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Kyoto University
Interlayer tunneling spectroscopy for deeply underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$: Spectroscopic evidence for inhomogeneous superconductivity

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By using a small mesa structure and a short-pulse technique, we have measured the interlayer tunneling spectra of deeply underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with a $T_c$ of $\sim$40 K realized by partially substituting Sr with La. The superconducting peak observed at around 60 meV is extraordinarily small and broad, presenting a sharp contrast to the optimally doped or slightly overdoped case. The most striking feature is, however, that the tunneling conductance displays a stepwise incremental change as $T$ decreases across $T_c$ in the wide voltage range observed. This behavior indicates that the superconducting state in the deeply underdoped region is inhomogeneous and phase separated on a length scale of less than several tens of nm.

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I. INTRODUCTION

It is now well known that high-$T_c$ superconductivity occurs when charge carriers are doped into a parent Mott-insulating cuprate. In order to elucidate the mechanism of superconductivity in cuprates, it is important to understand how electronic states evolve with the carrier doping when the system changes from a Mott insulator to a superconductor. Recent research into the vicinity of the Mott insulating state has revealed anomalous electronic properties.$^{1,2}$ For example, an unexpected metallic behavior was observed in the in-plane resistivity $\rho_{ab}$ in lightly doped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) near room temperature, even though its magnitude is far greater than the Mott limit.$^3$ Besides, angle-resolved photoemission spectroscopy measurements for lightly doped LSCO have revealed Fermi arcs in the zone-diagonal directions in $k$ space,$^{2}$ which partially explains the metallic behavior observed near room temperature. These anomalous features are considered to reflect a stripe structure,$^3$ a topological inhomogeneity in the normal state. Associated with these results, we are extremely concerned with the possibility of inhomogeneous superconducting (SC) states for high-$T_c$ cuprates. It is, however, a very difficult challenge to confirm that the SC state is inhomogeneous on a fine scale because the superconductivity makes all the sample dimension meaningless due to the disappearance of resistivity. Nonetheless, it is possible if we employ a stack of intrinsic Josephson junctions (IJJ’s),$^4$ tunnel junctions built in a layered crystal structure itself. In this paper, we present evidence for the inhomogeneous SC state in a deeply underdoped (lightly doped) Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) system based on tunneling spectroscopic experiments.

As long as surfaces are concerned the topological inhomogeneity of the SC state can be probed by the scanning tunneling spectroscopy and scanning tunneling microscopy (STS-STM) technique. As for the bulk, it can be probed by interlayer tunneling spectroscopy (ITS). This technique utilizes naturally built tunnel Josephson junctions in a layered crystal structure and hence probes the bulk properties.$^5$ This can be contrasted with the STS-STM technique, which probes only into the surface. We have adopted the ITS technique to study the SC state of deeply underdoped Bi2212.

It is rather difficult to obtain deeply underdoped specimens from Bi2212 crystals solely by oxygen reduction. Therefore, we employed the La substitution method, by which deeply underdoped specimens with a $T_c$ as low as 30 K were obtained. We have measured the interlayer tunneling spectra for these samples and found a rather strikingly anomalous result that the tunneling conductance $dI/dV$ displays a stepwise incremental change as the temperature $T$ decreases across $T_c$ in the whole voltage range observed. This is anomalous since in the usual tunneling spectra an increase in $dI/dV$ is observed only near the SC gap voltage when the sample undergoes the SC transition. It is shown in this paper that this result implies that the SC state is inhomogeneous and nonsuperconducting (NSC) regions coexist in the CuO$_2$ planes.

II. EXPERIMENTS

The single crystals used for the ITS measurements were grown by the CuO self-flux method. The starting composition was Bi$_{2.95}$Sr$_{1.95}$La$_{0.05}$Ca$_{2}$Cu$_{2}$O$_{8+\delta}$ and the analytical composition of the crystals grown was Bi$_{2.0}$Sr$_{1.75}$La$_{0.3}$Ca$_{2}$Cu$_{2}$O$_{8+\delta}$ by energy-dispersive x-ray analysis. The discrepancy between the nominal and actual compositions is similar to the case of Y-substituted Bi2212 crystals.$^6$ X-ray diffraction analysis of a single crystal reinforced the absence of impurity phases. The $T_c$ dependence of the $ab$-plane resistivity $\rho_{ab}$ for these crystals showed a broad SC transition; in many cases, $\rho_{ab}$ started to drop rapidly at 90 K and the temperature at which $\rho_{ab}$ becomes zero ranged from 30 K to 80 K from crystal to crystal. However, for a number of small mesa samples fabricated from these crystals, a rather sharp resistive transition was observed at a $T_c$ ranging from 30 K to 90 K, which implies that a homogeneous underdoped region is eventually extracted on the scale of the mesa dimension of 10 $\mu$m.

