

## Evidence of $d_{x^2-y^2}$ symmetry in the tunneling conductance density of states of $\text{Ti}_2\text{Ba}_2\text{CuO}_6$

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Tunnel junctions have been made on single crystals of  $\text{Ti}_2\text{Ba}_2\text{CuO}_6$  with a  $T_c \sim 91$  K using a mechanical point-contact method. Both superconductor-insulator-normal-metal (SIN) and superconductor-insulator-superconductor (SIS) junctions were obtained using Au and Nb tips, respectively. The tunneling conductances obtained are reproducible, with sharp, well-defined energy gap structures and are characterized by a cusplike feature at zero bias. These conductances can be fit to a simple, momentum-averaged density of states (DOS) obtained from a superconducting order parameter with  $d_{x^2-y^2}$  symmetry. The SIS data display a weak Nb gap feature which is consistent with the subgap DOS observed in the SIN data. [S0163-1829(98)51406-3]

Theoretical<sup>1</sup> and experimental results on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) (Refs. 2 and 3) and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212) (Refs. 4 and 5) present a strong case for  $d_{x^2-y^2}$  ( $d$ -wave) pairing in high temperature superconductors (HTS). Surprisingly, the quasiparticle tunneling data on these materials have not clearly and reproducibly exhibited the characteristic features of a  $d$ -wave density of states (DOS) (Refs. 6–8) such as a cusplike feature at zero bias, a linear increase in the subgap region, and sharp peaks at the gap voltage. Furthermore, there exist examples of flat subgap tunneling conductances in Bi-2212 (Ref. 9) and Hg-based cuprates<sup>10,11</sup> which are not easily reconciled with a  $d$ -wave gap parameter. These results might be due to surface effects in the tunneling experiment, preferential tunneling directions, or perhaps because none of the above systems have a pure  $d$ -wave symmetry gap.<sup>1</sup> We report here tunneling measurements of single-crystal  $\text{Ti}_2\text{Ba}_2\text{CuO}_6$  (TI-2201) which reproducibly exhibit a characteristic DOS that is consistent with  $d$ -wave symmetry. The gap parameter of  $\Delta = 20$ – $22$  meV was found on over 100 junctions measured on 15 different crystals. This reproducibility of gap value is rare among HTS cuprates.<sup>12</sup>

TI-2201 is the first member of the homologous series  $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $n = 1, 2, \text{ and } 3$ ). It has a tetragonal crystal structure with a single Cu-O layer per unit cell<sup>13</sup> which is relatively simple when compared to the bilayer and trilayer HTS. The optimally doped compound has a  $T_c$  of approximately 91 K and its value can be depressed by overdoping. Although tunneling measurements have been carried out on two-layer  $\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$  (TI-2212),<sup>14</sup> to the best of our knowledge, no tunneling data have been reported on single-layer TI-2201. Maximum gap values of  $\Delta \sim 27$ – $31$  meV for TI-2201 have been reported<sup>15</sup> using Raman scattering, and there has been an observation of half-integer flux quanta in tricrystal rings<sup>3</sup> consistent with  $d$ -wave pairing symmetry for this material.

Another tetragonal compound, polycrystalline  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg-1201) which has a single Cu-O plane per unit cell and similar  $T_c \sim 95$  K as TI-2201, was studied by Chen *et al.*<sup>10</sup> using the identical point-contact tunneling

(PCT) method. The data exhibit more BCS-like tunneling conductances for both SIN (Au tip) and SIS (Nb tip) junctions with low and flat subgap features. Because of the similarities in these two cuprates, tunneling in TI-2201 might be expected to be the same as Hg-1201. However, the PCT data on TI-2201 seem to be more consistent with a  $d$ -wave DOS. Further discussion on this comparison is reserved for later in this article.

