

STM STUDY OF THE ELECTRONIC DENSITY OF STATES IN THE SUPERCONDUCTING PHASE OF BizSrzCaCuzOs

Koichi Ichimura and Kazushige Nomura

Department of Physics, Hokkaido University, Sapporo 060, Japan

Fujio Minami

Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

Shunji Takekawa

National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

(Received 18 January 1992 by H. Kamimura)

Tunneling spectroscopic measurement was carried out in the superconducting phase of Bi₂Sr₂CaCu₂O₈ with use of a low temperature scanning tunneling microscope. Both the cleaved Bi-O surface and the lateral surface of a single crystal were investigated. The tunneling conductance shows an explicit superconducting gap structure at both surfaces. For the lateral surface the conductance curve is independent of the tip distance from the sample surface and gives directly the electronic density of states in the superconducting phase. The obtained gap structure is in good agreement with the BCS prediction. although it seems that the gap is slightly anisotropic. The obtained gap-ratio $2\Delta/k_BT_c=6.1$ indicates the strong-coupling nature of this superconductor. For the Bi-O surface, on the other hand, the normalized differential conductance increases with increasing the tip distance, especially at the outside of the superconducting gap as reported by Hasegawa et al. Such a dependence on the tip distance is attributed to series barriers of Bi-O, Sr-O layers and vacuum for the tunneling between the Cu-O layer and the tip metal.

In cuprate superconductors, it has been well recognized that the Cu-O plane plays an important role for the appearance of the superconductivity. Accordingly, the investigation of the electronic state of the Cu-O plane in superconducting phase gives a key to elucidate the mechanism of high-Tc superconductivity. Various tunneling spectroscopic measurements have been done [1-4] up to the present, in order to study the electronic density of states in the superconducting phase. However, these results are not consistent with each other and even values for the gap parameter show a significant scatter. Among several tunneling spectroscopic methods, the STM (Scanning Tunneling Microscopy) is the most appropriate probe for investigation of electronic properties at the surface, because the non-contacting configuration assures the least disturbance of the electronic state of the sample. In the previous STM measurement [5], we obtained the gap value Δ =22-30 meV, which shows a spatial variation, and correspondingly $2\Delta/k_{B}T_{c}{=}6{-}8$ for Bi₂Sr₂CaCu₂O₈, which suggests that it is the strong-coupling superconductor.

Recently Hasegawa *et al.* have reported [6] that the tunneling conductance (G=dI/dV) curve observed by STM is dependent on the tip distance from the sample surface. They argued

that such a behavior of the G-V curve makes the interpretation of tunneling data complicated and the absolute value of the gap cannot be determined uniquely. In order to make clear the mechanism of the dependence of the G-V curve on the tip distance and investigate the electronic state unambiguously, we performed the spectroscopic measurement not only at the cleaved Bi-O surface but also at the lateral surface of a single crystal of Bi₂Sr₂CaCu₂O₆ with STM.

The most important result is that the G-V curve obtained at the lateral surface is independent of the tip distance and gives directly the electronic density of states in the superconducting phase. For the tunneling at the Bi-O surface, we confirmed [7] the tip distance-dependent G-V curve similar to that observed by Hasegawa *et al.* [6].

The STM method, which avoids a direct contact between the sample and the counterelectrode (tip), enables us to investigate the local density of states on an atomic scale at the surface without modifying the physical properties of the sample. The tunneling current I is simply given as a function of the distance between the tip and the sample surface d as,

$$I = I_o(V) \exp[-d/d_o], \qquad (1)$$

where $I_o(V)$ is the characteristic current determined by the bias voltage V applied between the tip and the sample, and the length d_o characterizes the extension of electronic wave functions. One can therefore control the tip distance by keeping the tunneling current constant for a constant bias voltage; with increasing the tunneling current, the tip distance becomes small. Such a possibility of varying the tunneling resistance at the same position of the sample surface is one of advantages of the STM method.

