Anomalous band folding due to the BiO superstructure in $Bi_2Sr_2CaCu_2O_8$ studied by angle-resolved photoemission

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Angle-resolved photoemission measurement has been performed on a twin-free $Bi_2Sr_2CaCu_2O_8$ single crystal to study the band-folding effect due to the BiO superstructure. It was found that the superstructure running along the b axis considerably modulates the electronic structure near the Fermi level (E_F) in that direction, almost smearing out the dispersive feature of a band which crosses the Fermi level. In contrast with the energy region near E_F, the main body of the valence band (1 to 7 eV in binding energy) shows a comparable but different energy dispersion between the a- and b-axis directions. This indicates that the band-folding effect may be different between the near-E_F region and the whole valence band in $Bi_2Sr_2CaCu_2O_8$.

I. INTRODUCTION

The electronic structure and its relation to the mechanism of superconductivity in high-temperature superconductors (HTSC's) have been studied extensively by photoemission spectroscopy.[1] Among various HTSC's, Bi-system superconductors such as $Bi_2Sr_2CaCu_2O_8$ (Bi2212) have a unique crystal structure not existing in the other HTSC's; weakly bonded double BiO layers sandwiching the CuO_2 sheet. This weak van der Waals bonding between two BiO layers enables easy cleaving between them and a lot of angle-resolved photoemission spectroscopies have been done with an *in situ* cleaved surface of a single crystal.

The existence of BiO layers in the crystal has brought about several interesting problems. One of them is metallicity of the BiO layer since the band-structure calculation[2] on Bi2212 has predicted a substantial contribution to the density of states at the Fermi level (E_F) from the Bi-O band, suggesting its contribution to the higher superconducting transition temperature (T_c) compared with La- and Y-system HTSC's. However, scanning-tunneling spectroscopies[3,4] (STS) combined with photoemission and inverse photoemission spectroscopies observed a small semiconductorlike energy gap for the BiO layer, proposing its nonmetallicity contrary to the band calculation, while a photoemission study[5] has supported the existence of a small electron pocket at E_F originating in the Bi-O band. A recent precise angle-resolved photoemission study,[6] however, denied the previous interpretation[5] and clearly showed that the BiO band remains entirely above E_F, supporting the STS studies.[3,4]

Another interesting and important problem related to the above problem is an effect of the superstructure in BiO layers to the electronic structure through the band folding. It is well established[7] by the structural study

that an incommensurate superstructure of 4.7–5.2 times the period in the CuO_2 plane runs in the BiO plane along a crystal axis 45° away from the direction of the Cu-O bonding, making two unequivalent crystal axes in the plane, a and b axes; the b axis is defined as the crystal axis along which the superstructure runs. This BiO superstructure is expected to modulate the electronic structure of the CuO_2 plane through the band-folding effect and as a result may affect the symmetry of the superconducting energy gap. However, almost all the previous photoemission studies have overlooked the existence of the BiO superstructure and interpreted the experimental results as regarding the a and b axes as equivalent. This has caused a lot of controversy in the obtained band dispersions among the previous angle-resolved photoemission studies. Recently, Kelley *et al.*[8] performed a careful angle-resolved photoemission measurement distinguishing between the a and b axes and found a clear band-folding effect in the electronic structure near E_F, offering a useful caution that the two unequivalent crystal axes should be distinguished when the electronic structure is studied. In this paper, we report an angle-resolved photoemission study on a twin-free Bi2212 single crystal distinguishing the two unequivalent crystal axes (a and b). We expanded the previous study of Kelley *et al.*[8] by measuring both the near-E_F region and the whole valence band. While we confirmed the result of Kelley *et al.*[8] by observing almost dispersionless photoemission spectra near E_F along the b axis (ΓY direction in the Brillouin zone) caused probably by the incommensurate superstructure, we found an anomalously clear energy dispersion of bands even along the b axis in the main body of the valence band. We also found that the obtained energy dispersion in the b-axis direction is comparable to but different from that in the a axis (ΓX direction) along which no superstructure runs. We discuss some possible origins to produce such an anomalous band-folding effect in Bi2212.

