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Influence of the oxygen content on the tunneling characteristics of $YBa_2Cu_3O_{7-\delta}$

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We have formed planar tunnel junctions between Pb films and $YBa_2Cu_3O_{7-\delta}$ single crystals with different surface oxygen stoichiometries. Oxygen losses have been induced by heating the crystals at 400 °C in vacuum for different times. Low-leakage tunnel junctions have also been obtained in the case of the most "degraded" samples. As the oxygen deficiency increases, the Y-Ba-Cu-O gaplike structure gradually broadens and shifts towards higher energies. For thermally untreated samples, tunneling spectroscopy gives information on the local T_c.

As is well known, tunneling into high-T_c superconductors is complicated by the extremely short and anisotropic coherence lengths of these materials, with the highest values in the range of a few tens of angstroms, and by the easy oxygen desorption, at least in the case of the 1:2:3 structures. Tunneling probes the electronic density of states within a length ξ of a superconductor, requiring an atomic-level perfect surface that is very difficult to obtain in these compounds. The 92-K superconducting phase, $YBa_2Cu_3O_7$ (Y-Ba-Cu-O), is a remarkably complicated material; the oxygen content is variable and, for oxygen stoichiometries less than 7, the chain oxygen atoms can assume a number of possible orderings. The superconducting transition temperature, as well as other physical properties, depend sensitively on the oxygen content and orderings.[1] It seems reasonable that the tunneling would also be sensitive to the oxygen content of the sample in the surface region where the junction is formed.

In spite of a large effort expended by a number of groups to produce reliable tunnel junctions on this material, the literature contains very few examples of reproducible tunneling data.[2] In this paper, we start from the high reproducibility of the tunneling characteristics of junctions obtained on chemically etched Y-Ba-Cu-O single crystals,[3] and we describe an approach which allows us to follow the evolution of features in tunneling data as the surface oxygen stoichiometry is altered. Unambiguous, reproducible effects are thus induced in the tunneling characteristics of quality-controlled tunnel junctions. We show that tunneling gives information about the local T_c and that Y-Ba-Cu-O single crystals with $T_c = 90$ K and oxygen-reduced surfaces can have conductance curves similar to those of samples with $T_c = 80$ K, which is not surprising since tunneling is probing superconductivity on a scale of a few coherence lengths.

The Y-Ba-Cu-O single-crystal samples 1, 2, and 3 that we report on were grown in the same batch by the flux method.[4] According to dc and ac susceptibility measurements, they had superconducting transition temperatures of 91 K. They were etched for 20 min in a 1% Br solution in methanol (etching rate ≈ 50 Å/min). At this point, in vacuum, at about 10^{-6} mbar, they underwent different treatments: Sample 1 was not processed; sample 2 was heated at 10 °C/min to 400 °C where upon the furnace was turned off; sample 3 underwent the same processing as sample 2 but it was held at 400 °C for 60 min. The furnace cooling rate was approximately 100 °C/h. Subsequently the crystals were masked by epoxy glue to define the junction geometry and were exposed to the ambient air for about 20 min. The Pb counterelectrode, 5000 Å thick, was contemporaneously evaporated on the three samples through a metallic mask. At the end of the fabrication procedure, treated and untreated samples resulted to have spent the same total time in vacuum as well as in the ambient atmosphere. The same vacuum system, equipped with a cryogenic pump, has been used both for thermal treatments and evaporations. Analysis of the residual gases made by a mass spectrometer revealed the absence of any significant contaminant. Such fabrication conditions minimize the possibility of surface contamination. Junction areas were less than 0.1×1 mm^2, and Cu wires soldered with In dots were used for electrical contacts. Four terminal measurements of the differential resistances were performed using a standard low-frequency lock-in technique.

Heat treatments in vacuum at temperatures between 400–500 °C are known to reduce the Y-Ba-Cu-O compound.[1] We have investigated the influence of such treatments on the T_c's of the samples by near zero-field microwave absorption and by ac and dc susceptibility. We have found that samples briefly heated to 400 °C behave as untreated crystals, while samples held at 400° for 1 h showed evidence for a small fraction of 60-K material although the main part of the crystals remains 90 K. These results are consistent with degradation of a near surface region, which corresponds to oxygen loss as a result of the heat treatments.