Small and thin mesa structures were engraved on a cleaved crystal surface by the standard photolithograph and Ar-ion-milling technique. The thickness of a mesa is approximately 15 nm and the lateral dimensions are 10 $\times$ 10 $\mu$m$^2$ typically. After the Ar ion milling, a 350-nm-thick SiO$_2$ insulating layer was deposited by the self-alignment
method. A 350-nm Au upper electrode was finally deposited and patterned by the lift-off method. The schematic of a mesa structure is shown in the inset in Fig. 1. The \( c \)-axis resistivity \( \rho_c \) was determined from the mesa resistance \( R_c \) using the mesa dimensions. ITS measurements were carried out by the short-pulse method.\(^5\) Employing short pulses is requisite to reduce the self-heating effect sufficiently. The voltage values acquired were smoothed to give numerical differential \( dI/dV \)-\( V \) curves.

### III. RESULTS

#### A. \( c \)-axis resistivity \( \rho_c \): Zero-bias tunneling conductance

Figure 1 shows the \( \rho_c-T \) characteristics for three typical mesas (samples A–C) with different \( T_c \)'s fabricated from La-doped Bi2212 crystals. The semiconductive \( T \) dependence, which is due to the pseudogap development, is seen in the whole \( T \) range above \( T_c \). These samples exhibit a sharp resistive transition at 35 K, 44 K, and 52 K. The scatter of \( T_c \) values is probably caused by the variation of the amount of La substitution among these mesas. As for the doping level \( p \) for these samples, the parabolic formula \(^7\) \( T_c/T_{c\text{ max}} = 1 - 82.6 (p - 0.16)^2 \) is applied with \( T_{c\text{ max}} = 95 \) K to provide an estimate of \( p \) ranging from \( \sim 0.07 \) to \( \sim 0.09 \). The residual resistance seen below \( T_c \) represents the contact resistance \( R_{\text{cont}} \) between the upper electrode and the mesa structure. Since the influence of \( R_{\text{cont}} \) on the magnitude of the energy gap is estimated to be less than 10%, \( R_{\text{cont}} \) is neglected in the analysis which follows.\(^8\)

Figure 2 shows oscilloscope images of the current-voltage \( (I-V) \) characteristics at 7 K for the samples in Fig. 1. From these \( I-V \) characteristics, the maximum Josephson current densities \( J_c \) at 7 K for samples A, B, and C are evaluated to be 100 A/cm\(^2\), 240 A/cm\(^2\), and 300 A/cm\(^2\), respectively. These values are one order of magnitude smaller than that for an optimally doped sample. It is also seen that the maximum Josephson current tends to decrease as \( T_c \) decreases from sample C to sample A in the La-substituted Bi2212 system. This result is consistent with previous observations that \( J_c \) decreases with decreasing doping level in the Bi2212 system.\(^9\) All the samples show \( I-V \) curves with hysteretic branches; each branch corresponds to the voltage state of a constituent \( \text{IJJ} \) in the mesa. For each sample, the critical current magnitude and the voltage spacing for all the branches are almost the same, indicating uniformity of the junctions within a mesa. This rather homogeneous Josephson current together with its increase with increasing \( T_c \) reflects that the resistive SC transition observed is not caused by an accidental microshort. This is reinforced by the fact that these characteristics were observed reproducibly for different samples. This uniformity of the Josephson current for the constituent junctions is crucially important in relation to the inhomogeneity length scale, which is discussed later. The number of \( \text{IJJ} \)'s, \( N \), in each mesa is also found from these \( I-V \) characteristics to be \( N=8, 7, \) and 11 for samples A–C.

Figure 3 shows \( \rho_c-T \) characteristics under various magnetic fields parallel to the \( c \) axis for a mesa with almost the same \( T_c \) as that of sample B at a current density of 1 A/cm\(^2\). It is seen that the resistive transition exhibits a notable broad-
FIG. 3. $T$ dependence of $\rho_c$ for a La-substituted underdoped Bi2212 mesa in magnetic fields parallel to the $c$ axis at a current density of 1 A/cm$^2$.

FIG. 4. $I$-$V$ characteristics for sample $B$ measured by the short-pulse method at various temperatures. The abscissa scale represents the single junction voltage. (a) Above $T_c$, current decreases with decreasing $T$ due to the evolution of the pseudogap. (b) Below $T_c$, current increases with decreasing $T$.

