Reproducible Tunneling Data on Chemically Etched Single Crystals of $YBa_2Cu_3O_7$

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We have fabricated tunnel junctions between chemically etched single crystals of $YBa_2Cu_3O_7$ and evaporated metal counterelectrodes which exhibit reproducible characteristics. Above the bulk critical temperature of $YBa_2Cu_3O_7$, T_c, the conductance, $G(V)$, has a linear dependence with voltage and has some asymmetry. Below T_c, additional structure associated with the superconductivity appears in $G(V)$. At $T \ll T_c$ there is a reproducible, finite, zero-bias conductance which suggests that there are states at the Fermi energy in superconducting $YBa_2Cu_3O_7$. Junctions with Pb, Sn, Bi, Sb, PbBi, and Au counterelectrodes all show qualitatively similar behavior.

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As is well known, tunneling probes the density of electronic states within a coherence length ξ of the surface of a superconductor. In orthorhombic $YBa_2Cu_3O_7$, ξ is anisotropic, with $\xi_c \approx 2$–4 Å in the direction normal to the Cu-O planes, and $\xi_{ab} \approx 12$–30 Å along the planes.[1] Single crystals of $YBa_2Cu_3O_7$ are typically thin platelets oriented along the *a*-*b* planes. Considering the extremely short ξ_c, tunneling into these platelets requires monolayer-level perfection at the surfaces. This surface perfection is decisively lacking in as-prepared crystals subjected to long oxygen anneals. In addition, prolonged ambient exposure has been shown to affect surface stoichiometry.[2] Experimental approaches devised to overcome these problems include break junctions,[3] point-contact tunneling with tips driven into the surface,[4] tunneling into freshly cleaved surfaces,[5] and tunneling into freshly prepared films.[6,7] Despite these measures, the considerable scatter in the gap values found in the literature and the general lack of reproducibility in tunneling are quite disturbing.

We have fabricated tunnel junctions on chemically etched single-crystal $YBa_2Cu_3O_7$ with evaporated films of Pb, PbBi, Sn, Bi, Sb, and Au which have highly reproducible tunneling characteristics from junction to junction. In this Letter, we concentrate on results obtained from $YBa_2Cu_3O_7$/Pb junctions for which we are certain that the conductance is due to a single-step tunneling process. These junctions show reproducible structure in $G(V)$ which appears at temperatures below the critical temperature of $YBa_2Cu_3O_7$, T_c, and which we can attribute to structure in the superconducting density of states in the $YBa_2Cu_3O_7$. This structure includes gaplike features at about 4 and 19 mV and a finite zero-bias conductance. We will describe this structure and its temperature and magnetic field dependence. In addition, we will compare the $YBa_2Cu_3O_7$/Pb and $YBa_2Cu_3O_7$/Au results and discuss our results in relation to earlier tunneling measurements on $YBa_2Cu_3O_7$.

The single crystals of $YBa_2Cu_3O_7$ were grown by the flux method[8] and were annealed in oxygen for more than three weeks. The junctions were fabricated in the following manner. First, the crystals were etched either in 10 mM $HClO_4$, 1 M $NaClO_4$ in water[9] for 5–30 min (etch rate of 1000 ± 100 Å/min) or in 1.0% Br (by volume) in methanol[10] for 30–120 min (etch rate of 50 ± 20 Å/min). The surface of an etched crystal is dotted with crystallographically oriented square etch pits which were typically 20 μm on a side and ≈ 0.2 μm deep. We point out that the etching process exposes a large number of *a*-*b* plane terminations, while the initially flat surface was uniformly oriented in the *c*-axis direction. This may be of great benefit for tunneling studies, given the difference in ξ_{ab} and ξ_c.[1] The etched regions appear very clean and shiny when viewed in an optical microscope. Etched crystals were treated for 5–10 min at 100 °C in air in order to increase the tunneling resistance. The junctions were completed by evaporating the counterelectrode through a shadow mask. Junction dimensions were about 0.1×1.0 mm^2 and resistances were between 5 and 1000 Ω.

The nature of the barriers in the tunnel junctions is unknown, but the formation of high-quality tunnel junctions directly on the surface of oxide superconductors is quite common.[11] We have observed that the room-temperature resistance of the junctions increases with heat-treatment time and depends on the counterelectrode material; i.e., Pb produces greater resistances than Au.

Four-terminal measurements of the differential resistance were performed using standard low-frequency ac lock-in techniques. These resistances were inverted to obtain the differential conductance, $G(V)$. At low temperatures, $G(V)$ of a normal metal/insulator/superconductor tunnel junction is proportional to the density of states of the superconductor.

