Electron tunneling in the high-T_c bismuthate superconductors

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We have performed extensive tunneling measurements on some high-T_c superconducting oxides of bismuth: $BaPb_{1-x}Bi_xO_3$, $Ba_{1-x}Rb_xBiO_3$, and $Ba_{1-x}K_xBiO_3$. The results on high-quality single crystals and epitaxial films indicate that these materials are weak-coupled superconductors with $2\Delta/kT_c=3.5\pm0.3$. The observed quasiparticle excitation spectrum agrees with the BCS model. We also do not observe structure indicating electron-phonon coupling sufficiently strong to account for the T_c of these materials.

Many of the basic questions surrounding superconductivity in the high-T_c oxide superconductors remain unanswered. Of the more fundamental issues still to be resolved, two important ones are the existence and nature of the energy gap and the mechanism responsible for the binding of the pairs. The two classes of materials which are considered as "high-T_c oxides" are the layered copper oxides (cuprates) and the three-dimensional bismuthates.[1,2] We have performed extensive tunneling measurements on both classes of oxides and in this paper we report our results on the bismuth oxides. Measurements have been performed on $BaPb_{1-x}Bi_xO_3$ (Ba-Pb-Bi-O) (the original high-T_c bismuthate), and the higher-T_c $Ba_{1-x}Rb_xBiO_3$ (Ba-Rb-Bi-O) and $Ba_{1-x}K_xBiO_3$ (Ba-K-Bi-O). The results of these studies to date show clearly that these materials have a "traditional" BCS energy gap with a value $2\Delta/kT_c\sim3.5\pm0.3$. In this regard, substantial differences with the cuprates currently exist where simple gaps are not observed.[3] A remarkable similarity in the normal state tunneling density of states does exist between the two classes of materials, however. Both classes show a linear tunneling conductance at voltages well above the energy gap.

The tunneling measurements were performed on single crystals (Ba-Pb-Bi-O, Ba-K-Bi-O), sintered powders (Ba-Pb-Bi-O, Ba-Rb-Bi-O), and thin films (Ba-K-Bi-O, Ba-Rb-Bi-O). The most extensive results are on Ba-Pb-Bi-O and Ba-K-Bi-O. The latter work is the most recent and will be emphasized. The single crystals of Ba-K-Bi-O were grown by a modification of the electrochemical method of Norton which will be published separately.[4] The crystals studied had smooth faceted faces up to 6 mm^2 in area. The $Ba_{1-x}Rb_xBiO_3$ films are grown on MgO substrates by molecular beam epitaxy.[5] Growth was initiated at higher substrate temperatures to obtain (100)-oriented films on (100) MgO.[6]

Tunnel junctions were formed using a variety of techniques, all based on the formation of a "natural" barrier at the surface. In the case of the single crystals, a freshly cleaved surface most often gave the best results. Either a thin film evaporated onto this fresh surface (In, Au, Pb, and Sn have been used) or simply a pressed metal contact (In) has been employed. In fact, we have successfully fabricated Ba-K-Bi-O/Ba-K-Bi-O symmetric tunnel junctions using film-crystal contacts or crystal-crystal contacts.[7] In the thin film case (Ba-K-Bi-O), the most successful fabrication technique we have found is a surface degradation with a Kaufman-type ion miller, and a subsequent metal evaporation for the counter-electrode (most often Au). These techniques have resulted in extremely high-quality tunnel junctions with leakage conductances at zero bias in the energy gap often well below 1% of the above gap conductances. Furthermore, we have been able to control the junction resistance over several orders of magnitude. With junctions of this quality we can quantitatively compare both the magnitude of the energy gap and the shape of the density of states to BCS predictions. As a practical matter most of these structures are thin film and have substantially lower current densities than point contact, break junctions, or STM junctions. This results in more stable junctions with less spurious effects such as local heating.

The standard expression for a normal-metal–superconductor tunnel junction I-V characteristics is given by

$$I(V)=CN(0)\int_{-\infty}^{\infty}N(E)[f(E,T)-f(E+V,T)]dE\ , \quad (1)$$

where C is a constant containing all the tunneling probabilities (assumed energy independent on this scale), $N(0)$ is the normal metal density of states measured with respect to the Fermi energy (also assumed constant), f is the usual Fermi function at temperature T, and $N(E)$ is the superconducting density of states. In the case of a BCS superconductor

$$N(E)=\frac{E}{\sqrt{E^2-\Delta^2}}\quad (E>\Delta)\ . \quad (2)$$

At $T=0$, it is clear from Eq. (1) that a measure of dI/dV directly yields $N(E)$. At finite temperature the situation is a little more complex as the Fermi functions broaden the sharp structure at the gap edge. Nevertheless, it is a straightforward procedure to test whether these junctions are BCS-like and extract a value of the energy gap Δ.

