Hole-concentration dependence of band structure in $(Bi,Pb)_2(Sr,La)_2CuO_{6+\delta}$ determined by the angle-resolved photoemission spectroscopy

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Abstract

Energy–momentum (E–$\boldsymbol{k}$) dispersion and the shape of the Fermi surface (FS) in the $(Bi,Pb)_2(Sr,La)_2CuO_{6+\delta}$ (Bi2201) superconductors of various hole-concentrations were investigated by the angle-resolved photoemission spectroscopy (ARPES) with high energy and momentum resolutions ($\Delta E = 10$ meV and $\Delta k = 0.005$ Å^{-1}). The E–$\boldsymbol{k}$ dispersion is kept rigid and the chemical potential moves towards lower or higher energies with increasing or decreasing hole-concentration, respectively, over a wide hole-concentration range from the nearly optimal-doped condition with a transition temperature of 32 K to a heavily over-doped condition where the superconducting transition disappears. By comparing the shape of the FS determined for the present Bi2201 with that reported for the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212), we found that the area surrounded by the FS in the Bi2201 is fairly larger than that in the Bi2212. Estimated hole-concentration in the Bi2201 was found to vary from 0.25 to 0.43 holes/Cu, that is more than twice as large as that in the optimally doped $La_{2-x}Sr_xCuO_4$ (LSCO) and Bi2212 superconductors of 0.17 holes/Cu.
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1. Introduction

The superconducting transition temperature (T_c) in high-T_c superconductors is known to possess a strong hole-concentration dependence. In order to gain insight into this dependence, it is of great importance to investigate in detail the electronic structure as a function of hole-concentration.

Angle-resolved photoemission spectroscopy (ARPES) is a unique and powerful experimental technique that can reveal important information about the momentum and kinetic energy of the valence electrons. In this work, we investigate the hole-concentration dependence of the E–$\boldsymbol{k}$ dispersion by performing ARPES measurement on $(Bi,Pb)_2(Sr,La)_2CuO_{6+\delta}$ (Bi2201) of various hole-concentrations. We intentionally picked Bi2201 up rather than $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) because the hole-concentration in the Bi2201 can be widely controlled [1]. It is also very important to note here that

a clean surface of the Bi2201, which is one of the essential conditions of the ARPES measurement, can be easily prepared under an ultra-high vacuum condition because the doubly-stacked BiO layers in the unit cell are weakly connected by the Van der Waals' force. The determined E–$\boldsymbol{k}$ dispersion and Fermi surface (FS) in Bi2201 were compared with those in the Bi2212 to gain insight into the factors leading the difference in the transition temperature at the optimal condition, 36 K for Bi2201 and 92 K for Bi2212.

2. Experimental procedure

$(Bi,Pb)_2(Sr,La)_2CuO_{6+\delta}$ single crystals of a few cm in length were grown by the floating-zone (FZ) technique. The crystals are cut into typically 4 mm × 4 mm × 0.05 mm for the ARPES measurement. A partial substitution of Pb for Bi in Bi2201 was effective in weakening the superstructure along the b-axis, [2–6] which is often observed in the Bi-based superconductors and has prevented us from easily analyzing

the band structure.[7–9]. Hole-concentrations in the samples were controlled by the partial substitution of La for Sr and by different annealing conditions; the over-doped sample with $T_c < 2$ K (OD00) and $T_c < 7$ K (OD07) was obtained by annealing the as-grown sample of a nominal condition of $(Bi_{1.74}Pb_{0.38})Sr_{1.88}CuO_{6+\delta}$ with the annealing condition of 400 K for 72 h in a oxygen atmosphere and 550 K in a vacuum atmosphere, respectively. An over-doped sample with $T_c = 32$ K (OD32) and an under-doped sample with $T_c = 27$ K (UD27) were obtained from as-grown samples of nominal conditions of $(Bi_{1.35}Pb_{0.85})(Sr_{1.47}La_{0.38})CuO_{6+\delta}$ and $(Bi_{1.35}Pb_{0.85})(Sr_{1.4}La_{0.45})CuO_{6+\delta}$, respectively, both with the annealing condition of 650 K for 24 h in an Ar flow atmosphere. In the dc susceptibility measurement, all samples except for OD00 showed a sharp drop within a transition width less than 3 K. The OD00 possessed no evidence for the superconductivity in its dc susceptibility nor in the electrical resistivity at temperatures above 2 K.

