Different electronic states at crystallographically inequivalent CuO$_2$ planes on four-layered cuprates

HgBa$_2$Ca$_3$Cu$_4$O$_{10+\delta}$

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Abstract. We report tunneling conductances due to two kinds of crystallographically inequivalent CuO$_2$ planes on multi-layered cuprates Hg$_{0.95}$Ba$_2$Ca$_3$Cu$_4$O$_{10.05}$ (Hg1234) measured by a point-contact tunneling technique. One is an outer CuO$_2$ plane (OP) which has a pyramidal five-oxygen coordination, another is an inner CuO$_2$ plane (IP) which has a square four-oxygen coordination. These tunneling conductances exhibit two kinds of superconducting gaps $\Delta$ with clearly different sizes. That is, $\Delta$ on Hg1234 was 36 $\pm$ 2 meV and 55 $\pm$ 2 meV for OP and IP, respectively. Moreover, we report the correlation between the mode energy $\Omega$ and $\Delta$. The $\Omega/\Delta$ exhibits the common feature with other cuprates and does not exceed 2. This behaviour implies that the collective spin excitation is a candidate for the mediator on pair formation.

1. Introduction

High-$T_C$ cuprate superconductor has been over 30 years since its discovery, however mechanism for pair formation has not been elucidated yet, and therefore it is one of the challenging subject. Cuprates having three or more CuO$_2$ planes in a unit cell are called a multilayer cuprates (MLCs) and have two kinds of CuO$_2$ planes that are crystallographically inequivalent. In particular, the sufficient investigation for MLCs have not been collected since the complexity of crystal structure. Thus, it is one of the reasons why high-$T_C$ superconducting mechanisms remain unexplained. On the other hand, investigation for mono- or bilayered cuprates have been actively conducted. In particular, many common properties of cuprate superconductors have been revealed by spectroscopic studies such as point-contact/break-junction tunneling (PCT/BJT) [1, 2], scanning tunneling microscopy/spectroscopy (STM/STS) [3] and angle-resolved photoemission spectroscopy (ARPES) [4], since the electronic state can be observed directly. Specifically, for example on hole-doped cuprates, there is common understanding such as $d$-wave superconductor, bell-shaped superconducting phase diagram, and the decreasing of magnitude of the superconducting gap $\Delta$ with doping increasing.

As shown in Fig. 1, MLC such as Hg$_{0.95}$Ba$_2$Ca$_3$Cu$_4$O$_{10.05}$ (Hg1234) has two kinds of crystallographically inequivalent CuO$_2$ plane: an outer CuO$_2$ plane (OP) which has a pyramidal five-oxygen coordination, another is an inner CuO$_2$ plane (IP) which has a square four-oxygen coordination. Investigation for MLCs has been actively done in a few spectroscopic studies [5], and has been performed energetically in NMR [6, 7]. According to NMR results, the local carrier concentration at the OP is...
higher than that at the IP [6]. By combining NMR results with the doping dependence of the $\Delta$, it can be expected that $\Delta$s of different magnitudes will be observed in MLCs. However, in a spectroscopic experiment using a vacuum as a tunnel barrier, the information of the OP closest to the cleavage surface becomes the main and it is difficult to investigate the superconducting characteristics on the IP. On the other hand, the two kinds of superconducting gap originating at the OP and IP have been successfully observed by the PCT method by forming a direct junction to the OP and IP, as shown in the Fig. 1(b, c). Since the MLCs have CuO$_2$ planes (IP) distant from the charge supplying layer, there is a possibility that the nature of the essential superconducting CuO$_2$ surface can be clarified. Therefore, it is principal to investigate two kinds of CuO$_2$ planes of multi-layered cuprates. Hg-based cuprates are well known for having a flat CuO$_2$ plane and the higher $T_c$ among cuprate superconductors. Therefore, Hg1234 is one of the ideal material for the PCT method.