This is accomplished by fitting the tunnel conductance with the energy gap Δ being the only adjustable parameter. The constants are divided out by normalizing the superconducting conductance data to that of the normal state. This results in any energy dependence to C or $N(0)$ to be accounted for in first order.

In Fig. 1 we show previously published results for Ba-Pb-Bi-O.[8] In the inset we show the I-V characteristics for a Ba-Pb-Bi-O/In tunnel junction in which the In has been driven into the normal state by a magnetic field (0.1 T). The I-V curves show the excellent quality of the junction. The results of the BCS fit using a gap value of $\Delta = 1.65$ meV are shown in Fig. 1 and it can be seen that the agreement is excellent. A direct measurement of the T_c of this same crystal by measuring the temperature at which there is a discontinuity in the tunnel conductance yields $T_c = 11.0$ K and consequently, a value $2\Delta/kT_c = 3.5$, the BCS weak-coupling value.

Ba-K-Bi-O has been shown to be superconducting up to 30 K. We have been routinely successful in fabricating tunnel junctions on epitaxial thin films and the results for a typical Ba-K-Bi-O/Au junction are shown in Fig. 2. Here we have used an additional parameter Γ which injects a smearing into the density of states $N(E)$ by replacing E by $E'+i\Gamma$. This smearing could be due to lifetime effects, stoichiometry variations, noise smearing, etc.; in any case it is small (0.21 meV) relative to the energy gap (3.2 meV). In fact, the data are taken using an ac. modulation which was approximately half (0.1 meV) this broadening factor. Although the fit is better with this broadening term, the comparison is still quite good without its use. A BCS description of the quasiparticle excitation spectrum [Eq. (2)] is a good representation and nothing "anomalous" appears in the data. A transport measurement of T_c for this film shows a rather broad transition (consistent with a finite value of Γ) with a 10% to 90% transition from 20→23 K. This results in a ratio

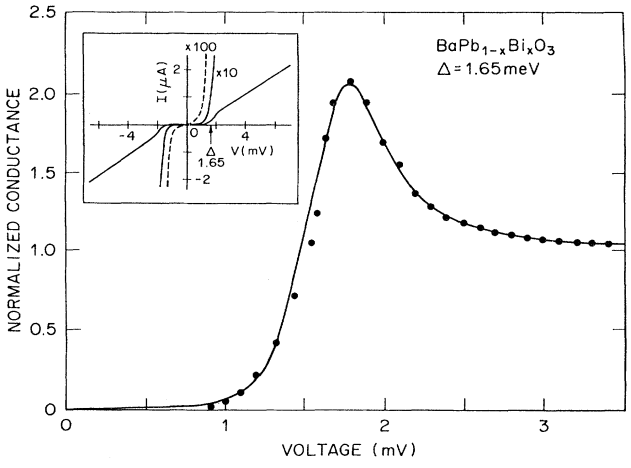

FIG. 1. Conductance dI/dV (circles) and a BCS fit (solid line) from Eq. (1) of a Ba-Pb-Bi-O/In tunnel junction at $T = 1.2$ K. The In is in the normal state and the energy gap Δ extracted from such a fit is $\Delta = 1.65$ meV. The insert shows an I-V curve for a similar junction.

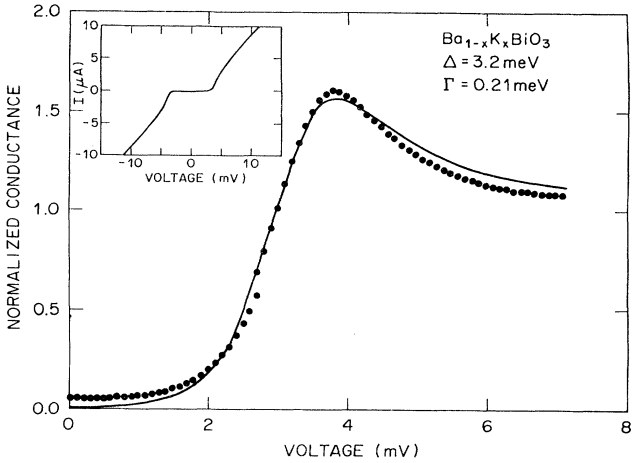

FIG. 2. Conductance dI/dV (circles) and a BCS fit (solid line) from Eq. (1) of a thin film Ba-K-Bi-O/Au tunnel junction at $T = 1.2$ K. An additional parameter Γ is used to accomplish this fit and the fitted values are $\Delta = 3.1$ meV and $\Gamma = 0.21$ meV. The inset shows an I-V curve for a similar junction.

of $2\Delta/kT_c = 3.5 \pm 0.3$, similar to the weak-coupling value extracted for Ba-Pb-Bi-O.