High-resolution ARPES spectra were accumulated using the Scienta SES 2002 hemispherical analyzer with the Gammadata VUV5010 photon source (He Iα) at the Institute of Solid State Physics (ISSP), the University of Tokyo. The angular and energy resolutions employed in this work were 0.15° and 10 meV, respectively. We intentionally measured the spectra at 200 K rather than that at low temperature below 10 K to obtain information about the conduction band above E_F.

3. Results and discussion

Fig. 1(a-A)–(a-C) shows OD00's mapping images of the ARPES intensity at 6 K as a function of binding energy and momentum $(Int(E, \boldsymbol{k}, 6K))$ along several momentum lines shown in the Fig. 1(f). Since E_F is located almost on the bottom of the parabolic E–k_x curve in Fig. 1(a-A), it particularly difficult to determine the peak position at $k_x = 0$. To
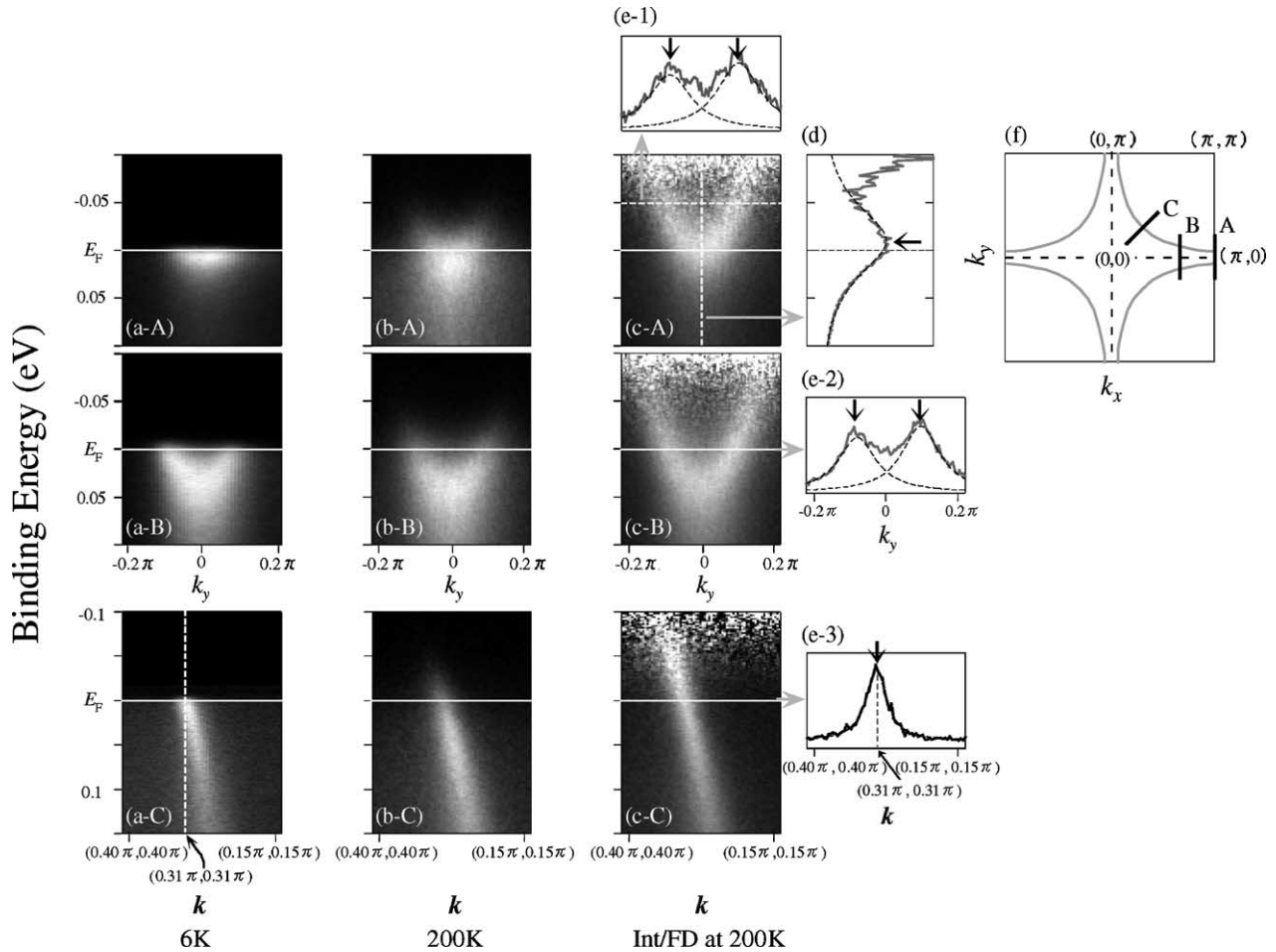