II. EXPERIMENT

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 Meissner-effect measurements, which showed a very sharp superconducting transition at 90.2 K with widths of about 1.5 K. The composition was determined by the electron-probe microanalysis to be Bi:Sr:Ca:Cu=2.15: 1.86: 0.98: 2.03 within an 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. Figure 1 shows a Laue diffraction pattern of the crystal, where the well-ordered distribution of a lot of sharp spots shows the high quality and twin-free nature of the crystal.

Photoemission measurement was performed with an angle-resolved photoemission spectrometer at UVSOR synchrotron-radiation facility in the Institute for Molecular Science, Okazaki. The energy and angular resolutions were 150 meV and 2°, respectively, for the photon energy used (21 eV). A clean and fresh surface of the single crystal for photoemission measurement was obtained by *in situ* cleaving in the spectrometer under the working pressure of 8×10^{-10} Torr. Photoemission spectra were recorded with cooling the sample at 150–170 K. No degradation of the sample was detected during the measure-
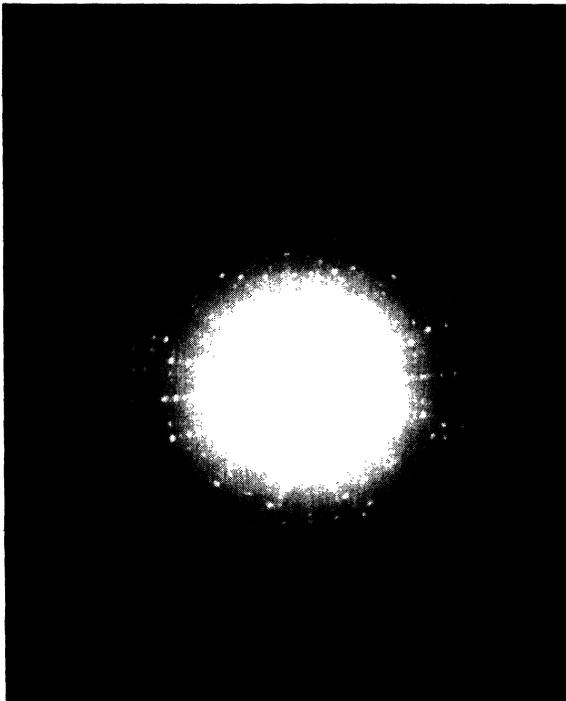
ment. The Fermi level of the sample was referred to that of a gold film deposited on the sample.

