RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Nature of the states near the Fermi level of the layered superconductors of $Bi_2Ca_1Sr_2Cu_2O_8$ and $Bi_2Sr_2CuO_6$

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(Received 4 August 1988)

Photoemission spectroscopy using synchrotron radiation has been used to investigate the electronic structure of the $Bi_2Ca_1Sr_2Cu_2O_8$ and the $Bi_2Sr_2CuO_6$ superconductors. The states near the Fermi level E_F, as observed in photoemission spectroscopy in these two compounds, have less Cu character than the $La_{1.8}Sr_{0.2}CuO_4$ and the $YBa_2Cu_3O_7$ superconductors. We suggest the coexistence of bandlike p states of Bi-O origin and correlated Cu $3d$–O $2p$ bands. The p bands of Bi-O are occupied differently in the $Bi_2Ca_1Sr_2Cu_2O_8$ and the $Bi_2Sr_2CuO_6$ superconductors, resulting in a different density of states near E_F and a slightly different valency of the Bi ions in the two compounds. We point out the correlation between the difference in the density of states near E_F and the difference in the superconducting transition temperatures of the $Bi_2Ca_1Sr_2Cu_2O_8$ and the $Bi_2Sr_2CuO_6$ superconductors.

Since the discovery of the high-temperature superconductors[1,2] much attention has been focused on the states at the Fermi energy E_F and their role for superconductivity. In the $La_{1.8}Sr_{0.2}CuO_4$ and the $YBa_2Cu_3O_7$ superconductors, one-electron band theory predicts that the states near E_F are dominated by Cu 3d–O $2p$ states from the Cu-O planes or the Cu-O chains.[3–5] This implies that the Cu $3d$ and O $2p$ states are the only ones that may be responsible for the superconductivity. Nevertheless, there has been increasing experimental evidence that the correlation effects play an important role, so that band theory cannot adequately describe the electronic structure. The density of states (DOS) at E_F observed in photoemission is much lower than that predicted by band theory. These experiments suggest that the Anderson Hamiltonian, which involves both the d-d Coulomb interaction and the p-d charge transfer, gives a good description of the electronic structure of the high-temperature superconductors.[6–8] The Anderson Hamiltonian has also been widely used as a starting point of different theories of the superconductivity.[3] Based on the localized picture of this Hamiltonian, the low DOS at E_F is attributed to the d-d correlation effects in the hybridized Cu$3d$–O $2p$ bands. For the two recently discovered superconductors of Bi-Ca-Sr-Cu-O and Th-Ca-Ba-Cu-O,[9–15] however, band theory for $Bi_2Ca_1Sr_2Cu_2O_8$ predicts that, not only the Cu $3d$–O $2p$ bands, but also the Bi $6p$–O $2p$ bands cross E_F.[16–18] Therefore, in the latter system, the Bi-O states may play an important role for the superconductivity. This hypothesis is reinforced by the experimental finding that $La_2SrCu_2O_6$, which can be derived from $Bi_2Ca_1Sr_2Cu_2O_8$ by removing the Bi-O planes and replacing Sr atoms by La atoms and Ca atoms by Sr atoms, is not superconducting.[19] Another very interesting property of the Bi-Ca-Sr-Cu-O superconductors is that the superconducting transition temperature T_c correlates with the number of Cu-O layers. The T_c for Bi-Sr-Ca-Cu-O superconductors with one, two, and three Cu-O layers is 10, 85, and 110 K, respectively.[20] Therefore, an investigation of the character of the states at E_F for the Bi-Ca-Sr-Cu-O superconductors, and the effects of changing the number of layers is well motivated.