Fig. 1. (a) The ARPES intensity images measured at 6 K, $Int(E, \boldsymbol{k}, 6K)$, as a function of binding energy and momentum for over doped Bi2201 with $T_c < 2$ K, where A, B, and C refer the measured momentum in (f). Because of the high energy resolution, no intensity was observed above E_F. (b) $Int(E, \boldsymbol{k}, 200K)$ along the momentum lines A, B, and C. Thermal broadening can be observed up to a few $k_B T$ above E_F. (c) $Int(E, \boldsymbol{k}, 200K)$ divided by the Fermi–Dirac distribution function at 200 K along the momentum lines A, B, and C. The E–k dispersion up to a few $k_B T$ above E_F can be clearly observed. (d) The energy distribution curve at $(\pi,0)$ point, and (e) momentum distribution curves at energies shown in (e-A), (e-B), and (e-C). Energy and momentum of the peaks in EDC and MDC were assigned as the Eigen value and Eigen vector, respectively.

determine the peak position at the $(\pi,0)$ point, we employed Int(E, $\boldsymbol{k}$, 200 K), which are depicted in Fig. 1(b-A)–(b-C). Although photoemission spectroscopy is in general known to measure only the occupied part of electronic states, it can also probe the conduction band in a very narrow energy range up to a few $k_B T$ above E_F owing to a finite value in the Fermi–Dirac distribution function (FD-function) [10,11]. It is obvious in Fig. 1(b-A)–(b-C) that the Int(E, $\boldsymbol{k}$, 200 K) has intensity above E_F. We divided the Int(E, $\boldsymbol{k}$, 200 K) by the FD-function at 200 K and the resulting images are shown in Fig. 1(c-A)–(c-C). This method is valid only if the energy resolution ΔE of the measurement is smaller than $k_B T$. ΔE in the present measurement was $\sim$10 meV, which was a half of the $k_B T \sim 20$ meV at 200 K. It is obvious from Fig. 1(c-A)–(c-C) that the E–k dispersion even above E_F can be clearly observed. By extracting the energy distribution curve (EDC) at $(\pi,0)$ point, we confirmed that the peak energy at $(\pi,0)$ point is located above E_F, as previously reported by Takeuchi et al. [12]. Therefore we stress that the heavily over-doped Bi2201 with T_c less than 2 K has an electron-like Fermi surface centered at (0,0).

By extracting EDC's and momentum distribution curves (MDC's) from Int(E, $\boldsymbol{k}$, 200 K) divided by FD-function at 200 K, we successfully determine the E–k dispersion in the energy range of $-50 \leq$ B.E. ≤ 300 meV for the OD00, OD07, OD32, and UD27 samples. Eigen value as a function of wave vector, $E(k_x,k_y)$, was determined as the peak position in the MDC's or EDC's. We used fitting function with a Lorentzian shape to precisely determine $E(k_x,k_y)$. Some examples of the extracted EDC's and MDC's with the fitting curve are shown in Fig. 1(d) and (e), respectively.

