

## Photoemission study of $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$

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The electronic structure of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  has been studied by photoemission and electron-energy-loss spectroscopy (EELS). From analysis of the Cu  $2p$  core-level photoemission spectra, the Cu  $3d$ - $\text{O}2p$  bond in the  $\text{CuO}_2$  layer is found to be more ionic than that in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , which leads to a weaker superexchange coupling between the  $\text{Cu}^{2+}$  spins within the layer. Valence-band photoemission and EELS spectra suggest a significant shift of the Bi  $6s$  contribution from the deep-lying Bi  $6s$ - $\text{O}2p$  bonding states to the antibonding states in the O  $2p$  band region as compared to the results of band-structure calculations on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . This is probably due to excess oxygen atoms around Bi, which may raise the Bi  $6s$  orbital energy and provide the system with holes.

### I. INTRODUCTION

Knowledge of the electronic structure is essentially important in studying the mechanism of high- $T_c$  superconductivity in the layered perovskite oxides. So far, high-energy spectroscopic studies<sup>1</sup> such as photoemission spectroscopy,<sup>2-4</sup> electron-energy-loss spectroscopy (EELS),<sup>5</sup> and x-ray-absorption spectroscopy<sup>6</sup> on the La-Sr-Cu-O and Y-Ba-Cu-O and related systems have revealed that Cu atoms are at most divalent and that the Cu  $3d$  electrons are nearly localized due to strong electron correlation and that doped holes enter the O  $2p$  band rather than the Cu  $3d$ . Starting from this picture, various spin-fluctuation<sup>7-10</sup> and charge-fluctuation-mediated<sup>11</sup> pairing mechanisms have been proposed. The recent discovery of high- $T_c$  superconductivity in the Bi-Sr-Ca-Cu-O (Ref. 12) and Ti-Ba-Ca-Cu-O (Ref. 13) systems naturally raises the question of whether or not the same picture holds for the new systems and can explain the similarities and differences between the new and previous systems.

In this paper, we have studied  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  by photoemission spectroscopy and EELS. The results indicate that the Cu  $3d$ - $\text{O}2p$  bond within the  $\text{CuO}_2$  layer is more ionic than in the La-Sr-Cu-O and Y-Ba-Cu-O systems. Further, a significant Bi  $6s$  contribution is found in the valence-band region. We will discuss implications of these results on the character of doped holes and also on the crystal structure and oxygen content of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  which have not been settled yet.

### II. EXPERIMENT

Sintered  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  samples were prepared by a solid-state reaction as described in Ref. 14. Single-crystal  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  was grown by the traveling-solvent floating-zone method<sup>15</sup> and showed a  $T_c$  of  $\sim 90$  K. Its chemical composition was determined to be  $\text{Bi}_{2.2}$ -

$\text{Sr}_{1.8}\text{Ca}_{1.0}\text{Cu}_2\text{O}_y$  by electron microprobe analysis. A single crystal of  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$  was grown from the melt by using CuO as a flux.

The samples were introduced into the spectrometer with a base pressure of  $\sim 1 \times 10^{-10}$  Torr via an airlock entry. Clean surfaces were obtained by scraping *in situ* with a diamond file. In order to minimize possible surface degradation,<sup>16</sup> the samples were cooled to liquid-nitrogen temperature during the measurements. X-ray and ultraviolet photoemission spectroscopy (XPS and UPS) spectra were excited with a Mg x-ray source ( $h\nu = 1253.6$  eV) and a He resonance lamp ( $h\nu = 21.2$  eV and 40.8 eV), and EELS spectra with a grazing-incidence electron gun. Electrons were collected using a double-pass cylindrical-mirror analyzer. The total resolution of XPS, UPS, and EELS was  $\sim 0.9$ ,  $\sim 0.15$ , and  $\sim 0.7$  eV, respectively. Signals due to the satellites of the x-ray source were numerically subtracted.

Spectra of the single-crystal  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$  were obviously of better quality than those of sintered samples as judged from the single-peaked O  $1s$  core-level XPS spectrum and the weakness of the UPS feature of unknown origin at a binding energy  $E_B \sim 9$  eV.<sup>16</sup> As for  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$ , spectra were virtually identical between the single-crystal and sintered samples, except for Cu deficiency in the latter as measured by core-level XPS intensities, and both were found to be clean from the O  $1s$  XPS and valence-band UPS. All spectra presented in this paper are those of the single crystals.

