Tunneling spectroscopy of Tl$_2$Ba$_2$CaCu$_2$O$_8$ single crystals and thin films

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(Dated: March 23, 2022)

PACS numbers: 74.50.+r 74.72.Jt 74.72.-h

Keywords: superconductivity, tunneling, superconducting gap, SIN, HTS, Tl-2212, TlBaCaCuO, thallium, cuprate

I. INTRODUCTION

Superconducting thallium-based cuprates were first made and studied by Sheng et al.$^{13,14}$ and Hazen et al.$^8$, followed by Ganguli et al.$^2$, Parkin et al.$^2$, Liang et al.$^2$, and Krantz et al.$^2$ shortly after the discovery of high-temperature superconductivity. The microscopic mechanism of superconductivity in cuprates is not agreed upon, but the macroscopic $d$-wave model$^9$ has been the most successful phenomenological one. While symmetry of the superconducting cuprates is different from conventional superconductors, still the maximal gap size $\Delta_{\text{max}}$ remains a key parameter of superconducting phenomena in cuprates. Continuing discussions are fueled by factors such as the quantitative differences between data measured on overdoped$^{11,12}$ and underdoped$^{12}$ cuprates, or by inconsistencies among superconducting parameters derived from data obtained by different techniques on nominally identical materials.$^{13,14}$ Our research presented in this article contributes to the resolution of inconsistency in superconducting gap parameters published to date on the Tl$_2$Ba$_2$CaCu$_2$O$_8$ cuprate (Tl-2212).

Electron tunneling techniques have proven to be important probes of electronic structure of superconductors. Most importantly, they provide a direct measure of the superconducting gap parameter, $\Delta$. Early electron tunneling studies by Takeuchi et al.$^{15}$ and Huang et al.$^{13}$ measured the Tl-2212 polycrystals and single crystals. Published values of $\Delta$ were $\sim 25$ meV and 16-28 meV, respectively. In the latter case, a majority of junctions exhibited $\Delta \sim 20$ meV, significantly smaller than expected based on the $T_c$. For example, optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) consistently exhibits $\Delta \approx 38$ meV for $T_c = 94$ K, as reported by Miyakawa et al.$^{18}$ The bulk $T_c$ of Tl-2212 films and crystals is typically above 100 K. Tunneling and Andreev reflection experiments on $c$-axis oriented Tl-2212 thin films$^{19,20,21,22}$ published more recently displayed gap sizes in the same range as in earlier reports, i.e. 20 and 25 meV. The early tunneling data can be characterized as showing smaller $\Delta$ than expected, large zero-bias conductance values (even above 50% of the “background”, i.e. the zero-bias normal state conductance extrapolated from high-bias voltage dependence of junction conductance) and poorly defined quasiparticle peaks. In contrast to the tunneling measurements, Raman scattering measurements on Tl-2212 single crystals by Kang et al.$^{18}$ gave $\Delta_{\text{max}} \sim 45$ meV. A more recent publication of Wang et al.$^{22}$ supported this result with data obtained by infrared spectroscopy of $c$-axis oriented thin film Tl-2212 samples. The published value was $\Delta_{\text{max}} \sim 43$ meV. Both groups considered the $d$-wave character of superconductivity in Tl-2212 to determine the gap size $\Delta_{\text{max}}$. A summary of all the values is given in Table I.

There is a large difference between Tl-2212 values obtained by bulk probes (Raman scattering, IR spectroscopy) and the surface probes (electron tunneling, Andreev reflection spectroscopy), which cannot be satisfactorily explained by the difference in the model used in data analysis. The possibility that the observed difference may be inherent in thallium-based superconductors owing to a significantly stronger chemical bonding between layers than Bi-2212 could be supported by the single-layered Tl-2201 data$^{22,23,24}$, where a similar in-
TABLE I: Overview of superconducting gap size and coupling strength values published previously, measured on thallium cuprates Tl-2201, Tl-2212, Tl-2223 and on bismuth cuprate Bi-2212.

