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Electronic structure of Bi-Ca-Sr-Cu-O superconductors studied by photoelectron spectroscopy

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Photoelectron spectroscopy has been used to study the electronic structure of the newly discovered Bi-Ca-Sr-Cu-O superconductors. A clear Fermi edge is observed showing a metallic behavior. The oxygen 1*s* core level shows only one peak, in contrast to previous results on $YBa_2Cu_3O_{7-\delta}$. We suggest that the Fermi edge observed is mainly due to electrons derived from Bi-O *p* bands.

The recently discovered superconductors of Bi-Ca-Sr-Cu-O (Refs. 1 and 2) show many similarities with the previously studied $YBa_2Cu_3O_{7-\delta}$, which has been extensively investigated using photoelectron spectroscopy.[3-7] The results of these studies show the importance of correlation effects among the copper 3*d* electrons as well as the charge transfer between the oxygen and copper ions. Two-band calculations have recently been published on the electronic structure of the $Bi_2CaSr_2Cu_2O_{8+\delta}$ superconductor.[8,9] In this Rapid Communication, we report a recent experimental study of the electronic structure of the Bi-Ca-Sr-Cu-O superconductors using photoelectron spectroscopy. Several interesting observations are made. First of all, in contrast to $YBa_2Cu_3O_{7-\delta}$, $Bi_2CaSr_2Cu_2O_{8+\delta}$ shows a clear Fermi edge. This implies a higher density of states (DOS) at the Fermi level (E_F). Second, there is a strong Coulomb interaction among the Cu 3*d* electrons in the Bi-Ca-Sr-Cu-O superconductors. We suggest that the states observed at E_F are mainly due to contributions from the Bi-O *p* bands. The results indicate that the band theory describes the states of Bi-O *p* bands fairly well. However, the correlation effects must be taken into account for the states of the Cu-O planes.

Two samples of Bi-Ca-Sr-Cu-O were prepared by dry mixing Bi_2O_3, $CaCO_3$, $SrCO_3$, and CuO. In the following, we call them samples *A* and *B*, respectively, and refer to them together as Bi-Ca-Sr-Cu-O superconductors. The mixture was heated in air for 48 h at 850 °C, ground, then pressed into pellets and reannealed for 48 h at 870 °C. The temperature dependence of the Meissner susceptibility was measured by a vibrating sample magnetometer. Sample *A* displays an abrupt single transition at 85 K, while sample *B* exhibits a small Meissner signal at 105 K and an abrupt transition at 85 K. The Meissner signal for sample *A* (*B*) at 4.2 K is 70% (55%) of diamagnetic shielding. Powder x-ray diffraction shows that sample *A* is a single 85-K T_c phase of 2:1:2:2 composition ($Bi_2CaSr_2Cu_2O_{8+\delta}$). Also, sample *B* has a majority phase of the 2:1:2:2 composition with a small amount of the 105-K T_c phase ($Bi_2Ca_2Sr_2Cu_3O_{10+\delta}$) and some impurity phases. Therefore, we expect the photoemission spectra (PES) from the two samples to be similar. PES experiments were performed in an ultrahigh vacuum chamber with energy resolutions of 0.5 eV ultraviolet-photoemission spectroscopy (UPS) and 1.2 eV x-ray photoemission spectroscopy (XPS). The Fermi level of the analyzer was determined by evaporating Ag *in situ*. The base pressure during the experiment was better than 5×10^{-10} Torr. The samples were scraped *in situ* by a diamond file. More details of the experiment can be found in our earlier paper.[6]

The O 1*s* and the O Auger spectra were measured in order to check the surface cleanliness. The results of these measurements are shown in Fig. 1. Two peaks were observed in the O 1*s* core-level spectra for the as-transfered samples. However, after scraping the sample surfaces, the higher-binding-energy feature becomes progressively weaker, and eventually disappears completely from the spectra, leaving a single O 1*s* core-level peak, as shown in the figure. This finding is in sharp contrast to the results from $YBa_2Cu_3O_{7-\delta}$, which generally show a double structure of the O 1*s* core level. Since many authors have attributed the higher binding-energy feature on $YBa_2Cu_3O_{7-\delta}$ to contamination, the result shown in Fig. 1 gives us confidence of the sample quality and surface cleanliness. In addition, the Auger peak is also sharper than that of the $YBa_2Cu_3O_{7-\delta}$ system.[7]