B. Tunneling spectra

Figures 4(a) and 4(b) show the $I$-$V$ characteristics for sample $B$ measured by the 300-ns-time-scale short-pulse method at various temperatures above and below $T_c$, respectively. In this figure, the abscissa scale represents the single-junction voltage. Above $T_c$, the nonlinearity of the $I$-$V$ curve becomes gradually enhanced with decreasing $T$, reflecting the evolution of the pseudogap. Below $T_c$, on the other hand, it is seen in Fig. 4(b) that the quasiparticle current at a fixed $V$ increases with decreasing $T$ in the whole $V$ range observed. This behavior is clearly at variance with the usual behavior in which the current decreases below $T_c$ since the gap structure develops at low $T$ (Refs. 12 and 13).

Figure 5 shows $dI/dV$-$V$ curves numerically obtained from the data in Fig. 4 at various temperatures. The abscissa scale also indicates the single-junction voltage. In these tunneling spectra, a sharp SC peak is not seen even at low $T$ unlike the case for optimally doped or slightly overdoped samples; instead, a broad shoulder structure is seen at around 60 mV at 5 K. Since this structure diminishes as $T$ increases and disappears near $T_c$, it is accepted that this shoulder structure reflects the SC peak of $2\Delta \sim 60$ meV. The $V$-shaped background structure represents the pseudogap. If the pseudogap peak is located outside the range observed, the pseudogap magnitude defined as half the peak separation is much greater than 280 meV. This result clearly excludes the possibility that the pseudogap is a precursor of the SC gap. This feature presents a sharp contrast to those observed in the Bi2212 system near the optimal doping level. Moreover, the zero-bias conductance of about 0.01 S seems to decrease very little or remains almost unchanged when $T$ falls even below $T_c$. This value is about 20% of the normal-state conductance at 240 K. When we take into account that we are dealing with IJJ’s in single crystals, it is difficult to ascribe the undiminished zero-bias conductance to imperfections involved in junctions. Rather, it is very likely that these characteristics are attributable to the nature intrinsic to deeply underdoped crystals.

Furthermore, the tunneling characteristics in Fig. 5 display a totally unknown behavior in that $dI/dV$ increases significantly with decreasing $T$ in an extended $V$ range. Figure 5(c) shows the $T$ dependence of $dI/dV$ at $V=100$ mV and 200 mV, representing a stepwise increase below $T_c$. These features observed for deeply underdoped mesas are difficult to understand in terms of a homogeneous tunnel Josephson junction and homogeneous superconductivity in CuO$_2$ planes.

Figure 6 shows a set of $dI/dV$-$V$ curves for sample $C$ whose $T_c$ of 52 K is higher than sample $B$ by 8 K. As shown...
in this figure, it is a common behavior for the La-substituted deeply underdoped Bi$_{2212}$ samples that $dI/dV$ increases significantly with decreasing $T$ in an extended $V$ range. Compared with the characteristics in Fig. 5(a), a small SC peak rather than a shoulder structure is seen at around 64 mV in the curves at 5 K and 20 K. This peak is clearly the SC peak and the SC gap magnitude determined from the peak position is 64 meV, which is larger than that of sample $B$ by $\sim4$ meV. Contrary to the optimally doped or slightly overdoped case, the SC gap magnitude appears to remain almost constant as $T$ increases from 5 K to 20 K. Above 20 K, the peak structure is totally absent.

Figures 7 and 8 show the $dI/dV$-$V$ curves under various magnetic fields $B$ and at various temperatures for sample $B$ and $C$, respectively. In Figs. 7(d) and 8(d), it is clearly seen that the background pseudogap structure is independent of $B$ for $B \leq 9$ T above $T_c$. The same behavior was seen at different temperatures above $T_c$. Therefore, we can conclude that the change brought about by applied magnetic fields in Figs. 7 and 8 is caused by the suppression of superconductivity. In Figs. 7(a) and 8(a), it is seen that the shoulder and a small peak structure gradually diminish with increasing $B$, suggesting again that these structures result from the SC peak. On the other hand, $dI/dV$ at $V=0$, the zero-bias conductance, does not change appreciably with increasing $B$ up to 9 T. This implies that there is no magnetic-field-induced density

**FIG. 5.** $dI/dV$-$V$ curves (a) below $T_c$ and (b) above $T_c$ obtained numerically from the data in Fig. 4 at various temperatures. The dashed lines indicate the curves close to $T_c$. In contrast to an optimally doped or overdoped case, a sharp SC peak is absent even at low $T$. (c) The $T$ dependence of the $dI/dV$ value at $V=100$ mV and 200 mV. The lines are guide to the eyes.

