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Electronic structure of Bi-based copper oxide superconductors: A comparative photoemission study of $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CuO_6$, and $Bi_2Sr_2CoO_{6+\delta}$

H. Eisaki, H. Takagi, and S. Uchida
Engineering Research Institute, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

H. Matsubara and S. Suga*
Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Tanashi, Tokyo 118, Japan

M. Nakamura, K. Yamaguchi, and A. Misu
Department of Physics, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

H. Namatame and A. Fujimori
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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Bi-based high-T_c copper oxide superconductors, $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CuO_6$, and a related material $Bi_2Sr_2CoO_{6+\delta}$ have been studied by photoemission spectroscopy. While common prominent structures at high-binding energies (> 2 eV) are attributed to oxygen $2p$ states in the Bi-O planes, emission near the Fermi level (E_F) is different from one other, indicating that these states are oxygen $2p$ states hybridizing with the transition-metal $3d$ states. For the states near E_F, the resonant behavior at the Cu $3p$-$3d$ absorption threshold and the photon energy dependence of the intensities are shown to be consistent with Cu $3d^9$-O $2p$ hole local singlets formed within the CuO_2 planes.

In the study of high-T_c copper oxide superconductors, high-energy spectroscopic methods have revealed their electronic structure on a large energy scale, which constitutes a framework to understand these materials.[1] On the other hand, it is also important to elucidate the electronic structure near the Fermi level (E_F) which is responsible for their transport and thermodynamic properties. For this purpose, $Bi_2Sr_2CaCu_2O_8$ has an advantage over the other materials in that the sample surfaces are stable under ultra-high-vacuum conditions so that clear Fermi edges are observable.

In a previous study,[2] we have investigated changes in the electronic structure near E_F across the metal-insulator transition in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ system, and have found a strong indication that doped holes go into the in-plane oxygen $2p$ orbitals which are coupled with the Cu $3d_{x^2-y^2}$ holes to form local singlets ($^1A_1$). These in-plane oxygen $2p$ holes are consistent with the polarization dependence of oxygen $1s$ core-level electron-energy-loss spectroscopy.[3] Angle-resolved photoemission studies have revealed dispersive states crossing E_F, which have been attributed to the electronic states of the CuO_2 planes in the metallic phase.[4] However, the atomic orbital character of these states still remains quite controversial. Arko *et al.*[5] have measured the valence-band ultraviolet photoemission spectroscopy (UPS) spectra of $YBa_2Cu_3O_7$ with various photon energies and found considerable Cu $3d$-derived emission intensities near E_F, which may contradict the predicted largely oxygen p-hole character of the $^1A_1$ final states.[1,2] On the other hand, according to band-structure calculations on $Bi_2Sr_2CaCu_2O_8$,[6] there may be significant contributions to the electronic states near E_F from a hybridized Bi $6p$-O $2p$ band as well as from the Cu $3d$-O $2p$ antibonding band. Indeed, Shen *et al.*[7] have performed a resonant photoemission study and ascribed the states near E_F to the Bi-O planes based on the lack of appreciable resonance at the photon energy near the Cu $3p$-$3d$ core absorption threshold. In this paper, we report on a photoemission spectroscopic study of $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CuO_6$, and $Bi_2Sr_2CoO_{6+\delta}$ to further investigate the nature of the electronic states near E_F in these systems.

Single-crystalline $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_6$ samples were synthesized as described in our earlier paper.[8] The $Bi_2Sr_2CaCu_2O_8$ sample has a transition temperature of 80 K. $Bi_2Sr_2CuO_6$ shows metallic behavior but no superconducting transition down to 4.2 K. The polycrystalline $Bi_2Sr_2CoO_{6+\delta}$ was synthesized by a solid-state reaction. The sample shows a semiconducting behavior with a resistivity of about 10 ohm cm at room temperature with an activation energy of about 200 meV.

