Tunneling STM/STS and break-junction spectroscopy of the Pb-doped Bi2223 superconductor

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Abstract. The combined scanning tunneling microscopy/spectroscopy (STM/STS) and the break-junction tunneling spectroscopy (BJTS) measurements of the three-layered Pb,Bi2Sr2CaCu2O10+δ cuprate superconductors were carried out. The averaged dI/dV spectrum obtained by the STS shows the gap δSTS ≈ 45 meV, while that of BJTS shows δBJ ≈ 35 meV. In case of the BJTS measurements, we also referred the zero bias (ZB) peak as being due to the maximum Josephson current IJc. The product of IJc and normal resistance RN (IJcRN) was obtained IJcRN ≈ 3.5 mV at T = 11 K, which is one order lower than that of the BCS-based Ambegaokar-Baratoff theory with δBJ =35 meV taken into account. With increasing the temperature, the IJcRN was reduced and vanished just below the Tc (≈ 106 K), indicating the bulk superconductivity. Simultaneously, from the temperature dependence of the gap features from 80 K to 120 K, the gap Δ was shown to persist across the Tc, indicating that the IJcRN product is a significant parameter for understanding the cuprate superconductivity.

1. Introduction

The character of the energy gap Δ in cuprate superconductors (SC) still remains an intriguing and important issue, even though many investigations have been done since its first observations. Among cuprate superconductors, the gaps of the Bi-based type one demonstrate relatively large gap-critical temperature (Tc) ratios 2Δ/kB Tc ≈ 10 as well as the nanoscale inhomogeneities [1-3], which are not seen in conventional superconductors. Furthermore, such gaps persist above Tc continuously merging into “pseudogaps” of the larger magnitude [4-6]. The temperature dependence of Δ is not completely correlated with Tc. Hence, it is very important to find out which parameter defines the Tc. The tunnel spectroscopy method is the powerful tool to observe the local density of state including the gap Δ coherent peaks. In addition, a junction of the superconductor–insulator–superconductor (SIS) type can detect the stationary Josephson current as a peak at the zero bias (ZB) energy. In the conventional SCs, the dI/dV curve (I and V are the tunnel current and voltage, respectively) for the appropriate barrier properties of SIS junctions leads to the sharp ZB Josephson-related peak, while, of course, the dI/dV for superconductor–insulator–normal metal (SIN) junctions do not. According to the well-known Ambegaokar and Baratoff (AB) relation [7], the Bardeen-Cooper-Schrieffer (BCS)-typed maximum Josephson tunnel current IJc is described as
\[ I_{Jc} = \frac{\pi \Delta(T)}{2eR_N} \tanh \frac{\Delta(T)}{2k_BT}. \]  

Here, the \( R_N \) and \( k_B \) is the normal resistance and Boltzmann constant, respectively. The parameter of “\( I_{Jc} R_N \)” product should be considered as one of the most important parameters characterizing Josephson junctions.

In this paper, we present the combined study of both the scanning tunneling microscopy/spectroscopy (STM/STS) and the break-junction tunneling spectroscopy (BJTS) measurements of the three-layer Pb doped \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y} \) (Bi2223) cuprate, that possesses the highest \( T_c \) among the Bi-based cuprates, focusing on the Josephson current and gap features around the critical temperature \( T_c \approx 106 \, \text{K} \). We also present the temperature dependence of \( I_{Jc} R_N \) parameter as the \( T_c \)-related property.

2. Experimental

The specimens of the tri-layered Pb doped Bi-cuprate superconductor \( \text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y} \) (PbBi2223, \( x=0.4 \)) were fabricated by a solid-state reaction technique. The details of the sample fabrications were described elsewhere [4]. Since the size of domain facet is about several tens of \( \mu \text{m} \), it is enough to carry out STM measurements by looking for suitable surfaces using the XY movable mechanism. The critical temperature was determined as the zero resistivity appearance as \( T_c \approx 106 \, \text{K} \).

The STM/STS apparatus used in this study is the commercially based system (Omicron LT-STM) with the above mentioned XY movement mechanism and upgrading modifications [8-9]. The high enough barrier height, \( \phi \approx 5 \, \text{eV} \), was found by measuring the dependence of tunneling current \( I \) on the tip-sample distance \( z \) (\( I-z \)-method) [10], indicating that the tunnel conditions were satisfactory to obtain the atomic resolution. The macroscopic tunneling measurements were done using the BJTS by a four-probe method. The BJTS were measured using an \( \text{ac} \) modulation technique with a lock-in amplifier. The \( I(V) \) curves were simultaneously obtained. By this method, fresh and clean SIS junction interface can be obtained along the crack of the micro-crystal [4].

