Valence-band and core-level photoemission study of single-crystal $Bi_2CaSr_2Cu_2O_8$ superconductors

Z.-X. Shen, P.A.P. Lindberg, and B. O. Wells
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

D. B. Mitzi
Department of Applied Physics, Stanford University, Stanford, California 94305

I. Lindau and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

A. Kapitulnik
Department of Applied Physics, Stanford University, Stanford, California 94305
(Received 29 August 1988)

High-quality single crystals of $Bi_2CaSr_2Cu_2O_8$ superconductors have been prepared and cleaved in ultrahigh vacuum. Low-energy electron diffraction measurements show that the surface structure is consistent with the bulk crystal structure. Ultraviolet photoemission and x-ray photoemission experiments were performed on these well-characterized sample surfaces. The valence-band and the core-level spectra obtained from the single-crystal surfaces are in agreement with spectra recorded from polycrystalline samples, justifying earlier results from polycrystalline samples. Cu satellites are observed both in the valence band and Cu $2p$ core level, signaling the strong correlation among the Cu $3d$ electrons. The O $1s$ core-level data exhibit a sharp, single peak at 529-eV binding energy without any clear satellite structures.

Since the discovery of the high-T_c superconductors, photoelectron spectroscopy has been used extensively to study their electronic structures.[1,2] Even though valence-band spectra for $Bi_2CaSr_2Cu_2O_8$ have been studied by various authors on both single-crystalline and polycrystalline samples,[3,4] no low-energy electron diffraction (LEED) study has been reported to characterize the surface structure of those samples studied by photoemission spectroscopy (PES). Furthermore, all the core-level data for $Bi_2CaSr_2Cu_2O_8$ were obtained from polycrystalline samples.[4] Therefore, concerns about the surface quality and its potential effects on the experimental results remain. In this paper, we report a study of single crystals of $Bi_2CaSr_2Cu_2O_8$ using LEED, ultraviolet photoemission spectroscopy (UPS), and x-ray photoemission spectroscopy (XPS). The LEED pattern shows that the surface structure is consistent with the bulk crystal structure. The experimental results from these well-characterized single-crystal surfaces are compared with previous reported results. The valence-band spectra obtained are very similar to earlier results obtained from single-crystalline and polycrystalline samples.[3,4] The important Cu d^8 satellite structures are identified in the valence band, confirming previous observations from polycrystalline samples.[4] The O $1s$ core-level and Cu $2p$ core-level spectra from these single crystals are also in good agreement with results from polycrystalline materials. Clear satellite structures are observed in the Cu $2p$ core-level spectra, consistent with the localized nature of the Cu $3d$ states. On the other hand, the O $1s$ core level, which has been controversial in $YBa_2Cu_3O_7$ and $(La_{1-x}Sr_x)_2CuO_4$, exhibits a single, sharp peak without any clear sign of satellite structures.

Single crystals of $Bi_2CaSr_2Cu_2O_8$ were prepared by mixing powders of Bi_2O_3, $Sr(CO_3)_2$, $CaCO_3$, and CuO. More details of the sample preparation can be found in our earlier paper.[5] x-ray diffraction measurements showed an almost pure phase of $Bi_2CaSr_2Cu_2O_8$ in the crystals. The superconducting transition temperature T_c was determined by magnetic measurements to be 90 K. The samples were transferred into a Varian photoemission chamber through a fast lock transfer system and then cleaved *in situ*. The orientations of the cleavage plane of the samples were determined by x-ray diffraction after the photoemission experiment.[5] The base pressure of the chamber was 1×10^{-10} torr. The surface area of the samples varied from 6 to 25 mm^2. The energy resolutions of the UPS and XPS experiments were 0.4 and 1.2 eV, respectively.