### III. RESULTS AND DISCUSSION

#### A. Cu-O bonds and superexchange interaction within the $\text{CuO}_2$ layer

As shown in Fig. 1, the Cu  $2p$  XPS spectrum of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  exhibits satellite structures charac-

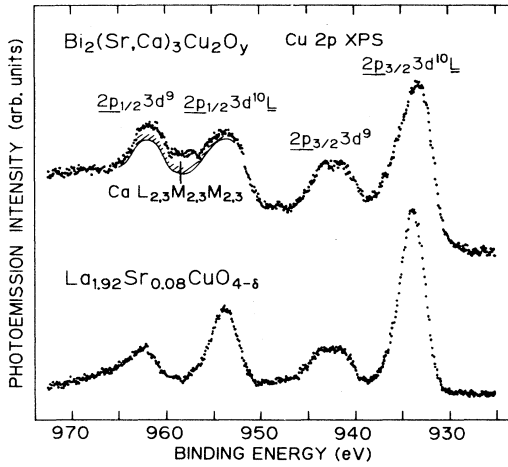


FIG. 1. Cu 2p core-level XPS spectra of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$ .

teristic of divalent Cu as in the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .<sup>1-4</sup> The figure also shows that the intensity of the satellite ( $2p3d^9$ , where  $2p$  denotes a Cu  $2p$  core hole) relative to that of the main peak ( $2p3d^{10}\underline{L}$ , where  $\underline{L}$  denotes an O  $2p$  ligand hole) is higher for  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  than for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . The relative intensities  $I_s/I_m$  and splittings  $\Delta E_{ms}$  of the main ( $m$ ) and satellite ( $s$ ) peaks of these compounds as well as those of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (Ref. 17) are listed in Table I.<sup>18</sup> From these values, one can estimate following the procedure of van der Laan, Westra, Haas, and Sawatzky<sup>19</sup> the  $d^9 \rightarrow d^{10}\underline{L}$  charge transfer energy,  $\Delta$ , the Cu  $3d$ -O  $2p$  transfer integral,  $T[\equiv -\sqrt{3}(pd\sigma)]$ , and the on-site Coulomb energy between the Cu  $2p$  core and  $3d$  electron,  $U_{cd}$ , by referring to Fig. 2, where  $\Delta$  and  $U_{cd}$  are plotted as functions of  $T$  for the given  $I_s/I_m$  and  $\Delta E_{ms}$  values of each compound. Considering that  $U_{cd}$  should not be much different between these compounds because of its intra-atomic nature nor  $T$  should because of nearly the same in-plane Cu-O bond lengths, we have estimated  $T$ ,  $\Delta$ , and  $U_{cd}$  as given in Table I. (Note that the  $\Delta$  and  $T$  thus obtained are those *within* the  $\text{CuO}_2$  layer because of the  $x^2-y^2$  character of the unoccupied  $d$  orbital of  $\text{Cu}^{2+}$ .) Thus, we find that a significant increase in  $\Delta$ , namely, in the ionic character of the in-plane Cu-O bond on going from  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  to  $\text{YBa}_2\text{Cu}_3\text{O}_y$  to  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  (though the small

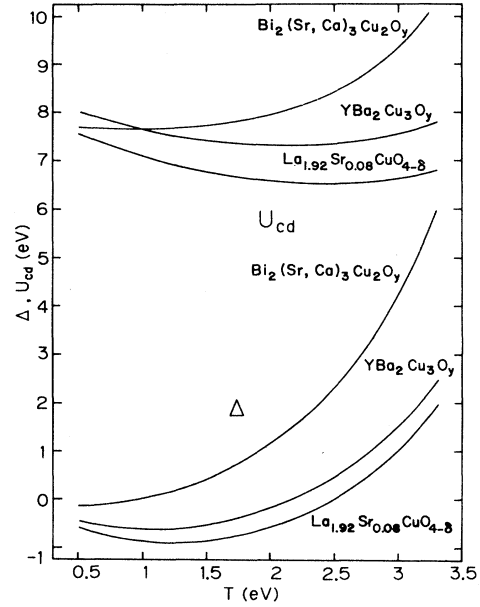


FIG. 2.  $d^9 \rightarrow d^{10}\underline{L}$  charge transfer energy  $\Delta$  and the on-site Coulomb energy  $U_{cd}$  between the Cu  $2p$  core and  $3d$  electrons as functions of the Cu  $3d$  to  $2p$  transfer integral  $T$  for the experimental  $I_s/I_m$  and  $\Delta E_{ms}$  values of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (Ref. 17), and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$ .