Figure 2 shows experimental energy distribution curves (EDC's) of the $Bi_2CaSr_2Cu_2O_{8+\delta}$ sample at photon energies of 21.2, 40.8, and 1253.6 eV. The theoretical curves were obtained by adding the theoretical partial density of states (DOS) from band theory[8] weighted by the photoionization cross section of the various elements at different photon energies.[10] By comparing the experimental and theoretical curves, one finds that the experimental results do not agree with the band theory very well. There are two obvious differences between the experimental and theoretical curves. First of all, the DOS observed at E_F is lower than what the band theory predicts. This is also observed in the other high-T_c superconductors.[3,4,6] Second,

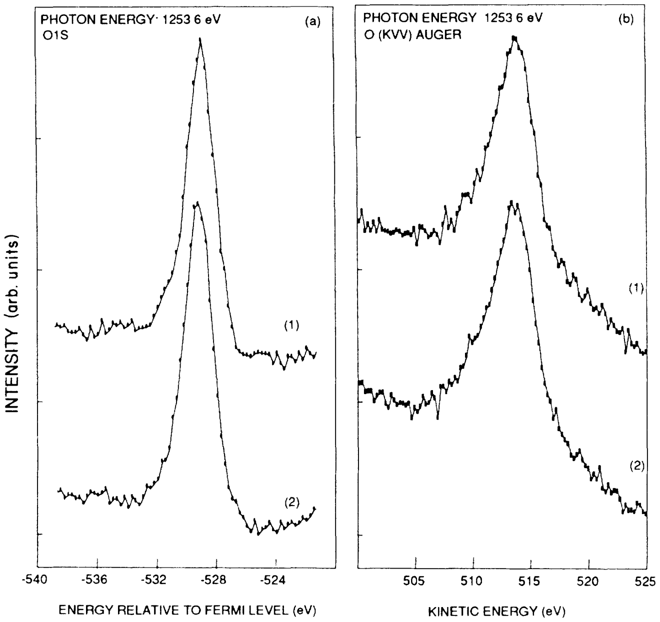

FIG. 1. Oxygen 1*s* core level and O Auger spectra of sample *A* (1) and sample *B* (2).

the centroid of the experimental valence band is shifted to higher binding energy by about 1.5 eV. This difference has often been observed in systems of transition-metal compounds like NiO,[11] and also the $YBa_2Cu_3O_{7-\delta}$ and La_2CuO_4 systems.[3,4,6] For the case of NiO, Sawatzky and Allen suggested that this difference is due to the Coulomb interaction U_{dd} of the 3*d* electrons.[11] Kubler and Williams also proposed that U_{dd} will cause a rigid shift of the bands.[12] However, a recent experiment on NiO by Shih *et al.* indicates that it is oversimplified to believe that the only effect of the correlations among the *d* electrons is a rigid shift of bands.[13] We believe the shift of the valence-band centroid observed in the Bi-Ca-Sr-Cu-O superconductor is due to a mechanism similar to that in NiO. These two differences between experiment and band theory reveal the necessity to go beyond the one-electron picture.