Samples of single crystal TI-2201 were synthesized using a method as described elsewhere.<sup>16</sup> The single crystals, approximately 0.5 mm on edge, were cleaved parallel to the  $a$ - $b$  plane, leaving a flat, shiny surface. All tunneling measurements were done with the PCT apparatus described in Ref. 17. In PCT, since the tip must be pushed into the surface of the crystals, the tunneling direction is undefined, although the tip approaches nominally along the  $c$  axis. Local variations in oxygen stoichiometry are expected to have a smaller effect than with a scanning tunnel microscopy (STM) probe because of the larger PCT contact area (estimated diameter  $> 100$  nm) (Ref. 18) compared to atomic dimensions.

Figure 1 shows  $dI/dV$  vs  $V$  from a representative set of five junctions from three different crystals. These data show a slight asymmetry in both the conductance peak and the background, displaying a higher peak at negative voltages (sample relative to tip). Sometimes (about 20%) the  $dI/dV$  display more broadening, with the conductance peaks reduced in size and shifted to higher voltages, and a more rounded zero-bias conductance. Examples are shown as the two bottom curves in Fig. 1. Further analysis is restricted to those junctions with a high ratio of peak to background conductance. Presumably, such junctions should be more reflective of the underlying DOS. Figure 2 shows four additional junctions from Sample A, where the conductances have been shifted for clarity. The unnormalized conductances are generally symmetrical and have an approximately flat or a weakly decreasing background. The average location of the conductance peak voltage ( $V_p$ ) is slightly more than 20 mV, while a cusplike feature is observed at zero bias. Asymmetric dip features are also present in some of the data and are

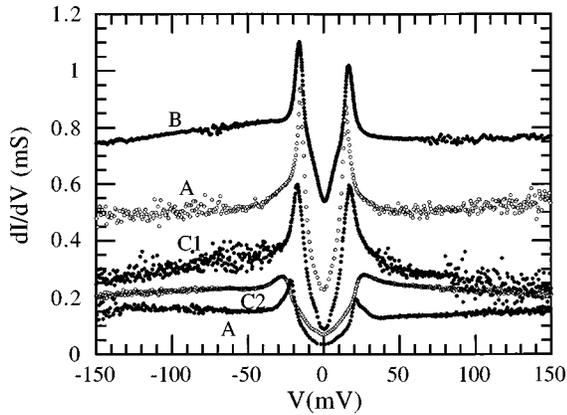


FIG. 1. Representative set of SIN (Au tip) junction conductances of three crystals (A, B, and C) of Tl-2201 at  $T=4.2$  K. The voltage  $V$  is that of the tip relative to the sample. For clarity, data B has been shifted by 0.4 mS and data C2 has been multiplied by 0.3.

consistent with but smaller than what is found in Bi-2212.<sup>6,8,9</sup> More detailed discussions of these background features are deferred to a future article.

We have also examined SIS junctions at various temperatures between 4.2 and 10 K, the latter being above the  $T_c$  for the Nb tip. In Fig. 3, the SIS conductance normalized by a constant value, 0.65 mS (open circles), again has a peak just above 20 mV (the solid line fit will be explained in the next section). This is expected since the Nb gap is  $\sim 1.5$  mV and should not significantly shift the conductance peak when compared to the SIN data. However, at 4.2 K, we observed a Nb gap inside the Tl-2201 gap. The Nb gap disappeared at 9.0 K (Nb tip becomes normal), revealing a small zero-bias anomaly (see inset of Fig. 3). This feature is consistent with SIN tunneling of Nb into the subgap states of Tl-2201. We believe the zero-bias anomaly is due to the presence of a  $\text{Nb}_y\text{O}_x$  insulating layer on the Nb tip, which has been shown in other tunnel junctions to produce a similar zero-bias peak.<sup>19</sup> The generally poorer quality of the Nb tip junctions may be a consequence of the Nb oxide.