III. RESULTS AND DISCUSSION

Figure 2 shows angle-resolved photoemission spectra near E_F of a Bi2212 single crystal measured for the $\Gamma X(a$ axis) and $\Gamma Y(b$ axis) directions in the Brillouin zone. Polar angle (θ) referred to the surface normal is denoted on each spectrum. As found in Fig. 2, a series of photoemission spectra in the ΓX direction shows a small but distinct angular dependence, while that of ΓY shows little change against the polar angle. In the ΓX direction, a small structure, which appears at 300 meV in binding energy in the spectrum of $\theta = 7.5°$, gradually approaches the Fermi level and at the same time becomes sharp with the polar angle. This dispersive band appears to cross the Fermi level around $\theta = 15°$ since the spectral intensity suddenly decreases at $\theta = 15° - 17.5°$, indicating the band enters the unoccupied states. While in the ΓY direction a slight change in the shape of the photoemission spectrum is also observed around $\theta = 10° - 17.5°$, the change against the polar angle is less remarkable. This experimental result showing a large apparent anisotropy of the electronic
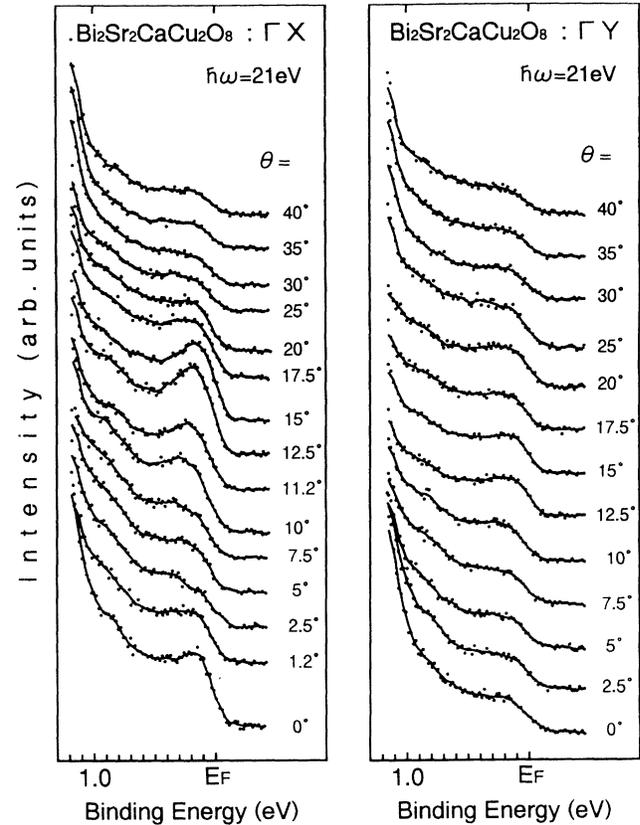

FIG. 1. Laue diffraction pattern of a $Bi_2Sr_2CaCu_2O_8$ single crystal used in this study. The near-horizontal direction along which a lot of small spots are aligned corresponds to the b axis, while another direction perpendicular to the former one is the a axis along which a relatively few spots are seen.

FIG. 2. Angle-resolved photoemission spectra near the Fermi level of $Bi_2Sr_2CaCu_2O_8$ measured at $h\nu=21$ eV for the a (ΓX) and b axis (ΓY) directions. Experimental results (points) are smoothed by lines for eyes. Polar angle (θ) referred to the surface normal is indicated on each spectrum. Note a monotonous feature of spectra against the polar angle in the ΓY direction.

structure near E_F between the ΓX and ΓY directions is in good agreement with the report by Kelley et al.[8] and is certainly due to the band-folding effect caused by the incommensurate superstructure of the BiO layer running along the b axis (ΓY direction). The incommensurate band-folding smears out k (wave-vector) dependence of the electronic structure in the ΓY direction, producing almost the same photoemission spectrum for every polar angle as shown in Fig. 2. This band-folding effect is expected to also work in the whole valence-band region and give an almost identical valence-band photoemission spectrum for all polar angles in the ΓY direction.

Figure 3 shows comparison of angle-resolved photoemission spectra of the whole valence-band region between the ΓX and ΓY directions. Contrary to the simple expectation mentioned above, the photoemission spectrum in the ΓY direction shows a clear angular dependence comparable to that in the ΓX direction. Also it should be remarked that the angular dependence, namely the energy dispersion of bands, is different between the two directions. The photoemission spectrum at $\theta = 0°$ corresponds to the Γ point, so that it is reasonable that the spectrum looks similar at this angle in both directions, while the shape of photoemission spectra of large polar angles appear to be considerably different from each other between the two directions. This remarkable angular dependence of valence-band photoemission spectrum in the ΓY direction shows a sharp contrast with the monotonous feature of the photoemission spectra near
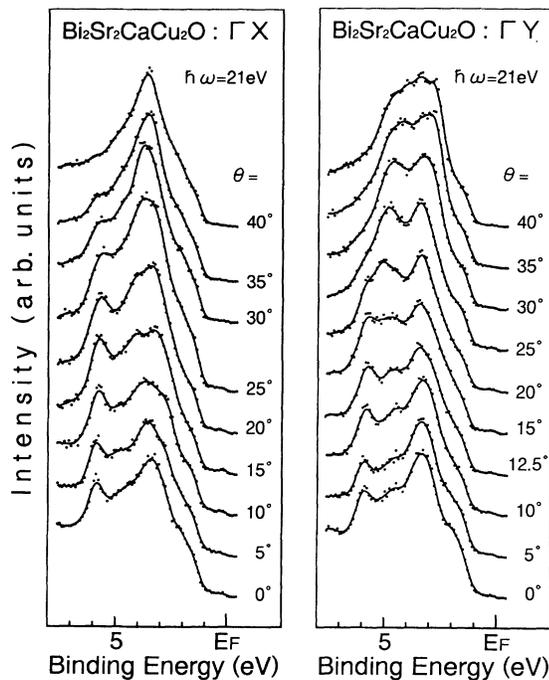
E_F as shown in Fig. 2 and obviously contradicts a simple expectation from the incommensurate band-folding effect due to the BiO superstructure. Figure 4 shows the angle-resolved photoemission spectra of the near-E_F and the whole valence-band region for the $\Gamma \overline{M}$ direction 45° away from both ΓX and ΓY directions for comparison.

