Anisotropy of the electronic structure and superconducting gap in $Bi_2Sr_2CaCu_2O_8$

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Existence of a large anisotropy of the superconducting energy gap in $Bi_2Sr_2CaCu_2O_8$ was confirmed by angle-resolved photoemission. The gap size, Δ (the full superconducting energy gap being 2Δ), is 0–4 meV for the ΓX and ΓY directions while that of the $\Gamma\overline{M}$ direction, 45° away from the former two, is 17–19 meV. Comparison with previous reports was made with regard to the symmetry of the superconducting order parameter. It was also found that the electronic structure of the normal state in the ΓY direction is considerably modified by the incommensurate superstructure in the BiO plane. In contrast, the size of superconducting gap is identical within the present accuracy for both ΓX and ΓY directions, suggesting that the superstructure has a negligible effect on the size of the superconducting energy gap.

The symmetry of the superconducting energy gap is the most essential physical parameter when we consider the superconducting mechanism in the layered high-T_c cuprates. A wide variety of experimental techniques (NMR,[1] Raman scattering,[2] penetration depth,[3] thermal conductivity,[4] microwave,[5] scanning tunneling spectroscopy,[6] Josephson junction,[7] photoemission,[8–14] etc.) have been applied to the high-T_c superconductors to elucidate the symmetry of superconducting gap. A great advantage of angle-resolved photoemission spectroscopy (ARPES) is its capability of **k** (wave vector)-resolved investigation of the electronic structure. ARPES enables a direct **k**-resolved mapping of the superconducting gap in the Brillouin zone. Olson *et al.*[9] performed a low-temperature ARPES measurement on $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and reported an isotropic (s wave) superconducting order parameter, while later Shen *et al.*[12] reported their observation of a large anisotropy of a superconducting gap in Bi2212, proposing a superconducting mechanism with $d_{x^2-y^2}$ or $s+id$ symmetry. In contrast, Kelley *et al.*[14] proposed a possibility of $d_{xz}+d_{yz}$ gap symmetry in Bi2212 based on their polarization-dependent ARPES measurement. Thus, ARPES experiments are not consistent with each other and support conflicting models.

In this paper, we present our high-resolution ARPES data of a high-quality Bi2212 single crystal. We expended great care to measure an accurate minimum superconducting energy gap, since whether or not the superconducting gap vanishes at a certain point in the Brillouin zone is key evidence in distinguishing the superconducting order parameter. Actually, Mahan pointed out in his Comment[15] that the minimum superconducting energy gap (Δ) observed by Shen *et al.*[12] in a sample is substantial ($\Delta \sim 10$ meV) and showed that the data is better fitted with an extended s-wave order parameter rather than a d-wave symmetry. We also paid special attention to a possible effect of the superstructure of BiO layers on the electronic structure and as a result on the superconducting energy gap. This point was overlooked in the previous two conflicting ARPES studies.[9,12]

A high-quality Bi2212 single crystal was prepared by the traveling solvent floating-zone method using an infrared mirror furnace. The superconductivity was characterized by resistivity and Meissner-effect measurements, which showed a very sharp superconducting transition at 86.4 K with widths of 1.5 and 0.6 K, respectively. The composition was determined by electron probe microanalysis to be Bi: Sr: Ca: Cu = 2.15: 1.86: 0.98: 2.03 within error of a few percent. The x-ray rocking-curve analysis has been done for the $(0,0,l)$ reflections and the width of the peak was sharp, being between 150 and 300 sec, which also proves the high-quality crystallinity of the sample.

Photoemission measurements were performed with a home-built ARPES spectrometer, which has a VSW electron energy analyzer (radius 150 mm) and a high-brightness discharge lamp. The base pressure was $7-8\times10^{-11}$ Torr. Since the analyzer is fixed to the vacuum chamber, angle-resolved measurements were achieved by rotating the sample with respect to the analyzer. The angle between the electron energy analyzer and the incident light is about 40°. In this setup, the direction of the electric vector of the incident light changes with the angle. This experimental setup is different from that of previous ARPES measurements[9,12] where the analyzer was rotated relative to the sample and the direction of the electric vector of the incident light was constant. So, if the present experimental result agrees with one of the previous ARPES measurements, it means that the superconducting order parameter is experimentally confirmed by two independent ARPES with different modes. The total energy resolution in the present study was about 25 meV, as estimated from the Fermi-edge cutoff of gold, including the thermal broadening at 25 K (about 7 meV at E_F) and the natural width of the He I resonance line (3 meV). The angular resolution was estimated to be 1–2°. ARPES measurements were performed for three high-symmetry directions in the Brillouin zone, namely ΓX, ΓY, and $\Gamma\overline{M}$, at 25 and 100 K. A clean surface of the crystal for ARPES measurements was obtained by *in situ*

