Quasiparticle Tunneling Spectroscopy of High-T$_c$ Cuprates

John Zasadzinski, L. Ozyuzer, Z. Yusof  
Science and Technology Center for Superconductivity  
Physics Department  
Illinois Institute of Technology, Chicago, IL 60616

Jun Chen, K.E. Gray, R. Mogilevsky, D.G. Hinks  
Materials Science Division  
Argonne National Laboratory, Argonne, IL 60439

J.L. Cobb, and J.T. Markert  
University of Texas at Austin, Austin, TX  78712


DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

*Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Science under Contract #W-31-109-ENG-38 (KEG, DH) and the National Science Foundation Office of Science and Technology Centers for Superconductivity under Contract #DMR91-20000 (JZ, JC, ZY).
ABSTRACT

Superconductor-insulator-normal metal (SIN) and superconductor-insulator-superconductor (SIS) tunnel junctions provide important information on pairing state symmetry and mechanism. Measurements of such junctions on high $T_c$ superconductors (HTS) are reported using mechanical point contacts, which generally display the optimum characteristics that can be obtained from HTS native-surface tunnel barriers. New tunneling data on the infinite-layer cuprate, $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ are reported which show a remarkable similarity to another electron-doped cuprate, $\text{Nd}_{1.85}\text{Ce}_{0.85}\text{CuO}_4$. In particular, there is a strong, asymmetric linear background conductance that is indicative of inelastic tunneling from a continuum of states. A discussion is given of the anomalous “dip” feature found in the tunneling and photoemission data on BSCCO 2212. It is shown that a similar feature is found in many cuprate junctions and that this dip scales with the gap energy over a wide range. New data on the single-layer, tetragonal cuprate, $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (Tl2201) are presented and discussed in light of recent published results on the similar compound $\text{HgBa}_2\text{CuO}_4$ (Hg1201). The Hg1201 data display a low, flat sub-gap tunneling conductance which is consistent with a BCS density of states whereas the Tl2201 data display a cusp-like feature at zero bias which is more consistent with $d_{x^2-y^2}$ symmetry.

1 INTRODUCTION

Quasiparticle (single-electron) tunneling spectroscopy has long been viewed as a powerful probe of the superconducting state. In conventional superconductors such as Pb and Nb, the gap in the density of states is seen in the tunneling conductance and the strong-coupling phonon structures are found as well. Inversion of the data allows the determination of the gap energy, the electron-phonon spectral function, $\alpha^2F(\omega)$, and the coulomb pseudopotential, $\mu^*$, thereby providing a complete description of the superconductivity in conventional metals. In the early studies of high $T_c$ superconductors (HTS) the tunneling spectroscopy results were plagued by poor reproducibility, however, more recent studies on better characterized samples has led to a consensus on energy gap values for a number of HTS. Tunneling data on BSCCO 2212, for example, are highly reproducible and consistent results have been reported by a number of groups using various junction methods. A good review of HTS tunneling is given by Hasegawa et al.

We report here progress made in the development of SIN and SIS junctions on oxide superconductors using a mechanical, point-contact tunneling (PCT) approach. All of the PCT data presented are from the Argonne/IIT tunneling group. For our instrument, the term “point contact” is somewhat of a misnomer in that the contact area of the tip and sample can be large compared to atomic dimensions. This is by design as the intention is not to obtain atomic scale images as with an STM but rather to obtain stable contacts with relatively low resistances of typically 1 k$\Omega$ to 20 k$\Omega$ for improved signal-to-noise. Barrier height analysis of such junctions on Nb using an Au tip indicated a contact diameter of ~2400 Å. Furthermore, the observation of the Nb phonon structures consistent with planar junctions demonstrated that this method could be used for sensitive spectroscopy. This mechanical method has proven to be a reliable and versatile tool for making many
2. TUNNELING DENSITY OF STATES

No discussion of tunneling data can proceed without a brief discussion of the density of states (dos) for cuprate superconductors. The tunnel current in an SIN or SIS junction can be written as,

\[ I(V) = C \int_{-\infty}^{\infty} \rho_1(E) \rho_2(E+eV)[f(E)-f(E+eV)]dE. \]  