In the case of single crystals, the anodic growth method produces specimens ranging from sharp onsets at 30.5 K to ones containing phases with transitions down to 15 K. The majority of samples we have examined are in the range $T_c = 18$–25 K. A representative tunneling curve for a single crystal of Ba-K-Bi-O is shown in Fig. 3 along with a fit to the BCS expression. Susceptibility measurements on single crystals show a sharp transition and consistent with that observation, we have not needed a smearing parameter Γ to obtain a fit. In this case, again, we obtain a very good fit to the simple BCS expression [Eq. (1)] for the tunneling conductance. We have also observed a range of T_c's both in the case of thin films

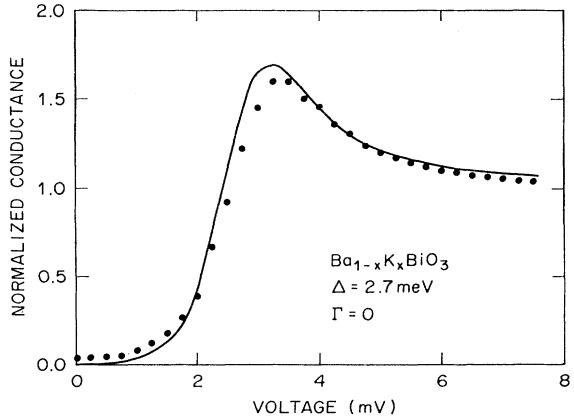

FIG. 3. Conductance dI/dV (circles) and a BCS fit (solid line) from Eq. (1) for a single crystal Ba-K-Bi-O/Au tunnel junction at $T = 1.2$ K. No additional parameter Γ was needed for this fit.

and single crystals which depends on stoichiometry of the material. (There is a solubility range of potassium in this system which allows this variation.) It appears, from the limited data that we have, that Δ scales with T_c continuously, and that the weak-coupling limit is independent of the stoichiometry of the material.

Since these results are highly reproducible[9,10] in both thin films and single crystals, we have confidence that for this class of high-T_c oxide superconductors, the excitation spectrum is of the traditional BCS form given by Eq. (2). This firm result is unlike the case of the copper oxides where tunneling spectroscopy has consistently shown substantial deviation from this form,[3] thus leaving ambiguity and controversy as to what is the value of the energy gap, or if needed a true "gap" exists in the cuprates.[11]

Tunneling spectroscopy in conventional superconductors has been very successful in quantitatively identifying the electron-phonon interaction as the coupling mechanism, and the technique has extracted the electron-phonon coupling function $\alpha^2(E)F(E)$ where $F(E)$ is the phonon density of states and $\alpha^2(E)$ is the strength of the electron-phonon coupling. The parameter which most simply characterizes the strength of this coupling is an integral over this function and is given by

$$\lambda=2\int_0^\infty \frac{\alpha^2(E)F(E)}{E}dE \ . \tag{3}$$

There have been several attempts to extract this function from tunneling data to address the issue of the coupling mechanism. In the case of Ba-Pb-Bi-O, we have seen clear evidence for substantial electron-phonon coupling at low energies and, using established techniques, have extracted a resultant $\alpha^2(E)F(E)$.[11] This function has its weight in the energy region representative of acoustic phonons. The resultant $\lambda=1$ in this spectral range is *not* adequate to account for a transition temperature as high as 11 K. We can, at the moment, only speculate on reasons for this inadequacy. A plausible explanation is that there is additional coupling to optical modes which would account for the necessary strength that is lacking. A model calculation of coupling to such a mode has been performed by solving the Eliashberg gap equations with a Lorentzian oscillator in the 25–40-meV range where one would expect optic modes. Parametrizing the strength of the coupling to account for the superconductivity indicates that the expected deviations from BCS theory in the tunneling conductance could easily be masked by the level of noise we typically see in Ba-Pb-Bi-O tunnel junctions. It is our experience that these tunnel junctions have a substantially higher level of noise than traditional materials for reasons which we will discuss shortly. Nevertheless, in the case of Ba-Pb-Bi-O, the conductance deviations expected in the regime of optical phonons are weak for an 11-K superconductor, approximately on the order of 1%. We cannot exclude the possibility that the deviations exist, and it may be *possible* that conventional electron-phonon interaction can account for all of the superconductivity in Ba-Pb-Bi-O.