In this paper we report a photoemission spectroscopy (PES) study, using synchrotron radiation, of the electronic structure of the Bi-Ca-Sr-Cu-O superconductors with two CuO_2 layers (2-Cu-L, with nominal composition $Bi_2Ca_1Sr_2Cu_2O_8$) and one CuO_2 layer (1-Cu-L, with nominal composition $Bi_2Sr_2CuO_6$). Compared to the $La_{1.8}Sr_{0.2}CuO_4$ and the $YBa_2Cu_3O_7$ superconductors, the states near E_F in the 2-Cu-L and the 1-Cu-L systems are found to have less Cu character. Even though both the $YBa_2Cu_3O_7$ and the 2-Cu-L compounds have two CuO_2

layers, the 2-Cu-L sample exhibits a clear Fermi edge, in contrast to the results from the $YBa_2Cu_3O_7$ compound.[7,8,21,22] Substantial differences of the states near E_F for the 2-Cu-L and the 1-Cu-L compounds are also observed. The 1-Cu-L system has a much lower DOS at E_F than the 2-Cu-L system. The corresponding core-level data indicate that the Bi ions in the 1-Cu-L system have a higher valency. We suggest that the differences in the DOS at E_F are due to the contributions from states of Bi-O p bands. Our data indicate that band theory adequately describes the Bi-O p bands. We also find strong evidence for correlation effects among the Cu $3d$ electrons as previously observed in the $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$ compounds.[6-8] Given the importance of states near E_F to superconductivity, we discuss the correlation between the difference of the DOS near E_F and the difference in the superconducting transition temperature T_c in the 2-Cu-L and the 1-Cu-L compounds.

The 2-Cu-L and the 1-Cu-L samples were prepared as described in our earlier paper.[22] The samples were characterized by x-ray diffraction and found to be of single phase. The magnetic and resistance measurements showed a superconducting transition at 85 and 10 K for the 2-Cu-L and the 1-Cu-L samples, respectively. The photoemission experiments were performed using the 3-m toroidal grating monochromator (TGM) beam line at the Synchrotron Radiation Center of the University of Wisconsin at Madison. The base pressure of the photoemission chamber was 4×10^{-11} torr. The photoelectrons were detected by a double-pass cylindrical mirror analyzer. The total-energy resolution of the monochromator and the analyzer was better than 0.3 eV. The pellet samples were scraped *in situ* by a diamond file. The photon flux was normalized by the beam current and the photon intensity variation of the beam line.

Figure 1 shows the valence-band spectra of the 1-Cu-L and the 2-Cu-L samples at photon energies of 70 (solid curves) and 74 (dotted curves) eV. All the spectra are normalized to have the same maximum intensity in the valence band. Comparing the PES spectra obtained from the 1-Cu-L and 2-Cu-L samples, one finds that the overall line shape of the valence band is rather similar, although measurable differences exist. First, the 2-Cu-L sample shows a clear Fermi edge, and exhibits much higher DOS at E_F, while the DOS of the 1-Cu-L sample tails off gradually as one approaches the E_F. It is worthwhile to note that the 2-Cu-L sample has higher T_c than the 1-Cu-L sample, such that T_c and the DOS at E_F appear related. Second, the centroid of the valence band of the 1-Cu-L sample is shifted to higher binding energy by about 0.5 eV relative to that of the 2-Cu-L sample. The lower binding-energy shoulder C, which can be seen in the 2-Cu-L sample, is not visible in the spectrum of the 1-Cu-L sample. We also notice that the Bi $5d$ core level of the 1-Cu-L sample is shifted to higher binding energy by 0.3 eV as compared with the 2-Cu-L sample [panel (2) of Fig. 1]. This indicates that the Bi ions of the 1-Cu-L sample have slightly higher valency than in the 2-Cu-L sample. Finally, as has been found in the $La_{1.8}Sr_{0.2}CuO_4$ and the $YBa_2Cu_3O_7$ compounds,[6-8] the enhancement of the features centered near -12.3 eV, $S1$ and $S2$ (shaded areas), in going from $h\upsilon=70$ to 74 eV is roughly proportional to the number of Cu states in the two samples. Measurement of the areas shows that they have approximately the ratio relation $A1{:}A2=1{:}2$, which is consistent with the fact that the Cu content in the 2-Cu-L system is higher than that in the 1-Cu-L system. The existence of such Cu satellite features at high binding energy reflects the strong correlations among the Cu $3d$ electrons.[6-8]