Recording PES spectra at different photon energies can help us to understand the character of the valence-band states better. For the three photon energies used in Fig. 2, the valence-band emission is mainly from Cu or O states, and the contributions from Bi and other elements are negligible due to the small photoionization cross section.[10] The photoionization cross sections of Cu and O are comparable at photon energies of 21.2 and 40.8 eV. At a photon energy of 1253.6 eV, however, the Cu contribution dominates the spectra because its cross section is about 40 times that of the O cross section. In Fig. 2(a), we can identify, within our resolution, three features, noted as *A*, *B*, and *C*. The photon energy dependence of feature *B* indicates that it has more oxygen character. For the feature extending from −10 to −12.5 eV binding energy, the fact that it is more pronounced at a photon energy of 1253.6 eV suggests that it has Cu 3*d* characters. Since this feature is so broad, it is also possible that there are oxygen or even Bi 6*s*, which will have small photoionization cross section, states contribute to the feature. However, resonance photoemission spectroscopy (RESPES) measurements are needed to identify this feature.[5,6] Our result of RESPES measurements indicate that only the higher-binding-energy part (−12.3 eV) of the feature exhibits strong resonance across the Cu threshold.[14]

We notice that the discrepancy between experiment and band theory is largest in Fig. 2(c). This is not surprising since we are essentially looking at Cu states at this photon energy. The band theory does not account for the *d*-*d* Coulomb interaction U_{dd} explicitly. Therefore, one would expect the *d* partial DOS to be severely altered by the correlation effects.[13] Even in Figs. 2(a) and 2(b), the experimental and the theoretical curves do not agree very

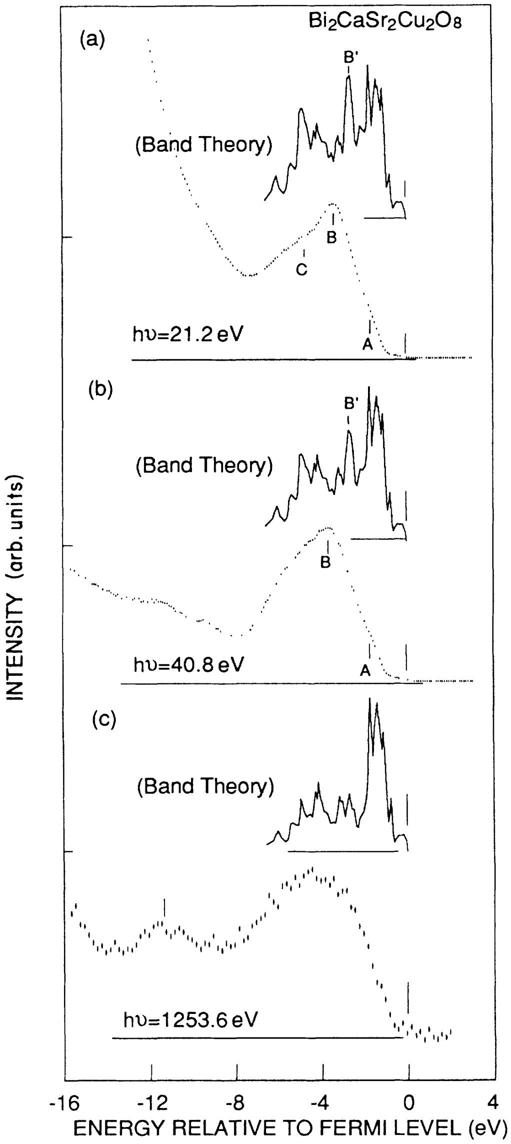

FIG. 2. Valence-band EDC's of sample *A* ($Bi_2CaSr_2Cu_2O_{8+\delta}$) at three different photon energies, (a) 21.2 eV, (b) 40.8 eV, and (c) 1253.6 eV, in comparison with band-theory predictions, weighted by the photoionization cross section at different photon energies. See text for more details.

well. As has been pointed out earlier, feature *B* has more O character. We think this might indicate that this feature reflects oxygen states from the Bi-O *p* bands. The band theory shows that the position of the oxygen states in the Bi-O *p* bands peak at *B*′. Since the key elements of the crystal structure are the Cu-O planes and Bi-O sheets,[8] one would expect the strongly hybridized Cu and O states in the Cu-O planes to be severely affected by the strong Coulombic interaction U_{dd}. On the other hand, it is conceivable that the band theory will give reasonable results for the 6*p*-2*p* bands of the Bi-O planes (even though it will be affected by the Cu-O planes). This argument makes it plausible that feature *B* corresponds to *B*′. Also the calculation by Krakauer and Pickett gives an O peak from the Bi-O *p* bands near the feature around −2.8 eV.[9] In addition, the fact that we can see the Fermi edge shows that the stoichiometric material is a metal, in agreement with the band-theory predictions.[8,9]