The measurements using synchrotron radiation were done at the Synchrotron Radiation Laboratory using a modified Rowland-mount monochromator. We also used a He resonance lamp as a photon source. During the measurement, the pressure in the spectrometer was kept in the 10^{-10}-torr range. Clean surfaces were obtained by scraping the samples *in situ* with a diamond file, so that the obtained spectra are of the angle-integrated type. The samples were cooled to liquid-nitrogen temperature except for $Bi_2Sr_2CoO_{6+\delta}$, for which measurement at low temperatures was unsuccessful due to a charging effect.

Figure 1 shows valence-band spectra taken with photon energy 21.2 eV. The main O $2p$ band at higher binding energies (> 2 eV) resemble one another, characterized by a peak at about 3.5 eV (labeled A) and a shoulder at about 5.5 eV (labeled B) independent of the $3d$ transi-

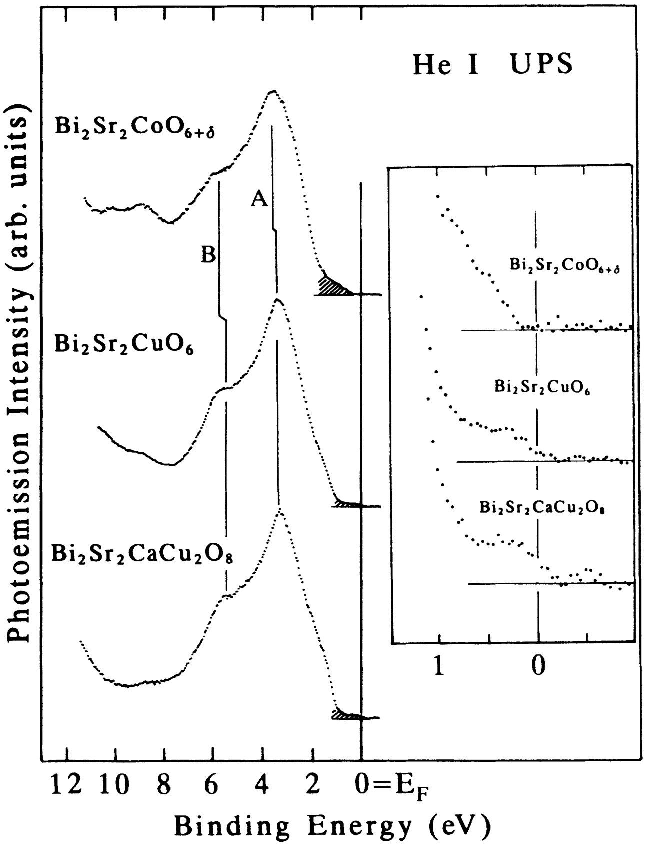

FIG. 1. Valence-band photoemission spectra of $Bi_2Sr_2CoO_{6+\delta}$, $Bi_2Sr_2CuO_6$, and $Bi_2Sr_2CaCu_2O_8$ taken with $h\nu = 21.2$ eV. The inset shows the spectra near the Fermi level on an enlarged scale.

tion-metal elements. On the other hand, the angle-integrated photoemission spectrum of single-crystalline $(La,Sr)_2CuO_4$ taken with the same photon energy shows no such distinct structures as A and B,[9] suggesting that these structures are associated with the Bi-O planes although the O $2p$ band as a whole has contributions from both the Bi-O and CuO_2 planes as well as from the SrO planes. Further, the fact that $Bi_2Sr_2CuO_6$, which has the same CuO_6 octahedrons as $(La,Sr)_2CuO_4$, clearly shows structures A and B also suggests that these structures are not related to the CuO_6 octahedra nor to the CuO_2 planes.

On the other hand, the states near E_F (the shaded part of Fig. 1) show a significant difference between these compounds. In the inset of Fig. 1, we plot the spectra in this region. [Here, the spectrum of $Bi_2Sr_2CoO_{6+\delta}$ has been shifted by 0.2 eV to smaller binding energies in order to align the valence-band peak position (peak A) with that of $Bi_2Sr_2CuO_6$.] For the Cu compounds, clear Fermi edges are observed as reported before.[2,9] Further, the intensity near the Fermi edge increases with the increasing number of CuO_2 planes per unit cell, indicating that the density of states at E_F correlates with the number of CuO_2 planes. On the other hand, the spectrum of $Bi_2Sr_2CoO_{6+\delta}$ has higher intensity at binding energies around 1 eV than that of the Cu compounds, but there is no emission at E_F. This indicates that the emission in the vicinity of E_F originates from the CuO_2 planes and not from the Bi-O planes since the emission from the Bi-O planes is expected to be nearly the same for these compounds with the same Bi-O planes.