Here, \( \rho_1(E) \) and \( \rho_2(E) \) are the quasiparticle dos in the two electrodes and \( C \) is a constant which depends on (among other things) junction area. The Fermi functions, \( f(E) \) account for thermal population of quasiparticle states. Here, \( \rho(E)=1 \) for a normal metal which points out an often neglected fact that all band structure effects have mysteriously disappeared from the integral. The absence of the band structure dos in the tunneling data of conventional superconductors is experimentally established and a theoretical argument for this has been given by Harrison (see chap. 2 of ref 1). The tunneling matrix element, \( t^2 \), has an energy dependence which is assumed to be weak over the voltage range of interest (energy gap region) and has been taken out of the integral. In the limit, \( T=0 \) K, the tunneling conductance, \( \sigma_s = dI/dV \), for an SIN junction becomes,

\[ \sigma_s = C t^2 \rho(E) \]  

where we have now set \( E=eV \). Eq. 2 simply states that a measurement of the tunneling conductance at low temperatures should reveal the quasiparticle dos, which for a BCS superconductor is given by \( \rho(E)=E/(E^2-A^2)^{1/2} \). An exact determination of \( \rho(E) \) requires a measurement of the weak, voltage-dependent background (or normal state) conductances to divide out the prefactors of eq. 2, however such a measurement can be difficult due to the high critical fields and temperatures of HTS. Also, in some cases the background conductances are far from having a weak voltage dependence as we will show. In the absence of a normal state measurement, it is common to normalize the data by a constant taken at some arbitrary high bias voltage.

To examine the dos of HTS cuprates, we take a simple model identical to that described by Fedro and Koelling.6 The two-dimensional Cu-O2 planes are represented by a single, tight-binding band with nearest neighbor (NN) and second NN hopping described by \( t \) and \( t' \). We choose \( t'=0 \) for simplicity and a hole concentration of 0.18 which shifts the van Hove singularity above the Fermi energy at \( E=0 \). Fig. 1 shows what the superconducting energy gap looks like in the dos.

Figure 1  Two-dimensional, tight-binding band dos with (a) isotropic gap and (b) d-wave gap.
3. Experimental Results

d-doped samples. As will be shown, this can have significant effects, which is a striking feature of the data presented in the manuscript. While the most obvious difference in the two curves of Fig. 1 is the drop in the data for the doped sample, the trend is similar to that of Fig. 1, i.e., the peak height is dependent on the concentration of the superconducting phase in the sample. This results in a clear enhancement of the CDG peak, which is a consequence of the fact that the superconducting phase dominates the CDG signal. The CDG signal is also observed in the presence of the doped sample, which shows a similar trend. The difference is shown in Fig. 2. In our simple model, the data is fitted by (a). The CDG peak enhancement is attributed to the HTS phase.

The energy scale (750 K) is marked by 2 J and the full band width is 10 K, which is approximately the HTS transition.
The general behavior of the three-site compounds we have studied by PET-101.11 is as follows: for each compound

\[ \text{Conductance} = \frac{q}{4}\left( 1 + \sin \theta \right) \]

where \( q \) is the charge on the ion with respect to sample.

![Graphs showing conductance and voltage relationships.](image)

The experimental data for the PET-185798A1504 compound.

![Graphs showing superconducting behavior.](image)

The experimental data for the PET-185798A1504 compound.

The conductance of the sample decreases with increasing temperature. At low temperatures, the conductance is proportional to the square of the magnetic field. At higher temperatures, the conductance becomes independent of the magnetic field. The conductance is also dependent on the applied voltage, with a quadratic dependence.

The conductance is given by the expression:

\[ \text{Conductance} = \frac{q}{4}\left( 1 + \sin \theta \right) \]

where \( q \) is the charge on the ion with respect to sample.

The conductance is plotted against voltage in the graphs shown above.

The conductance is also plotted against temperature in the graphs shown above.

The conductance is plotted against magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.

The conductance is plotted against the temperature in the graphs shown above.

The conductance is plotted against the magnetic field in the graphs shown above.