We are led to ask the same question of the higher-T_c material Ba-K-Bi-O. In this case, the same model solutions of the Eliashberg gap equations predict substantially larger deviations in the tunneling conductance for electron–optical-phonon coupling. For example, for a Lorentzian optic phonon at 40 meV, a deviation in the tunneling conductance of 5% is needed to account for a T_c of $\sim$26 K. In Fig. 4 we show the results of such a calculation where we have modeled $\alpha^2(E)F(E)$ as a Lorentzian centered at 40 meV. To account for a $T_c\sim26$ K we require a $\lambda=0.9$ and the resultant energy gap $\Delta=3.9$ meV, for a Coulomb repulsion $\mu^*=0.11$. These reasonable parameters lead to $2\Delta/kT_c=3.5$, which is observed. Motivated by this calculation, we have performed extensive measurements on thin films and single crystals of Ba-K-Bi-O over this voltage range in an attempt to identify structures of the type illustrated here. We consistently observe structure similar in shape to that observed in Ba-Pb-B-O at low energies (<10 meV) which we identify as acoustic phonon coupling. While there is substantial structure in the tunneling conductance curves over the energy range expected for optic phonons, we find that this structure cannot confidently be assigned as being due to electron-phonon coupling. The uncertainty stems from the following observations.

(1) The structures are *not* reproducible from junction to junction. While we consistently see structure in this region, the details are vastly different for different tunnel junctions.

(2) The structure is *not* symmetric about zero voltage. Since these materials have asymmetric conductance above zero bias, it is straightforward to check whether the structure is symmetric in current or voltage. Upon investigation, we have concluded that the structure we see is symmetric with the bias current. This leads us to suspect that the structure is due to spurious effects such as microshort paths changing in the film or flux line motion induced by the applied current. It is also possible that the fluctuations are intrinsic, either in the barrier or the material.

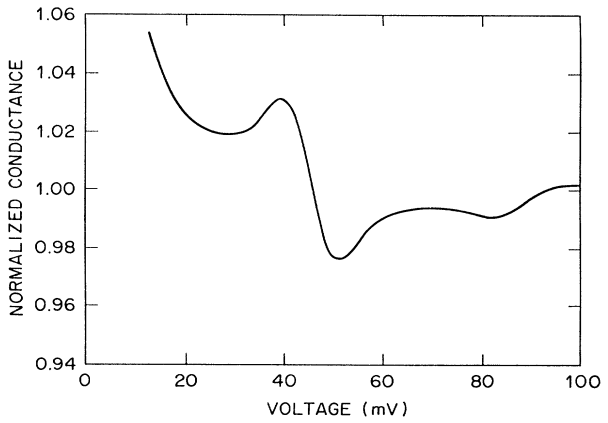

FIG. 4. Results of a model calculation for the conductance of a Ba-K-Bi-O tunnel junction with Lorentzian $\alpha^2(E)F(E)$ at 40 meV. The strength of the oscillator coupling was chosen to be enough to account for the superconductivity in this material ($T_c=26$ K).

(3) The structure exists at high bias voltages, well beyond the optical-phonon energy range. Furthermore, the amplitude of the structure also increases with bias, leading us to conclude that the effect is not due to optical phonons. We continue to pursue these issues, but at the moment we are not able either to assign a value to the electron-phonon coupling constant λ, or to exclude it as the coupling mechanism.

For these reasons, based on our extensive study of many high-quality single crystals and epitaxial films, we do not yet feel confident of the conclusions of other investigators[9] that these materials are electron-phonon superconductors. Extraction of an $\alpha^2(E)F(E)$ from the data awaits solution of these problems.

One of the remarkable similarities between the tunneling results of the bismuth oxides and the copper oxides is the approximate linear background at higher voltages. This linear conductance is of the form $dI/dV=\sigma_0+\alpha|V|$ and has previously noted in the cuprates (most notably in Y-Ba-Cu-O but also in Bi-Sr-Ca-Cu-O and Ta-Ba-Ca-Cu-O) and in Ba-Pb-Bi-O. We believe this linear conductance to be an intrinsic measure of the density of states in these materials. We also believe that the slope of this conductance is related to the superconducting transition temperature of the bismuthates.[12]

In summary, extensive measurements of the bismuth oxide high-T_c superconductors have been performed. On both $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$ we determine that a traditional BCS energy gap is the proper description of the quasiparticle excitation spectrum. In addition, a determination of the value of the energy gap indicates that these superconductors are in the weak-coupling limit (i.e., $2\Delta/kT_c=3.5$). Although we see indications of acoustic electron-phonon coupling, we have not yet observed reproducible structure which we can determine as due to optic phonon-electron coupling. Electron-phonon coupling may be responsible for the observed transition temperature in this system, but the issue remains to be experimentally proven.

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