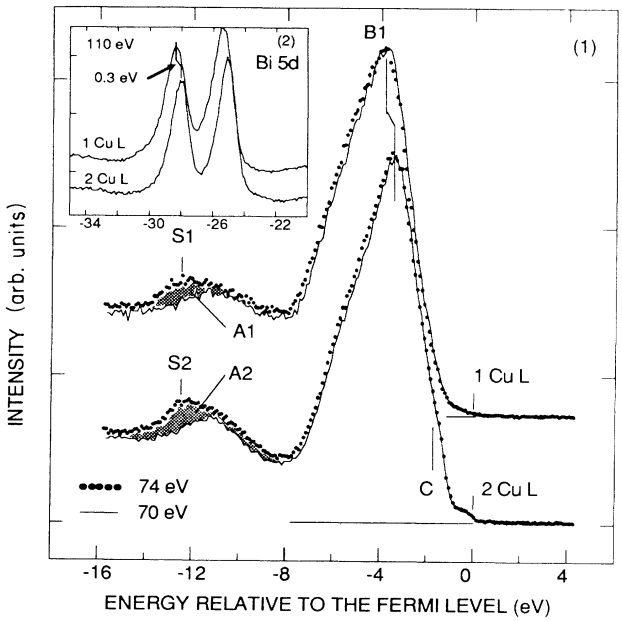

FIG. 1. Comparison of valence-band spectra for the 2-Cu-L and the 1-Cu-L samples at photon energies of 70 (solid line) and 74 eV (dotted curve). The inset of the figure shows the Bi $5d$ core levels at a photon energy of 110 eV.

To investigate the characters of the states in the valence band, we also performed constant initial-state (CIS) measurements, the results of which are presented in Fig. 2. Figures 2(a) and 2(b) show the CIS spectra of the 2-Cu-L and the 1-Cu-L samples, respectively. For the 2-Cu-L (the 1-Cu-L) sample, the satellite at an initial energy E_i of -12.3 eV (-12.6 eV) shows a Fano resonance line shape at the threshold of 74 eV. On the other hand, the main valence band with E_i of -3.2 eV (-4.0 eV) exhibits antiresonance behavior around the 74-eV threshold. Unlike the $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$ compounds, the states very close to E_F, at -0.5 and -0.8 eV for the 2-Cu-L and 1-Cu-L samples, respectively, do not show resonant behavior at the Cu $3p$-$3d$ absorption threshold.

To further explore the character of states near E_F, we present in Fig. 3 the CIS spectra with E_i in the vicinity of -0.5 eV for four different samples: (a) $YBa_2Cu_3O_7$, (b) $La_{1.8}Sr_{0.2}CuO_4$, and (c) the 2-Cu-L and (d) the 1-Cu-L (with $E_i=-0.8$ eV) Bi-Ca-Sr-Cu-O superconductors. The CIS spectra (a) and (b) are taken from earlier measurements.[7] The $YBa_2Cu_3O_7$ sample (a) shows a strong resonant behavior in the vicinity of 74 eV, while the $La_{1.8}Sr_{0.2}CuO_4$ sample (b) has a somewhat weaker resonant behavior. On the other hand, the Bi-Ca-Sr-Cu-O samples (c) and (d) do not exhibit any resonant behavior.