A discrete data set of $E(k_x,k_y)$ in the OD07 is shown in Fig. 2(a). The presence of the van Hove singularity (vHs) at the $(\pi,0)$ point can be clearly observed at the energy slightly below E_F. In order to get continuous data sets rather than the discrete one, we employed the tight-binding fitting method proposed by Norman et al. [13], that is performed on the ARPES data of a Bi2212 superconductor. The resulting $E(k_x,k_y)$ for OD07 is depicted in Fig. 2(b).
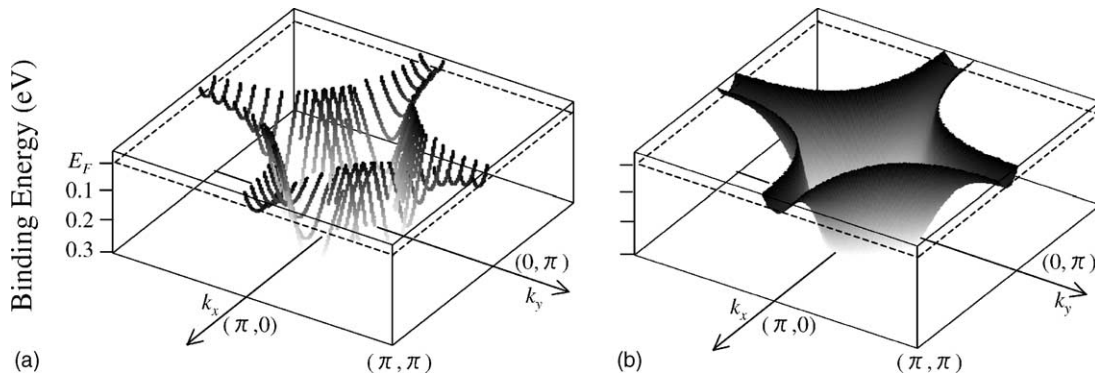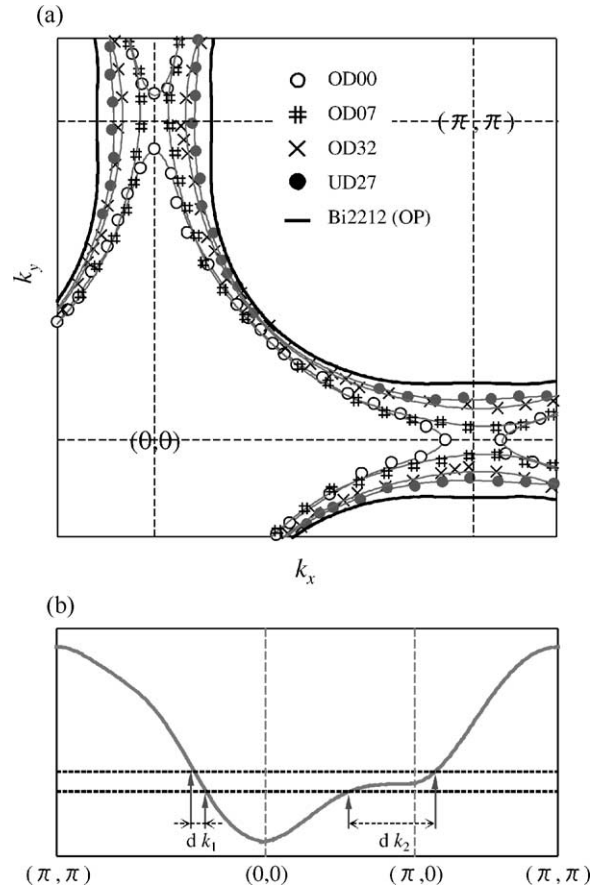

Fig. 3. (a) Fermi surfaces of Bi2201 with various hole-concentrations deduced from the ARPES measurement. (b) The E–k dispersion on the high-symmetry line for Bi2201. When E_F moves towards higher or lower energy, k_F at small v_g moves more than that with large v_g.

Fig. 3 shows the FS's in the OD02, OD07, OD32, and UD27 determined from the ARPES data. The area surrounded by the hole-like FS gets larger with increasing hole-concentration and the hole-like FS eventually transforms into an electron-like FS in the case of OD00. The shape of the FS is remarkably deformed around the $(\pi,0)$ point with increasing or decreasing hole-concentration, while that around the k_F along the diagonal direction shows

Fig. 2. (a) The E–k dispersion determined by the ARPES measurement for the over-doped Bi2201 with $T_c = 7$ K. (b) The E–k dispersion obtained by the tight-binding fit on the data set in (a).

less significant doping dependence. This hole-concentration dependence of FS can be accounted for by considering the momentum dependence of the group velocity $v_g(k_x, k_y) = (\partial E/\partial \boldsymbol{k})/\hbar$. The FS is more expanded around wave vectors k_F's corresponding to a small v_g more than to a large v_g with varying carrier concentration, as schematically drawn in Fig. 3(b). Since v_g in the vicinity of the vHs is smaller than that in other portion, FS is naturally expected to expand near the $(\pi, 0)$ point.