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cleaving. The Fermi level of the sample was referenced to that of a gold substrate. We took great care to avoid a possible time- and/or temperature-dependent drift of the Fermi level. We measured the Fermi level of the gold reference for every set of ARPES measurements along one direction and at each temperature.

Figure 1 shows ARPES spectra in the vicinity of the Fermi level measured for the ΓX direction. We find that a dispersive band appears at $\theta=6°$ around 300 meV binding energy, approaches the Fermi level (E_F) with increasing polar angle and finally crosses it at $\theta=13-14°$. The photoemission intensity at E_F is drastically reduced at $\theta=14-15°$, showing that the band enters the unoccupied states. We have performed a similar measurement for two other directions (ΓY and $\Gamma \overline{M}$) and determined the point of Fermi-level crossing with considerable accuracy.

Figure 2 shows photoemission spectra near the Fermi level of a Bi2212 single crystal in the normal ($T=100$ K) and superconducting ($T=25$ K) states measured at the

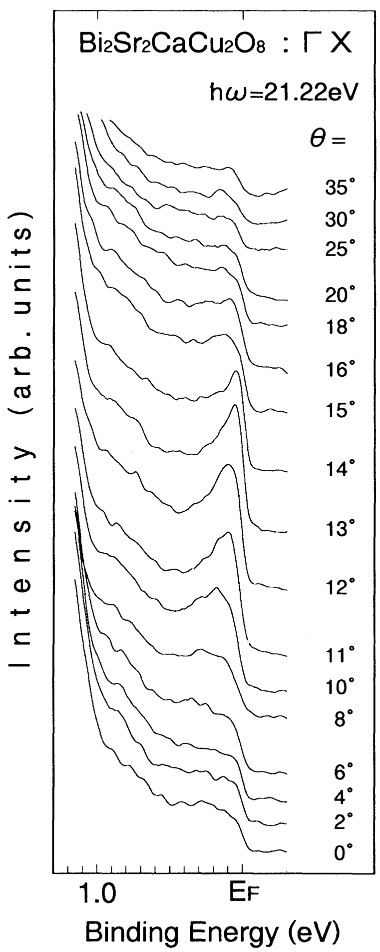

FIG. 1. Angle-resolved photoemission spectra of a Bi2212 single crystal ($T_c=86.4$ K) in the ΓX (a-axis) direction measured with the He I resonance line (21.22 eV) at about 100 K. Polar angle (θ) referred to the surface normal is indicated on each spectrum. Note a remarkable reduction of photoemission intensity near the Fermi level at $\theta=14-15°$, which is a clear indication of the Fermi-level crossing of a band.

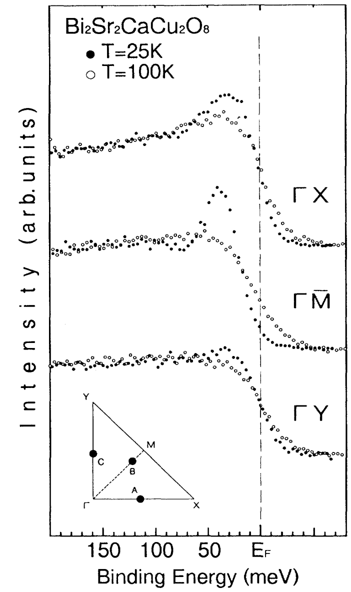

FIG. 2. High-resolution angle-resolved photoemission spectra of a Bi2212 single crystal ($T_c=86.4$ K) in the vicinity of the Fermi level measured at 100 K (normal state) and 25 K (superconducting state). Photoemission spectra were recorded at the three points in the Brillouin zone (see the inset, points A, B, and C for the ΓX, $\Gamma \overline{M}$, and ΓY directions, respectively), at which we observe a band crossing the Fermi level as seen in Fig. 1. The spectra are normalized with respect to the total intensity.

