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Quasiparticle tunneling in Bi-Sr-Ca-Cu-O thin films

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Tunnel junctions were formed by depositing a thin layer of Al_2O_3(20 Å) and Al counter electrodes onto sputtered and annealed Bi-Sr-Ca-Cu-O films. Differential conductance spectra displayed low conductivity at low bias, and two pairs of peaks, symmetric with respect to zero bias, which correlate in energy and relative magnitude with the two superconducting Bi-Sr-Ca-Cu-O phases present in the film (110 and 85 K). The measured values of the peak positions and the reduced gap parameter are $\Delta_1 = 18$–21 meV (85-K phase), $\Delta_2 = 25$–28 meV (110-K phase), $2\Delta/k_BT_c = 5.5 \pm 0.6$ for both phases. The shape of the conductance curves at higher bias is parabolic. This effect can be explained by the presence of a composite barrier. Such a barrier is likely to be the result of insulating or semiconducting grain surfaces in addition to the artificial barrier.

INTRODUCTION

Tunnel junctions made on conventional superconductors[1] have allowed measurements of the energy gap,[2] the quasiparticle density of states,[2] the phonon density of states,[3] and many other important physical parameters such as spin-orbit-scattering rates[4] and Fermi liquid parameters.[5] It is expected that tunneling experiments on high-T_c superconductors similarly will give information about the mechanisms leading to superconductivity in these compounds.

Significant effort has been made already by many groups to produce tunnel junctions based on high-T_c materials. Very few results are available on Bi-Sr-Ca-Cu-O so far, and there is still an uncertainty regarding the value of the superconducting energy gap 2Δ, and the value of $2\Delta/k_BT_c$. Ikuta *et al.*[6] find $2\Delta = 60$ meV with tunnel junctions made by depositing a silicon barrier and a silver counter electrode on bulk ceramic. By the point-contact technique on bulk and thin-film materials, Ekino and Akimitsu[7] find $\Delta_\perp = 25$–27 meV and $\Delta_\parallel = 40$–44 meV for the 110-K phase material and $\Delta_\perp = 19$–20 meV, and $\Delta_\parallel = 34$–35 meV for the 85-K phase material where perpendicular and parallel refer to the angle between the tunneling direction and the CuO planes. Shiping *et al.*[8] interpret their data using classical strong-coupling theory with a complex gap $\Delta_1 = 18$ meV, $\Delta_2 = 10$ meV. Assuming a real gap, they obtain $\Delta = 23$ meV. Lee *et al.*[9] obtain $\Delta = 25$ meV with a tunnel junction made by depositing a Pb counter electrode on a single crystal. With a scanning tunneling microscope on a polished bulk sample of composition 4:3:3:4, Vieira *et al.*[10] find a distribution of gaps between 15 and 23 meV, with maxima at 16 and 21 meV. They suggest that the two values are the gaps of the two superconducting phases present in their films. We report conductance measurements on a tunnel junction made on a thin film of Bi-Sr-Ca-Cu-O containing both the 110- and the 85-K phases, using a conventional superconductor, Al, as a counter electrode. We find

$$\Delta_1 = 18\text{–}21 \text{ meV (85-K phase)},$$

$$\Delta_2 = 25\text{–}28 \text{ meV (110-K phase)},$$

and

$$2\Delta/k_BT_c = 5.5 \pm 0.6$$

for both phases.

We explain the observed small asymmetry and parabolic background of the differential conductance (dI/dV) curves in the framework of conventional normal metal-insulator-normal metal (NIN) and superconductor-insulator-normal metal (SIN) junction theory at zero temperature. This procedure justifies a simple approximate method of separating the density-of-states contribution to the tunneling current from the contribution due to the dependence of the barrier height on the applied bias.

JUNCTION PREPARATION

The thin films were sputtered from a pressed, nonreacted powder target, containing Pb_3O_4, Bi_2O_3, $CaCO_3$, $SrCO_3$, CuO, with Pb:Bi:Sr:Ca:Cu in the ratios 0.3:1.7:2:2:3.0. The sputtering gas was Ar with about 20% O_2. Cleaved MgO crystal substrates were resistively heated in a Pt foil to 860 °C (evaluated by pyrometer) during deposition.

The films were annealed for a short time (furnace heat up to 860 °C, then 10 min at that temperature, followed by quenching to room temperature), and x-ray diffraction patterns showed mostly the peaks corresponding to a *c*-axis oriented film of the 85-K material (2:2:1:2). The resistive transition (Fig. 1, inset) shows the presence of the 110-K (2:2:2:3) phase, and the resistance was zero by 78 K. X-ray photoemission spectroscopy (XPS) measurements showed that Pb was almost completely gone after the anneal.