The doping dependence of the FS discussed above seems to indicate a rigid E–$\boldsymbol{k}$ dispersion; the E–$\boldsymbol{k}$ dispersion in all samples possesses a common $v_g(k_x, k_y)$ and the E_F is shifted toward higher or lower binding energy with decreasing or increasing hole-concentration, respectively. In order to confirm the rigidity of the band structure more clearly, we compare equi-energy surfaces at given $B.E._{norm}$ in the two-dimensional momentum space, where $B.E._{norm}$ are determined by $B.E._{norm} = B.E. - B.E._{vHs}$, so that the energy at the vHs is zero.

Fig. 4(a–d) shows the equi-energy surfaces of the OD00, OD07, and OD32 at $B.E._{norm} = -50, 0, 70$, and 150, respectively, determined by ARPES measurement. Since the spectra of UD27 were too broad to accurately determine the band stricture, we avoided using the band structure determined for UD27K. One may think that anti-ferromagnetic ordering gradually develops with decreasing hole-concentration towards that in the Mott insulator. This ordering creates a pseudo zone boundary along a momentum line connecting

$(0, \pi)$ and $(\pi, 0)$. If this scenario comes true, the E–$\boldsymbol{k}$ dispersion would be distorted about the newly generated pseudo zone boundary. Notably, however, the deduced equi-energy surfaces for all samples fall on a common curve at each $B.E._{norm}$. This result strongly indicates that the E–$\boldsymbol{k}$ dispersion is never distorted with varying hole-concentration at least in the over-doped condition, even though $T_c/T_c^{optimal}$ varies widely from 0 to 0.9. Thus we confidently argue that anti-ferromagnetic ordering never arise in the Bi2201 at least in the over-doped to nearly optimal doped conditions.

It is of great interest to compare the FS in the Bi2201 with that in the Bi2212, because the Bi2201 has the single CuO_2 plane in a unit cell and shows relatively low $T_c^{optimal} = 36$ K, while the Bi2212 has the double CuO_2 planes and a much higher $T_c^{optimal} = 92$ K. The FS reported for optimal doped Bi2212 [7–9,14] is superimposed on those determined for the Bi2201 in Fig. 3. Obviously, the area surrounded by the FS's in the present Bi2201 is considerably larger than that of the Bi2212.

For a quantitative comparison, hole-concentration in each sample was calculated from the area surrounded by the FS. It is widely known that uncertain oxygen concentration δ and the mixed valence of Bi in the $Bi_2Sr_2Ca_nCu_{n+1}O_{6+2n+\delta}$ ($n = 1, 2$, and 3) prevents us from easily estimating the precise hole-concentration in these high-T_c superconductors [16]. Notably, the method we used in this study to evaluate the hole-concentration is reliable as long as the wave number
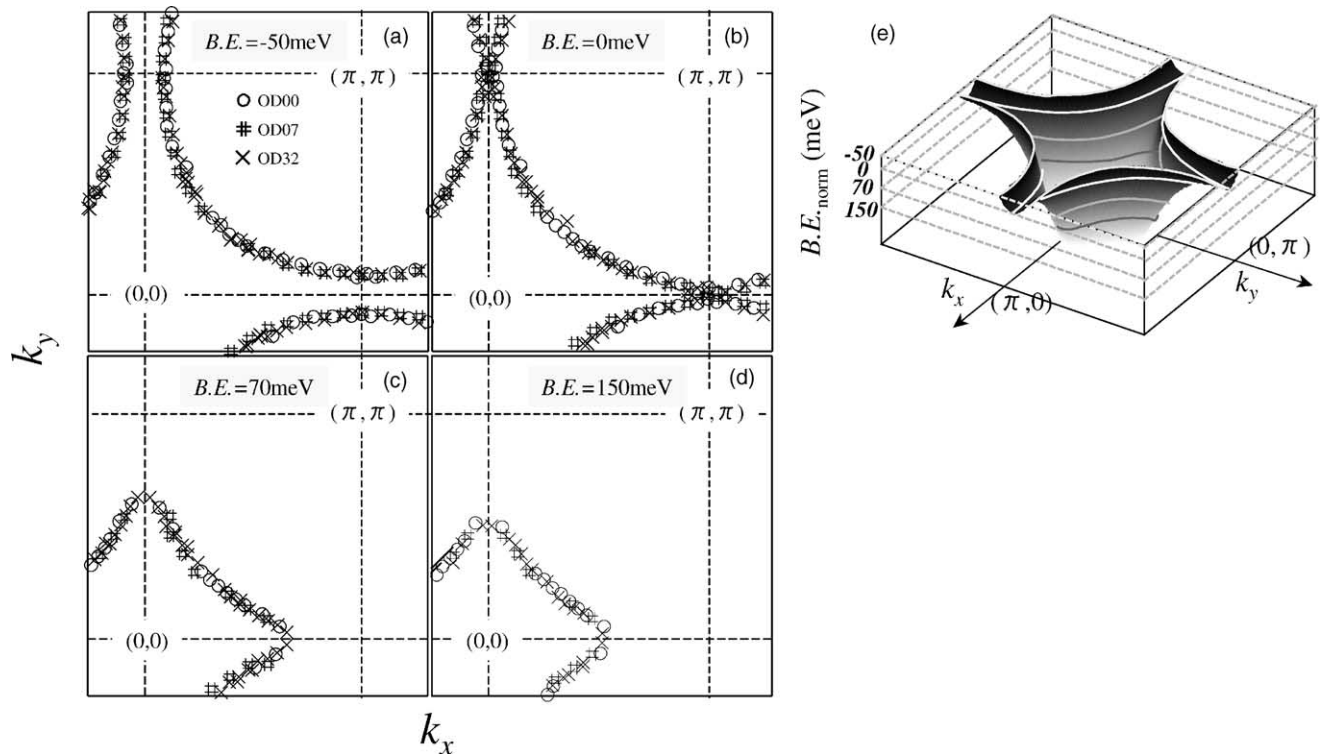