For uniformity, we present data that come from one Pb and one Au junction that are representative of the results we have obtained on many (over 100) similar junctions. For all measurable junctions, the structure in

$G(V)$ below T_c was similar for different counterelectrode materials. The sharpness and amplitude of the predominant features did vary somewhat from junction to junction, but remained nonetheless essentially identical in a large number of junctions.

Structure first appears in $G(V)$ at T_c. We show this in Fig. 1(a) where we have plotted the temperature dependence of $G(V=0)/G(100\text{ mV})$. At T_c there is a discontinuity in $dG(V=0)/dT$ which is similar to what one would see due to the opening of the energy gap at T_c in a metal/insulator/BCS-superconductor tunnel junction. We believe that these results are compelling evidence that the electrons are tunneling directly into *superconducting* $YBa_2Cu_3O_7$—there is no thick (on the scale of ξ) reduced-T_c layer at the surface.

In Fig. 1(b) we show $G(V)$ normalized to $G(100\text{ mV})$ of a $YBa_2Cu_3O_7$/Pb junction at temperatures both above and below $T_c=89$ K. The high-voltage conductance depends on temperature, decreasing by approximately 15% from 10 to 180 K. For clarity, we have not shown data for temperatures below the superconducting transition of Pb where the phonon structure and energy gap of Pb adds even more structure to the data. This structure is well understood and is not the focus of this paper. It is important to note, however, that all the structure due to the Pb is of the correct amplitude and at the correct energies. Thus, we are confident that $G(V)$ is determined by a single-step tunneling process.

Above T_c, $G(V)$ is linear in V, as has been observed in other experiments.[12] This background has some asymmetry: The slope at positive bias is about 10% greater than that at negative bias.

Additional structure and the asymmetry in $G(V)$ are evident in Fig. 2 where we have plotted $G(V)$ at 10 K and zero magnetic field (solid line) on a finer voltage scale. The prominent features in $G(V)$ are peaks located at approximately ± 19 and $+36$ mV and minima at ± 49 mV. There are reproducible asymmetries in both the height of the ± 19-mV peaks and the number of peaks at each bias. There are two smaller broader peaks at approximately -31 and -41 mV. The sharpness of these features varies a little from junction to junction but their positions remain constant. Below about 25 K features at ± 4–5 mV begin to emerge. In $YBa_2Cu_3O_7$/Au and $YBa_2Cu_3O_7$/Bi junctions these last features are even sharper and actually appear as peaks.

In addition, we have consistently measured a zero-bias conductance on the order of 50% of the junction conductance at 100 mV at temperatures well below T_c. We know that this is not due to leakage because the ratio of the junction zero-bias conductance with the Pb in the su-

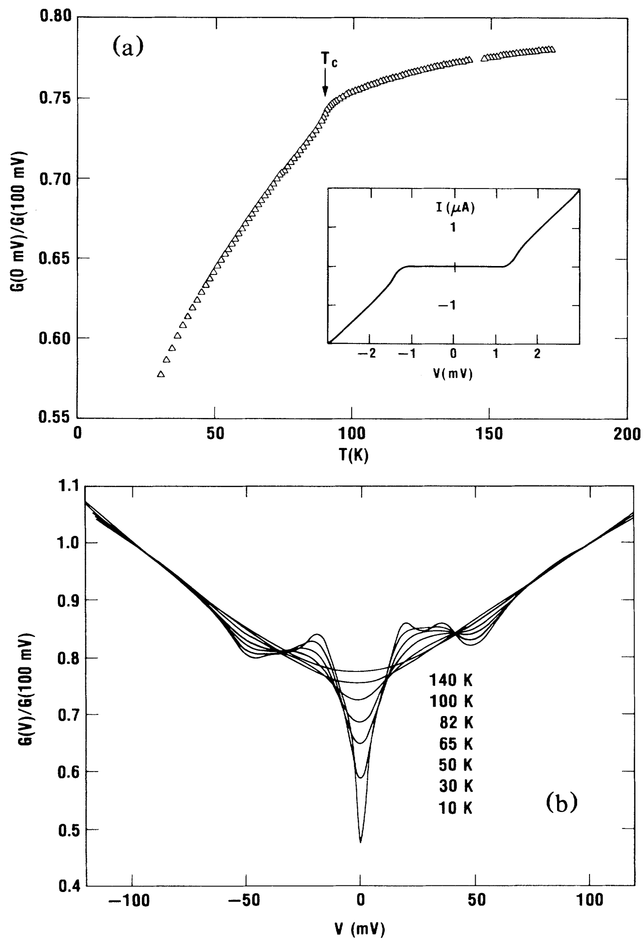

FIG. 1. (a) Temperature dependence of $G(0\text{ mV})/G(100\text{ mV})$ of a $YBa_2Cu_3O_7$/Pb junction. Inset: Current vs voltage for a typical junction for $T<1$ K. Note the absence of leakage. (b) Voltage dependence of $G(V)/G(100\text{ mV})$ for the temperatures indicated for the junction in (a). The lowest-temperature curve has the lowest zero-bias conductance. The polarity refers to the $YBa_2Cu_3O_7$ electrode.