Figure 1 presents a LEED pattern of a single crystal of $Bi_2CaSr_2Cu_2O_8$ recorded at 45 eV beam energy and 24 h after cleaving. The LEED pattern, exhibiting sharp, distinct spots without streaking, is typical of a well ordered single crystalline surface. The LEED pattern shows that the single-crystal cleaves along the a-b plane, in agreement with the results of x-ray diffraction measurements.[5] The closely spaced diffraction spots along one axis reveal that also the surface exhibits a one-dimensional superstructure, consistent with the bulk crystal structure.[5] Even though this LEED pattern was taken 24 h after cleaving, it appeared identical to the LEED pattern taken from the freshly cleaved surface except for somewhat fuzzier diffraction spots. This result demonstrates that the surface of $Bi_2CaSr_2Cu_2O_8$ is very stable in vacuum, which

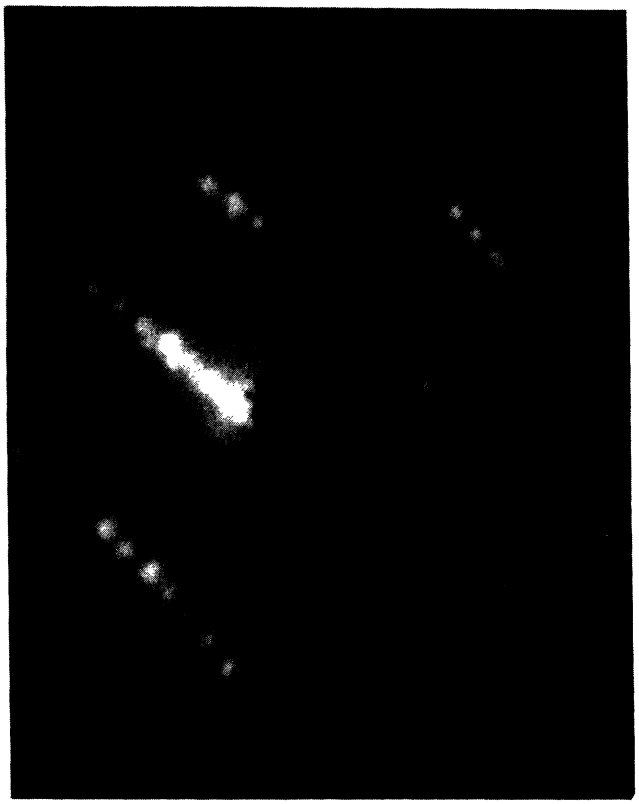

FIG. 1. Low-energy electron diffraction (LEED) pattern from a single-crystal $Bi_2CaSr_2Cu_2O_8$ superconductor recorded at a beam energy of 45 eV and 24 h after cleaving.

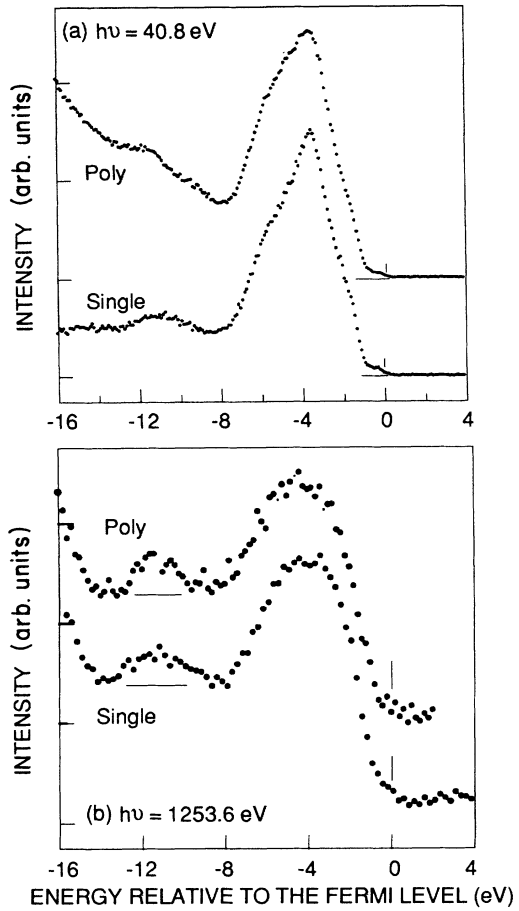

FIG. 2. Valence-band energy distribution curves (EDC's) from a single-crystal sample in comparison with results from a polycrystalline sample at different photon energies : (a) 40.8 eV, (b) 1253.6 eV.

might be important for their potential applications.