An artificial barrier of aluminum oxide was sputtered onto the annealed films. The thickness, evaluated by a previous calibration, was on the order of 20 Å. The cross strips were evaporated aluminum (1000 Å). Other barriers and counter electrodes were tried, but did not yield any tunneling features which could be associated with superconductivity in Bi-Sr-Ca-Cu-O.

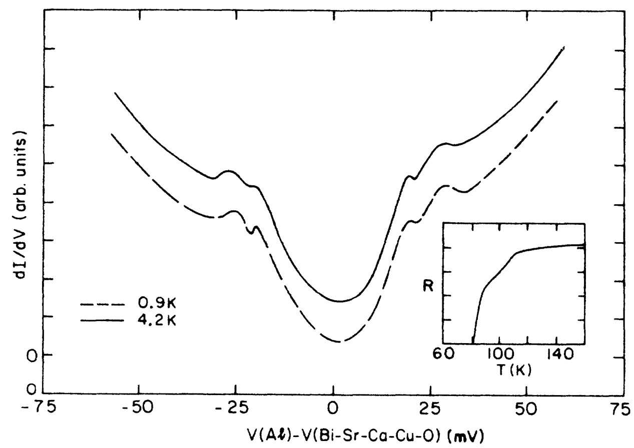

FIG. 1. Plot of low-temperature dI/dV as a function of V. The curve taken at 0.9 K was shifted down vertically by one division (as shown) for clarity. The same bias convention is used in all the figures. Inset: Resistive transition of the film used for the tunneling.

EXPERIMENTAL RESULTS

Figures 1 and 2 show the differential conductance as a function of the bias at different temperatures. As the temperature falls, several features appear and become sharper. At 4.2 K and below, there is a region of low conductivity (in comparison to the background), with two pairs of peaks. At 0.9 K, below the T_c of Al, the peaks further sharpen, as expected for a transition from normal-metal-insulator-superconductor (NIS) to superconductor-insulator-superconductor (SIS) tunneling.

These peaks can be regarded as two pairs at nearly equal positive and negative biases, although there is a slight asymmetry in the magnitude of tunneling conductance. If we consider the junction as consisting of many parallel junctions formed between the Al film and the grains of various phases of Bi-Sr-Ca-Cu-O, we can relate these peaks to the gaps of the two superconducting phases seen in the resistive transition, obtaining

$$\Delta_1 = 18\text{--}21 \text{ meV for the } (2{:}2{:}1{:}2) \text{ phase},$$

$$\Delta_2 = 25\text{--}28 \text{ meV for the } (2{:}2{:}2{:}3) \text{ phase},$$

and

$$2\Delta/k_B T_c = 5.5 \pm 0.6$$

for both phases. The agreement of the presumed reduced gap parameters is supportive of the association of the observed features and the superconducting energy gaps of the phases. The value of the parameters is higher than the BCS weak-coupling value of 3.5, but is not extraordinary in comparison to that for Pb (Ref. 3) and amorphous Ga (Refs. 5 and 11) which have shown values up to 4.5. The relative size of the two peak amplitudes is also in rough agreement with the relative amounts of the two phases present, as estimated from the resistivity measurement.

Various characteristics of the measured data obstructed efforts to interpret the conductance directly in terms of the quasiparticle density of states (DOS). There was some leakage conductance at low temperatures, probably due to normal regions in the Bi-Sr-Ca-Cu-O surface. Although this level of leakage would be intolerable in conventional superconducting tunnel junctions, it is fairly respectable in high-T_c samples.[12,13] Tunneling from superconducting Al ($T_c = 1.2$ K for 1000-Å films) into another superconductor should split the gap peaks into sum and difference peaks. The splitting would be only a few tenths of a meV, however, and could probably not be seen because the gaps of the other superconductors are so much larger. A tunnel junction over a normal region should give two symmetric peaks at the Al gap voltage. But again this is a very small voltage on our voltage scale, and the resolution of our measurement was lowered by the presence of noise due to the very high resistance of our junctions near zero bias (several hundred $k\Omega$). A sharpening of the peaks when temperature was lowered through 1.2 K was observed. It is reasonable to assume that if there is a superconductor with a gap of several tens of meV on the other side of the barrier, the opening of the Al gap will not have an effect big enough to be detected under the conditions of this experiment.