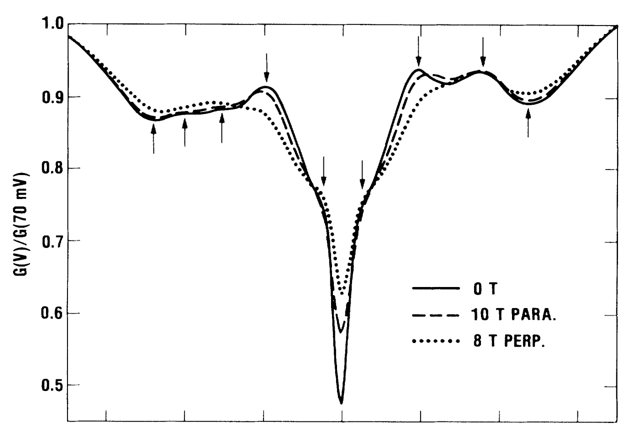

FIG. 2. $G(V)$ for $YBa_2Cu_3O_7$/Pb junction in 0 T (solid line), 10.0 T (dashed line), and 8.0 T (dotted line) magnetic fields at $T=10$ K. Arrows indicate features which are discussed in the text.

perconducting state ($T < 1$ K) to the junction zero-bias conductance with the Pb in the normal state is much less than 1% [see inset of Fig. 1(a)]. This finite zero-bias conductance could be due to several things, such as (a) the presence of states at the Fermi energy of superconducting $YBa_2Cu_3O_7$, (b) the presence of both superconducting and normal metallic phases within the junction area, or (c) a normal-metal surface on $YBa_2Cu_3O_7$ which superconducts due to the proximity effect. We believe that the reproducibility of the size of the zero-bias conductance between junctions prepared in many different ways and the observed onset of structure at the bulk T_c argue against the latter two possibilities.

Further evidence that most of the observed structure below T_c is related to the superconducting density of states of $YBa_2Cu_3O_7$ comes from the magnetic field dependence of $G(V)$. In Fig. 2, we show the conductance in magnetic fields parallel (dashed line) and perpendicular (dotted line) to the plane of the junction, respectively. The features which appear to be most strongly affected by a parallel magnetic field are the zero-bias conductance, which increases, and the peaks at ± 19 and ± 4 mV, which broaden and shrink in a manner qualitatively similar to the smearing of a BCS density-of-states peak in a parallel magnetic field. The effect of a perpendicular field on $G(V)$ is more dramatic. For this field orientation, normal-vortex-core regions are present at the surface of $YBa_2Cu_3O_7$. Quasiparticles can tunnel into these regions, reducing the size of the structure in $G(V)$ due to superconductivity.

To illustrate the variation in $G(V)$ with counterelectrode material we compare data from $YBa_2Cu_3O_7$/Au and $YBa_2Cu_3O_7$/Pb junctions in Fig. 3. While the main features are similar, the background conductance is steeper and the overall shape (e.g., the position of peaks near ± 24 mV) of $G(V)$ is more asymmetric for the $YBa_2Cu_3O_7$/Au junction.

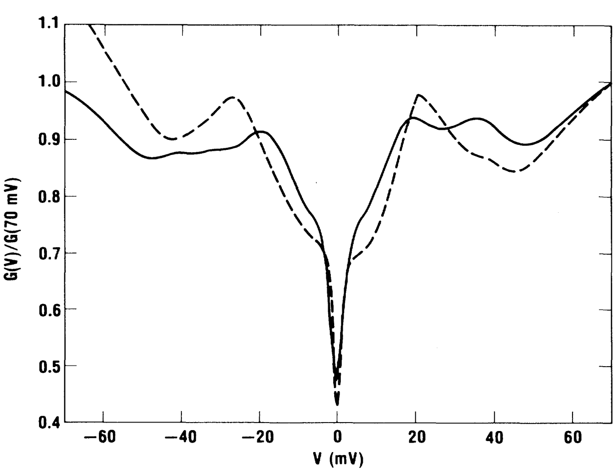

FIG. 3. $G(V)$ of a $YBa_2Cu_3O_7$/Pb junction at $T=10$ K (solid line) and $G(V)$ of a $YBa_2Cu_3O_7$/Au junction at $T=1.4$ K.