difference between  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_y$  may be within the experimental uncertainty).<sup>20</sup>

Since the in-plane superexchange coupling  $J$  between the  $\text{Cu}^{2+}$  spins decreases as  $\Delta$  increases,<sup>3,21</sup> the present results suggest a decrease in  $J$  in going from La-Sr-Cu-O to Y-Ba-Cu-O to Bi-Sr-Ca-Cu-O. Indeed,  $J$ 's obtained from two-magnon Raman scattering experiments have shown this tendency,<sup>22</sup> suggesting a correlation between  $J$  or  $\Delta$  and  $T_c$  (including results on Ti-Ba-Ca-Cu-O). If this correlation is real and the superconductivity occurs within the  $\text{CuO}_2$  layer, spin fluctuations will be favored over charge fluctuations as the origin of the high- $T_c$  superconductivity, since spin fluctuations generally become dominant with increasing  $\Delta$  while charge fluctuations become dominant with decreasing  $\Delta$ . However, one cannot conclude this at this stage because layers other than the  $\text{CuO}_2$  layer may be actively participating in the superconductivity.<sup>23,24</sup>

TABLE I. Relative intensities  $I_s/I_m$  and splittings  $\Delta E_{ms}$  of the main ( $m$ ) and satellite ( $s$ ) peaks in the Cu  $2p_{3/2}$  core-level XPS spectra. Electronic-structure parameters,  $\Delta$ ,  $T$ , and  $U_{cd}$  (for definition, see text) evaluated from the  $I_s/I_m$  and  $\Delta E_{ms}$  for each compound are also given. Energies are in eV.

	$I_s/I_m$	$\Delta E_{ms}$	$\Delta$	$T$	$U_{cd}$
$\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$	0.60	7.9	$2.0 \pm 0.5$	$2.4 \pm 0.2$	$8.1 \pm 0.2$
$\text{YBa}_2\text{Cu}_3\text{O}_y$	$0.33^a$	$8.5^a$	$0.7 \pm 0.2$	$2.6 \pm 0.2$	$7.3 \pm 0.1$
$\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$	0.25	8.2	$0.4 \pm 0.3$	$2.7 \pm 0.2$	$6.5 \pm 0.1$

<sup>a</sup>Taken from the spectrum of Meyer *et al.* (Ref. 17).

### B. Valence bands and possible Bi 6s contribution

In Fig. 3, the valence-band XPS and UPS spectra<sup>25</sup> of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  are compared with theoretical spectra calculated using band theory.<sup>26</sup> As in the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,<sup>16,17,27</sup> the experimental spectra are shifted to higher binding energy relative to the band-structure calculations (in this case as much as  $\sim 2$  eV). This together with the presence of a valence-band satellite at  $E_B \sim 11$  eV demonstrates the inapplicability of one-electron band theory to this material.

Thus, we calculated valence-band spectra using the configuration-interaction cluster model, which considers an octahedral  $\text{CuO}_6$  or a pyramidal  $\text{CuO}_5$  cluster and takes into account Coulomb and exchange interactions on the Cu site.<sup>28</sup> First, we fitted the calculated spectrum to the XPS spectrum of  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$ , using  $\Delta = 1.0$  eV,  $T = 2.4$  eV, [i.e.,  $(pd\sigma) = -2.2(pd\pi) = -1.4$  eV. Transfer integrals between the Cu 3d and off-plane O 2p orbitals were taken to be about 40% of the in-plane values<sup>28</sup>], and  $U_{dd} = 6.5$  eV. (The values are similar but not identical to those estimated from the Cu 2p XPS because of the effective nature of the parameters.<sup>29</sup>) Agreement with experiment is excellent as shown in Fig. 4. Here, the line shape and intensity of the O 2p band contribution have been derived, respectively, from the  $h\nu = 21.2$ -eV UPS spectrum for which the O 2p cross section is by far dominant, and the theoretical O 2p to Cu 3d XPS cross-section ratio.<sup>30</sup> Following the Cu 2p XPS results, we used a slightly larger  $\Delta$  (1.2 eV) and  $U_{dd}$  (7 eV):  $U_{dd}$  is expected to increase with  $U_{cd}$  (Ref. 29)], and a slightly smaller  $T$  (2.3 eV) for  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , and obtained again nearly perfect agreement with the XPS spectrum in Ref. 17. Accordingly, we took  $\Delta = 2.0$  eV,  $T = 2.2$  eV, and  $U_{dd} = 7.0$  eV for  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$ . However, using