In $Bi_2Sr_2CoO_{6+\delta}$, the valence of Co is considered to be 2+ or 3+, or their mixture depending on the oxygen content. For Co^{2+}, which has a $3d^7$ electron configuration, the photoemission spectra should exhibit a high intensity near E_F as in CoO.[10] For Co^{3+}, which has the same electron configuration $3d^6$ as FeO, the photoemission final state closest to E_F is a high spin $^6A_1$ state, and should show a high photoemission intensity as in FeO.[11] In the case of CuO with $3d^9$ configuration, the final state closest to E_F has $^1A_1$ symmetry with an oxygen hole lying in the Cu-O plane,[12] and the intensity of the states closest to E_F is weak compared to that of CoO or FeO, consistent with the present result.

The low photoemission intensity near E_F of the Bi-based Cu oxides may be further lowered due to the large width ($\sim$3 eV) of the $^1A_1$ band,[13] which may result in an intensity distribution extending into the main O $2p$ band region. In the high-T_c copper oxide superconductors, the square-planar CuO_4 units are connected two dimensionally in a corner-sharing way, in which the Cu $3d$-O $2p$ orbitals with x^2-y^2 symmetry in a CuO_4 unit strongly overlaps with those in the neighboring units, resulting in the formation of the wide $^1A_1$ band. In CuO, the CuO_4 units are connected in an edge-sharing way.[14] Then the overlap between neighboring (x^2-y^2)-symmetry orbitals is much reduced, and the $^1A_1$ final state does not show such a strong dispersion.

In Fig. 2, we show the valence-band spectra of the three materials measured at a higher photon energy $h\nu = 120$ eV. The photoionization cross section of the O $2p$ orbitals for this energy is $\frac{1}{10}$ compared with that for $h\nu = 21.2$ eV, while the cross sections of the Cu and Co $3d$ orbitals are not much reduced.[15] The cross section of the Bi $6s$-$6p$ orbitals for this photon energy is negligibly small. Thus, in these spectra, the contribution from the Cu or Co $3d$ orbitals is enhanced compared to that in Fig. 1. In Fig. 2, we see that the main O $2p$ band is similar among these materials, with a peak at around 3.5 eV. The main difference among them appears in the region near E_F, as in the case of $h\nu = 21.2$ eV, but more clearly in this case. This provides further evidence that these states are associated with the CuO_2 or CoO_2 planes and not solely with the Bi-O planes, since any contributions from the Bi-O planes should decrease with increasing photon energy. For $Bi_2Sr_2CoO_{6+\delta}$, the emission ranging from 0 to 1.4 eV is intense compared with the Cu compounds, indicating appreciable contributions from the Co $3d$ orbitals to this region. For the Cu compounds, as in the case of $h\nu = 21.2$ eV, the states within $\sim$1 eV of the Fermi level are also seen and the intensity of these states increases with the number of CuO_2 planes, indicating contributions from the CuO_2 planes to these states.

Such a photon energy dependence of the emission intensity near E_F as described above has led Arko *et al.*[5] to conclude that the states near E_F have a considerable amount of Cu $3d$ character as predicted by band-structure calculations. This photon energy dependence, however, can be reconciled with the largely oxygen p character of