Although we do not have compelling evidence that Au produces tunnel junctions, the strong similarities in $G(V)$ between Au and Pb junctions indicate that at least a large portion of the conductance is due to quasiparticle tunneling. Differences in the tunnel barriers could account for the differences in $G(V)$. If the $YBa_2Cu_3O_7$/Au barrier were more asymmetric and lower than the $YBa_2Cu_3O_7$/Pb barrier, then it would have a more asymmetric and steeper background which could mask and distort features in the density of states.[13] In particular, because of the steeper background conductance of the Au junction, peaks in the superconducting density of states will appear at higher voltages in the Au-junction $G(V)$ (24 mV) than in the Pb-junction $G(V)$ (19 mV).

One of the most striking features of this work is the reproducibility of the results. Our past attempts to tunnel into high-T_c oxide materials have yielded a wide variety of results characterized by vague structures in the tunnel junction conductances which sometimes appeared and sometimes did not. In the present studies, we have varied junction preparation parameters rather extensively (etchants, etching time, counterelectrodes, etc.) and obtained similar results. It is this remarkable reproducibility which gives us additional confidence in the intrinsic nature of the data.

Recently there have been other tunneling studies by Fournel *et al.*[5] (single-crystal $YBa_2Cu_3O_7$/Pb) and Geerk, Xi, and Linker[6] ($YBa_2Cu_3O_7$-film/In) which show results that are rather similar to ours. Both of these groups observe structure at approximately ± 4–5 mV and a finite zero-bias conductance in the superconducting state of $YBa_2Cu_3O_7$ as we do. In addition, Fournel *et al.* and Geerk, Xi, and Linker observed features at ± 30 and ± 16 mV, respectively, which probably correspond to those which we observe in $YBa_2Cu_3O_7$/Pb junctions at ± 19 mV. We believe that differences in the position of the higher-energy feature could be due to aspects of these experiments which are not intrinsic to the properties of $YBa_2Cu_3O_7$. That is, the conductance of the junction of Fournel *et al.* showed evidence (i.e., a shift in the Pb phonon spectrum) for transport via non-single-step tunneling processes. Such processes have the effect of broadening and moving structures in the density of states to higher energies. In the case of Geerk, Xi, and Linker, the junctions showed on the order of 30% leakage. To analyze their data they have subtracted out this leakage. The positions of features in the data could be very sensitive to this process.

Our data suggest interesting possibilities for the superconducting density of states in $YBa_2Cu_3O_7$. The nature and reproducibility of the structures at 19 and 4 meV offer the possibility that there are two separate energy gaps in $YBa_2Cu_3O_7$; the first associated with the a-b plane and the second with the c axis. Indeed, the nonplanar etched surfaces provide for tunneling in both directions, as was pointed out above. If this interpretation is correct then we estimate the geometric mean Δ_m

$=(3)^{-1/2}(2\Delta_{ab}^2+\Delta_c^2)^{1/2}$ to be 15.7 meV which corresponds to a $2\Delta/k_BT_c$ ratio of approximately 4.1; a number which is closer to the weak-coupling limit of 3.5 than many other measurements. We further speculate that the minima at ± 49 meV are analogous to the phonon structure seen in strong-coupled superconductors. If this speculation is correct, then the sharp decrease in $G(V)$ at ≈ 42 meV would correspond to a peak in the phonon density of states at $42-19=23$ meV. However, the McMillan formula[14] for T_c predicts a high value for λ if one uses an average phonon energy of 23 meV and $T_c=89$ K, while the analysis of the linear resistivity suggests a small λ.[15]

The question concerning the observation of finite conductance at zero bias at low temperatures continues to perplex us. As we have discussed earlier, it is possible that this feature may not be intrinsic. However, the reproducibility of the relative size of this feature makes it difficult to imagine that is not related to the density of states of superconducting $YBa_2Cu_3O_7$. There continue to be reports of electronic states extending below the gap from other investigations.[16-18] This result, taken at face value, certainly implies that there is a continuum of states below the gap.

In summary, we have reported tunneling measurements into single crystals of $YBa_2Cu_3O_7$. The reproducibility of these results gives us confidence in them. At T_c, we see an abrupt change in the zero-bias conductance which shows that we are tunneling into the superconducting state. There are two gaplike features at 4–5 meV and at 19 meV. This structure does not have a BCS shape and we consistently see a zero-bias conductance which is $\approx 50\%$ of the conductance at 100 mV suggesting the possibility of states at the Fermi energy.

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Note added.—Takeuchi *et al.*[19] have published $G(V)$ data on a sintered-$YBa_2Cu_3O_7$/pressed-Pb junction which shows structure which is similar to that shown in Fig. 2.

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