In Fig. 1 we show the conductances $G(V)$ normalized to $G(75\text{ mV})$ for junctions on samples 1, 2, and 3 at 4.2 K. Tunneling characteristics of samples like sample 1, including their behavior in magnetic fields and at very low temperatures, have been discussed in Refs. 3. The main features on the conductance curves are a finite zero-bias conductance, gaplike structures at ± 19 mV, and peaks at ± 36 mV. We observe that for sample 1, the structures at ± 36 mV represent a variation of about 3.5% on the

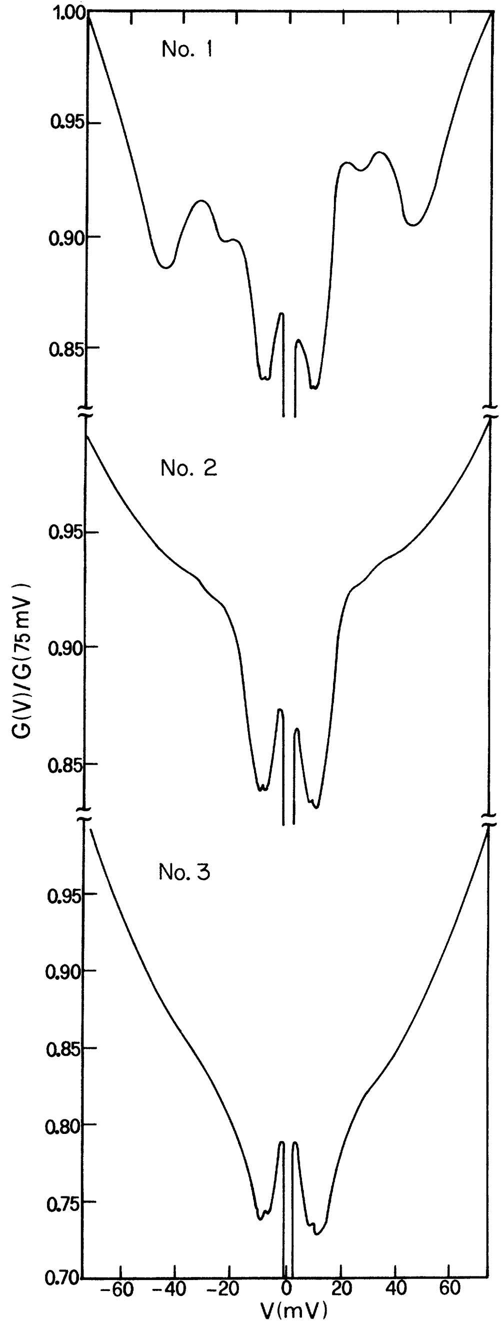

FIG. 1. Voltage dependence of $G(V)/G(75\text{ mV})$, at $T=4.2$ K, for Y-Ba-Cu-O/Pb junctions made on Y-Ba-Cu-O single crystals that, after the growth process, underwent different thermal treatments. Sample 1: not processed; sample 2: stayed a few minutes at 400 °C in vacuum; sample 3: same process as sample 2 but stayed at 400 °C for 60 min.

dI/dV vs V curve. We have found in about 10% of the more than 100 measured samples, that this feature, on the negative bias, splits into two smaller peaks at -31 and -41 mV (signs refer to the Y-Ba-Cu-O polarity). Heating treatments have been made on more than 30 samples. A reduction of the amplitude of the ±36-mV peaks can be observed on the conductance curve of the junction made on sample 2 that show the same features as before but smeared out and a little shifted towards higher energies. These variations are consistent with what we have found on single crystals grown in different batches showing transition temperatures $89\text{ K} \leq T_c \leq 91$ K and on epitaxial films with $T_c = 91$ K,[5] and can indicate small variations of the superficial oxygen stoichiometries. The effect of the thermal treatment becomes more dramatic on the curve relative to sample 3. For this "degraded" junction, all details of the Y-Ba-Cu-O structures were lost; the only relevant feature is the change in the conductance slope at about ±25 mV.

We have chosen to show the data in Fig. 1 at 4.2 K, since the Pb gap and phonon structure can be observed at low voltages on the three curves. These features were at the correct energies indicating a tunneling process through a high-quality tunnel barrier. The nature of this barrier is unknown. However, since the resistances, at $V=75$ mV, of the junctions 1, 2, and 3 at room temperature were 510, 200, and 500 Ω, respectively, and small differences in the junction areas can account for these different values, it seems that the heating process does not have a dramatic effect on the shape of the tunnel barrier.