The conductance is plotted against the flux density in the graphs shown above.

The conductance is plotted against the magnetic field strength in the graphs shown above.

The conductance is plotted against the applied voltage in the graphs shown above.
only ones observed? In PCT studies of hole-doped cuprates, a variety of background shapes are found including decreasing with bias\textsuperscript{3,14} as will be shown in the next section.

3.1 The anomalous "dip" feature

PCT data on Pb-doped Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} (BSCCO 2212) with a T\textsubscript{c}=96 K were reported\textsuperscript{14} in 1989. Two SIN tunneling conductance curves (Au tip) from that article are reproduced in Figs. 4(a) and 4(b) for the temperatures, 4.2 K and 77 K respectively. The background conductances decrease with applied voltage, an anomalous feature in itself but one which is typical for BSCCO 2212. In Fig. 4(a) the positive bias (Au tip is + with respect to the sample) is characterized by a sharp conductance peak at -22 mV, a pronounced dip near 45 mV followed by another peak near 70 mV. For the negative bias direction, the dip feature is weaker (but nevertheless observable) and we originally described it as a shoulder. The observation of a dip feature near 2\Delta in the SIN junctions on BSCCO and at 3\Delta in SIS junctions has been found by many groups using various junction methods.\textsuperscript{2} Note that features are shifted by an additional factor of \Delta in SIS junctions compared to SIN. The dip is clearly a reproducible feature and appears to be connected to a similar dip feature found in the spectral weight function measured in photoemission experiments.\textsuperscript{15} To gain some insight into this feature we have constructed estimates of the normal state curves by fitting the data for IV\textless;40 mV to a high order polynomial. These curves are shown as dashed lines in Fig. 4. Considering the different conductance values for the two junctions and noting the different sensitivities in the ordinates, the inferred background shapes are quite similar. The reduced gap features of the 77 K junction put a greater focus on the peak near 70 mV and perhaps it is this feature to which attention should be paid. Similar dip features are found in other cuprate junctions including the electron-doped NCCO, although in that case it is a subtle feature exposed only because of the ability to measure the normal state conductance. SIN junctions on Tl\textsubscript{2}Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} (TBCCO)\textsuperscript{16} generally displayed pronounced dips for both bias values, again at a voltage nearly twice that of the conductance peak.

The dip features are symmetric and much more pronounced in SIS junctions\textsuperscript{2} and for this reason we have chosen to plot the SIS characteristics of various cuprate junctions on a single plot and this is shown in Fig. 5. In the cases of NCCO and TBCCO we generated the SIS curves from SIN data using eq. 1 and the superconducting dos for each electrode. The T\textsubscript{c} values of the cuprates range from 5.5 K for BSCCO 2201 to 100 K for TBCCO and to plot the data on a single graph we have normalized the voltage axis by V\textsubscript{p}/2 where V\textsubscript{p} is the voltage of the conductance peak. Using this normalization, the x-axis is in units of \Delta. It is clear from Fig. 5 that the dip and subsequent peak features scale with the superconducting gap, which varies by a factor of 30 over the cuprates examined.

![Figure 4](image-url)
Figure 5. Representative SIS normalized tunnel conductances for various cuprate superconductors ($T_c$ from 5.5 K to 100 K) plotted on a voltage axis renormalized in units which are $\Delta$. Left scale: NCCO (solid line), BSCCO 2212 (dashed line). Right scale: TBCCO (dashed-dot line), BSCCO 2201 (solid line), BSCCO film (dashed line).