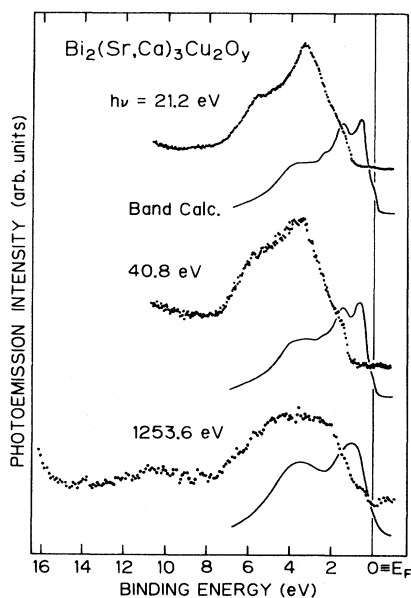


FIG. 3. Valence-band XPS and UPS spectra of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  (dots) compared with band-theoretical spectra (solid curves) calculated by Marksteiner *et al.* (Ref. 26).

these parameters or varying them somewhat around these values, we could not obtain a reasonable fit, particularly in the main-band region with binding energy  $E_B < 8$  eV as shown in Fig. 4. (As for the satellite region, there may be a contribution from Bi 6s-O 2p bonding states at  $E_B \sim 10$  eV, as discussed below; see, e.g., the valence-band XPS spectrum of  $\text{Bi}_2\text{O}_3$  in the inset of Fig. 5.)

The above discrepancy would be attributed to states other than Cu 3d and O 2p, probably related to Bi 6s states. The presence of Bi 6s character within several eV of the Fermi level ( $E_F$ ) is supported by the following argument. In Bi oxides, Bi 6s-O 2p bonding states are formed at  $E_B \sim 10$  eV and antibonding states within or just above the O 2p band,<sup>31</sup> both being occupied in  $\text{Bi}^{3+}$  oxides. The splitting between the bonding and antibonding states is largely determined by the strong Bi 6s-O 2p hybridization, particularly when the Bi 6s and O 2p levels are close to each other, and is relatively insensitive to the position of the Bi 6s level.<sup>31</sup> In the EELS spectra shown in Fig. 5, one can see that structures A at  $E_{\text{loss}} \lesssim 6$  eV and B at  $E_{\text{loss}} \sim 10$  eV are observed for  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  but absent for  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ . We attribute these structures to transitions from the Bi 6s-O 2p bonding and antibonding states to Bi 6p states above  $E_F$ . This assignment is obvious for structure B of  $\text{Bi}_2\text{O}_3$ , since its XPS spectrum (inset of Fig. 5) shows a bonding feature at  $E_B \sim 10$  eV; structure A is weak because the Bi 6s component is small

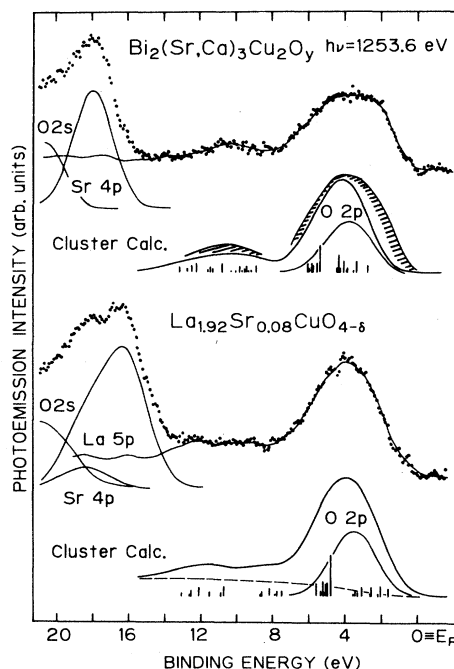


FIG. 4. Valence-band XPS spectra of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$  compared with those calculated using the configuration-interaction cluster model. Shallow core levels have been subtracted from the raw data (dots), yielding satellites at  $E_B = 10$ -12 eV. The shaded area for  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  indicates discrepancy between the experiment and theory. [For  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$ , an inelastic background has been subtracted.]