| Material  | Reference | sample character   | experimental method | Tc (K) | ∆(meV) | $\frac{2\Delta}{k_B T_c}$ |
|-----------|-----------|--------------------|---------------------|--------|--------|--------------------------|
| Tl-2201   | 2         | single crystal     | PCT                 | 91     | 20 − 22| 5.1 − 5.6                |
|           | 26        | single crystal     | PCT                 | 86     | 19 − 25| 5.1 − 6.7                |
|           | 20        | single crystal     | PCT                 | 93     | 20     | 5.0                      |
|           | 21        | single crystal     | Raman               | 80     | 28 − 31| 8.0 − 9.0                |
|           | 27        | single crystal overdoped | Raman             | 85     | 22     | 6.0                      |
|           | 22        | single crystal doping varied | Raman        | 78     | 24     | 7.2                      |
|           | 28        | single crystal     | Raman               | 90     | 27 − 30| 7.0 − 7.8                |
|           | 29        | single crystal     | Raman               | 85     | 29     | 8.0                      |
|           | 30        | single crystal     | Raman               | 80     | 27     | 7.7                      |
| Tl-2212   | 13        | single crystal     | PCT                 | 112    | 16 − 28| 3.3 − 5.8                |
|           | 15        | polycrystal        | tunneling           | 94.5   | 25     | 6.1                      |
|           | 16        | thin film          | break junction tunneling | 91 | 25 | 6.3 |
|           | 17        | thin film          | Andreev reflections | 104    | 20     | 4.5                      |
|           | 18        | single crystal     | Raman               | 102    | 45     | 10.2                     |
|           | 14        | thin film          | IR response         | 108    | 43     | 9.2                      |
| Tl-2223   | 15        | polycrystal        | PCT                 | 114    | 25 − 35| 5.1 − 7.1                |
|           | 23        | polycrystal        | STS                 | —      | 20 − 24| —                        |
|           | 24        | single crystal     | Raman               | 118    | 38     | 7.4                      |
|           | 25        | thin film          | Raman               | 111    | 33     | 7.0                      |
| Bi-2212   | 12        | single crystal     | PCT                 | 95     | 30 − 40| 7.3 − 9.8                |
|           | 11        | single crystal     | PCT                 | 95     | 38     | 9.3                      |
|           | 31        | single crystal     | Raman               | 90     | 38     | 8.5                      |
|           | 32        | single crystal     | Raman               | 95     | 34     | 8.3                      |

*Abbreviations: Raman = Raman scattering, PCT = point contact tunneling, STS = scanning tunneling spectroscopy.*

consistency is observed. The suggestion fails, though, in case of the tri-layered Tl-2223, where results of surface and bulk probes are closer. Values published in references have been added to Table I.

Research of thallium-based cuprates has suffered from the poisonous quality of one of its base chemicals, the $\text{Tl}_2\text{O}_3$. Owing to this, larger part of the world-wide sample manufacturing efforts were focused on compounds safer to work with. Having reviewed the published electron tunneling data we believe that samples available for the experiments might have been of an insufficient crystalline quality (i.e. not single-phase crystals), not uniform oxygen doping or a combination of these, due to difficulties in the fabrication processes. Advances in the development of manufacturing procedures of thallium cuprate samples allow us to do tunneling measurements with the currently available high-quality Tl-2212 samples. Results of our point contact tunneling experi-
ments on one TI-2212 single crystal and two c-axis oriented thin-films are presented below.

The key results are the following. Junctions exhibit improved gap region characteristics including relatively low zero bias conductances and well-defined conductance peaks. The sub-gap region is consistent with a d-wave density of states. A majority of junctions display \( \Delta > 30 \text{ meV} \), higher than previous reports, and more consistent with bulk measurements. Finally, there is reproducible evidence of a spectral feature for \( eV > \Delta \) similar to the well known dip feature observed\(^{29}\) in Bi-2212.

II. SAMPLES AND INSTRUMENTATION

Single crystal samples were grown from a stoichiometric mixture of Ba\(_2\)CaCu\(_2\)O\(_x\) precursor and Ti\(_2\)O\(_3\). The precursor powder was mixed with Ti\(_2\)O\(_3\) powder and pressed into a pellet. The pellet was placed in an alumina crucible and covered with Al\(_2\)O\(_3\) lids to prevent the thallium vapors from escaping. The mixture was allowed to melt at high temperature in a furnace with steady O\(_2\) flow and then cooled down gradually. This procedure is described in detail in Ref. \(^{35}\). The resulting critical temperature of the single crystal was obtained as the onset temperature in bulk \( \rho(T) \) measurement, \( T_c = 103 \text{ K} \).