According to the simple tunneling theory, the characteristic current $I_o(V)$ in Eq. (1) is given as a function of the bias voltage V between the tip and the sample, as

$$I_{\circ}(V) \propto |M|^{2} \int_{-\infty}^{\infty} (E) N_{*}(E + eV) \{f(E) - f(E + eV)\} dE, \quad (2)$$

where N, and N_o are the electronic densities of states for the tip metal and the sample, respectively, and |M| denotes the tunneling matrix element which is assumed to be independent of E. If N₁ is constant with respect to E, we obtain the well-known equation for absolute zero temperature as

$$dI/dV \propto N_s(eV)$$
. (3)

Since in the STM method the electron tunneling occurs at a restricted area which contains at most a few atoms near the tip, one can study the local density of states of the sample surface with varying the tip position with use of STM.

Single crystals of Bi₂Sr₂CaCu₂O₈ were synthesized by the floating-zone method. Many single crystals were grown sticking together. After separating them, most crystals showed cleaved surfaces along the Bi-O layer (the a-b plane) and rough side surfaces. In rare cases, the extremely clean lateral surface appeared, however. This surface is parallel to the a-axis and oblique in the direction of the b-axis. This lateral surface looks slightly rough and grey under a optical microscope, while the cleaved Bi-O surface is finely flat and shiny. Yamanaka et al. [8] succeeded to obtain the (ZZ) Raman spectra at this lateral surface and confirmed little surface disorder. The typical dimension of such a clean lateral surface area is 0.2×0.2 mm². We investigated both the cleaved Bi-O and the extremely clean lateral surface with STM immediately after obtaining the surface. The superconducting transition temperature T_c was determined as T_c=87 K from the midpoint of the resistive transition after the STM measurement.

Details of our low temperature STM apparatus were described in our previous article [9]. A mechanically sharpened thin wire of Pt is used as the scanning tip, the density of states of which is known to vary slowly near the Fermi level. The sharpness of the tip was tested by taking an STM image of graphite surface at room temperature.

The distance between the tip and the sample surface was adjusted by making the tunneling current I_o constant for a constant bias voltage V_o with use of the electronic feedback circuit prior to the voltage sweep in the spectroscopic



Figure 1. Differential tunneling conductance obtained at the cleaved Bi-O surface at various tip distances. The tip distance is denoted by I_o as described in the text. Curves for $I_o=3$, 6, 8 and 10 nA at $V_o=150$ mV are shown together, normalized at 30 mV. The dotted curve represents the fit of the curve at $I_o=10$ nA to eq. (4) with fitting parameters $\Delta=29$ meV and $\Gamma=5$ meV.

measurement. During the voltage sweep, the tip distance was kept constant by turning the feedback circuit to the hold mode. The tunneling bias voltage was swept in the form of a 15-30 sec triangular wave. AC (0.5-1 kHz) modulation of small amplitude (0.5 mV peak to peak) was superimposed to the sweep voltage for the differential detection. The differential conductance was directly obtained as a function of the bias voltage with use of a lock-in amplifier.

Figure 1 shows G-V curves obtained at a fixed position of the cleaved Bi-O surface at 4.2 K [7]. We obtained essentially the identical curve at different positions of the same surface with varying the tip position as reported previously [5]. The tip distance is denoted by the initial tunneling current $I_0=3$, 6, 8 and 10 nA at the constant bias voltage $V_o=150$ mV, which is far larger than the superconducting energy gap. With increasing Io, the tip distance is reduced as described above. Each curve is normalized at V=30 mV. The dotted curve in the figure is a fit of the curve of $I_o=10$ nA to the broadened BCS density of states with the gap parameter Δ =29 meV and the quasiparticle lifetime broadening parameter Γ =5 meV described as [10],

$$N_{s}(E) = \operatorname{Re} \left(\frac{E - i\Gamma}{\{(E - i\Gamma)^{2} - \Delta^{2}\}^{1/2}} \right) N_{N}, \quad (4)$$

where N_N is the density of states in the normal state and is supposed to be almost constant near the Fermi level. In each G-V curve the sharp drop of conductance is found and the differential conductance is reduced to almost zero around zero bias voltage; the

superconducting energy gap structure is clearly revealed in these curves.