Despite numerous experimental studies, there is still no unified understanding for the mechanism of pair formation on cuprate superconductor [8]. As a probe to explore the mechanism of the pair formation, the dip structure observed outside the coherence peak of the tunneling conductance has been drawing attention. As one of the interpretation, the dip structure has been interpreted as a result of the contribution of bosonic excitations and has been reproduced by strong coupling analysis reflecting pairing interaction [1, 9, 10]. These result are consistent with the theory that the peak due to the mode energy $\Omega$ is located inside $2\Delta$ in the pairing function for the collective spin excitation model [11]. Furthermore, it has been found that the doping dependence of the $\Omega$ estimated from the dip structure coincides with the magnetic resonance mode energy observed in inelastic neutron scattering (INS) [1, 12]. Thus, the magnetic interaction has been interpreted one of the candidate playing a role of glue for the Cooper pair.

Figure 1. (a) Crystal structure for Hg1234. Hg1223 exhibits two kinds of CuO$_2$ plane [the inner plane (IP) with four-fold oxygen coordination and the outer plane (OP) with five-fold oxygen coordination]. (b, c) Schematic structure of SIN point contact tunneling junction at the OP (b) and IP (c) for Hg1234. (d-f) Characterization of Hg1234 sample. (d) X-ray diffraction measurement. Diamonds indicate unknown phase that is not cuprates with other layered. The lattice parameters of $a$ and $c$-axis are 3.854 Å and 19.043 Å, respectively. (e) Temperature dependence of DC resistivity and (f) magnetic susceptibility measurements. The $T_c$ for Hg1234 was determined as 127 K from both measurements.
2. Experimental details

The polycrystalline Hg1234 sample was synthesized under high pressure of 4.5 GPa at 850 °C for 1 h. The nominal composition of the sample corresponds to Hg0.95Ba2Ca_{3}Cu_{4}O_{10.05} (Hg1234). HgO, BaO, BaO_{2} and Ca_{2}Cu_{3}O_{5} was used as the source material. BaO was prepared by removing CO_{2} from BaCO_{3} with condition at 1025 °C for 24 h in vacuum of 1.2 × 10^{-4} Torr. BaO_{2} was prepared from the BaO at 600 °C for 24 h in O_{2} atmosphere. Ca_{2}Cu_{3}O_{5} was synthesized from CuO and CaCO_{3} whose mixture was heated at 950 °C for 20–40 h five times in air. It was confirmed that all precursors do not contain impurities by XRD measurement. The oxygen content of Hg1234 was adjusted by the ratio between BaO and BaO_{2}. MLCs such as four-layered Hg1234 are known to be easily mixed with superconducting impurities having different number of CuO_{2} planes in a unit cell. However, as shown in Fig. 1(d), we succeeded to synthesize the Hg1234 which does not have superconducting impurities such as three-layered and five-layered Hg-based cuprates. The lattice parameter of Hg1234 corresponds to \( a \sim 3.854 \text{ Å} \) and \( c \sim 19.043 \text{ Å} \), respectively. The \( T_{C} \) for Hg1234 was determined as 127 K by resistivity measurement [Fig. 1(e)] and magnetic susceptibility measurement [Fig. 1(f)]. The average doping level between IP and OP was estimated as \( p \sim 0.13 \) (under-doped region) by iodometry method.

Tunneling conductance by a superconductor-insulator-normal metal (SIN) junction have been measured by the PCT method using a Au tip. The insulating layer corresponds to blocking layers such as HgO, BaO and Ca. CuO_{2} planes are regarded as superconducting layer. Thus, the Au tip was gradually brought close to the sample surface, and the SIN junction was formed by using the block layer as the insulating layer. Figure 1(b, c) are the schematic illustrations for the two type of SIN junction. In the PCT measurement, we have reported that the electronic state at the OP and IP can be observed by forming a junction by contacting a tip on the sample surface. That is, in the case for Hg1234, as shown in Fig. 1(b), it is considered that the \( S_{(OP)} \)-I-N junction is formed by adopting the HgO and BaO layers as the insulating layer. On the other hand, as shown in Fig. 1(c), when the HgO layer supplying charge to CuO_{2} planes are scraped off by the Au-tip, it is considered that the OP cannot become the superconducting state due to the carrier deficiency. In such the situation, it is considered that the \( S_{(IP)} \)-I-N junction is formed by adopting the non-superconducting OP and Ca layer as the insulating layer. \( dI/dV \) s were measured by an ac lock-in technique at 4.2 K. The negative (positive) bias in the tunneling conductance corresponds to the occupied (unoccupied) state of superconductivity.