Figure 5 shows the experimental band structure for the three high-symmetry directions in the Brillouin zone (ΓX, ΓY, and $\Gamma \overline{M}$) derived from the angle-resolved photoemission spectra in Figs. 2–4. A representative band-structure calculation of Bi2212 by Massidda, Yu, and Freeman[2] is shown by thin solid lines for comparison. It is noted that the calculation assumes a quasitetragonal unit cell when neglecting the BiO superstructure and consequently gives an almost identical energy band along the ΓX and ΓY directions. Strong or prominent structures in the photoemission spectra are indicated by shading the experimental points. In the ΓX direction, we find a prominent dispersive band near E_F showing good agreement with the calculated Cu-O antibonding band which crosses midway between the Γ and X points. Although a weak feature corresponding to this dispersive band is recognized also in the ΓY direction (see Fig. 2), the structure is almost smeared out, giving a nondispersive band running near E_F along the ΓY direction. This is, as described above, due to the incommensurate band-folding effect caused by the BiO superstructure. We also find a small structure near the Γ point which is clearly seen in the ΓX direction, but almost disappears in the ΓY direc-

FIG. 3. Angle-resolved photoemission spectra in the whole valence-band region of $Bi_2Sr_2CaCu_2O_8$ measured at $h\nu = 21$ eV for the ΓX and ΓY directions. Polar angle (θ) referred to the surface normal is indicated on each spectrum. Note a comparable but different energy dispersion of bands in the spectra between the ΓX and ΓY directions.
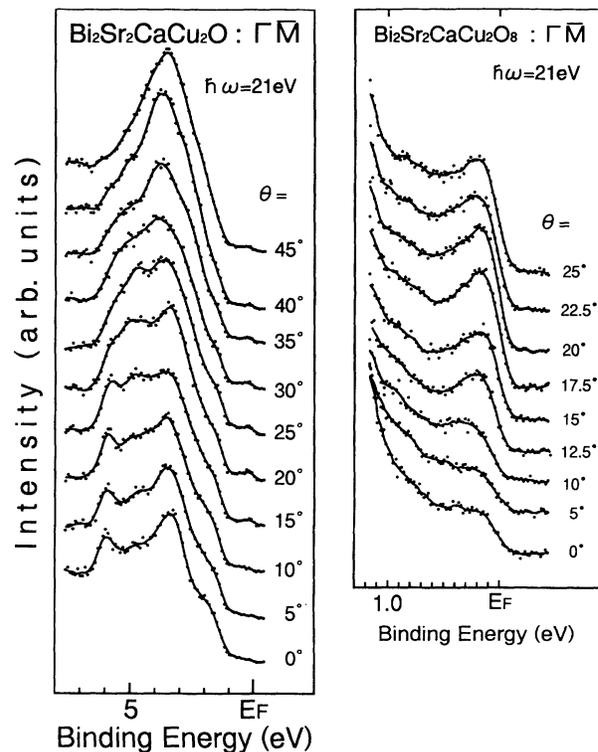
FIG. 4. Angle-resolved photoemission spectra near the Fermi level (right panel) and of the whole valence-band region (left) of $Bi_2Sr_2CaCu_2O_8$ measured at $h\nu = 21$ eV for the $\Gamma \overline{M}$ direction.
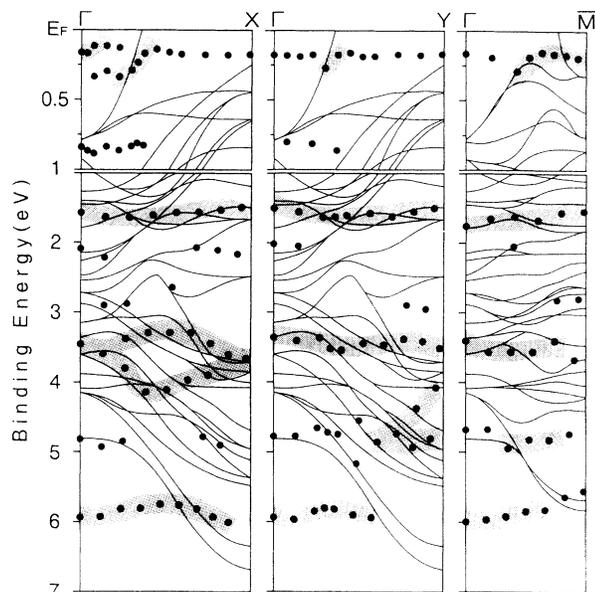