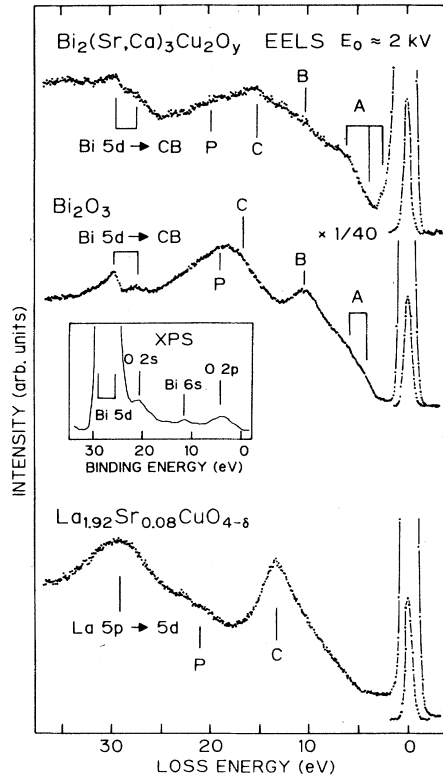


FIG. 5. EELS spectra of  $\text{Bi}_2(\text{Ca},\text{Sr})_3\text{Cu}_2\text{O}_y$ ,  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$ , and  $\text{Bi}_2\text{O}_3$ . *P* denotes plasmon satellites, and *C* transitions from O  $2p$  to higher conduction bands. Structures *A* and *B* are assigned, respectively, to transitions from the Bi  $6s$ –O  $2p$  bonding and antibonding states to the Bi  $6p$  states above  $E_F$  as discussed in the text. The inset shows an XPS spectrum of  $\text{Bi}_2\text{O}_3$ .

in the antibonding states. In going from  $\text{Bi}_2\text{O}_3$  to  $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_y$ , the intensity is shifted from *B* to *A*, which we interpret as due to a shift of the Bi  $6s$  weight from the bonding to antibonding states resulting from the upward shift of the Bi  $6s$  level.

Band-structure calculations on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  show no appreciable Bi  $6s$  character in the O  $2p$  band region.<sup>24,32,33</sup> As the local-density approximation is expected to be reliable in predicting the Bi  $6s$ - and O  $2p$ -level positions and hybridization between them, we suspect that the crystal structure used in the calculations is not sufficiently accurate. Namely, the superstructure of the  $\text{Bi}_2\text{O}_2$  layers has so far precluded accurate determination of the crystal structure.<sup>34</sup> Even the oxygen-coordinated number and geometry for the Bi atom nor the exact oxygen content  $y$  has not yet been determined. It is, therefore, probable that the oxygen content is greater than that assumed in the band-structure calculations ( $y=8$ ) and that the excess oxygens are coordinated to Bi, resulting in the upward shift of the Bi  $6s$  level. Indeed,  $y \approx 8.25 \pm 0.1$  has been obtained from thermogravimetry.<sup>35</sup> Since charges are balanced with  $y=8$  for valences of  $\text{Bi}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{O}^{2-}$ , excess oxygens are able to supply holes to the otherwise insulating system. (Alternatively, a “self-doping” mechanism has been proposed by

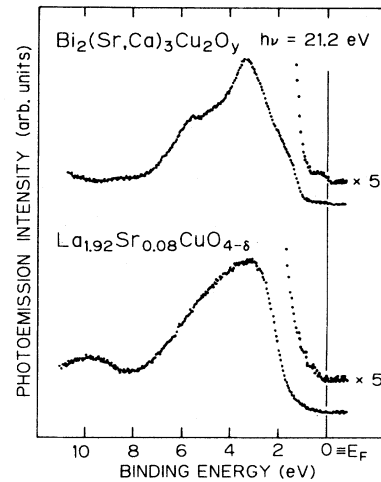


FIG. 6. UPS spectra of  $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_y$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_{4-\delta}$ .

Hybertsen and Mattheiss<sup>32</sup> and Krakauer and Pickett.<sup>33</sup> Even with  $y=8$  the bottom of the Bi  $6p$  band is populated by electrons, thus providing holes to the system. Due to the large uncertainty in the crystal structure, however, discussions on such a detail of the band structure would not be quite meaningful.) If there is significant Bi  $6s$  mixing near  $E_F$ , the holes may have partially Bi  $6s$  character or a fraction of Bi atoms may be converted to  $\text{Bi}^{4+}$  or  $\text{Bi}^{5+}$ , but its possible role in superconductivity is not clear at present.