The epitaxial c-axis oriented thin films of thickness \( \sim 40 \text{ nm} \) were prepared using D.C. magnetron sputtering from a stoichiometric target on a LaAlO\(_3\) substrate, and post-deposition annealing. Details of the thin film growth are published elsewhere\(^{33-34}\). The thin film samples (TFa and TFb) investigated had \( T_c = 106 \text{ K} \) and 102 K, respectively, obtained by SQUID magnetometer.

Our point-contact tunneling system allows measurements of junctions within a large range (across \( \sim 10^2 \text{ K} \), respectively, obtained by SQUID magnetometer. Details of the thin film samples (TFa and TFb) investigated had \( T_c = 106 \text{ K} \) and 102 K, respectively, obtained by SQUID magnetometer.

Our point-contact tunneling system allows measurements of junctions within a large range (across \( \sim 8 \text{ orders of magnitude} \)) of normal-state junction resistances. A differential micrometer is used for fine approach of the tip and to create the point contact junctions. The junction areas are typically less than, or in the order of, \( 1 \mu \text{m}^2 \). Two electrical leads are connected to the sample using silver paint. Together with the tip they constitute a three-point measurement setup. Sample is affixed to a holder so that the gold tip approaches along the c-axis of the sample. Tips are mechanically sharpened and chemically cleaned (aqua regia etching) before every experimental run. Details of the point-contact tunneling measurement system were published in Ref. \(^{37}\).

All data presented and discussed in this article were measured using gold tips on samples at 4.2 K. To avoid interference of thermal contraction, the system was cooled down to LHe temperature with tip retracted. Junctions were created and measured after system reached thermal equilibrium. As the tip is moved towards the sample, the \( I(V) \) signal is monitored on an oscilloscope screen. The approach is stopped, when a characteristics of a superconducting tunnel junction appears on the oscilloscope screen. The point contact is open between every two junctions measured to inadvertent data duplicity. A lock-in technique is used for direct measurement of the differential conductance, \( G(V) = dI/dV \). Both \( I(V) \) and lock-in signals are recorded simultaneously in data files for later data processing.

The cuprates are known to have many stable phases and doping levels, and the superconducting parameters have been shown\(^{28}\) to vary along the cuprate surfaces at the nanometer length scale, even for very high quality samples. Local surface probes, such as the STM and PCT, are much more sensitive spread of quasiparticle gap sizes much larger than global probes. It has been stated earlier\(^{29}\) that the PCT method can produce a variety of junctions on a single sample. In PCT the tip can be used to scrape, clean, and in some cases cleave the surface of a sample. Cleaving of a superconductor may result in an attachment of superconducting particles to the metallic tip and creation of a homogeneous superconductor-insulator-superconductor (SIS) junction (see Ref. \(^{11}\), for example). Care needs to be taken to distinguish the types of junctions in order to interpret the superconducting gap features correctly. Additionally, the lack of control over the local properties of the sample surface and the junction atomic-level geometry leads to a varying quality of junctions. Association of many obtained characteristics with a simple enough model is then difficult, or worse, impossible. Therefore, data presented here are representatives of junction characteristics that exhibited superconducting gap features, which is not the whole set of characteristics obtained on our samples.

III. EXPERIMENTAL RESULTS

Figure 1 shows two differential conductance curves for each sample type, thin film and single crystal. All presented data was measured at 4.2 K using a lock-in amplifier and subsequent calibration with the numerical derivative of current-voltage characteristics. The data presented here constitutes a substantial improvement from previously published tunneling data on TI-2212 in all aspects. The quasiparticle peaks are very well defined, the zero-bias conductance is low, and the sub-gap regions of the conductance curves are in an excellent agreement with the d-wave model. Additionally, there is evidence of the same “dip” feature (indicated by arrows in Fig. 1) consistently observed in published Bi-2212 tunneling data\(^{39}\), which is evidence\(^{40}\) of strong electron coupling to a boson mode. We observe that the tunneling background has a strong asymmetric linear dependence \( \propto |V| \), is very reproducible and common to all presented data sets. As discussed in Ref. \(^{11}\), this linear dependence of tunneling background is likely due to an additional, inelastic tunneling channel in the junctions. This behavior is common for superconducting cuprates without an easy cleavage plane.

