Tunneling Density of States in the Lead-Bismuth-Oxide Superconductors

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We have performed an extensive set of tunneling measurements on the high-T_c perovskites $BaPbO_3$, $BaPb_{0.75}Sb_{0.25}O_3$, $BaPb_{0.75}Bi_{0.25}O_3$, and $Ba_{0.7}K_{0.3}BiO_3$. In these materials, the superconducting transition temperature varies from less than 1 to 30 K. Tunneling data show a linear background conductance similar to that observed in the cuprates and we have strong experimental evidence that this linear conductance results from intrinsic properties of the density of states in these materials. We also observe a remarkable correlation between T_c and the slope of this linear background conductance.

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The mechanism responsible for superconductivity and the interactions leading to the anomalous density-of-state effects in the high-T_c oxide materials continues to be poorly understood and extensively studied. Electron tunneling has traditionally been an incisive probe of superconductors and the technique has been exploited for the oxides by several investigators with various degrees of success [1-6]. An early observation revealed that the "normal-state" background conductance was unlike conventional materials in that this conductance scaled linearly with the bias voltage. There have been several theoretical attempts to understand this linear behavior in terms of either elementary excitations in the materials [7,8] or inelastic-tunneling processes [9]. However, there has been no experimental study of the systematics of this peculiar behavior over various materials.

In this paper, we report the results of our extensive studies of this effect in the class of compounds referred to as the bismuth oxides [10,11]. The superconducting transition temperature T_c ranges from below 1 K (if superconducting at all) in $BaPbO_3$ to 30 K in $Ba_{0.7}K_{0.3}BiO_3$. We have prepared tunnel junctions in films or single crystals of $BaPbO_3$ ($T_c < 1$ K), $BaPb_{0.75}Sb_{0.25}O_3$ ($T_c = 3.5$ K), $BaPb_{0.75}Bi_{0.25}O_3$ ($T_c = 11-12$ K), and $Ba_{0.7}K_{0.3}BiO_3$ ($T_c = 24-30$ K) (BKBO). The range of T_c's quoted reflects variations in stoichiometry we observe from sample to sample. There were no systematic differences in the data obtained from thin films compared to the single crystals.

We chose this class of materials for systematic study for three reasons.

(1) We are confident that extremely high-quality tunnel junctions can be fabricated. Tunneling studies of the superconducting state show a BCS energy gap with very low leakage current, assuring us that tunneling is the dominant conduction mechanism [12,13].

(2) The large range of T_c's in these materials allows us to search for possible correlations between the anomalous normal-state density of states and the superconducting properties.

(3) These materials are structurally and electronically less complex than the cuprates. Unlike the cuprates, Bi-Pb oxides are cubic rather than two dimensional and have no anisotropy. It is also generally agreed that there are no spin fluctuations leading to magnetic moments in these compounds. This is also unlike the cuprates where antiferromagnetic ordering is observed.

The tunnel junctions studied are of the type (high-T_c oxide)/barrier/(non-high-T_c metal). The counterelectrodes used were Au, Pb, In, and Ag. Although the junction resistances depended on the counterelectrode materials used for a given preparation procedure, the results described here are independent of the counterelectrode type or preparation procedure. The junctions were prepared by a variety of techniques ranging from cleaving of the crystal followed by counterelectrode evaporation to ion-mill formation of a damage layer on high-T_c films followed by evaporation. The latter technique was most reproducible and by changing the ion-milling parameters, such as beam voltage and current and milling time, we were able to change the junction resistance/area rather controllably [14]. We used the observations of a well-characterized superconducting energy gap (of either the high-T_c oxide or the counterelectrode) as the criterion for junction quality. Except for the compound $BaPb_{0.75}Sb_{0.25}O_3$ the results reported here represent at least twenty high-quality junctions for each high-T_c material.