FIG. 5. Experimental band structures of $Bi_2Sr_2CaCu_2O_8$ in the ΓX, ΓY, and $\Gamma \overline{M}$ directions in the Brillouin zone (filled circles) derived from the present angle-resolved photoemission spectra in Figs. 2–4. Strong or prominent structures in the spectra are indicated by shading. A representative band-structure calculation (Ref. 2) is shown by thin solid lines for comparison. Note that the energy scale near the Fermi level is doubly expanded.

tion. As shown in Fig. 2, the photoemission intensity at E_F in the ΓX direction gradually decreased from $\theta = 0°$ to $2.5°$, suggesting the existence of a small electron pocket at the Γ point. This is in good agreement with a previous angle-resolved photoemission study[9] with a different photon energy (18 eV) and also with an angle-resolved inverse photoemission study.[10] The origin of this electron pocket is not known at present nor explained in the framework of the band-structure calculation which does not take into account the BiO superstructure.

As for the $\Gamma \overline{M}$ direction, the photoemission spectrum near E_F shows a gradual increase in intensity with the polar angle from $\theta = 0°$ to $15°$ and the intensity stays almost constant even after that angle (see Fig. 4). This shows a clear contrast with the spectral feature in the ΓX direction where the photoemission spectral intensity near E_F suddenly decreases just after the peak approaches closest to E_F around $\theta = 15°$ (see Fig. 2). This suggests the existence of two bands near E_F in the $\Gamma \overline{M}$ direction and one of them disperses across the Fermi level midway from the Γ and $\overline{M}$ points, while the other disperses together with the former band until the Fermi-level-crossing point but after that it separates from the former one, running just below the Fermi level near the $\overline{M}$ point. A similar flat band near the $\overline{M}$ point has been also observed by Dessau et al.,[6] who attributed the existence of these two close bands to an anisotropic strong electron-correlation effect between the ΓX and $\Gamma \overline{M}$ directions.