In the curve at $I_0=10$ nA, for which the tip distance is the smallest in the present experiment, the essential feature of the BCS density of states is reproduced as shown in Fig. 1. With increasing the tip distance the normalized differential conductance outside the gap is strongly enhanced and has a positive slope of dG/d|V|. The slope becomes steeper with increasing the tip distance. On the other hand, the G-V curve is insensitive to the tip distance at the midgap region.

Figure 2 shows G-V curves obtained at a fixed position of the extremely clean lateral surface. We investigated the G-V curve at different positions with varying the tip position, but we could not find any spatial variation of the G-V curve on an atomic scale. We obtained essentially the identical curves in every measured position, as in the case of the Bi-O surface. In Fig. 2, four curves for different tip distances, corresponding to the initial current $I_{0}{=}2,\;4,\;8$ and 20 nA at $V_{0}{=}200$ mV, are shown together. They are normalized at V=25 mV. We find that the normalized G-V curve is independent of the tip distance at the entire region of voltage shown in Fig. 1, in contrast with the case of the Bi-O surface. The dotted curve is a fit of the curve at $I_0=2$ nA to Eq. (4) with fitting parameters Δ =23 meV and Γ =3 meV. The shape of these G-V curves measured at the lateral surface is similar to that at I_{o} =10 nA at the cleaved Bi-O surface shown in Fig. 1. As shown in Fig. 2, the differential conductance is again reduced to almost zero around zero bias voltage and the G-V curve is almost flat at far outside of the gap.

We could observe the superconducting gap



Figure 2. Differential tunneling conductance obtained at the lateral surface at various tip distances. Curves for $I_0=2$, 4, 8 and 20 nA at $V_0=200$ mV are shown together, normalized at 25 mV. The dotted curve represents the fit of the curve at $I_0=2$ nA to eq. (4) with fitting parameters $\Delta=23$ meV and $\Gamma=3$ meV.

structure at both the cleaved Bi-O and the lateral surfaces. The dependence of G-V curve on the tip distance is however very different between these two cases. For a test of our apparatus we measured the tip distancedependent G-V curve for a typical conventional superconductor, lead with AC modulation of 50 μV peak to peak. We obtained the G-V curve independent of the tip distance at the surface of bulk poly-crystalline lead. Figure 3 shows a typical G-V curve measured at 4.2 K at the tip distance for the initial current Io=15 nA at V_{o} =20 mV. Although the differential conductance near zero bias voltage is slightly enhanced from the BCS, the G-V curve is clearly BCS like. We confirmed that the differential conductance gives the electronic density of states of the sample directly, irrespective of the tip distance; we have proven the reliability of our apparatus.

The tip distance dependent G-V curves shown in Fig. 1 suggest that in the tunneling at the Bi-O surface the tunneling matrix element |M|in Eq. (2) depends on the energy except for the low bias voltage region ($|eV|<\Delta$), where the normalized G-V curve is almost independent of the tip distance. The energy dependence of the tunneling matrix element appears to become stronger with increasing the tip distance. The differential conductance is no longer proportional to the electronic density of states of the sample for the tunneling at the Bi-O surface. One must therefore discuss the tunneling result at the Bi-O surface with great care, as pointed out by Hasegawa *et al.* [6].

The transmission coefficient for the electron tunneling was calculated for various interface barrier height [11] for the normal metal-superconductor tunneling. The G-V curve is dependent on the barrier height especially at the midgap region; the midgap conductance is



Figure 3. Differential tunneling conductance obtained at the surface of bulk lead at 4.2 K. The tip distance corresponds to the initial current $I_0=15$ nA at $V_0=20$ mV. The gap parameter is determined as $\Delta=1.3$ meV.

increased with decreasing the barrier height. The tip distance-dependent G-V curve observed at the Bi-O surface might be partly explained by such a mechanism. However, the tip distance dependence was observed only at the cleaved Bi-O surface especially at the outside of the gap, but was not at the lateral surface nor lead in the similar configuration.