**FIG. 6.** $dI/dV$-$V$ curves for sample $C$ at various temperatures below $T_c$. In contrast to sample $B$, a small SC peak is observed at low $T$.

**FIG. 7.** $dI/dV$-$V$ curves for sample $B$ in the presence of different magnetic fields parallel to the $c$ axis at various temperatures. It is seen in (d) that the background pseudogap structure is independent of $B$ for $B \leq 9$ T. In (a)–(c), a significant $B$ dependence is clearly seen, presenting a sharp contrast to the overdoped case.
The stepwise increase in the $dl/dV$ magnitude below $T_c$ is the unique consequence of the inhomogeneous SC state in the CuO$_2$ layers. Since it is obvious that the DOS transfer associated with the SC transition is not conserved as seen in Figs. 5 and 6, the stepwise increase in $dl/dV$ by no means reflects an increase in the quasiparticle DOS. It is attributable to inhomogeneous transport on a fine scale. When the SC state is inhomogeneous and NSC regions coexist in the CuO$_2$ planes, the local $c$-axis interlayer tunneling conductivity $\sigma_t$ varies spatially and from layer to layer. In this case, the tunneling current in the $c$-axis direction is no longer uniform on a fine scale within the CuO$_2$ plane. When the doping level decreases and $\sigma_t$ varies significantly in the $c$-axis direction, the current is forced to have lateral components to fulfill the continuity condition; i.e., the total current is forced to have lateral components that flow within the CuO$_2$ planes. The lateral current fraction is considered to increase as the fraction of the NSC region increases—i.e., as the doping level decreases profoundly. In the normal state, the current in the lateral direction is dissipative, whereas in the SC state, it flows with no dissipation. Therefore, in the normal state, the voltage drop arises both from the interlayer tunneling and from the dissipation in the CuO$_2$ planes, while in the SC state, most of it arises from the interlayer tunneling. Then, at a constant current, the voltage drop decreases below $T_c$, exhibiting a stepwise increase in $dl/dV$. Therefore, a stepwise incremental change in $dl/dV$ below $T_c$ is the consequence of the inhomogeneous superconductivity, and the data in Figs. 5–8 provide its evidence.

To confirm the above-mentioned scenario semiquantitatively, we have calculated $dl/dV$ curve based on a simple model in which the lateral current component is represented by an in-plane resistance connected in series with a tunnel junction. In this model, the measured voltage is expressed as follows:

$$V = V_l(I) + R_{ab}(I)I,$$

(1)

where $V_l(I)$ is the real $I$-$V$ characteristics for a tunnel junction and $R_{ab}(I)$ is the $I$ dependent effective in-plane resistance. Here we assume for simplicity that $V_l(I)$ is independent of $T$ below $T_c$, which seems reasonable since $dl/dV$ is almost $T$ independent for $T_c < T < 80$ K as seen in Fig. 5(b). We assume further that $R_{ab}(I)=R_0$ at 45 K, where $R_0$ is a constant, and that $R_{ab}(I)=\alpha |I| - I_c$ at 5 K, where $I_c$ is the critical current. The $V_l(I)$ curve is obtained using the experimental $I$-$V$ curve together with Eq. (1) and then the $I$-$V$ curve at a lower $T$ is calculated using $R_{ab}(I)$ at 5 K. Figure 9 shows a fit (dashed line) to the experimental $dl/dV$ curve at 5 K for sample B together with the experimental data at 45 K. In the calculation, values of $R_0=43 \Omega$, $I_c=3.5$ mA, and $\alpha = 1.012 \Omega/mA$ were used. It is clearly seen that the calculated curve compares with the experimental result pretty well for $V > 100$ mV. The deviation for $V < 100$ mV results from the evolution of the SC gap. Thus the experimental results are explained semiquantitatively in terms of the lateral current component model. Thus, it follows that the results in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Sample_C.png}
\caption{$dl/dV$-V curves for sample C in the presence of different magnetic fields parallel to the c axis at various temperatures. The $B$ dependence is similar to that for sample B.}
\end{figure}

IV. DISCUSSION

It is found that the present ITS results are difficult to explain in terms of tunneling between homogeneous superconductors. We show in the following that they are explicable when the superconductivity is inhomogeneous and that the SC state in the deeply underdoped La-substituted Bi2212 system is essentially inhomogeneous as a bulk nature.