Fig. 4. Equi-energy surfaces of various hole-concentrations at (a) $B.E._{norm} = -50$ meV; (b) $B.E._{norm} = 0$ meV; (c) $B.E._{norm} = 70$ meV; and (d) $B.E._{norm} = 150$ meV. All data in each panel falls on a common curve, indicating a presence of a rigid band independent of hole-concentration.
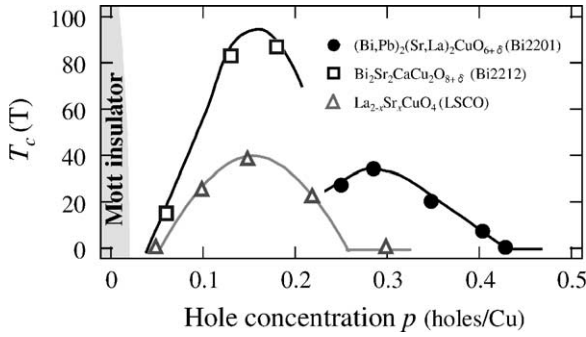
Fig. 5. T_c vs. p curves evaluated from the area surrounded by the FS for the Bi2201, Bi2212 [14], and LSCO [15].

is regarded as a good quantum number. Fig. 5 shows the transition temperature as a function of hole-concentration in the present Bi2201 together with those in the Bi2212 and the $La_{2-x}Sr_xCuO_4$ (LSCO) deduced from the reported FS's [14,15]. The areas surrounded by the FS for the OD02, OD07, OD32, and UD27 were determined to be 72, 70, 64, and 62% of full area in the first Brillouin zone (BZ), respectively. The resulting hole-concentrations (p) for the OD02, OD07, OD32, and UD27 turned out to be 0.43, 0.40, 0.28, and 0.25 holes/Cu, respectively. Surprisingly, the concentration of hole in the present Bi2201 is more than twice as large as that deduced from the optimal doped Bi2212, $p = 0.17$ holes/Cu. The T_c versus p curve for the present Bi2201 obviously extends towards the region in much higher hole-concentrations than that for the Bi2212 and LSCO centered at about $p = 0.17$ holes/Cu. The fact that $T_c^{optimal}$ in the Bi2201 is much lower than that in the Bi2212 might have a close relation with the difference in the hole-concentration revealed in this work. Further analysis is strongly required

to confirm this scenario. It is now in progress. We should stress that the transition temperatures in the high-T_c superconductors cannot be universally scaled by the hole-concentration.