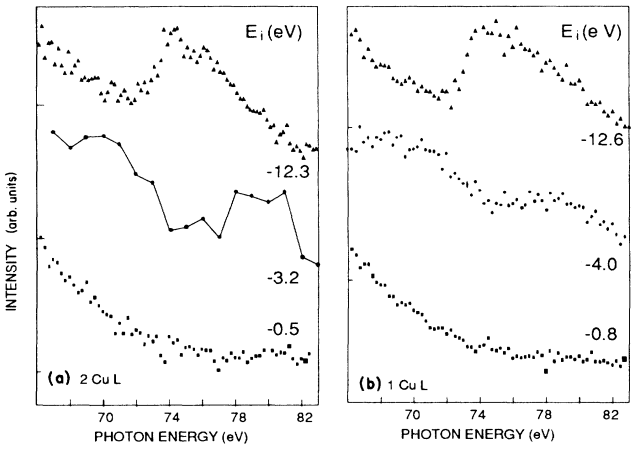

FIG. 2. CIS spectra of the 2-Cu-L (a) and the 1-Cu-L (b) samples at three different initial energies. The satellite $(-12.3, -12.6)$ shows resonance and the main band $(-3.2, -4.0)$ shows antiresonance, while the states near E_F show neither resonance nor antiresonance.

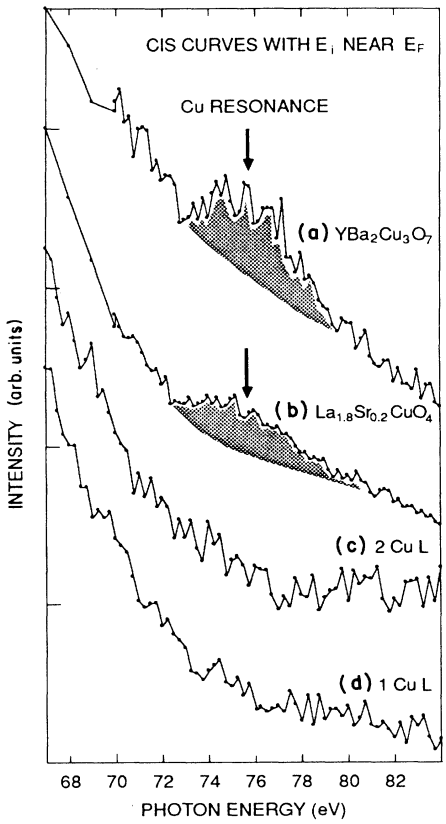

FIG. 3. CIS spectra of the states near E_F for four different samples, (a) $YBa_2Cu_3O_{7-\delta}$, (b) $La_{1.8}Sr_{0.2}CuO_4$, (c) 2-Cu-L sample, and (d) 1-Cu-L sample. The spectra were taken at following initial energies: $E_i = -0.5$ eV for (a), (b), and (c), and $E_i = -0.8$ eV for (d).

Based on this, we believe that the states near E_F for the Bi-Ca-Sr-Cu-O compounds have less Cu character than $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$ systems. A similar conclusion has also been drawn by Takahashi *et al.*[23] This is consistent with what we pointed out earlier that the Fermi edge might mainly arise from the states of the Bi-O p bands, as predicted by band theory.[16-18,22]