The DOS for SIN tunneling at  $T=0$  K is equal to the ratio of the conductance in the superconducting state ( $\sigma_s$ ) with the

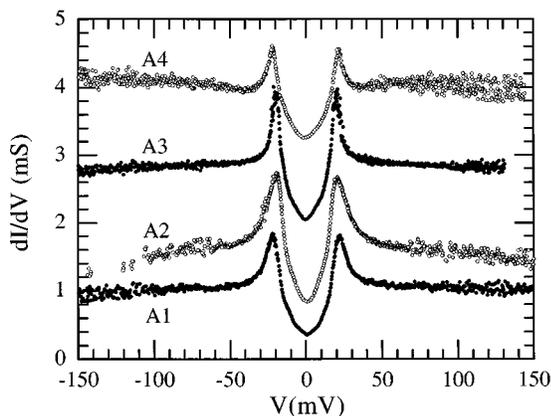


FIG. 2. Representative set of SIN (Au tip) junction conductances of Sample A at 4.2 K. Junction A2, A3, and A4 have been shifted vertically by  $1\sigma$ ,  $3\sigma$ , and  $5\sigma$ , respectively, for clarity ( $\sigma=0.6$  mS).

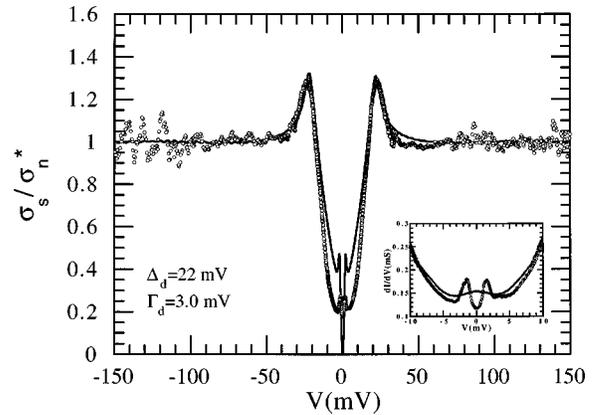


FIG. 3. Normalized experimental SIS with Nb tip ( $T=4.2$  K) data (open circles) and numerical fit (solid line) using a  $d$ -wave gap symmetry, tight-binding band structure for Tl-2201, and a BCS DOS for Nb. The inset shows the subgap feature which corresponds to the Nb gap. Data taken at 9.0 K (filled circles) show that the Nb gap has disappeared, revealing a zero-bias anomaly.

conductance in the normal state ( $\sigma_n$ ).<sup>20</sup> Unfortunately, the normal state conductance for HTS is not easily obtained. It means sustaining the junction while raising the temperature to a value above  $T_c$ . This is unfeasible since thermal expansion alters, if not destroys, the junction. Furthermore, the tunneling process may be temperature dependent such that the conductance would not reflect the true background shape at lower temperatures. Therefore, since we expect the value of  $\sigma_s$  to approximate  $\sigma_n$  at voltages much higher than the gap, we extrapolate the values of  $\sigma_s$  at high voltages and get an approximation,  $\sigma_n^*$ , thus obtaining an approximate DOS from the ratio of  $\sigma_s/\sigma_n^*$ .

Because the shape of the gap-region tunneling conductances suggests a  $d$ -wave symmetry, a quantitative fit of the normalized conductance was carried out using a two-dimensional tight-binding band structure and the  $d$ -wave gap parameter, similar to the one used by Li *et al.*<sup>21</sup> for the case where the band structure is restricted to the nearest-neighbor interaction. For the  $d$ -wave fit, the gap symmetry used is  $\Delta_{\mathbf{k}}=(\Delta_0/2)[\cos(k_x a)-\cos(k_y a)]$ . As expected, this model displays a pronounced van Hove singularity (VHS) in the DOS near  $\varepsilon_F$ . No such feature was ever observed in our data (see Figs. 1 and 2) and the absence of the VHS is consistent with the general result that elastic tunneling does not probe band structure effects.<sup>12,22,23</sup> We removed the VHS from the calculation of  $\sigma_s$  by using an artificially large value of the chemical potential  $\mu$  which produced a flat DOS from the band structure.