Before closing the discussion, we should comment on the incident photon energy dependence of the spectrum shape and topology of the FS, that is now one of the controversial issues in the field of photoemission spectroscopy on the high T_c superconductors. Two different topologies of the FS, electron-like and hole-like FS's, were reported for Bi2212 on the basis of ARPES measurement with different incident photon energies [8,9]. This behavior can be accounted for in two different ways. The first explanation is based on the bi-layer splitting associated with double CuO_2 planes separated by the Ca layer in the unit cell [17,18]. One band is enhanced at certain incident photon energy such as 22 eV and the other at 33 eV [8,9,19]. This explanation cannot be used for the Bi2201 because it has only one CuO_2 plane per unit cell. The second way is associated with the umklapp bands generated by the structure modulation in the BiO layer [7–9]. The main band would be enhanced at certain energies where umklapp bands is reduced, and vice versa. Note here that we employed, in our present study, the Bi2201 free from structure modulation. That was confirmed by the X-ray diffraction patterns. Indeed no evidence of the presence of unklapp band was observed in the present measurement. We measured ARPES spectrum of Bi2201 especially near the (π,0) point with various incident photon energies from 16 to 33 eV in a synchrotron radiation facility SRC in Madison, Wisconsin. No significant variation that indicates the presence of two or more bands was found in the Brillouin zone as shown in Fig. 6. We strongly believe, therefore, that the electronic structure of Bi2201
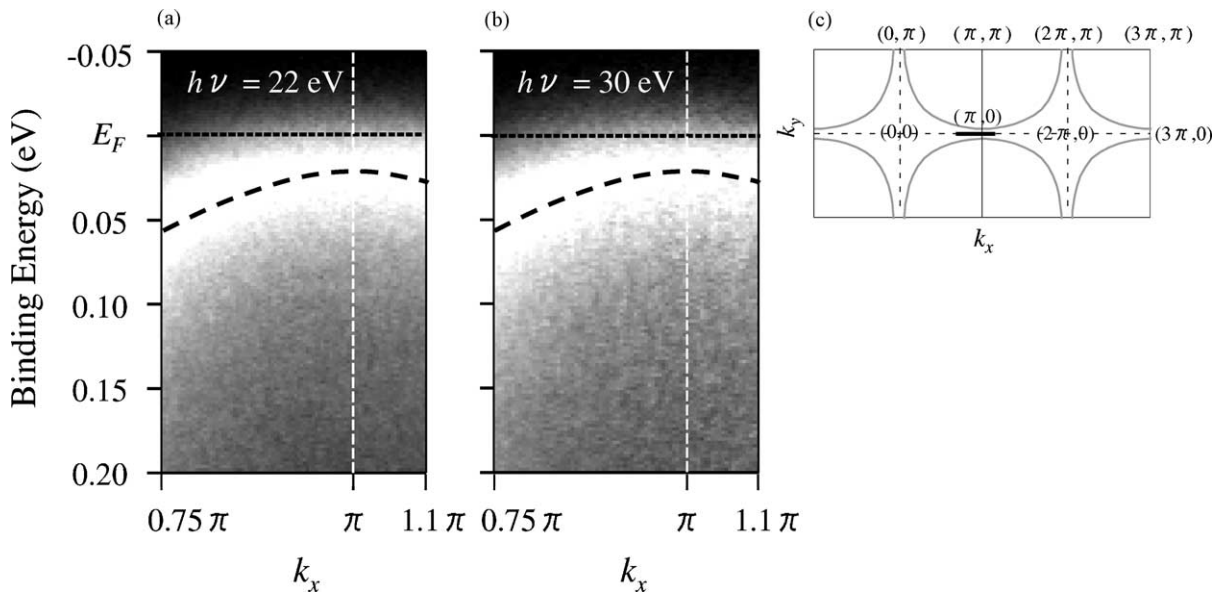

Fig. 6. E–k dispersion measured at a momentum line shown in (c) through (π,0) point along (0,0)-(π,0) direction with incident photon energies of (a) 22 and (b) 30 eV. No significant difference can be observed.

revealed in this study reflects intrinsic nature in the Bi2201 superconductor.

4. Conclusion

In the present study, the angle-resolved photoemission spectroscopy measurements were performed on the Bi2201 with various doping states. By measuring the spectra at 200 K, we determined the E–$\boldsymbol{k}$ dispersion in a binding energy range of $-50\,\text{meV} \leq \text{B.E.} \leq 300\,\text{meV}$, and found that the E–$\boldsymbol{k}$ dispersion is kept rigid over a wide hole-concentration range in the over-doped condition. Hole-concentration in the Bi2201 was quantitatively deduced from the area surrounded by the FS and compared with that in the Bi2212 and LSCO. We found that the hole-concentration in the present Bi2201 were distributed from $p = 0.25$ to 0.43 holes/Cu, that is twice as large as that in the Bi2212. Transition temperatures in the high-T_c superconductors cannot be universally scaled by the hole-concentration.

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