To gain further insight into the electronic structure of the Bi-Ca-Sr-Cu-O samples, we also measured the Cu 2*p* core level. The Cu 2*p* core levels of two Bi-Ca-Sr-Cu-O samples are presented in Fig. 3. The general line shapes are very similar to that of the other high-T_c materials and CuO.[3,6] However, the line shapes are distorted a little because of the Ca(*LMM*) Auger (∼ −960 eV) and Bi 4*s* core level (∼ −940 eV). The Bi 4*s* is not very strong, so the Cu $2p_{3/2}$ spectral features are basically not affected. These peaks are assigned to d^9 and $d^{10}\underline{L}$ configurations using the configuration interaction model.[3,6] The existence of the d^9 satellite in the Cu 2*p* core level again suggests the importance of strong correlation. The energy separation between the d^9 and $d^{10}\underline{L}$ states reflects the Coulomb interaction U_{cd} between the Cu 3*d* hole and Cu 2*p* core hole.[3,6]

To compare the electronic structure of the Bi-Ca-Sr-Cu-O compounds and $YBa_2Cu_3O_{7-\delta}$, in Fig. 4 we show the valence-band spectra of samples *A* and *B*, together with the valence-band spectrum of $YBa_2Cu_3O_{7-\delta}$. The $YBa_2Cu_3O_{7-\delta}$ spectrum is from Fig. 1 of our earlier paper.[6] An important difference between the Bi-Ca-Sr-Cu-O compounds and $YBa_2Cu_3O_{7-\delta}$, can be seen in Fig. 4. The DOS at E_F of Bi-Ca-Sr-Cu-O compounds is higher than for $YBa_2Cu_3O_{7-\delta}$. [A clear Fermi edge is shown in Fig. 4(b) for the $Bi_2CaSr_2Cu_2O_{8+\delta}$ sample.] The difference suggests that the Bi-Ca-Sr-Cu-O compounds have more metallic character than $YBa_2Cu_3O_{7-\delta}$. In addition, the Bi 4*f* core-level spectrum has an asymmetric line shape which also discloses the metallic nature of the Bi-Ca-Sr-Cu-O compounds. We suggest that the more metallic behavior of the Bi-Ca-Sr-Cu-O compounds as compared to $YBa_2Cu_3O_{7-\delta}$ is due to the 6*p*-2*p* states of the Bi-O bands. Comparing the crystal structure of $YBa_2Cu_3O_{7-\delta}$ and Bi-Ca-Sr-Cu-O compounds, we can see that the main difference is that the Cu-O chains in $YBa_2Cu_3O_{7-\delta}$ are replaced by the Bi-O planes in the Bi-Ca-Sr-Cu-O compounds.[8] According to the band calculations for the two compounds, these structural changes result in changes in the electronic structure. For the case of $YBa_2Cu_3O_{7-\delta}$, the states which cross E_F are the 3*d*-2*p* states from the Cu-O planes and the Cu-O chains.[15] For the case of Bi-Ca-Sr-Cu-O, the states which cross E_F are 3*d*-2*p* states of the Cu-O planes and 6*p*-2*p* states of the Bi-O bands.[8] Now, if the correlation effects arising from the Coulomb interactions among the 3*d* electrons are taken into account, the Cu-O states near E_F will be pushed away.[8,11–13] That probably explains why it is difficult to see emission at E_F from $YBa_2Cu_3O_{7-\delta}$ compounds. Since the Cu-O planes in the Bi-Ca-Sr-Cu-O compounds are very similar to those of $YBa_2Cu_3O_{7-\delta}$, we expect the same thing to happen for the Bi-Ca-Sr-Cu-O compounds. On the other hand, for the Bi 6*p*-O 2*p* states, the correlation effects are not strong, and we expect the band theory to describe the electronic structure of the Bi-O *p* bands