3. Results and discussion

Two kinds of the superconducting gap originating from the OP and IP for MLCs have been reported by our PCT method [19–24]. As shown in Fig. 2, two kinds of spectra with different gap magnitudes have also been observed non-selectively for Hg1234. Figure 2(a) shows the typical tunneling conductance on Hg1234. In the PCT measurement, the electronic state at the OP and IP can be observed by forming a junction by contacting a tip on the sample surface. The tunneling conductance for Hg1234 exhibits similar features to the monolayer cuprates Bi_{2}Sr_{2}Cu_{3}O_{8} (Bi2201) [25], Tl_{2}Ba_{2}CuO_{6} (Tl2201) [26] and the bilayer cuprates Bi_{2}Sr_{2}CaCu_{2}O_{y} (Bi2212) [27], TlBa_{2}CaCu_{2}O_{y} (Tl1212) [28]. That is the tunneling conductances exhibits not only the peak-dip-hump structure [as indicated by allows in Fig. 2(a)] but also the \( d \)-wave like shape sub-gap region. In Fig. 2(a), the upper curve corresponds to the tunneling conductance due to the electronic state at the OP and the lower curve corresponds to that at the IP, respectively. As shown in Fig. 2(a), the tunneling conductance at the OP exhibits sharp and high coherence peaks, and the dip structure (indicated by allows) was observed on both positive and negative bias sides. We note that the dip structure is clearly observed also on the positive bias side. On the other hand, the tunneling conductance at the IP is more asymmetric and exhibits the coherence peak broader
Figure 2. (a) Two kinds of the typical tunneling conductances originating from the OP (top) and IP (bottom) on Hg1234 at 4.2 K, respectively. Arrows indicate the dip structure. (b) Histogram of the superconducting gap magnitudes at 4.2 K on Hg1234. The superconducting gap \( \Delta \) was estimated as \( \Delta = e V_p \), where \( V_p \) is a differential voltage at the coherence peak of the tunneling conductance. Hg1234 exhibits two distinct distributions originating the OP and IP. The \( \Delta \) on Hg1234 was \( 36 \pm 2 \) meV at the OP and \( 55 \pm 2 \) meV at the IP, respectively. The green and blue curves are fitted with a Gaussian distribution.

and lower than that at the OP. Furthermore, the dip structure is observed more strongly at the negative bias side than at the positive bias side. Such features have been discussed in strong coupling analysis considering Van Hove singularity at the \( M \) point in the Brillouin zone [10, 29]. That is, the small coupling constant reproduces the coherence peak which becomes higher on the negative bias side. On the other hand, the large coupling constant reproduces that the coherence peak on the positive bias side becomes higher than that on the negative bias side.

As shown in Fig. 2(b), the histogram of the gap magnitudes on Hg1234 exhibits two distinct distributions. That is, it indicates that there are two kinds of gap due to different electronic states at the OP and IP, respectively. Based on the statistical distribution, the gap magnitudes of Hg1234 are determined \( 36 \pm 2 \) meV and \( 55 \pm 2 \) meV for the OP and the IP, respectively. The existence of two kinds of superconducting gaps has also been observed by the PCT method [19–24]. According to the NMR results, MLCs exhibit different local carrier concentration at the OP and IP, and \( p_{\text{OP}} \) is larger than \( p_{\text{IP}} \) [7]. On the other hand, as investigated in spectroscopic studies, it is well known that the gap magnitude decreases with hole concentration increasing [2–4]. These two experimental facts lead to a conclusion; the gap magnitude at the OP is smaller than that at the IP. Therefore, the tunneling conductance which exhibits the smaller (larger) gap magnitude reflects to the electric state at the OP (IP).