As a further test of the quality of the junctions, in Figs. 2(a) and 2(b) we show the normalized zero-bias conductance $G(0)/G(100\text{ mV})$ as a function of temperature for samples 1 and 3 and, in the insets, their I-V curves at low voltages. The jump in the curve in Fig. 2(a) relative to sample 1 is due to the contribution of the single-crystal resistance going to zero at $T=T_c$, and the different behavior above and below T_c is similar, though less pronounced, to what one would expect due to an opening of an energy gap in a metal-insulator-BCS-superconductor junction. The curve in 2(b) for sample 3 shows no discontinuity.

These data demonstrate that local T_c's, measured by tunneling spectroscopy, can be different from the bulk ones—a result already known, but worth emphasizing for high-T_c superconductors. We observe that in evaluating the ratio $2\Delta/kT_c$, critical temperature values measured from curves like those of Fig. 2 for sample 1 should be used. If for sample 1 we assume that the peak at ±19 mV represents the energy gap in Y-Ba-Cu-O, we can estimate a ratio $2\Delta/kT_c$ of about 5.0.

The insets of Figs. 2(a) and 2(b) show the I-V characteristics of junctions 1 and 3 at low voltages, at 4.2 K, together with the theoretical fittings obtained from the expression for the current flowing through an S-N junction at finite temperature. We have considered the Y-Ba-Cu-O as normal since in the studied energy range it shows a finite conductance. The satisfactory agreement between experiments and theory indicates negligible leakage currents and the barriers are thus proven to be continuous and pin hole free.

As a corollary to the previous results in Fig. 3 we show the normalized conductances $G(V)/G(75\text{ mV})$ at $T=10$ K of junction 3, the curve in 3(a), and of an Y-Ba-Cu-O/Pb junction representative of the behaviors found on single crystals that underwent a different oxygen annealing following growth, the curve in 3(b). Due to a lower

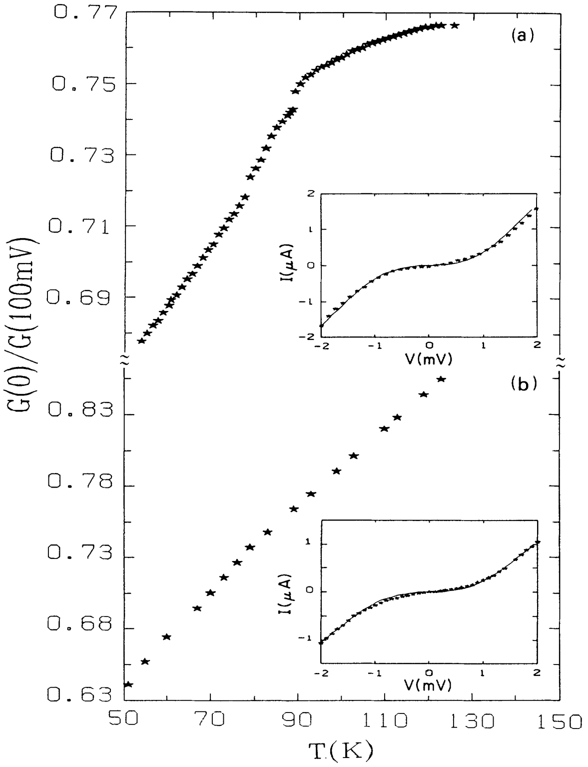

FIG. 2. Temperature dependence of $G(0)/G(100\ \mathrm{mV})$ for Y-Ba-Cu-O/Pb junctions made on (a) sample 1 and (b) sample 3. Insets show I-V characteristics for the same junctions at low voltages at 4.2 K; the solid lines are the theoretical fittings for the current flowing through an S-N junction at the same temperature.

oxygen content, these latter samples had superconducting transition temperatures of 80 K. The fabrication procedure used for the 80-K junctions was the same as for sample 1. The striking similarity of these data is indicative of a similar oxygen content at the surfaces of single crystals with different "bulk" T_c's. It is interesting to note that the structure at ±4–5 mV, already found in tunneling characteristics of junctions on stoichiometric Y-Ba-Cu-O,[3,5-7] are present on both curves of Fig. 3. This structure, sometimes attributed to gap anisotropy or to proximity effects, is sensitive to a magnetic field and disappears at about 25 K.

Junctions realized on chemically etched Y-Ba-Cu-O single crystals with resistive $T_c = 60$ K, have also been measured. As is known,[1] the 60-K phase corresponds to an oxygen content $6.5 < \delta < 6.7$. These junctions have steeper background conductances and sometimes lose the details of the Pb structures, so we cannot always be confident of a clear tunneling process; but no matter how degraded the crystal or the crystal surface, the conductance characteristics show an enhanced broadening of the Y-Ba-Cu-O structures that often just appear as a relevant change of slope at about 30 mV.