![Figure 1](image)

**Figure 1.** (a) STM image of the cleaved PbBi2223 crystal \( (T = 4.9 \, \text{K}) \). (b) The averaged \( dI/dV \) spectrum obtained on the whole surface of the STS area. (c) The spatial gap distribution (\( \Delta \) map) at \( T = 4.9 \, \text{K} \).

3. Results and Discussion

Figure 1(a) shows an STM image of the typical surface on the cleaved PbBi2223 crystal at \( T = 4.9 \, \text{K} \). The atomic structures with the super-modulation of \( 4-5 \, \text{nm} \) were clearly observed. The basic lattice structure of Bi and Pb (brighter spots) sites had the period of \( \sim 0.36 \, \text{nm} \). These surface features obtained by STM measurements show good enough sample quality to apply the tunnel spectroscopy. The averaged \( dI/dV \) spectrum obtained on the whole surface at \( T = 4.9 \, \text{K} \) is shown in Fig. 1(b). The quasiparticle peaks of the gap are clearly observed. Because the STS measurements are dealing with
SIN junctions, the peak-to-peak voltage corresponds to $2\Delta/e$, where $e$ is elementary charge. The typical value of the gap is $2\Delta_{STS}/e = V_{pp} \approx 90$ mV. Fig. 1(c) shows the spatial gap distribution ($\Delta$ map) on the area of the sample, the latter taken from the same batch as that in Fig. 1(a). The magnitude of $\Delta$ is defined as the half peak-to-peak ($V_{pp}$) voltage difference as is indicated in Fig. 1(b) ($V_{pp} = 2\Delta/e$). The $\Delta$ map reveals the patchy inhomogeneity at the nanometer scale with the length scale of 3–5 nm with the standard deviation of $\sigma \sim 8$ meV. The details of these STS results were described elsewhere [3].

Generally, such gap peaks do not completely correlate with the bulk superconductivity, because those gaps do not vanish at the bulk $T_c$ in various cuprates [4-6]. In order to investigate the relation between STS gap features and bulk superconductivity, especially the ZB-peak features characterizing the Josephson current, the BJTS measurements of SIS junctions were carried out. In the BJTS experiment, the ZB peaks were not always observed due to unsatisfactory barrier properties. The result depends on whether its barrier condition is “leaky” or “capacitive”. The Josephson current was frequently observed on leaky junctions. However, in such junctions, the apparent gap signals were weak. We fabricated junctions where manifestations of both the gap coherent peaks and the ZB Josephson peak were found in the single $dI/dV(V)$ curve simultaneously. Such a typical BJTS $dI/dV(V)$ curve measured at $T = 11$ K is displayed as the red curve in Fig. 2(a). It is natural that for this SIS junction the peak to peak voltage $V_{pp}$ corresponds to $V_{pp} = 4\Delta/e$. The distance between gap peaks is $V_{pp} = 4\Delta_{BJ}/e \sim 140$ mV. Hence, the magnitude of the $\Delta_{BJ}$ is estimated as $\Delta_{BJ} \sim 35$ meV, which is smaller than that from the STS measurement: $\Delta_{STS} \sim 45$ meV. The discrepancy may be caused by the difference of the tunnel conditions. Indeed, in the STS case, tunneling was highly directional and occurred only along the $c$-axis direction, whereas in the BJTS case the tunnel currents between crystal fragments may flow along different crystal axes. Of course, the STS results may reflect the inhomogeneity effects. The latter may alter the BJTS results as well [11].

![Figure 2](image-url)
$R_N$ is 1 order lower than $(\pi/2)\Delta_{BJ} / e \sim 55$ mV obtained on the basis of the AB theory. We note that one order lower values were also found in the intrinsic Josephson junction (IJJ) experiments [12]. Those issues are touched upon below.

Figure 3. (a) Temperature evolution of the $dI/dV(V)$ curves obtained by the BJTS. (b) Temperature dependence of the characteristic voltages, $V_{pp}/4 \sim \Delta_{BJ}/e$ and $I_{Jc}R_N$ product from BJ $dI/dV(V)$ and $I(V)$ curves. The red dashed line show the theoretical curve based on Eq. (1).