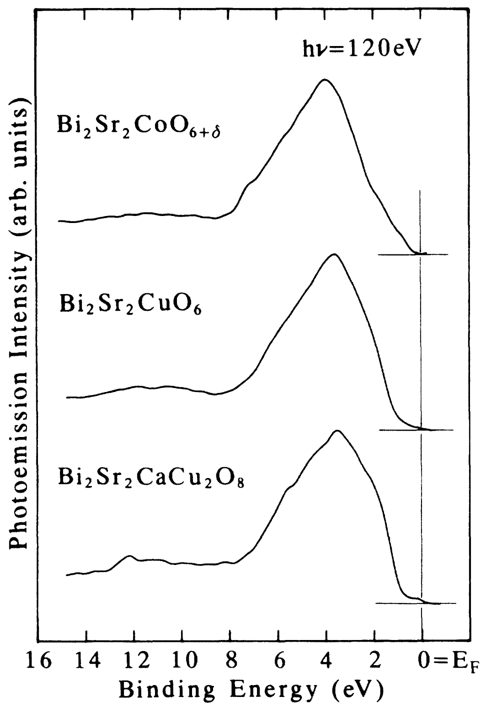

FIG. 2. Valence-band photoemission spectra of $Bi_2Sr_2CuO_{6+\delta}$, $Bi_2Sr_2CuO_6$, and $Bi_2Sr_2CaCu_2O_8$ taken with $h\nu=120$ eV.

the doped holes as predicted by the strong electron correlation picture[1] as follows. The ground state (without extra holes) shows strong hybridization between the Cu $3d$ and O $2p$ orbitals[1,13] and may be written as

$$\Psi_g \sim \sqrt{0.6}\,|d^9\rangle + \sqrt{0.4}\,|d^{10}\underline{L}\rangle \qquad (1)$$

in the cluster model. The $^1A_1$ final state close to E_F has a very small d^8 contribution because of the strong on-site Coulomb interaction between the two $3d$ holes, and may be given as

$$\Psi_f \sim \sqrt{0.05}\,|d^8\rangle + \sqrt{0.55}\,|d^9\underline{L}\rangle + \sqrt{0.4}\,|d^{10}\underline{L}^2\rangle . \qquad (2)$$

This means that ~95% of the dope hole is located on the O sites. On the other hand, the Cu $3d$-derived photoemission intensity of this final state is proportional to $|\langle\Psi_f|d|\Psi_g\rangle|^2 \sim 0.41$, which is as large as 40–50% of the O $2p$-derived intensity, $|\langle\Psi_f|L|\Psi_g\rangle|^2 \sim 0.95$, where d and L denote the annihilation operators of the Cu d and O $2p$ electrons. Thus the strong Cu $3d$-derived photoemission near E_F is totally consistent with the largely O $2p$ character of the doped holes.

In order to further investigate the contribution of the transition-metal $3d$ orbitals to the valence band, we have measured constant-initial-state (CIS) spectra of $Bi_2Sr_2CuO_6$ and $Bi_2Sr_2CoO_{6+\delta}$ using synchrotron radiation as shown in Fig. 3. For $Bi_2Sr_2CuO_6$ the satellite structure at $E_B = 12.7$ eV, which results from $3d^8$ final states, shows a strong resonant behavior around the photon energy of the Cu $3p$-$3d$ absorption, ~74 eV, but there is no appreciable resonance for $E_B = 3.6$ eV and at $E_B = 0.5$ eV. In the case of $Bi_2Sr_2CoO_{6+\delta}$, the resonance behavior can be seen at the Co $3p$-$3d$ absorption energy ($h\nu \sim 62$ eV) in the whole valence-band region. In particular, the existence of resonance for $E_B = 0.8$ eV indicates contributions of the Co $3d$ states to the spectra near E_F. A similar behavior is also observed in divalent $3d$ transition-metal oxide: For CoO,