We were not easily able to follow the gap to temperatures higher than 60 K, because the background became too strong compared with the interesting features. But, as we explain below, when the parabolic background was divided out, structure in the dI/dV curve related to the gap could be seen. Unfortunately, the thermal broadening at this temperature, together with the presumed double-gap structure, make extracting the numerical value of the gap difficult. Although it is possible to deconvolve this broadening in many cases, we were not able to do it with our experimental curves, presumably because even the dI/dV curves at very low temperature lack sharp features. This makes a deconvolution difficult to perform in practice. We note that suppression of sharp features at the gap voltage has been observed in conventional superconductor junctions using semiconductor barriers such as amorphous silicon.[14] The very low barrier and electron traps in these barriers cause rounding of these features. The surface layer of the Bi-Sr-Ca-Cu-O may have caused

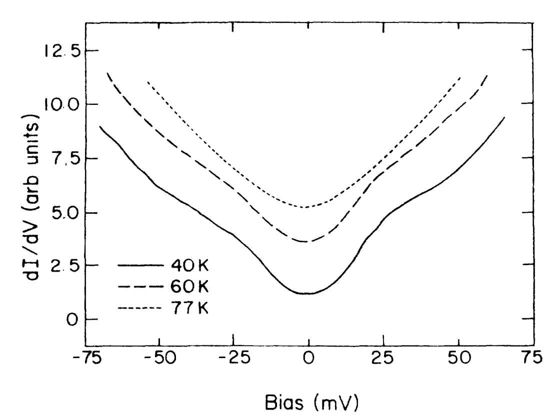

FIG. 2. Measured dI/dV at higher temperatures. These data were taken on the same junction as in Fig. 1. The zero corresponds to the curve taken at 77 K.

this effect in the present experiment.

The values obtained for the gap are very close to values measured on Bi-Sr-Ca-Cu-O samples by others. The agreement is particularly good with the values Ekino and Akimitsu[7] find for Δ of the 85-K phase and of the 110-K phase. Although our films are oriented with the c axis perpendicular to the substrate, scanning electron micrographs of the surface indicate the jumbled polycrystalline morphology commonly observed in post-annealed films. Thus, we have no knowledge of the crystal direction sampled by our tunnel data. The agreement is also good with the data of Vieira *et al.*[10] Their resistance measurement showed an onset of a superconducting transition at about 110 K. As they scan the sample with a tip, they record dI/dV curves showing single peaks. The distribution of the gaps is peaked around two values, $\Delta_1 = 16$ meV and $\Delta_2 = 21$ meV. The approximate proportionality of these gap values to the T_c's of the two phases leads them to attribute the two gap values to the two phases. It should be mentioned that double peak structures have been observed on Y-Ba-Cu-O tunnel junctions where presumably only one phase is present.[12,13,15] Geerk, Xi, and Linker[13] suggest the second peak in their data and also in the data of Kirtley *et al.*[12] as possibly due to inelastic processes. Gurvitch *et al.*[15] make a similar comment on their recent data. Our data show two very similar features, which makes an interpretation in terms of inelastic processes, such as phonon interactions very unlikely. In Pb, where inelastic peaks due to phonons are easily observed, they never exceed a few percent of the conductance and are much weaker than density-of-states peaks. Thus, we feel that in our case, the explanation of the double peaks as belonging to two phases present in the sample is more straightforward.

DISCUSSION

Tunneling theory

The high-bias part of the measured conductance curves can be well fitted by second degree polynomials $G = G_0(1+bV+cV^2)$, where $b = 0.0025$ and $c = 0.00025$ when V is given in mV. In our data the linear term always gives a contribution of less than 10% to the total conductivity in the bias range between 0 and 60 mV. For physical reasons, even powers of V should not contribute much to the current, which entails that odd powers of V should be small in the derivative dI/dV.

It has been previously observed,[1] with conventional superconductors, that tunnel junctions show a parabolic conductance, although in most cases the V^2 term only becomes important at biases of the order of 100 mV, far away from the gap of conventional superconductors. There is also very often a slight asymmetry, due to a small linear correction.

The quasiparticle part of the tunneling current can be written as[16]

$$J \propto \int_0^{+\infty} dE\, \rho_L(E)\rho_R(E-eV)\,|T|^2[f(E)-f(E-eV)]\,,$$

where E is the quasiparticle energy, ρ_L and ρ_R are the quasiparticle densities of states in the two electrodes, V is the bias, $|T|^2$ is the square of the modulus of the tunneling amplitude, and f is the Fermi function. The influence of different terms on the conductivity as a function of bias is well known. When $|T|^2$ is independent of E and V, the densities of states are the only bias-dependent factors and their influence on the conductivity is then very easy to evaluate, and leads to conventional SIN and SIS theory. In the SIN case, the existence of the gap Δ leads to a zero conductivity below Δ/e, followed by a peak and a region of constant conductivity. In fact, in this case, $dI/dV(V)$ is proportional to $\rho_s(eV)$. The SIS case is similar, and one observes a small peak at the difference of the gaps, and a larger peak at the sum of the gaps of the two superconductors. The influence of the $|T|^2$ term by itself has been studied by Stratton on planar NIN junctions.[17] He finds a current of the form

$$J \propto V + aV^2 + bV^3\,,$$

where a is zero for a symmetric barrier, and b is of order $\frac{1}{6}\alpha^2 t^2/\phi$, where ϕ is the barrier height, t the thickness, and $\alpha = 1.025$ eV$^{-1/2}$ Å^{-1}. In most experiments, one observes both kinds of behavior: The rapid variations due to the densities of states, and a slowly rising parabolic background due to $|T|^2$.