three Fermi-level-crossing points (A, B, and C, as shown in the inset to Fig. 2). These points are located on the three different high-symmetry directions, ΓX, $\Gamma \overline{M}$, and ΓY, in the Brillouin zone, respectively. Firstly, we find that the change of spectra with temperature across the superconducting transition temperature (T_c) is very similar in the ΓX and ΓY directions, while that of the $\Gamma \overline{M}$ direction is considerably different from the former two. The observed similarity in the behavior of superconducting-gap opening in the ΓX and ΓY directions is in sharp contrast with the remarkable difference in the electronic structure in the normal state between the two directions.[16] Figure 3 shows angle-resolved photoemission spectra of the valence-band region in the normal state for the ΓX and ΓY directions.[17] While the spectrum at $\theta=0°$, which represents the Γ point in the Brillouin zone, appears almost the same in both directions, the spectral profile gradually becomes different between the two directions with increasing polar angle. For example, a prominent structure at 6 eV in the normal-emission spectrum ($\theta=0°$) holds its position in the ΓX direction, while that of the ΓY direction merges into a peak at 3.5 eV with increasing polar angle. The observed large difference in the photoemission spectra between ΓX and ΓY directions is ascribed to the incommensurate superstructure in the BiO plane which runs only along the b-axis (ΓY direction). However, as shown in Fig. 2, the change of the electronic structure with temperature across the T_c is very similar in the two directions. This indicates that the effect of the BiO superstructure on the

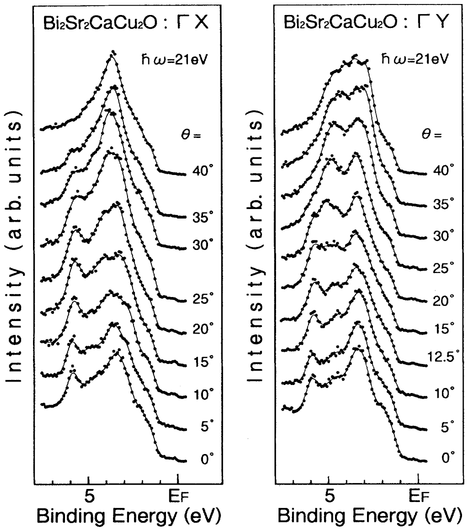

FIG. 3. Angle-resolved photoemission spectra of a Bi2212 single crystal ($T_c = 86.4$ K) along the ΓX and ΓY directions measured with synchrotron radiation of 21 eV at about 100 K (Ref. 17). An incommensurate superstructure of BiO layers runs only along the *b*-axis (ΓY) direction. Note the considerable difference in the spectral shape for the larger polar angles between the two directions.

superconducting gap and consequently on the superconducting state is very small or negligible, meaning that the superconducting state is entirely dominated by the square-planar CuO_2 network in the crystal.