Figure 4 shows representative fits of the experimental data with the DOS obtained using this model which includes  $\Gamma$ , a quasiparticle lifetime factor.<sup>24</sup> The model produced a particularly good overall fit to the experimental data when compared to other HTS cuprate tunneling,<sup>8,14</sup> although, at zero bias, the experimental data have a higher conductance. A total of ten experimental data sets were fitted, yielding values of  $\Delta=20$ – $22$  meV and similar gap values could be inferred from the raw data of more than 100 junctions. Attempts to fit these data with a BCS DOS (including lifetime smearing) resulted in much poorer agreement, especially in the subgap region.

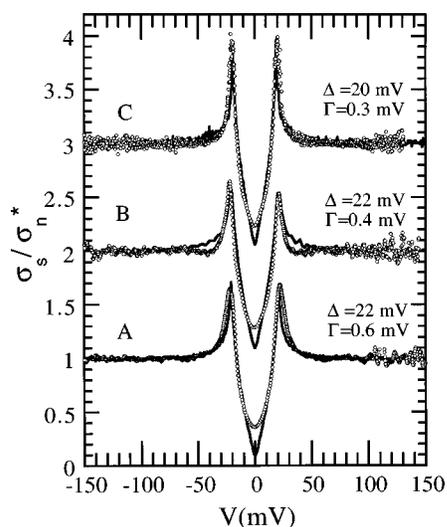


FIG. 4. Quantitative fits of normalized experimental SIN data (open circles) to the DOS obtained from a tight-binding band structure with  $d$ -wave gap symmetry (solid line). Data *B* and *C* have been shifted vertically by 1 and 2 units, respectively, for clarity.

To fit the SIS data, we generated the DOS for Nb using the standard BCS model and  $\Delta=1.5$  meV. This is then convoluted with the DOS generated using the identical  $d$ -wave model. In Fig. 3, the result (solid line) is comparable to the SIS data, reproducing the observed Nb gap feature, although the magnitude of the conductance in the Nb gap region is not reproduced. This may be due to the zero-bias anomaly which was not accounted for in our model. Our analysis showed that the Nb gap feature was found in the model even for the case  $\Gamma=0$  and therefore implied that this experimental feature is consistent with the subgap states in the  $d$ -wave DOS, and does not require any other source of gaplessness in the TI-2201.

The simple model used here cannot explain all of the features seen in our data such as the asymmetric peak heights, dip features (in some cases), or the decreasing background conductances found in some junctions. However, the observation of a similar shape to the gap region conductance in so many different junctions suggests that it is a consequence of the underlying DOS. While the observation that the DOS of TI-2201 has  $d$ -wave symmetry may not be too surprising in light of the tricrystal ring experiments;<sup>3</sup> *this tunneling measurement consistently and convincingly displays the  $d$ -wave DOS.*

It is tempting to assert that it is the simple tetragonal structure of TI-2201 which is responsible for our observations. This structure allows a pure  $d$ -wave state with no admixture of  $s$ -wave components which might otherwise round out or distort the cusp feature in the DOS. Earlier tunneling studies<sup>14</sup> of TI-2212, which is also tetragonal, displayed many of the features found here for TI-2201 including flat or decreasing backgrounds and very sharp conductance peaks at nearly the same voltages,  $\sim 20$  mV.