Figure 1 shows a typical background conductance versus bias voltage for a BKBO-Au tunnel junction at 4.2 K. The inset is the current-voltage characteristic at 4.2 K of a similar junction showing the low leakage and high quality of the junction. The observed linear tunnel conductance is similar to that seen in the cuprates [1]. It has been suggested that this effect is caused by the reduced dimensionality of the cuprates [7] or possibly inelastic scattering from the magnetic moments in the cuprates during the tunneling process [9]. However, since the bismuth oxides are three dimensional and exhibit no magnetic moments, we think it is unlikely that the above explanations correctly explain this observed behavior. To invoke inelastic-tunneling processes, one would have to invoke charge-density waves rather than spin-density

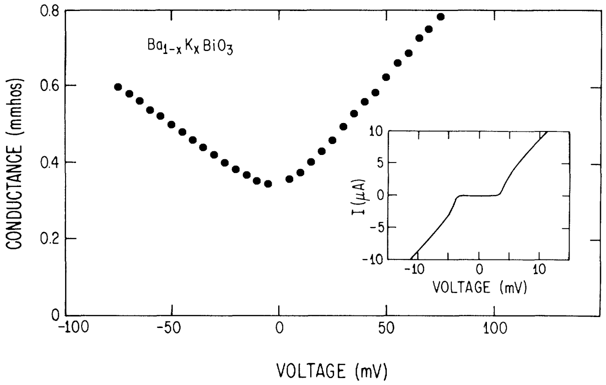

FIG. 1. Background conductance (normal state) for a BKBO-Au tunnel junction. Inset: An *I-V* curve of a similar junction in the gap region. Both measurements are at 4.2 K.

waves and it seems unlikely that these two separate processes would result in identical behavior.

To see whether this effect is an intrinsic measure of the density of states and not due to the barrier, we have formed tunnel junctions of various resistances in this material by adjusting the milling parameters. (The change in the junction areas was minimal.) Figure 2 shows the background slope versus zero-bias conductance for a variety of BKBO-Au junctions with different resistances. The line through the data is a least-squares fit with a slope of 1.04. Insofar as this is linear, we believe it implies that the background conductance is intrinsic in the density of states and not dependent on barrier effects.

As indicated in Fig. 2, these investigations have involved a rather large number of samples. The transport properties of the samples we have looked at [$\rho(T)$, for example] show a wide variation but this background-conductance effect seems, by comparison, remarkably reproducible. This is understood if we believe that these tunneling measurements are revealing an intrinsic spectroscopic property, while transport measurements are terribly sensitive to grain boundaries, etc.

The central result of this study is shown in Fig. 3. We show here a composite plot of the conductance versus bias voltage, normalized at zero bias, for the four compounds studied at 1.2 K. The data sets are typical of the respective compounds in the magnitude of the observed linear conductance and reflect many junctions. It should be noted that junction-to-junction variations within a particular compound are much smaller than the differences observed between compounds. We believe this is a meaningful way to represent the data since the plot in Fig. 2 leads us to believe that this effect is intrinsic.

There are two aspects we would like to emphasize. We find it striking that the magnitude of the slope of this linear background conductance scales with the superconducting transition temperature T_c. This is illustrated in Fig. 4 where we show a plot of the slope of the background conductance for positive bias (dG/dV) as a function of T_c for the different materials. The horizontal error bars represent the range of T_c's for a particular compound due to stoichiometry variations. The correlation in this figure is striking and suggests to us that this phenomenon is intrinsically linked to the superconducting properties. We propose that these effects are the result of strong renormalization in the carriers due to many-body effects. Any theory which is capable of describing the superconductivity in these unique compounds must also be able to describe these linear-density-of-state effects. We also point out that similar behavior observed in the cu-

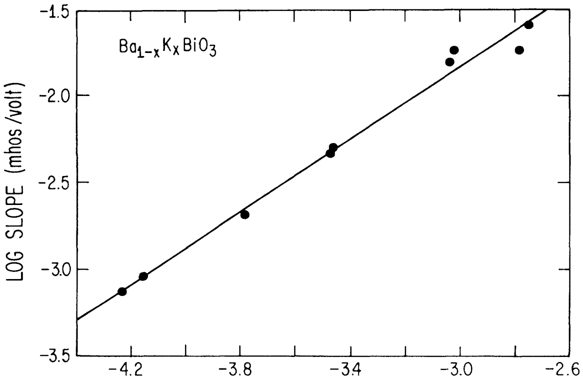

FIG. 2. The dependence of the slope of the linear background conductance on the zero-bias conductance for various BKBO junctions. The line through the data is a least-squares fit with a slope of 1.04. This implies that the background conductance observed in these tunnel junctions is not a barrier effect and is intrinsic in the density of states.