The present observations of a large anisotropy in the superconducting energy gap between the ΓX or ΓY and the $\Gamma\overline{M}$ direction is qualitatively consistent with the report by Shen *et al.*,[12] but different from that of Olson *et al.*[9] For estimating the gap size and comparing it with the previous reports, we assumed the energy interval between the midpoint of the leading edge of the spectrum[18] and the Fermi level as the size of the superconducting energy gap (Δ), as has been conventionally employed in the previous studies. Although this simple and conventional method provides a rough estimate of the gap and its **k** dependence in the Brillouin zone, a line-shape analysis with an appropriate model function would be useful and necessary for more detailed discussion as demonstrated in the study of $TiTe_2$ (Ref. 19). According to the present method, we obtained $\Delta = 1-2$ meV, 0–1 meV, and 17–19 meV for ΓX, ΓY, and $\Gamma\overline{M}$ directions, respectively, with the accuracy of ± 2 meV. The observed maximum superconducting gap in the $\Gamma\overline{M}$ direction agrees well with that of samples 2 and 3 of Shen *et al.* (17–22 meV), but is different from that of sample 1 (12–13 meV). This difference in the maximum superconducting gap has been ascribed to the difference in the oxygen concentration in samples, namely the T_c; T_c of sample 1 is 78 K, while that of samples 2 and 3 is 88 K, being in the same range as the present sample ($T_c = 86.4$ K). On the other hand, the minimum superconducting energy gap observed in this study (0–4 meV including the experimental error for the ΓX or ΓY direction) agrees well with those of samples 1 and 3 of Shen *et al.* (1–2 meV), but is considerably different from that of sample 2 (about 10 meV). Mahan pointed out the significance of the size of the minimum superconducting energy gap and commented that the data of sample 2 is better fitted with an extended *s* symmetry rather than the *d*-wave model.[15] Shen *et al.* have attributed this apparently large minimum superconducting energy gap in the $\Gamma Y(X)$ direction to the poorer quality of sample surface and an aging effect due to adsorption of residual gases on it, both of which worsen the **k** resolution by causing scatter of photoelectrons at the surface. Actually, we also observed a similar aging effect which brought about an apparent increase of superconducting gap for ΓX and ΓY directions and a decrease for the $\Gamma\overline{M}$ direction after we kept the sample at low temperature (25 K) for a few hours. Since it was found that this aging effect was removed when the sample was warmed to room temperature, it is certainly due to physisorption of residual gases. In order to avoid this aging effect, all spectra shown in Fig. 2 were recorded within 1–2 h after cooling. We also found that the gap size is very sensitive to the position in the Brillouin zone, in particular, in the area where the minimum gap was observed. For example, when we changed the angle by 1–2° at point *A* in the ΓX direction (see the inset of Fig. 2), it led to an opening of a gap of 3–4 meV. So, in the course of this study, we took great care to find the position which gives a minimum superconducting gap, recording ARPES spectra in 0.5° intervals near the Fermi-level-crossing point. From our experience, the large scatter in the size of the minimum superconducting gap observed by Shen *et al.*[12] may also be due to a slight misalignment of angle as well as to the poor surface quality and the aging effect.

Thus, the present experimental result agrees qualitatively well with that of Shen *et al.*,[12] favoring an anisotropic symmetry superconductivity such as the *d* wave. However, the large scatter of data in the minimum superconducting energy gap in the ARPES experiment by Shen *et al.*[12] leaves a possibility for an extended *s* or $s+id$ symmetry as pointed out by Mahan.[15] In the present ARPES experiment (Fig. 2), we observed a nearly zero (0–4 meV, this being a limit of the present resolution) superconducting energy gap in the two high-symmetry directions (ΓX and ΓY) as well as a substantial (17–19 meV) gap in the $\Gamma\overline{M}$ direction 45° away from the former two. This observation clearly contradicts the d_{xy} symmetry, since a maximum superconducting gap should open in ΓX and ΓY directions in the d_{xy} symmetry. The present experimental result is also inconsistent with the d_{xz+yz} symmetry proposed by Kelley *et al.*[14] from their polarization-dependent ARPES. This is because the superconducting gap with d_{xz+yz} symmetry has a twofold symmetry in the *x-y* plane with two equivalent nodes on it, while the present result clearly shows a fourfold symmetry of the superconducting gap in the *x-y* plane. Although the possibility of mixed symmetries or strongly anisotropic *s*-wave gap is not finally ruled out at present because of limited experimental resolution, the present ARPES data suggests existence of a node on ΓX and ΓY lines, suggesting a $d_{x^2-y^2}$ symmetry as the most probable superconducting order parameter. However, there is still a large scatter of experimental results on the superconducting symmetry obtained by various experimental methods.[1–14] One possibility to produce such a variety may be a doping-[20] and/or temperature-[21] dependent alteration of the superconducting order parameter. Further theoretical and experimental studies on the doping (or T_c) and temperature dependence of the superconducting energy gap are needed.

In conclusion, we have performed a high-resolution angle-resolved photoemission spectroscopy experiment on a high-quality Bi2212 single crystal. We observed a large anisotropy of the superconducting energy gap; $\Delta=0-4$ meV for both ΓX and ΓY directions, while $\Delta=17-19$ meV for the $\Gamma\bar{M}$ direction. This result is explained in terms of a $d_{x^2-y^2}$ or a strongly anisotropic extended s-wave superconducting order parameter, while it is qualitatively inconsistent with a d_{xy} or d_{xy+yx} order parameter. We also found that the size of superconducting gap is almost identical for ΓX and ΓY directions, which suggests that the incommensurate superstructure running along the ΓY direction has a negligible effect on the size of the superconducting energy gap.

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