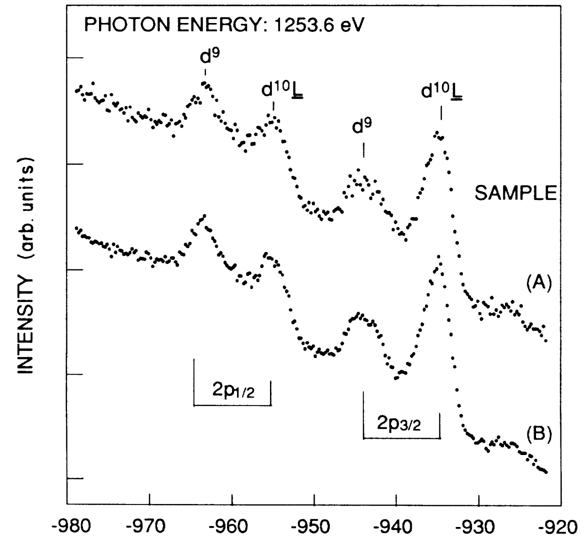

FIG. 3. Cu 2*p* core levels for samples *A* and *B*.

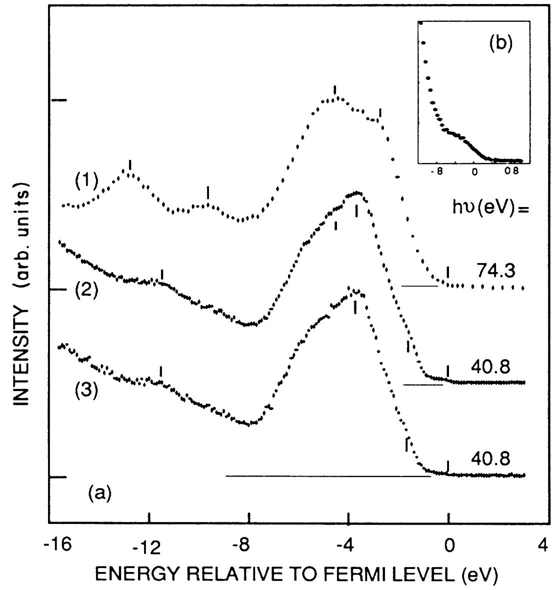

FIG. 4. (a) Valence-band spectra of samples *A* (2) and *B* (3) in comparison with the valence-band spectrum of $YBa_2Cu_3O_{7-\delta}$ (1). (b) Fermi level cutoff for $Bi_2CaSr_2Cu_2O_{8+\delta}$.

fairly well. Based on the above considerations, we believe that the states we observe at the Fermi level are mainly due to the contributions from the Bi-O p bands. Another interesting difference between the Bi-Ca-Sr-Cu-O compounds and $YBa_2Cu_3O_{7-\delta}$ is that the mysterious −9.2 eV peak in the $YBa_2Cu_3O_{7-\delta}$ valence band[6] is almost not visible in the Bi-Ca-Sr-Cu-O compounds.

To summarize, we have found that (1) the O 1s core level exhibits a single peak; (2) the experimental EDC's are different from the predictions of the one-electron band theory suggesting the importance of correlation effects among the 3d electrons; and (3) a clear Fermi edge is observed, which is believed to be derived from states of the Bi-O p bands. These results show that the stoichiometric material of the Bi-Ca-Sr-Cu-O compounds is more metallic due to the Bi-O p bands as predicted by the band theories.[8,9] However, the electronic structure of the Cu-O planes in the Bi-Ca-Sr-Cu-O compounds is similar to that of $YBa_2Cu_3O_{7-\delta}$. Since the Cu-O planes are believed to be responsible for the superconductivity, the underlying physics for the superconductivity is expected to be the same; however, the screening in the Cu-O plane and U_{dd} may be changed by the more metallic character of the Bi-O p bands.

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