For the case of a typical $Al/Al_2O_3/Al$ junction with $\phi = 1$ eV and $t = 10$ Å, the coefficient of V^2 is close to 50 V^{-2}. Our curves can be fitted with coefficients of the order of 300 V^{-2}. To see if this can be explained by reasonable barrier characteristics; we assume a barrier composed of two sections: between 0 and t_1, the barrier height is ϕ_1, and between t_1 and t_2, it is ϕ_2. This incorporates the effect of a bad surface in addition to the artifical barrier. We assume that the artificial barrier has a thickness of 15 Å and a height of 1 eV. Then an additional 5 Å of a barrier of height 0.5 eV gives the desired curvature, while the linear term associated with the asymmetry remains very small.

Application to our data

There are at least three contributions to the total conductivity: A contribution from superconducting regions with a T_c close to 80 K; a second contribution from regions containing the 110-K phase; and a third contribution called a leakage current, which we assume to be due to nonsuperconducting regions in the thin film. We assume that these conductances add up as for parallel circuits. The current through a tunnel barrier being an exponential function of $-t\sqrt{\phi}$, variations in the barrier thickness of a few Å or variations in the barrier height of a few tenths of a volt, change it by several orders of magnitude. Thus, if different regions give contributions to the current which are comparable in magnitude, then the barrier characteristics associated with these contributions must be almost identical. It is then reasonable to assume that the curvature of the differential conductance, which is a much smoother function of the barrier parameters, is the same. Figures 3 and 4 show the result of dividing out the parabolic dependence. Because of the various assumptions and approximations made, these curves can probably

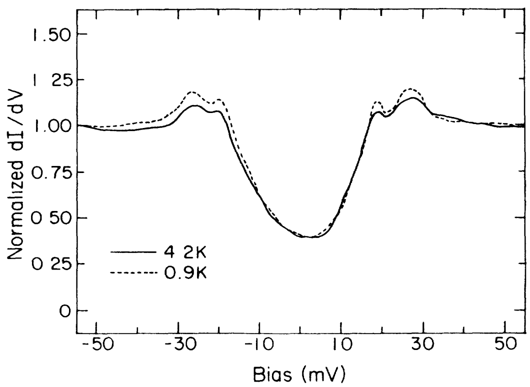

FIG. 3. Low-temperature dI/dV after dividing by the parabolic background.

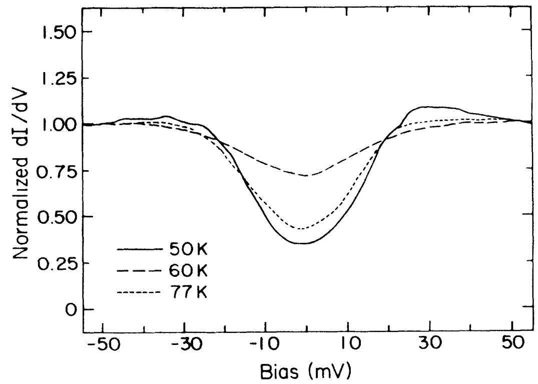

FIG. 4. dI/dV at higher temperatures after parabolic background was divided out.

not be directly interpreted as being thermally broadened densities of states, but they show several features that one would expect from the quasiparticle DOS of a superconductor: A region of low conductance, which looks like the indication of a gap although there is a slow and continuous rise, followed by a peak which is not as high as would be a BCS peak. All of these features were already visible in the original data, but they become much clearer after this numerical treatment. The upper and lower bounds given for Δ stay valid. The derived barrier thicknesses and heights are reasonable considering the roughness of the Bi-Sr-Ca-Cu-O surface and the possibility of imperfect material near the surface onto which the barrier was sputtered.

CONCLUSION

The tunneling conductance of our Bi-Sr-Ca-Cu-O/Al_2O_3/Al junctions displays features all of which have been seen before in conventional superconducting tunnel junctions. At low temperature, the conductance curves display peaks which can be interpreted as arising from the gaps of the two superconducting phases present. The voltage at which these peaks appear are in the ratio of the T_c's of the two phases and give a ratio of $2\Delta/kT_c \sim 5.5$. The parabolic behavior of the conductance is consistent with tunneling theory and can be understood by assuming that a surface layer of the superconducting material is semiconducting and gives an additional barrier. The rounding and attenuation of the peaks is reminiscent of similar structure seen in tunneling conductances of conventional superconducting junctions with semiconducting barriers.[14] The nonzero conductance at low temperature and small bias is also likely to be the result of poor surface quality. We therefore feel these conductance data demonstrate the existence and magnitude of the energy gap in Bi-Sr-Ca-Cu-O superconducting material.

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