Because of the strong linear character of the background, direct normalization of the differential conduc-
FIG. 1: (Color online) Tunneling junctions data measured on Tl-2212 a) thin films and b) single crystal represented by red (grey) markers. Black arrows have been added at voltages of local minima corresponding to the spectral “dip” features. Horizontal scales of the top and bottom plots are the same.

FIG. 2: (Color online) Tunneling junctions data represented by red (grey) line with empty circle markers, as measured on Tl-2212 a) thin films and b) single crystal. The data is here overlaid with the $d$-wave model superconducting density of states, which is represented by black line with small dot markers. Parameters $\Delta_{\text{max}}$ and $\Gamma$ of the $d$-wave model curves are displayed in text boxes in upper right corners of the respective plot areas. Horizontal scales of the top and bottom plots are the same.

The same fitting as shown in Figure 2 was applied to all measured $dI/dV$ curves, which featured sharp quasiparticle peaks. There were 37 such junctions on thin film samples and 12 on the single crystal. Thus obtained $\Delta_{\text{max}}$ values are presented in histograms in Figure 3. The histograms show that $\Delta_{\text{max}}$ values consistently fall in ranges $\approx 25 - 50$ for thin films and $\approx 24 - 47$ for single crystals. More than 70% of the junctions exhibited $\Delta > 30$ meV. Variation of $\Delta$ throughout the measured set of tunneling junctions can be due to several reasons, intrinsic or extrinsic. In case of the intrinsic reasons we can point out the measurements of McElroy et al., who reported large doping variation along Bi-2212 cuprate surface. For the extrinsic causes of the spread of values we can mention the possibility of surface damage-induced change in oxygen doping. The spread in $\Delta_{\text{max}}$ not inconsistent with historical results of optical methods and there was little correlation between measurement conditions and the data taken. On one thin film sample, there seemed to be the tendency to measure smaller gaps at the beginning of the experiment and larger towards the end, suggesting the repeated contact of the tip was scraping through the surface. But this was not the case with other two Tl-2212 samples. This observation indicates that the influence of extrinsic doping changes is minor. We conclude that the spread of gap sizes is largely intrinsic to the samples. These ranges have been put together in the graphics in Figure 4 for comparison with the historical Tl-2212 values, which we already summarized in Table 1 in the Introduction.

To interpret the tunneling data correctly and to obtain the true $\Delta_{\text{max}}$, we had to make sure that the junctions included in the analysis had no other but SIN character. The alternative junction type, which has the same general features, is the SIS break junction. An incorrectly applied SIN model would result in $\sim 2 \times$ the actual $\Delta_{\text{max}}$. Observing that the historical inconsistency in the $\Delta_{\text{max}}$ values determined by bulk and surface probes is almost by a factor of 2, we consider this point worthy of special attention.

General features common to SIN and SIS tunneling characteristics of high-$T_c$ superconductors are existence of quasiparticle peaks, approximately cusp-like shape of
FIG. 3: (Color online) Histograms of $\Delta_{\text{max}}$ values of SIN junctions measured on Tl-2212. a) 37 SIN junctions on 2 thin film samples, and b) 12 junctions on 1 single crystal sample. Note that 70% junctions overall exhibited $\Delta_{\text{max}} \geq 30$ meV.