In this material the Bi-O layer is reported as semiconducting at room temperature [12,13], while it is generally accepted that metallic electronic states localize within the Cu-O layer. In the case shown in Fig. 1 the tunneling electrons appear to be coming mainly from the Cu-O layer, because each curve shows the characteristic superconducting gap structure. If it is correct, the electron tunneling occurs through series tunneling barriers, i.e. Bi-O, Sr-O layers and the vacuum gap. The allowed electronic level is different in energy among these barriers. Increase of the tip distance corresponds to widening of the vacuum gap. It is considered that such a complicated interface barrier structure is closely connected with the observed energy dependence of tunneling matrix element.

Muldoon et al. [14] have reported the electron tunneling experiment between aluminum and lead through the tunneling barrier which consists of aluminum-oxide and some kinds of organic compounds. They found non-linear tunneling I-V curves and explained them by the model calculation of the tunneling current assuming the elastic tunneling through two barriers in series, which are different in height and width. Our present configuration at the Bi-O surface is similar to that of Muldoon et al. [14]. Our results for the tip distance dependence might be explained in terms of series tunneling barriers. Detailed model calculation for our present results will be presented separately. It is naturally expected from such a model that the energy dependence of the transmission coefficient is weak near zero bias voltage. It explains that with increasing the tip distance the normalized G-V curve is varied significantly at high bias voltage region, while it is almost unchanged at low bias voltage region ($|eV|<\Delta$). Such a property of electron tunneling, which is sensitive to the barrier structure, may also explain existing controversial tunneling experiments for cuprate superconductors, in which the structure of tunneling gap was not much controlled microscopically, because of the layered structure of this material.

We should also point out the possibility of the inelastic scattering of electrons at Bi-O or Sr-O layer. If the tunneling electron is scattered by excitations within barriers, the inelastic tunneling process becomes important. Then the G-V curve is modified according to the spectra of excitations. However, it is questionable that the inelastic scattering process depends strongly on the relative width of Bi-O and Sr-O layers to the vacuum gap. We deduce that the inelastic tunneling is not main reason for the tip distance dependence of the G-V curve.

As shown in Fig. 2, G-V curves measured at the lateral surface show the gap structure of a characteristic superconductor irrespective of

the tip position. It is expected that Cu-O, Bi-O and other layers come out periodically in the lateral surface of Bi₂Sr₂CaCu₂O₈ single crystal. The spatial period is estimated to be larger than 3 nm, if we take into account of the slight inclination of the lateral surface. We can accordingly approach to each layer alternatively with scanning the tip. However, we could obtain only the identical G-V curve in every measured point of the lateral surface. Metallic electrons are likely confined within the Cu-O layer. In the range of voltage sweep in the present experiment, the electron tunneling occurs almost through electronic states in the Cu-O layer, because there is little available electronic level in other layers. It is deduced that even if the tip is closest to the Bi-O layer, the tunneling current flows obliquely between the Cu-O layer and the tip metal. It is understood under these circumstances that we could obtain only the identical G-V curve irrespective of the tip position in the lateral surface.

The Cu-O layer and the tip are separated only by the vacuum gap in this configuration as in the case of lead shown in Fig. 3. It is naturally expected that the tunneling matrix element is independent of energy. The electronic density of states for the superconducting state in this material can be obtained directly from the differential conductance observed at this lateral surface.

We note that G-V curves at the lateral surface is again BCS like. Although Hasegawa et al. [6] argued the ambiguity of determination of the gap parameter Δ at the Bi-O surface, we can determine Δ uniquely as Δ =23 meV and correspondingly $2\Delta/k_{\rm B}T_{\rm c}$ =6.1 for T_c=87 K from the result at the lateral surface. This value is consistent with that obtained at the Bi-O surface, if we take account of the spatial variation of Δ [5]. It indicates the strong-coupling superconductivity.