As shown in Fig. 6, the UPS spectrum of  $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_y$  is different from that of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  in that it shows a flat region within  $\sim 1$  eV of  $E_F$  and a clear Fermi edge. [The spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  are rather similar to those of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , although a less clear Fermi edge has been observed for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with higher  $x$  (Ref. 27) and for  $\text{YBa}_2\text{Cu}_3\text{O}_y$ .<sup>36</sup> As the above comparison between the XPS spectrum and the cluster calculation has suggested extra spectral intensity within several eV of  $E_F$  (Fig. 3), which we have attributed to the effect of Bi  $6s$ , the characteristic behavior of the  $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_y$  UPS spectra near  $E_F$  might be related to the presence of the Bi  $6s$  character in this region. The fact that the extra intensity identified by XPS is not observed by UPS is consistent with the decrease of the Bi  $6s$  to O  $2p$  cross-section ratio by a factor of  $\sim 10^{-3}$  in going from XPS to UPS.<sup>37</sup>

### C. Character of doped oxygen holes

It is now established that the doped holes in the La-Sr-Cu-O and Y-Ba-Cu-O systems are O  $2p$ -like rather than Cu  $3d$ -like,<sup>1-6</sup> but it is controversial whether the holes are created on the  $p\sigma$ ,<sup>7-9</sup>  $p\pi$ ,<sup>10,38</sup> or  $p_z$  (Ref. 39) orbitals of oxygen in the  $\text{CuO}_2$  layer or on the  $p_z$  orbitals of the off-plane (i.e., BaO- or LaO-layer) oxygen above the Cu atom.<sup>23</sup> The recent polarized Cu  $L_{2,3}$ -edge x-ray absorption study has given microscopic evidence for the presence of off-plane  $p_z$  holes.<sup>24</sup> Indeed, band-structure calculations on  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_y$  have shown that the average energy (center of gravity) of the off-plane O  $2p$  partial density of states (DOS) is higher than that of

the in-plane O  $2p$ .<sup>20,40,41</sup> Although this is not obvious in the band-structure calculations of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ,<sup>32,33,42</sup> if oxygen content is higher than  $y=8$  and these oxygens are located in or near the  $\text{Bi}_2\text{O}_2$  layer, the O  $2p$  level in the SrO layer which is adjacent to the  $\text{Bi}_2\text{O}_2$  layer will be raised and may be preferentially doped with holes.

#### D. Core levels of Bi, O, and Sr

The XPS spectra of Bi core levels exhibit a slight asymmetry. Although the core-level asymmetry is often due to excitations of conduction electrons across  $E_F$  and suggests a finite density of states (DOS) at  $E_F$  at the core-level site,<sup>43</sup> the Bi  $4f$  core-level XPS spectrum (Fig. 7) could be better fitted by assuming an additional component on the high binding-energy side (solid curve) rather than by a Doniach-Sunjić-type<sup>43</sup> asymmetric Lorentzian ( $\alpha \approx 0.1$ , dashed line) which represents the excitations of conduction electrons in a wide band with a sufficiently large Fermi energy. The high binding-energy component is at least partly due to energy loss satellites (see the EELS spectrum in the inset of Fig. 7), and an intrinsic high binding-energy tail, if it exists, appears to be restricted within a narrow ( $\ll 1$  eV) range from the main peak. The narrow tail is consistent with a small Fermi energy ( $\ll 1$  eV) for the doped hole carriers. As for the possibility of Bi mixed valency, the core-level shifts between  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  in oxides are unfortunately very small<sup>44</sup> and would not give useful information.