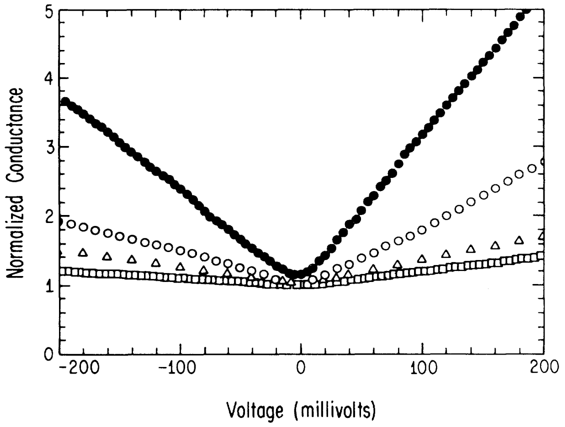

FIG. 3. Normalized conductance for tunnel junctions on BKBO (solid circles), $BaPb_{0.75}Bi_{0.25}O_3$ (open circles), $BaPb_{0.75}Sb_{0.25}O_3$ (triangles), and $BaPbO_3$ (squares) at 1.2 K. Note that the slope of the linear conductance scales with the superconducting transition temperature T_c and that there is an asymmetry of approximately a factor of 2 about zero bias for all four materials.

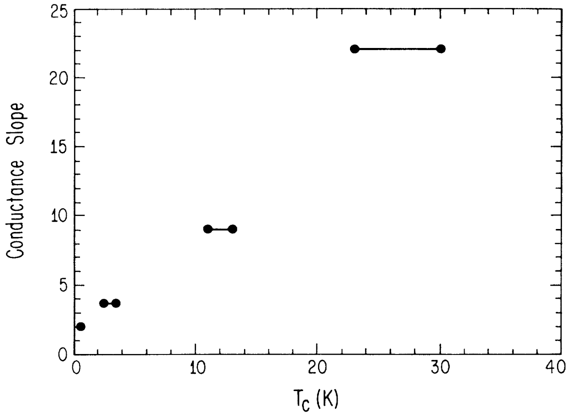

FIG. 4. Magnitude of the slope of the conductance positive bias vs the superconducting transition temperature T_c. Error bars reflect variations of T_c in a particular compound due to stoichiometry differences.

prates may have the same origin. We suggest that the slope of this linear background is a measure of the coupling strength of the mechanism responsible for superconductivity.

A second aspect of the data is the asymmetry between positive and negative bias seen in Fig. 3. (Positive bias corresponds to the oxide being positive.) This asymmetry is similar in all the compounds and is about a factor of 2. We do not have an explanation for this asymmetry but note that it is reversed about zero bias in studies of the cuprates, with the positive side being less steep. We speculate that this difference may be due to the difference in the sign of the carriers in the two materials. We recognize the possibility of a more straightforward explanation based on barrier-shape effects. We cannot exclude this possibility insofar as the asymmetry is concerned.

Besides theories based on two dimensionality and magnetic moments, it has been proposed that these materials be considered as "marginal Fermi liquids" [8] with very strong correlation effects. It may well be that one can understand the systematics reported here and the remarkable correlation with T_c in the context of this picture and we hope that these data stimulate quantitative theoretical investigation. We should point out that these effects are not due to renormalization effects as a result of static disorder [15]. These disorder effects have been extensively studied by tunneling experiments and in three dimensions [16] the corrections to the density of states depend on $E^{1/2}$. The strength of these corrections has been shown theoretically and experimentally to scale with the disorder [15,16]. These present results show neither this $E^{1/2}$ dependence nor the dependence on disorder. In fact, for most of the samples in this study the disorder is sufficiently small that we would expect to see no influence from these effects.

In summary, we have performed extensive tunneling measurements on the Pb-Bi oxide superconductors. The tunneling density of states shows an intrinsic linear behavior much like that observed in the cuprates. The strength of this linear behavior scales with the transition temperature of the material. We speculate that this linear density of states is a fingerprint of the mechanism responsible for superconductivity in these materials.

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