The widely recognized features distinguishing between SIN and SIS $d$-wave model characteristics are the detailed shape of sub-gap region, and higher (peak-to-background ratio) quasiparticle peaks of the SIN characteristics. There are other distinctive properties of experimental $dI/dV$ characteristics, which cannot be derived from the $s$-wave or $d$-wave models. Homogeneous SIN junctions have symmetrical characteristics, both in peak height and background shape. The strong asymmetry of tunneling background we observed is not consistent with SIN junction character, but SIN characteristics are often asymmetrical. Another distinguishing element is the position and magnitude of the “dip feature”, which has been consistently observed in Bi-2212 and is likely a result of strong electron-boson coupling in HTS. The dips are less pronounced in SIN curves, while positioned at $V_{SIN}^{\text{dip}} \approx 2\Delta_{\text{max}}/e$. In SIS characteristics, dips are symmetrical and sharper (these dips were observed to go negative in some SIS junctions on Bi-2212) and it is located at $V_{SIS}^{\text{dip}} \approx 3\Delta_{\text{max}}/e$ (see Ref. 40). The set of $dI/dV$ curves displayed in Figures 1 and 2 show that all conductance curves are asymmetrical to some degree. At the same time, the “dip” features accentuated in Figure 1 are present and located consistently at $V_{SIN}^{\text{dip}} \approx 1.8 - 2.3\Delta_{\text{max}}/e$. Finally, the sub-gap regions are consistently more alike the SIN model characteristics, rather than the SIS ones (for SIS model curves see for example Ref. 36). Using these attributes we were able to justify that all characteristics included in our analysis were of SIN type, and that superconducting gap parameters summarized in Figures 3 and 4 are correct.

IV. CONCLUSIONS

We have created and measured 49 high-quality SIN tunneling junctions on three different Tl-2212 cuprate samples, which exhibited $\Delta_{\text{max}}$ in the range 25–50 meV for c-axis oriented thin films and 24–47 meV for a single crystal. About 80% of all the $\Delta_{\text{max}}$ values were greater than 30 meV, which is in stark contrast with previous tunneling studies of Tl-2212 samples, where published $\Delta_{\text{max}}$ were all below 30 meV, most of them in the range 20–25 meV. These results are most likely a consequence of improved sample quality and homogene-
ity. The new $\Delta_{\text{max}}$ values were obtained from tunneling characteristics with sharp quasiparticle peaks, low zero-bias conductance, and an obviously $d$-wave character of the sub-gap region. There is a clear consistency between data measured on thin films and single crystals. Our results, including the spread of energy gaps $\Delta_{\text{max}}$ are in agreement with bulk measurements on Tl-2212 thin films and single crystals published in\textsuperscript{29} and\textsuperscript{34}. As there was no convincing correlation between the gaps sizes measured and experiment progress, we conclude that the spread of values is most likely due to a real spread of doping across the samples, while the influence of the measurement procedure on our result is minute. Additionally, the tunneling characteristics exhibit a high-bias ”dip” feature, which has been consistently observed in Bi-2212 and is likely a result of strong coupling of the superconducting electrons to a boson. It has been proposed that the dip in tunneling is linked to peak in optical self-energy\textsuperscript{40} in Bi-2212. Now a similar linkage is formed in Tl-2212, which also exhibits\textsuperscript{14} a peak in optical self-energy.

Acknowledgments

The first author would like to thank Dr. Lütfi Özyüzler for valuable advice and leadership. Dr. N. L. Wang acknowledges support from the National Science Foundation of China and the Ministry of Science and Technology of China (973 project No. 2006CB601002). The submitted manuscript has been authored by the UChicago Argonne, LLC, Operator of Argonne National Laboratory under the Contract No. DE-AC02-06CH11357 with the U.S. Department of Energy.
Technology \textbf{7}, 681 (1994).

Y. C. Ma and N. L. Wang, Physical Review B \textbf{72}, 104518 (2005).

P. Romano, L. Ozyuzer, Z. Yusof, C. Kurter, and J. F. Zasadzinski, Physical Review B \textbf{73}, 092514 (2006).

L. Ozyuzer, J. F. Zasadzinski, and K. E. Gray, Cryogenics \textbf{38}, 911 (1998).

K. McElroy, J.-H. Lee, J. A. Slezak, D.-H. Lee, H. Eisaki, S. Uchida, and J. C. Davis, Science \textbf{309}, 1048 (2005).

L. Ozyuzer, J. F. Zasadzinski, and N. Miyakawa, International Journal of Modern Physics B \textbf{13}, 3721 (1999).

J. F. Zasadzinski, L. Ozyuzer, L. Coffey, K. E. Gray, D. G. Hinks, and C. Kendziora, Physical Review Letters \textbf{96}, 017004 (2006).

J. F. Zasadzinski, in \textit{The Physics of Superconductors}, edited by K. H. Bennemann and J. B. Ketterson (Springer-Verlag, Berlin, Heidelberg, Germany, 2003), vol. I: Conventional and high-\textit{T_c} superconductors, chap. 8, pp. 591–646.