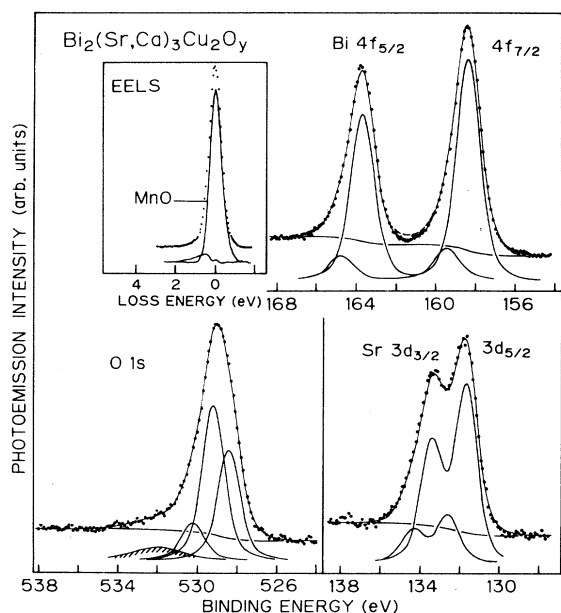


FIG. 7. Core-level XPS spectra of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$  and their line-shape analyses. The dashed curves for Bi  $4f$  is a Doniach-Sunjić line-shape fit. The shaded part for the O  $1s$  spectrum is due to contamination. The inset shows the elastic peak of an EELS spectrum (dots,  $E_0 \approx 2$  kV) decomposed into the purely elastic part (represented by the EELS spectrum of a wide-gap insulator MnO) and a low energy-loss signal ( $E_{\text{loss}} \sim 1$  eV).

The recent studies on single-crystal  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (Ref. 16) and well-characterized sintered  $\text{YBa}_2\text{Cu}_3\text{O}_y$  samples<sup>43</sup> have revealed that the O  $1s$  XPS spectrum consists of a single peak at  $E_B \sim 529$  eV rather than two peaks at  $E_B \sim 529$  eV and 531 eV as observed in earlier studies and that the 531-peak is due to surface degradation or grain-boundary contamination. The single peak, however, is considerably broader than the other core levels, suggesting the presence of overlapping multicomponents. Using approximately the same Gaussian width as for the other core levels, the O  $1s$  spectrum could be decomposed into three components (plus one, the shaded area in Fig. 7, due to contamination as judged from its time and filing-sequence dependence) as was done for La-Sr-Cu-O and Y-Ba-Cu-O by Weaver *et al.*<sup>45</sup> We assign the lowest binding-energy component to oxygens in the SrO and “ $\text{Bi}_2\text{O}_2$ ” layers, the second one to those in the  $\text{CuO}_2$  layers (plus an energy-loss satellite accompanying the first one), and the highest binding-energy component to the energy-loss satellite of the  $\text{CuO}_2$ -layer oxygen signal. The O  $1s$  binding energies deduced from the band calculation on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  are, on the other hand, such that  $\text{Bi}_2\text{O}_2 > \text{SrO} \sim \text{CuO}_2$ , and cannot explain the relative intensities of the deconvoluted peaks. As band calculations on  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_y$  have given O  $1s$  binding energies consistent with experiment,<sup>45</sup> the discrepancy would be attributed to the crystal structure used in the calculation. We suspect that the excess oxygens in or near the  $\text{Bi}_2\text{O}_2$  layer raise the O  $1s$  orbital in the same layer most significantly and that in the adjacent SrO layer to a lesser extent, resulting in the ordering of the O  $1s$  binding energies  $\text{CuO}_2 > \text{Bi}_2\text{O}_2 \sim \text{SrO}$ . Attempts to fit the O  $1s$  spectrum using the Doniach-Sunjić line shape gave unsatisfactory results as in the case of Bi  $4f$  XPS.

The high binding-energy component of the Sr  $3d$  core-level XPS (Fig. 7) appears too intense ( $\sim 30\%$  of the main component) to be assigned to an energy-loss satellite. This signal probably arises largely from Sr replacing Ca sites as has been suggested by a recent electron microscopy study.<sup>46</sup>

#### IV. CONCLUSIONS

We have found an increase in the  $d^9 \rightarrow d^{10}\underline{L}$  charge transfer energy  $\Delta$  or in the Cu–O bond ionicity within the  $\text{CuO}_2$  layer in going from  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  to  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_y$ , which leads to a decrease in the in-plane superexchange coupling  $J$ . A significant Bi  $6s$  contribution is suggested within several eV of  $E_F$ , although band-structure calculations on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  predict most of the  $6s$  weight to be in the Bi  $6s$ –O  $2p$  bonding states well below  $E_F$ . As the atomic arrangement of and around the  $\text{Bi}_2\text{O}_2$  layer and the oxygen concentration  $y$  have not been established yet, we propose that the discrepancy is caused by excess oxygens accommodated in or near the “ $\text{Bi}_2\text{O}_2$ ” layers.

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