As another of the characteristic common features of tunneling spectra of cuprate superconductors, a dip structure has been observed outside the coherence peak of tunneling conductance. This structure has been interpreted as an effect by collective excitation mode by strong coupling theory [1, 10]. This feature has also been observed for MLCs [24]. As shown in Fig. 2(a), Hg1234 also exhibits the dip structure outside the coherence peak. According to the collective spin excitation model, the resonance peak at the mode energy in the paring function corresponds to the position of the dip minimum [10, 11]. Thus, we can estimate the mode energy from the dip structure as \( \Omega = e V_p - e V_{\text{dip}} \). The \( V_p \) and \( V_{\text{dip}} \) were estimated from the point that the second derivative of the tunneling current becomes zero at the peak and dip position, respectively.

We now discuss the correlation between mode energy and superconducting gap. Figure 3 exhibits the \( \Omega/\Delta \) estimated from the dip structure as function of \( \Delta \). As shown in Fig. 3, we compare \( \Omega/\Delta \) vs \( \Delta \) on Hg1234 with that on other materials such as Bi2212 [1], Bi_{2}Sr_{2}Ca_{2}Cu_{3}O_{y} (Bi2223) [10],...
Figure 3. Comparison of the $\Omega/\Delta$ vs $\Delta$ between Bi2212 [1], Bi2223 [10], TI1223 [24] and Hg1234. Squares are for Hg1234. Circles, diamonds and triangles represent results for Bi2212 [1], Bi2223 [10] and TI1223 [24], respectively. The shaded region is a guide to the eye.

TIBa$_2$Ca$_2$Cu$_3$O$_{y}$ (TI1223) [24]. Squares correspond to the average value of $\Omega/\Delta$ on Hg1234 containing error bars. The dataset on TI1223 includes values estimated at the OP and IP from the PCT results. As shown in Fig. 3, the $\Omega/\Delta$ vs $\Delta$ is in good agreement between the these cuprates despite the difference in the number of CuO$_2$ planes and the charge supplying layer. That is, the $\Omega$ correlates with the $\Delta$, indicating that $\Omega/\Delta$ increases with $\Delta$ decreasing, and its value is less than 2 for both IP and OP. Thus, this result is not inconsistent with the model that the excitation exhibits excitonic character. According to the result on Bi2212, it is concluded that this behavior is based on the spin resonance mode from the coincidence of the mode energy estimated from BJT [1] and that observed in INS [12]. Furthermore, these results are also consistent with the results on Bi2223 [10] and TI1223 [24]. Although, there has not been report of the spin resonance mode on Hg1234 in INS measurement, it will be consistent with the mode energy on Hg1234 reported by our PCT.

4. Conclusion
We have succeeded in observing the two kinds of the supeconducting gap originating from the different electronic states at the OP and IP on Hg1234. The tunneling conductance on Hg1234 exhibits the common features with mono- and bilayered cuprates such as $d$-wave like gap shape and the dip structure. The $\Delta$ on Hg1234 was 36 ± 2 meV at the OP and 55 ± 2 meV at the IP, respectively. In the analysis of the mode energy estimated from the dip structure, the $\Omega/\Delta$ increases with $\Delta$ decreasing but does not exceed 2. The $\Omega/\Delta$ vs $\Delta$ for Hg1234 is in good agreement with that for other cuprates such as Bi2212, Bi2223, and TI1223. This behavior is consistent with the model that the excitation exhibits excitonic character. Thus, this common feature implies that the collective spin excitation is a candidate for the mediator on pair formation for cuprate superconductors.

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