.2 cm in thickness, and heated in oxygen for 10 to 13 h at 1070 °C.

The samples were examined by x-ray diffraction and microprobe analysis to establish their structure and to confirm their composition. The interpretation of the x-ray data is not yet entirely clear. We unambiguously observe the cubic perovskite structure. There is some indication of the K_2NiF_4 structure, but we see other phases as well. In particular, we see evidence for some of the higher-order perovskite structure recently claimed to be the high-T_c phase by Cava *et al.*[14]

The superconducting properties of these materials were examined using four-terminal dc resistance measurements. The superconducting transition was observed at about 92 K with a width of about 5 K. Magnetization measurements on the samples show 40% complete diamagnetism in the dc shielding and a 10% Meissner effect. The critical current density at 77 K was about 50 A/cm^2.

The point-contact tunneling was done using a cryogenic scanning-tunneling microscope.[15] 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. As a result, the tunneling most likely occurred through the native barrier. No continuous scanning was possible under these conditions, although several spots within a 1-μm by 1-μm region could be examined on the same sample by retracting and moving the probe to a new location. Some areas of the sample were found to be insulating, and no tunneling was possible in these locations.

The curves shown in Figs. 1 and 2 are representative of the best results obtained on Y-Ba-Cu-O at 4.2 K. The bias voltage is positive with respect to the tungsten probe. The three curves in Fig. 2 were taken at one location of the sample. Figure 1 was taken at a different location. The dI/dV curve shown in Fig. 3 was measured at 77 K at yet another location. The best curves were obtained when the tunneling current was stable and free from noise. The noise that was observed appeared to be the result of the tunneling current switching rapidly between two or more current paths, indicating a poorly formed point contact. This switching noise was much more common on the sintered Y-Ba-Cu-O material than the La-Sr-Cu-O thin films studied earlier.[5] Only on stable junctions would the

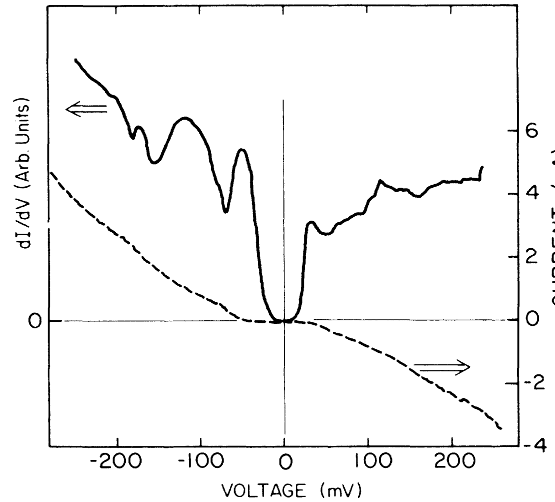

FIG. 1. I vs V and dI/dV vs V measured at 4.2 K on a point-contact tunnel junction formed by a tungsten probe and a sample of Y-Ba-Cu-O.

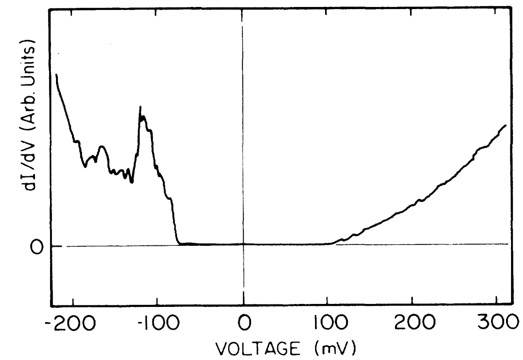

FIG. 3. dI/dV measured on Y-Ba-Cu-O at 77 K.

conductance reach zero bias and show any well-defined peaks. Junctions measured at room temperature never showed this behavior.

The interpretation of the peaks observed in Figs. 1–3 is not entirely straightforward. In all the curves the initial peak is suggestive of a peak at the energy gap in the BCS density of states. However, two features make the curves look quite different from typical density-of-states measurements on superconductors. The first is the very strong asymmetry between the positive and negative biases. This asymmetry is extreme for the data in Fig. 2 but much less in Fig. 1, which is more like our data for La-Sr-Cu-O.[5] The second is the frequent presence of very strong peaks above the energy of the initial peak. We suspect that the asymmetry is the result of tunneling through a native Schottky barrier that exists on the surface of the Ya-Ba-Cu-O. The sense of the asymmetry we observe is consistent with a p-type doping of the Y-Ba-Cu-O surface. Several pieces of evidence point toward Schottky-barrier formation. Large portions of the sintered material displayed semiconducting behavior at room temperature. (Some metallic and insulating regions were also present.) It was also very easy to form a tunnel junction, and we were never able to form a junction with a resistance below 100 kΩ. Moreover, the junction resistance was relatively insensitive to the pressure applied to the tungsten probe. This is in marked contrast to our experience in tunneling to other conducting surfaces. Finally, when we attempted point-contact measurements on a sample of Y-Ba-Cu-O which displayed more metallic behavior, we were unable to form a good tunnel junction because the barrier resistance was too low.