To study the quantitative properties of both the Josephson current and the gap $\Delta$ near $T_c$, we carried out precise BJTS measurements in the temperature range $80 \, K < T < 120 \, K$. Figure 3(a) shows a temperature evolution of BJTS. As was found in our previous measurements and other reports [4-6], the gap features survived above $T_c$ and continuously merged into the pseudogap-related broad peaks. On the other hand, ZB peaks, which can be seen just below $T_c$, are completely smeared out at $T \approx T_c$. Figure 3(b) shows $T$ dependences of the characteristic BJTS properties, namely, the gap magnitude $V_{pp}/4 \sim \Delta_{BJ}/e$ and $I_{Jc}R_N$. The quantity $I_{Jc}R_N$ almost linearly decreases with $T$ and completely vanishes at $T_c \approx 106 \, K$, while the finite gaps exist both below and above $T_c$. The red-dashed line in Fig. 3(b) show the curve $I_{Jc}R_N(T)$ calculated according to the Eq. (1) with the values $\Delta_{BJ}(0) \approx 35$ meV and $T_c \approx 106 \, K$. As has been mentioned above, the measured $I_{Jc}R_N$ product is one-order lower than the theoretical value, whereas it completely disappears at $T_c$. It may mean that the actual gap is not linked to the superfluid density $\langle n_s \rangle$ calculated according to the basic BCS theory. Since the gap survives the superconducting transition, its origin might be partially due to some other reason than the Cooper pairing, e.g., charge density waves [6a]. We can also suggest that the unconventional electron pairing in the oxide, when Eq. (1) is no longer valid, might lead to some corrections. However, this factor does not seem to be decisive because the order-of-magnitude renormalization could not be obtained assuming, e.g., $d$-wave superconductivity. Thus, the discrepancy is too large to be fully interpreted taking into account only the two indicated reasons. The intrinsic sample inhomogeneity, revealed in Fig. 1(c), may be another factor to suppress the averaged superfluid density leaving the apparent (maximal) gap features almost intact. For instance,
the 6 % reduction of the Josephson current might be result of the effective 25% fraction of the superconducting phase in each part of the broken sample taking part in tunneling across the SIS junction (25% × 25% ≈ 6.3%).

The information contained in the T-dependent Josephson current (i.e., the ZB peak in the dI/dV curve) characterize superconductivity of the Bi-based cuprate more directly than the gap ∆, even determined in the precisely STS measurements. It must be noted that, ZB peaks in dI/dV spectra can be seen in the case of SIN junctions as well, being, e.g., the consequence of the Andreev-Saint James zero energy bound states for the non-conventional order parameter symmetry. It seems that here it is not the case.

4. Summary

The combined STM/STS and the BJTS measurements of the three-layered PB2223 cuprate were carried out. The averaged dI/dV spectrum obtained by the STS reveals the gap ∆_{STS} ≈ 45 meV, while that of the BJTS shows ∆_{BJ} ≈ 35 meV. The \(I, R_N\) product is about 3.5 mV at \(T = 11\) K according to the BJTS measurements, which is one-order lower than that given by the AB theory based on the s-wave BCS superconductivity. With increasing \(T\), the quantity \(I, R_N\) is reduced and vanishes below the \(T_c (≈ 106\) K), reflecting the bulk superconductivity, while the gap \(\Delta\) persists above \(T_c\). It means that the measurements of the \(I, R_N\) product give us a very important parameter to understand the cuprate superconductivity.

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References

[1] Lang K M, Madhavan V, Hoffman J E, Hudson E W, Eisaki H, Uchida S and Davis J C 2002 Nature(London) 415 412
[2] Sugimoto A, Kashiwaya S, Eisaki H, Kashiwaya H, Tsuchiura H, Tanaka Y, Fujita K and Uchida S 2006 Phys. Rev. B 74 094503
[3] Sugimoto A, Iwano M, Ishimitsu S, Ekino T and Gabovich A M 2020 Supercond. Sci. Technol. 33 095011
[4] Ekino T, Hashimoto S, Takasaki T and Fujii H 2001 Phys. Rev. B 64 092510
[5] Ekino T, Sezaki Y and Fujii H 1999 Phys. Rev. B 60 6916
[6] Matsuda A, Sugita S, Fujii T and Watanabe T 2001 J. Phys. Phys. Chem. 62 65
[7] Ambegaokar V and Baratoff A 1963 Phys. Rev. Lett. 10 486
[8] Ekino T, Takasaki T, Ribeiro R, Muranaka T and Akimitsu J 2007 J. Phys.:Conference Series 61 278
[9] Sugimoto A, Yanase Y, Ekino T, Muranaka T and Gabovich A M 2019 Low Temp. Phys. 45 1209
[10] Sugimoto A, Ekino T and Eisaki H 2008 J. Phys. Soc. Jpn. 77 043705
[11] Ekino T, Gabovich A M, Li M S, Szymczak H and Voitenko A I 2020 Low Temp. Phys. 46 400
[12] Suzuki M, Hamatani T, Anagawa K and Watanabe T 2012 Phys. Rev. B 85 214529