Note that in the case of NCCO the dip is about 3.5 meV from the conductance peak, far below any phonon peak energies (typically 10 meV-70meV) and therefore does not interfere with the determination of $\alpha^2F(\omega)$. Linking the dip feature to a superconducting energy scale is important to understanding its origin. D. Coffey has argued\textsuperscript{17} that a natural explanation is an intrinsic, energy dependent quasiparticle decay mechanism, $\Gamma(\omega)$, put into the dos of eq.3, which turns on at a characteristic energy, $2\Delta$ or $3\Delta$, for d-wave and s-wave respectively. He further argues that the location of the dip at $3\Delta$ in SIS in Fig. 5 (consequently $2\Delta$ in the dos) is evidence for d-wave superconductivity. This is an attractive explanation however, the dip is found at the same location in NCCO which we have shown is most likely an s-wave superconductor. Perhaps the focus at the present time should not be on the precise location of the experimental dip as it might be affected by tunneling background shapes for example. An alternative explanation put forth recently by L. Coffey and K. Kouznetsov (CK)\textsuperscript{18} is in terms of inelastic quasiparticle scattering processes off a strong spin fluctuation spectrum arising from an oxygen deficient layer on the surface of the HTS. It is clear that the inelastic tunneling processes are present in many HTS junctions and by treating such processes using a realistic spin fluctuation spectrum, it is possible that the dip and peak features can be explained for the tunneling data and photoemission as well. If indeed, the anomalous dip is due to an inelastic tunneling process arising from a surface layer, then this might explain the observation by Shimada et al\textsuperscript{19} of phonon structures in BSCCO 2212 using Schottky type junctions. This experiment is one of the few to not show the pronounced dip in BSCCO 2212. Perhaps in this case, the intimate contact of the semiconductor to BSCCO inhibits any oxygen-deficient, surface layer allowing predominantly elastic tunneling to be observed.

3.2 PCT junctions on Tl$_2$Ba$_2$CuO$_6$

It was recently reported by Chen et al\textsuperscript{20,21} that PCT junctions on the single-layer Hg based cuprate, HgBa$_2$CuO$_4$ (Hg1201) exhibit BCS-like tunneling conductances for both SIN (Au tip) and SIS' (Nb tip) junctions. Given the choice of the two curves shown in Fig. 1, it was clear that the Hg1201 data were more compatible with an s-wave order parameter. Furthermore, the SIS' $I(V)$ data exhibited sharp current onsets at the gap voltage making the Hg1201 material a potential candidate for quasiparticle based devices such as mixer-based photon detectors\textsuperscript{21}. Typical gap parameters were $\Delta$=13-16 meV, but one junction had $\Delta$=24 meV. Considering that Hg1201 is tetragonal and has a single Cu-O layer per unit cell, we decided to examine a very similar compound, Tl$_2$Ba$_2$CuO$_6$ (Tl12201), which has the same structural properties as Hg1201 and a similar $T_c$ (91 K-95 K). Single-crystals of Tl12201 approximately 0.5mm on edge were grown by Mogilevsky and
Hinks at Argonne. The PCT method offers distinct advantages for the study of such small crystals. Over 200 junctions have been made on 20 different crystals using both Au and Nb tips. The data are reproducible and we show a representative set of four junctions from two samples in Fig. 6. Note here the voltage is that of the sample relative to the tip.

Fig. 6. Representative set of SIN (Au tip) junction conductances for two crystals of Ti2201. The curves are labelled (a) through (d) going from top to bottom. Junction (b) is represented by dots, all others by solid lines. The voltage, V, is that of the sample relative to the tip.

First note the background shape which is weakly decreasing with applied bias voltage similar to that typically found in BSCCO 2212. The junction conductances are characterized (in many cases) by very sharp conductance peaks located near 20 mV. Estimating $\Delta=20$ meV and using 91 K for $T_c$ one obtains $2\Delta/kT_c=5.1$. We note that the ratio of peak conductance to the estimated normal state at 20 mV is often greater than 2 and in some cases is as high as 3.5, the latter value being one of the largest ratios we are aware of for any SIN cuprate junction.

Figure 7. Normalized conductances of Ti2201 junctions (a) and (d) of Fig. 7.
Junction (c) of Fig. 6 is the most broadened of the four and the conductance peak voltage has been shifted to a slightly larger value. This shift of the conductance peak voltage to higher values for broadened junctions is a common effect in oxide superconductors. We argue that those junctions with the sharpest conductance peaks are the most representative of the bulk dos of Ti2201 and thus junctions (a) and (d) from two different crystals are chosen for further consideration. The curves were normalized by a constant and are shown in Fig. 7. Comparing the normalized conductances to the dos plots of Fig. 1, it appears that Ti2201 more closely resembles a superconductor with d_{x^2-y^2} symmetry. This is evident from the pronounced cusp feature in the data at zero bias. This cusp can be seen in all of the junctions of Fig. 6 and is a general feature of most of the SIN junctions we have studied. Quantitative fits of the data using the d-wave model discussed above are currently underway. In comparing these data to those of Hg1201, an obvious question arises. Why would two such similar compounds display junction characteristics indicating different gap symmetries?