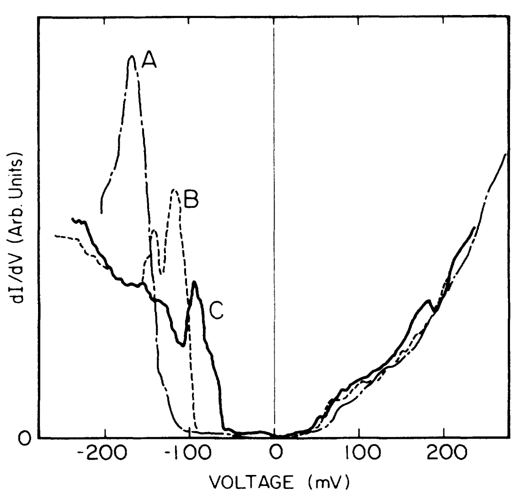

FIG. 2. dI/dV measured three times at the same location. This location was different from the one measured in Fig. 1.

In their study of tunneling between superconducting metal surfaces and a degenerate GaAs point probe, von Molnar, Thompson, and Edelstein[11] noted that their junctions displayed asymmetry with respect to the sign of the bias voltage. The asymmetry in their junctions was small compared to the effect we see, presumably because the energy gap of the superconductors they measured was only about 3 meV, small compared to the Fermi energy of the degenerate GaAs electrons. We anticipate that the energy gap of this high-T_c material will be much larger. Our earlier experiments on La-Sr-Cu-O (Ref. 5) show asymmetry in all the point-contact and thin-film junctions consistent with an n-type doping of the La-Sr-Cu-O surface. The asymmetry, though smaller than with the results on Y-Ba-Cu-O, increases at higher bias voltages.

The question of multiple peaks in the dI/dV curves is more challenging. From junction to junction, the energies of the peaks exhibit an intriguing pattern which is displayed in Fig. 4. Here we show the energy distribution of peaks in dI/dV for all the junctions in Figs. 1–3 and similar data taken with point-contact junctions on La-Sr-Cu-O, some of which was reported earlier.[5] The circled points for Y-Ba-Cu-O are the data taken at 77 K (Fig. 3). For both Y-Ba-Cu-O and La-Sr-Cu-O, the data appear to cluster into three groups. The La-Sr-Cu-O data fit this trend better, perhaps because of the higher quality of the thin-film junctions. In the best La-Sr-Cu-O junction produced so far (shown in Fig. 3 of Ref. 5 and indicated here

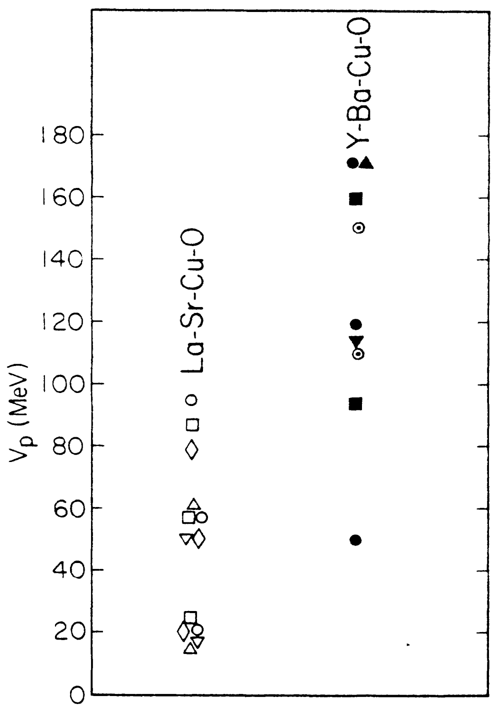

FIG. 4. Energy (V_p) distribution of peaks in dI/dV observed with point-contact tunnel junctions on La-Sr-Cu-O and Y-Ba-Cu-O. Each symbol represents a different sample. The data for Y-Ba-Cu-O is from Figs. 1–3. For La-Sr-Cu-O, the data points noted by open circles are from Ref. 5.

by the open circles), the peak energies follow almost exactly the ratio 1:3:5. Note, however, that the Y-Ba-Cu-O curves shown in Figs. 2 and 3 do not have peaks which fall in the lowest energy group. Although a pattern in the data seems evident, its basis is not yet clear.

Another interesting relation is that the ratio of the lowest energy peaks for Y-Ba-Cu-O and La-Sr-Cu-O is 50 to 20 meV or 2.5 to 1. The ratios of the T_c's are 90 to 35 K or 2.6 to 1. As a result, $2\Delta/k_BT_c$ for the two materials are both equal to about 13. The fact that the initial peaks do scale with T_c supports our interpretation that the observed behavior is connected with the superconductivity of these materials.

In summary, we have observed structure in the tunneling I-V characteristic of Y-Ba-Cu-O similar to that seen previously in La-Sr-Cu-O. A particularly intriguing pattern in this structure is seen that appears common to both materials. Independent of the specific interpretation of the data, there appears to be some commonality in the underlying physics of these two materials.

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