The tests made on oxygen-deficient single crystals with $T_c = 80$ and 60 K further confirm that possible surface contamination is playing a minor role in the heat-treated samples.

Tunneling characteristics such as those given in Fig. 3 lacking details of the Y-Ba-Cu-O structure and only showing a change of slope are frequently found in literature.[8] They usually come from samples with $T_c < 89$ K, in which more reduced surfaces are likely. Since oxygen deficiency in the Y-Ba-Cu-O compound results in semiconducting and not in metallic material, we cannot think of a proximity effect in the usual sense, even if we cannot exclude that a position-dependent order parameter, decreasing at the interface, can play a significant role in these experiments. Particularly puzzling for us is that junction 3 shows no evidence for a local T_c [Fig. 3(b)] and we do observe structures at ±5 and ±25 mV on the conductance curves.

On the basis of the present results, small differences in

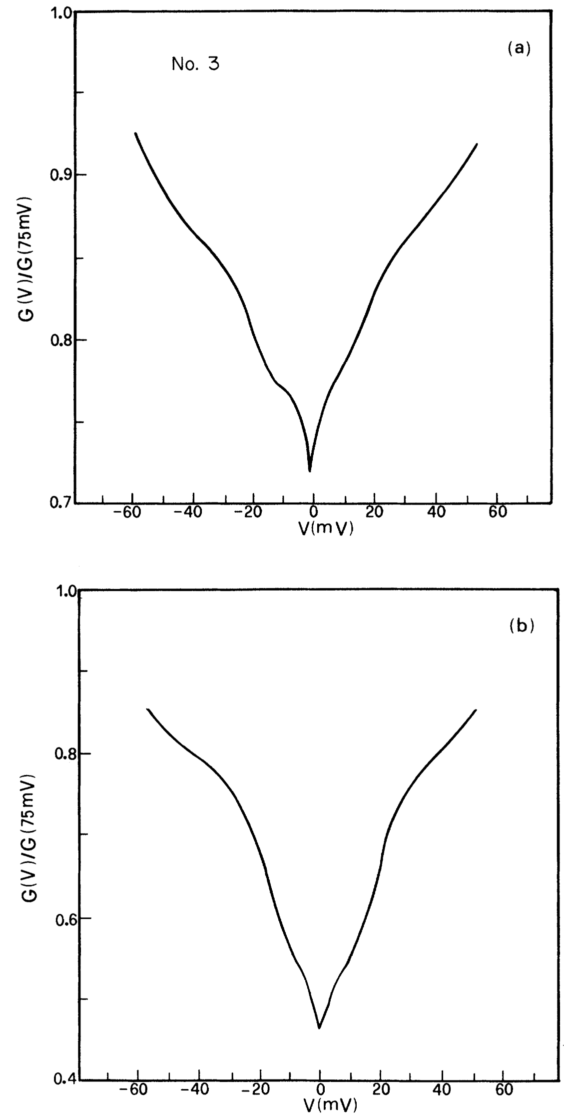

FIG. 3. $G(V)/G(75\ \mathrm{mV})$ vs voltage, at $T = 10$ K, for Y-Ba-Cu-O/Pb junctions made on (a) Y-Ba-Cu-O sample 3 and (b) Y-Ba-Cu-O single crystal with $T_c = 80$ K.

the oxygen content can account for small differences in the tunneling data obtained on Y-Ba-Cu-O films,[5,9] single crystals[3,7] and sintered pellets.[6,10] Furthermore, neither break nor point contact junctions avoid the oxygen problem. In the first case, breaks most likely occur along the grain boundaries of the samples exposing the poorest quality material. The second case, where the tip is driven directly into the samples, should, in principle, be less sensitive to this problem; but, very rarely are reproducible tunnel characteristics obtained by this method and the fact that the data vary somewhat from point to point of the same sample could also be ascribed to oxygen inhomogeneties.

In conclusion, we demonstrate that tunneling spectroscopy can probe the oxygen content at the Y-Ba-Cu-O surface, and we mainly attribute the spread of the experimental values of the gaplike structures found in the literature to different superficial oxygen stoichiometries. It is our opinion that only rigorous controls on the quality of the junctions can solve the remaining ambiguities in the behavior of this compound.

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