In the higher-binding-energy region of 1–7 eV, the

angle-resolved photoemission spectrum in the ΓY direction, along which the incommensurate BiO superstructure runs, shows a clear energy dispersion comparable to that in the ΓX direction (Figs. 3 and 5). This contradicts a simple expectation that the incommensurate band folding smears out the dispersive feature, giving an almost identical photoemission spectrum against the polar angle as seen in the measurement near E_F (Fig. 2). It should be also noted that the obtained band dispersion is considerably different between the two directions. This indicates that the effect of the band folding may be different between the near E_F region and the main body of valence band. An explanation for this strange band-folding effect is a lattice distortion in the CuO_2 plane. If the CuO_2 square lattice is distorted along the a and/or b axis in a span of the original unit cell (not in the period of the superstructure), it should give a considerably different band dispersion within the original Brillouin zone between the two directions as shown in Fig. 5. Several structural studies such as x-ray and neutron-diffraction and x-ray-absorption studies[11,12] have reported a substantial deviation of the atom position from the average crystal structure in T1- or Bi-HTSC's. However, the reported out-of-plane distortion of oxygen atoms in the CuO_2 plane[11] has an equivalent effect on both the a and b axis directions. Another structural study[12] reported that the copper and oxygen atoms are slightly displaced from the average position, showing a modulation of about five times the original unit cell matching the BiO superstructure. These distortions are not expected to give such a large difference in the band dispersion between the two directions shown in Fig. 5. Even if there is a substantial distortion in the CuO_2 plane not observed so far, it should give a large difference in the electronic structure near E_F comparable to that in the main body of the valence band as shown in Fig. 3. However, the present experimental result shows that a similar band dispersion is formed near E_F in both directions although the dispersive feature appears to be vague in the ΓY direction. This contradicts the above conjecture that the CuO_2 square lattice itself should be substantially distorted in a span of the original unit cell in a way to give two unequivalent crystal axes, a and b. An alternative explanation to the binding-energy-dependent band-folding effect may lie in the nonuniform distribution of the density of oxygen $2p$ states in the valence band. According to the band-structure calculation[2] on Bi2212, the electronic states near E_F originate mainly in the Cu-O band while the main body of the valence band has a mixed nature of the Cu-O and the Bi-O band. The observed insensitive behavior of the angle-resolved photoemission spectrum near E_F against the polar angle in the ΓY direction is explained in terms of the incommensurate band folding of the Cu-O band due to the BiO superstructure. This band-folding effect appears not to work well in the main body of the valence band as described above. If the observed valence-band dispersion in the ΓY direction was similar to that of the ΓX direction as a whole, it is explained by a weakened band-folding effect in the valence-band region. However, the band dispersion itself is considerably different between the two directions (see

Figs. 3 and 5). This suggests that the BiO plane should have a substantial anisotropy between the a and b axes in the original unit cell. The most probable cause for this is an anisotropic distribution of oxygen and bismuth atoms in the BiO plane as reported by an x-ray and neutron-diffraction study.[13] This anisotropy would serve as an origin of the incommensurate superstructure in the BiO plane. The previous band-structure calculation[2] did not take into account such anisotropic distribution in the BiO plane nor the incommensurate superstructure. When taken properly into account the correct distribution of oxygen and bismuth atoms in the BiO plane and its superstructure, the band-structure calculation may explain the nonmetallic nature of the BiO plane and/or the existence of a small electron pocket at the Γ point. However, such anisotropy in the distribution of atoms in the BiO plane has not yet been observed by high-resolution electron microscopy.[7,14] Further structural studies on the distribution of oxygen and bismuth atoms in the BiO plane are needed to understand the strange properties of Bi2212 such as a large anisotropic electronic structure between the a and b axes observed in this study.

IV. CONCLUSION

We have performed an angle-resolved photoemission spectroscopy on a twin-free $Bi_2Sr_2CaCu_2O_8$ single crystal by distinguishing the a and b axes in the crystal in order to study the effect of the incommensurate superstructure of the BiO plane on the electronic structure in the normal state. We found that the electronic structure near E_F is remarkably modulated by the superstructure running along the b axis, giving an almost identical angle-resolved photoemission spectrum for all wave vectors (k) along the ΓY direction (b axis). This would be due to the incommensurate band-folding effect caused by the BiO superstructure. In contrast with the electronic structure near E_F, the photoemission spectrum of the main body of the valence band shows a comparable but different energy dispersion between the ΓX (a axis) and ΓY (b axis) directions. This indicates that the band-folding effect may be different between the near-E_F region and the main body of the valence band. We have proposed a possible origin to be an anisotropic distribution of oxygen and bismuth atoms in the BiO plane.