This simple picture breaks down for the tetragonal compound Hg-1201 (Ref. 10) in which PCT indicated a more BCS-like shape to the tunneling data including a flat conductance near zero bias, and for Hg-1212 where in one case the STM spectroscopy showed a flat subgap conductance.<sup>11</sup> Other STM studies of the Hg-based cuprates revealed subgap

shapes which were more compatible with a  $d$ -wave DOS but no quantitative fits were obtained.<sup>25</sup> In one spectrum of Hg-1212 the zero-bias conductance is flat which is in clear disagreement with the cusp feature expected for a  $d$ -wave DOS.<sup>25</sup> We enumerate a few possibilities to explain these inconsistencies, but admit that a definitive explanation awaits further experiment. First is the possibility that despite their similarities, TI-2201 and Hg-1201 are not identical electronically. Band structure calculations show that Hg-1201 has a simple, single pocket to the Fermi surface,<sup>26</sup> whereas TI-2201 has two pockets owing to another metallic layer in addition to the Cu-O plane.<sup>27</sup> This allows the possibility for some type of interplane coupling in the TI-2201 unit cell which might favor a  $d$ -wave state or might provide characteristics which mimic such a state.<sup>28</sup> Certainly it would be useful for experimental probes such as angle-resolved photoemission to examine the electronic structures in both these compounds.

Another possible explanation has to do with directionality effects in tunneling. The reasonable fit of the TI-2201 data to the  $d$ -wave gap symmetry indicates that the entire Fermi surface is being probed as would be expected if all possible tunneling directions were contributing to the current. Such a situation could easily be imagined in our case if the tip indents the surface leading to a tunnel current which projects radially outward from the tip. a similar situation could also be true for a STM measurement where the tip is suspended above the cleaved crystal and the cone of tunnel current probes the whole Fermi surface. Certainly, STM results on Hg-based cuprates<sup>25</sup> and Bi-2212 (Refs. 6 and 9) more often exhibit subgap shapes which seem to be compatible with a  $d$ -wave gap symmetry. However, it is also possible in PCT to have preferential tunneling along a lobe of the  $d$ -wave gap that would result in a BCS-like tunneling DOS (Refs. 12 and 22) such as those seen by Chen *et al.*<sup>10</sup> Such a situation could explain the seemingly contradictory results on Hg-1201. A similar situation has also been observed in PCT spectroscopy of Bi-2212,<sup>9</sup> where it is possible to obtain a BCS-like subgap shape in the tunneling conductance. For Bi-2212 there is little question that the gap parameter is highly anisotropic and likely of  $d$ -wave symmetry.<sup>4,5</sup> Thus the observation of both flat and cusplike subgap shapes in different junctions (with the same gap value) is most likely due to tunneling directionality effects. The question remains as to why preferential tunneling might take place for PCT junctions on Hg-1201 and Bi-2212 but not for TI-2201. This might be related to material properties of TI-2201. The highly reproducible value for the gap ( $\Delta=20$ – $22$  meV) implies a very stable surface morphology and doping value. That this gap is slightly reduced from Raman measurements on optimally doped samples suggests that the stable surface is slightly overdoped. Further evidence of this is found in PCT studies of Bi-2212 which display a gap value of  $\Delta=37$  meV for  $T_c=95$  K samples, but rapidly decreasing values with overdoping.<sup>9</sup> The strong dip features of optimally doped Bi-2212 at  $eV=2\Delta$  are also diminished with overdoping<sup>9</sup> and this is consistent with the weak dip features found in TI-2201.

To summarize, PCT tunneling data on TI-2201 are highly reproducible and in many cases exhibit a normalized conductance that is well fit by a simple superconducting DOS with  $d$ -wave symmetry. The relatively flat background conductances show no indication of a van Hove singularity in the underlying electronic DOS and suggest that for this material

such band structure effects are not observed in tunneling. These PCT results are different from those found on Bi-2212, which exhibits a wide variety of subgap conductance shapes and more sharply decreasing background. The observation of flat, BCS-like tunneling conductances in Hg-1201 and in some cases Bi-2212 indicates that tunneling directionality effects play an important role in those materials but apparently not in Tl-2201. The gap values obtained in over 100 junctions are in the range  $\Delta=20\text{--}22$  meV, smaller than expected for a  $91\text{ K } T_c$  and may indicate that the surface is slightly overdoped.

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