4. SUMMARY

Quasiparticle tunneling data on HTS cuprates can potentially give important information on pairing state symmetry and mechanism. However, it is clear that in many cases unusual background shapes occur in the tunneling conductances. The fact that these background shapes can vary from increasing with bias (often in a linear fashion) to decreasing with bias for the same cuprate suggests that they are arising from a conduction process which is not elastic tunneling. A strong likelihood is inelastic tunneling which has been shown to produce linearly increasing backgrounds when the spin fluctuation spectrum is flat. Perhaps a more rigorous treatment of inelastic tunneling, including a realistic spin fluctuation spectrum, a tight binding band structure and directional tunneling effects will result in an explanation of all of the background shapes. The background must be understood before a quantitative analysis of the elastic tunneling part can be undertaken. One way of minimizing the problem is to focus on those junctions which have a relatively weak voltage dependent background at least for one bias direction. This approach worked with NCCO where a^2T(o) spectra have been obtained.

The origin of the anomalous dip feature is still not understood. Our observation that the dip feature scales with the energy gap puts severe constraints on its interpretation. The possibility of an energy dependent decay rate, \( \Gamma(o) \), is an attractive one and readily leads to the observed scaling behavior. However, there are still aspects of the dip feature which are not explained by this model, for example, the observed asymmetry of the effect with bias voltage as found in BSCCO 2212. There is also the possibility that the dip feature is associated with the same inelastic tunneling processes that affect the general background shape.

Quasiparticle tunneling cannot probe the sign of the order parameter and therefore cannot directly determine the pairing state symmetry. However, strong inferences can be made. For example, the observation of highly reproducible gap values in NCCO strongly supports an isotropic s-wave state and this is verified by a number of other experiments on NCCO including penetration depth and Raman scattering. The origin of the small sub gap conductance remains a puzzle. Other electron doped systems, including the infinite layer cuprate, Sr_{1-x}Nd_xCuO_2 display similar gap reproducibility which leads to the suggestion that they may be s-wave as well. Another way to probe the pairing state is to note that the s-wave and d-wave densities of states are quite different and should be reflected in the quasiparticle tunneling spectra. The observation of low, flat sub-gap conductances in junctions of Hg1201, for example, are difficult to reconcile with a d-wave pairing state. Strong directional tunneling effects must be invoked to explain the Hg1201 data within a d-wave scenario. In the case of the similar compound, Ti2201, the tunneling dos looks very much like the d-wave dos, including a pronounced cusp feature. In this case one must argue that there are no preferred tunneling directions and the total dos is being probed. For other cuprates, the presence of sub-gap conductance without any obvious cusp feature gives little information about pairing symmetry.

Finally, it should be mentioned that under no circumstances has the van Hove singularity feature ever been observed in PCT or to our knowledge, any other tunneling method. Such a distinctive feature as seen in Fig. 1 might be expected to show up in the tunneling data. Being strictly a band structure effect, its absence is probably linked to the common absence of band structure effects in the tunneling dos as found in conventional metals.

5. ACKNOWLEDGEMENTS

We acknowledge the assistance at Argonne of Qiang Huang and Paola Romano for tunneling measurements, John Wagner for bulk sample preparation, R. T. Kampwirth and C. Romeo for thin films of BSCCO; This work is partially supported by the U.S. Department of Energy, Division of Basic Energy Sciences-Materials Sciences (KEG,DH), under contract No. W-31-
109-ENG-38 and the National Science Foundation, Office of Science and Technology Centers (JZ, JC, ZY), under contract No. DMR 91-20000.

6. REFERENCES