As shown in Fig. 2, the entire G-V curves are similar to the BCS density of states. However, the differential conductance is slightly enhanced at the midgap region $(|eV|<\Delta)$, as compared with that expected from the BCS. Such a deviation from the BCS might be explained by the gap anisotropy as we already pointed out [5].

In summary, the tunneling spectroscopic measurement was carried out with use of STM both at the cleaved Bi-O and the lateral surfaces of a single crystal of Bi2Sr2CaCu2O8. The tunneling spectra at the Bi-O surface show the strong tip distance dependence at the outside of the gap. This is attributed to the tunneling through different barriers in series, *i.e.* Bi-O, Sr-O and vacuum. In the case of the lateral surface, the tunneling barrier is only the vacuum gap and the G-V curve do not show the tip distance dependence. The differential conductance is directly proportional to the density of states in the superconducting phase. The obtained gap indicates the strong coupling superconductivity.

Acknowledgements - We would like to thank Prof. T. Sambongi for valuable discussion and critical reading of our manuscript. We are also thankful to Dr. A. Yamanaka for discussion and helpful advice on the property of single crystal sample. We are also indebted to Dr. T. Okada and Dr. T. Takase of Olympus Optical Co., Ltd., for their useful advices on the STM.

REFERENCES

- 1. VIEIRA, S., RAMOS, M. A., VALLET-REGI, M. and GONZALEZ-CALBET, J. M., Phys. Rev. B38, 9295 (1988).
- 2. IKUTA, H., MAEDA, A., UCHINOKURA, K. and TANAKA, S., Jpn. J. Appl. Phys. 27, L1038 (1988). 3. EKINO, T. and AKIMITSU, J., Phys. Rev. B40, 6902 (1989).
- 4. MIYAKAWA, N., SHIMADA, D., KIDO, T. and TSUDA, N., J. Phys. Soc. Jpn. 59, 2473 (1990).
- 5. ICHIMURA, K., NOMURA, N., MINAMI, F. and TAKEKAWA, S., J. Phys.: Condens. Matter 2, 9961 (1990).
- 6. HASEGAWA, T., NANTOH, M. and KITAZAWA, K., Jpn. J. Appl. Phys. 30, L276 (1991).
- 7. ICHIMURA, K., NOMURA, N., MINAMI, F. and TAKEKAWA, S., Proc. 3rd Int. Conf. Materials and Mechanisms of Superconductivity High-Temperature Superconductors, Kanazawa, 1991, Physica C 185-189, 941 (1991).
- 8. YAMANAKA, A., private communication; YAMANAKA, A., TAKATO, H., MINAMI, F., INOUE, K. and TAKEKAWA, S., Proc. 3rd Int. Conf. Materials and Mechanisms of Superconductivity High-
- Temperature Superconductors, Kanazawa, 1991, Physica C 185-189, 1027 (1991). 9. NOMURA, K. and ICHIMURA, K., Solid State Commun. 71, 149 (1989); Proc. 4th Int. Conf. on Scanning Tunneling Microscopy/Spectroscopy, Oarai, 1989, J. Vac. Sci. Technol. A8, 504 (1990).
- 10. DYNES, R. C., NARAYANAMURTI, V. and GARNO, J. P. Phys. Rev. Lett. 41, 1509 (1978). 11. BLONDER, G. E., TINKHAM, M. and KLAPWIJK, T. M., Phys. Rev. B25, 4515 (1982); BLONDER, G. E. and TINKHAM, M., Phys. Rev. B27, 112 (1983).
- 12. TANAKA, M., TAKAHASHI, T., KATAYAMA-YOSHIDA, H., YAMAZAKI, S., FUJINAMI, M., OKADA, Y., MIZUTANI, W., ONO, M. and KAJIMURA, K., Nature 339, 691 (1989). 13. SHIH, C. K., FEENSTRA, R. M., KIRTLEY, J. R. and CHANDRASHEKHAR, G. V., Phys. Rev. B40, 2682
- (1989).
- 14. MULDOON, M. F., DRAGOSET, R. A. and COLEMAN, R. V., Phys. Rev. B20, 416 (1979).