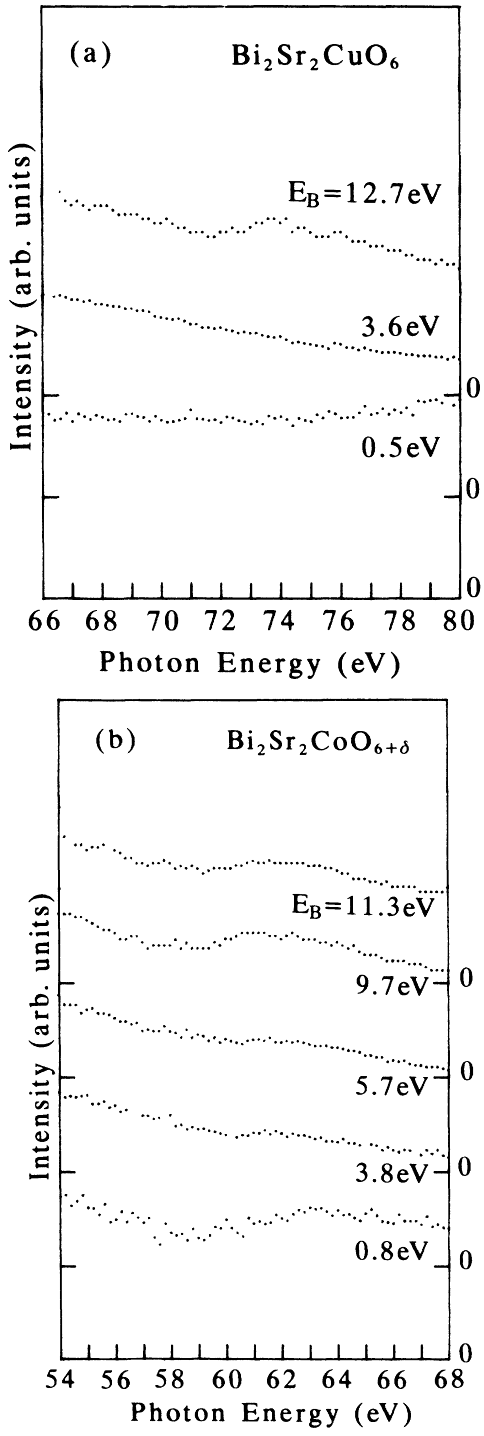

FIG. 3. Constant initial-state spectra of (a) $Bi_2Sr_2CuO_6$ and (b) $Bi_2Sr_2CoO_{6+\delta}$ taken in the $3p$-$3d$ core absorption region of the $3d$ transition metals.

resonant enhancement is seen both in the main valence band and the satellite,[10] consistent with the present result. On the other hand, the CIS study of CuO has revealed that a strong enhancement occurs in the satellite region but that only a very weak antiresonance behavior is seen for the main peak.[16] So the lack of appreciable resonance behavior for the states near E_F of the Bi-based copper oxides does not necessarily mean the lack of contribution of CuO_2 planes to the spectrum near E_F. As the resonance behavior near the Cu $3p$-$3d$ absorption energy occurs through the interference between the direct d-electron emission $3p^63d^9 \rightarrow 3p^63d^8\epsilon f$ and the $3p$ core excitation followed by a super Coster-Kronig decay[17] $3p^63d^9 \rightarrow 3p^53d^{10} \rightarrow 3p^63d^8\epsilon f$, the resonance behavior occurs for the $3d^8$ component in the final states. Therefore, the lack of appreciable resonance behavior can be attributed to the very small $3d^8$ component in the ${}^1A_1$ final state in Eq. (2), and is compatible with the Cu $3d$-derived photoemission which becomes stronger for higher photon energies.

In summary, we have measured valence-band ultraviolet photoemission spectra of a series of $3d$ transition-metal oxides with the Bi-O planes, $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CuO_6$, and $Bi_2Sr_2CoO_{6+\delta}$. Although some prominent structures at high-binding energies are attributed to the oxygen states in the Bi-O planes, the oxygen states which are hybridized with the transition-metal $3d$ states are located within 2 eV of the Fermi level. The states which cross E_F in the Cu compounds increase in intensity with an increasing number of the CuO_2 planes, and are not observed in $Bi_2Sr_2CoO_{6+\delta}$. The result suggests that these states reflect the electronic states of the CuO_2 planes. The photon energy dependence of the intensities of these states and the resonant behavior in the Cu $3p$-$3d$ absorption region are shown to be consistent with the local singlets consisting of the Cu d^9 local spins and the extra oxygen $2p$ holes within the CuO_2 planes.

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[*] Present address: Department of Materials Physics, Osaka University, Toyonaka 560, Japan.

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