ACKNOWLEDGMENTS

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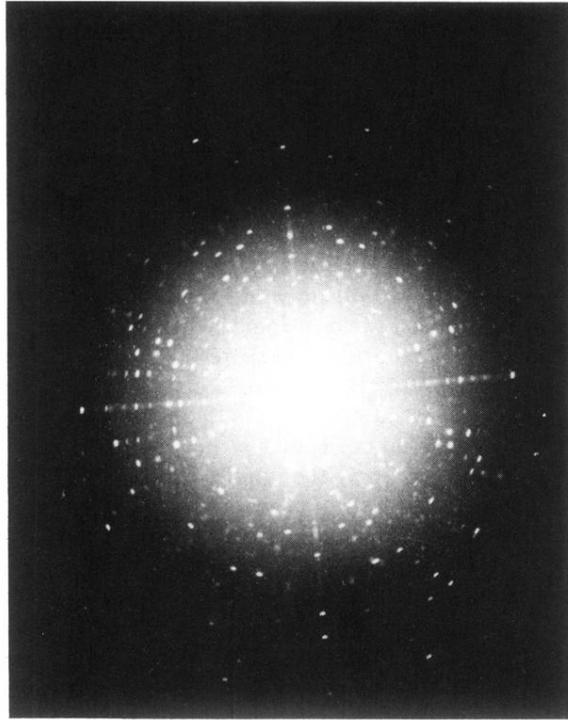[14] K. Hiraga, M. Hirabayashi, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. **27**, L573 (1988).

FIG. 1. Laue diffraction pattern of a $Bi_2Sr_2CaCu_2O_8$ single crystal used in this study. The near-horizontal direction along which a lot of small spots are aligned corresponds to the b axis, while another direction perpendicular to the former one is the a axis along which a relatively few spots are seen.
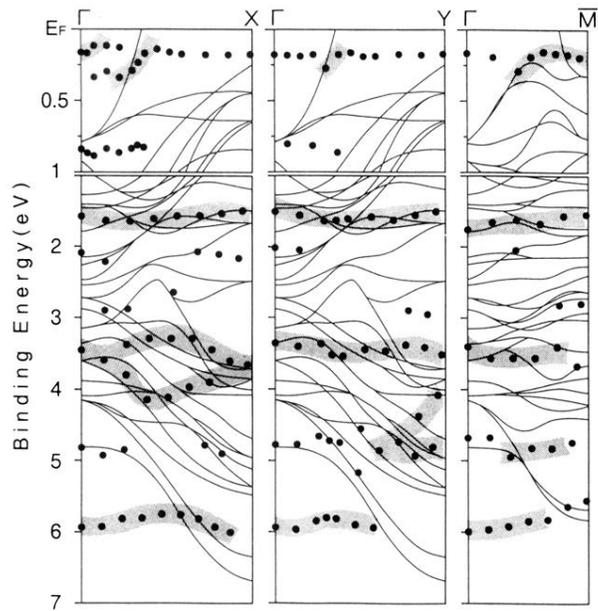
FIG. 5. Experimental band structures of $Bi_2Sr_2CaCu_2O_8$ in the ΓX, ΓY, and $\Gamma \overline{M}$ directions in the Brillouin zone (filled circles) derived from the present angle-resolved photoemission spectra in Figs. 2–4. Strong or prominent structures in the spectra are indicated by shading. A representative band-structure calculation (Ref. 2) is shown by thin solid lines for comparison. Note that the energy scale near the Fermi level is doubly expanded.