When the superconductivity is inhomogeneous and the SC and NSC regions coexist in CuO$_2$ planes, there is additional quasiparticle current in the voltage-state IJJ’s at low $T$ by the tunneling between NSC regions and between SC and NSC regions in CuO$_2$ planes. In this case, the tunneling involving the NSC regions is thought to reflect the background pseudogap structure. Such tunneling might be compared with the local DOS at the vortex center observed by STM. As a matter of course, the tunneling spectra involving the NSC regions lack the SC peak. Therefore, when the fraction of the NSC regions increases, the SC peak becomes extraordinarily small, as seen in Figs. 5(a) and 6. The difference in $T_c$, $J_c$, and the SC peak between sample B and C is probably caused by the difference in the area of SC region.

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Figs. 5–8 provide evidence for the inhomogeneous SC state in the La-substituted deeply underdoped Bi2212 system. The significant resistive transition broadening shown in Fig. 3 is also reasonably explicable in terms of the inhomogeneous superconductivity in CuO2 layers. When the magnetic fields are applied parallel to the c axis, most of the vortices are considered to reside in the NSC regions. In this case, the vortex structure favors a liquid state in which the vortex core is a random distribution of two kinds of typically different regions. If we regard these regions as the SC and NSC regions, then in the SC regions the peak is broad and the gap magnitude is large, reflecting the pseudogap, while in the SC region the conductance peak is sharp, reflecting the SC gap, and its width becomes comparable to the size of the SC regions in the present model is larger than that of less than 9 T to make the electrical transport as dissipative as in the normal state. Such an abrupt decrease in the melting point of the vortex solid is likely to occur when the SC state is inhomogeneous and the length scale of the SC regions is much smaller than the penetration depth of $\lambda \sim 200 \text{ nm.}$

The data in Figs. 3–8 and the model calculation results imply that the inhomogeneous superconductivity is a bulk nature of underdoped cuprates. There are many possible explanations for the origin of this inhomogeneity. One explanation is that the inhomogeneous SC state is a consequence of essential electronic phase separation in the underdoped region. This phase separation can be induced by a conflict between the itinerancy of the carriers and the magnetic ordering in a correlated system. The present experimental results are important in that various models are proposed theoretically for such inhomogeneity in relation to the occurrence of high-$T_c$ superconductivity.

The other explanation invokes microscopic chemical compositional inhomogeneity. If the La substitution causes a change in the electronic states in that local region, the inhomogeneous superconductivity can be induced. In this case, it is required that the inhomogeneous scale for a single region be less than several tens of nm, as inferred above. The change in the electronic states is considered to be brought about via a lattice deformation or local inhomogeneous charge distribution caused by La substitution in the SrO-BiO block layers. These two factors appear to be involved also in substituted oxygen-reduced underdoped samples. Therefore, it is unlikely that the inhomogeneous superconductivity is solely brought about by the La substitution but it is rather essential in underdoped Bi2212 irrespective of the method of doping, though the doping is always accomplished by chemical doping.

Finally, we note that the present results are consistent with our previous report that $J_c$ decreases while $\Delta$ increases in the underdoped region and with a recent STS surface observation of underdoped Bi2212. The latter revealed a granular distribution of two kinds of typically different regions. If we regard these regions as the SC and NSC regions, then in the NSC region, the peak is broad and the gap magnitude is large, reflecting the pseudogap, while in the SC region the conductance peak is sharp, reflecting the SC gap, and its magnitude $\Delta$ is 30 meV. This value is consistent with the shoulder structure at around 60 meV in Figs. 5 and 6. The size of the SC regions in the present model is larger than that of the STS results by an order of magnitude. This difference probably comes from the simpleness of the present model.
V. CONCLUSION

We have measured the interlayer tunneling spectra of deeply underdoped Bi2212 by partially substituting Sr with La. In the tunneling spectra of deeply underdoped Bi2212, the sharp superconducting peak is absent even at low T. Instead only a shoulder structure or a small peak is found at around 60 meV, which is consistent with the STS result. It is also found that the T dependence of the dI/dV-V curve shows a characteristic shift below Tc. All these features strongly suggest that the superconductivity in underdoped cuprates is essentially inhomogeneous as a bulk nature.

Acknowledgments

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\[ \text{REFERENCES} \]

8. I-V characteristics of R_{cont} is nonlinear like I \propto V^n so that R_{cont} \propto I^{-1+1/n} becomes rather small at higher currents. Moreover, the voltage drop due to the contact resistance is divided by the number of layers. Therefore, the tunneling characteristics for I > ~10 mA are subjected to little influence of the contact resistance, and hence so is the gap magnitude.
14. A large zero-bias conductance would usually imply a leaky tunnel junction. In the present case, however, it is difficult to attribute this leakage behavior to some defect structures in the tunnel junctions since they are atomically flat intrinsic tunnel junctions built in a crystal structure. Such characteristics are not seen in mesas fabricated from optimally or overdoped crystals.