It is interesting to relate our observation of the electronic structure with the crystal structure of the 2-Cu-L, the 1-Cu-L, and the $YBa_2Cu_3O_7$ systems. First, we focus on the 2-Cu-L and 1-Cu-L samples. Obviously, the main difference between the 1-Cu-L sample and the 2-Cu-L sample is the absence of one of the Cu-O plane and the Ca layer in the 1-Cu-L sample. In addition, the bond length in the z direction of the two types of samples is different. For the 1-Cu-L (2-Cu-L) sample, the Bi—O(2) bond length in the Bi-O(2)-Cu chain along the z axis is 1.97 Å (2.22 Å), while the O(2)—Cu bond length is 2.58 Å (2.16 Å).[14,15,20] [Here O(2) denotes the bridging oxygen in the Sr-O plane.] These structural results agree generally with others.[24] It is clear that the Bi—O(2) bond length in the 1-Cu-L sample is shorter than that of the 2-Cu-L sample. Therefore one would expect the Bi valency in the 1-Cu-L to be slightly higher than that in the 2-Cu-L sample. This is exactly what we see in our data, we find that the Bi $5d$ core level of the 1-Cu-L sample shifts by 0.3 eV to higher binding energy than that of the 2-Cu-L sample (Fig. 1). Since Bi has higher valency in the 1-Cu-L sample, it will have less $6p$ states filled, resulting in a lower DOS near E_F than the 2-Cu-L sample. This consistency of the core-level shift and the DOS near E_F strongly implies that the Fermi edge observed in the 2-Cu-L sample is mainly due to Bi-O p bands. The absence of Cu character in the CIS measurements (Fig. 3) at E_F strongly supports this conclusion. Several band calculations have been performed to investigate the electronic structure of the 2-Cu-L compounds.[16-18] According to them, one Bi-O band disperses strongly so that it dips through E_F and hybridizes with the occupied Cu-O bands. As a result, Bi, unlike the Sr and Ca ions, is not fully ionized, but retains a small but potentially important amount of valence charge. We expect that the band approach will give a fairly good description of the states of the Bi-O p bands. Going back to the 1-Cu-L sample, we note that since the Bi—O bonding along the z direction is shortened, the Bi ions will be more ionized, as observed experimentally, and will lose the small amount of the valence charge that is retained in the 2-Cu-L compound. We anticipate that this might lead to no Bi-O band dipping below E_F, partly explaining why we see a lower DOS near E_F and higher valency of Bi ions for the 1-Cu-L sample. Kasowski has provided us with his new calculation on the 1-Cu-L compound.[25] Based on his calculation, the Bi-O bands do not dip through E_F, and therefore no electron pocket is formed so that no occupied states near E_F form the Bi-O band. These results are consistent with our experimental observation. Now, let us examine the difference in the DOS near E_F of the 2-Cu-L and the $YBa_2Cu_3O_7$ compound. The main difference in the crystal structure between the $YBa_2Cu_3O_7$ and the 2-Cu-L compounds, as far as the electronic structure is concerned, is the replacement of the Cu-O chains by the Bi-O planes. According to band calculations for the $YBa_2Cu_3O_7$ system, the states which cross E_F are due to

Cu $3d$-O $2p$ states derived from both the CuO_2 planes and Cu-O chains.[5] Since the Cu $3d$-O $2p$ bands are highly correlated, correlation effects tend to push the states away from E_F, which may explain why no clear Fermi edge has been observed for $YBa_2Cu_3O_7$.[7,8] On the other hand, for the 2-Cu-L compound, the states which cross E_F are Cu $3d$-O $2p$ states from the CuO_2 planes and Bi $6p$-O $2p$ states.[16-18] The Cu $3d$-O $2p$ states are expected to be pushed away from E_F by the correlation effects, but since the correlation of the Bi $6p$-O $2p$ bands is very weak, they remain near E_F as predicted by band theory. In essence, for the Bi-Ca-Sr-Cu-O compounds, there are two types of states, one is the correlated band of Cu $3d$-O $2p$, the other one is more bandlike states of Bi-O origin which dominates the DOS at E_F. This is consistent with the results of a recent angle-resolved photoemission study of the 2-Cu-L superconductor.[23]

To summarize, we have performed a photoemission study of the 2-Cu-L and the 1-Cu-L systems of Bi-Ca-Sr-Cu-O superconductors. CIS data show that the states near E_F have less Cu character than the $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$ compounds. We suggest the existence of bandlike p states in the Bi-Ca-Sr-Ca-O compounds of Bi-O origin, which dominate the spectral weights near E_F in the 2-Cu-L compound. These states are occupied differently in the 1-Cu-L and the 2-Cu-L compounds, resulting in a sharp difference in the DOS near E_F and a slightly different valency of the Bi ions.

We would like to thank J.-S. Kang and Dr. J. W. Allen for letting us use CIS spectra of $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$. We are grateful to Dr. R. V. Kasowski for providing us with the DOS calculation before publication. We thank the staff at the Synchrotron Center of the University of Wisconsin-Madison for skillful technical assistance during the measurements. We especially acknowledge the assistance of Yeh Chang. This work is supported by the U. S. National Science Foundation through the NSF-MRL program at the Center for Material Research at Stanford University, and through Northern Illinois University with Contract No. ONR-84-05173, and Air Force Contracts No. AFOSR-87-0389 and No. F49620-88-C-0004.

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