Figure 2 shows experimental energy distribution curves (EDC's) of the same $Bi_2CaSr_2Cu_2O_8$ single crystal at photon energies of 40.8 and 1253.6 eV in comparison with our earlier results from an *in situ* scraped polycrystalline sample.[4] It is clear that the valence-band spectra obtained from the single crystal are very similar to the valence-band spectra obtained from the polycrystalline sample, except for the difference in the background in panel (a). This consistency between the spectra from single-crystalline and polycrystalline samples validates earlier results obtained from polycrystalline samples.[6] Among these results is the poor agreement with one-electron band calculations and the existence of the Cu d^8 satellite, signaling the necessity to include many-body effects in describing the electronic structure of the superconductors. Since comparisons with one-electron band calculation have been made in detail earlier,[4] we will discuss only the satellite structure in the rest of the paragraph. The broad feature extending from -9.5 to -13 eV, clearly seen for both the single-crystalline and polycrystalline samples, is probably due to Cu $3d$ states since it is more pronounced at a photon energy of 1253.6 eV. Such a Cu $3d$ feature located at high binding energy in the valence band, which is not predicted by the one-electron band theory, is usually assigned to a d^8 satellite. However, our resonance photoemission measurements indicate that only the higher binding energy part (-12.3 eV) of the feature exhibits evident resonance behavior across the Cu $3p$ to $3d$ threshold.[6] This finding cannot be explained by the differences in the resolution of XPS (1.2 eV) and UPS (0.3 eV) (Ref. 6) measurements. However, it might be due to the fact that the photoemission and resonance photoemission involve different photoionization channels.[7] The d^8 final states can have different multiplet components S, P, D, F, G, among them; the F and G components are the strongest.[8] The resonance photoemission involves an Auger process and it has very different transition-matrix elements for the different components. The high binding energy component probably has larger transition-matrix elements, causing the stronger resonance behavior. Similar effects have been observed by Ghijsen *et al.* in the CuO system.[9] It is worthwhile to note here that a similar feature exists in the 40.8 eV spectra where Cu and O have comparable photoionization cross sections. Therefore, one cannot rule out contributions also from Bi $6s$ states and O-related states to this broad feature.

To gain further insight into the electronic structure of the $Bi_2CaSr_2Cu_2O_8$ compound, we also measured the Cu $2p$ core level from the single-crystalline sample. A Cu $2p$

core-level spectrum of the single crystal is presented in Fig. 3, together with a spectrum of a polycrystalline sample from our earlier experiments.[4] The spectra of the two kinds of samples are in good agreement. The general line shapes of the spectra are very similar to that of the other high-T_c materials and CuO.[10] 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 unaffected. These peaks are assigned to d^9 and $d^{10}\underline{L}$ configurations using the configuration interaction model.[1,10] 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 $d^{10}\underline{L}$ lines, which reflects the Coulomb interaction U_{cd} between a Cu 3*d* hole and a Cu 2*p* core hole, is about 9 eV, close to that of other high-T_c superconductors.[10] The satellite and the main-line intensity ratio, which reflects the Cu valency, is about 33%, similar to that of the other high-T_c superconductors.[10] Given the fact that the intensity ratio and the energy separation between the satellite and the main line of the Cu 2*p* core level, as well as the valence-band satellite position, are similar to results from $YBa_2Cu_3O_7$ and $(La_{1-x}Sr_x)_2CuO_4$ superconductors,[10] the parameters for the cluster model are expected to be nearly the same.

The O 1*s* core-level data for the high-T_c superconductors have been somewhat controversial. The results from most polycrystalline samples of earlier superconductors of $YBa_2Cu_3O_7$ and $(La_{1-x}Sr_x)_2CuO_4$ have two components at different binding energies.[1,11-17] Some of the authors attribute the two components to the different oxygen sites in the crystals.[13-15] Recent data from polycrystalline $Bi_2CaSr_2Cu_2O_8$ and single-crystalline $(La_{1-x}Sr_x)_2CuO_4$ reveal a single O 1*s* core peak.[4,16] In Fig. 4, we present an O 1*s* core-level spectrum from a well characterized $Bi_2CaSr_2Cu_2O_8$ single-crystal surface together with a spectrum from a polycrystalline sample from our earlier study, in which the O 1*s* core level showed to have only one sharp peak near -529 eV. These data conclusively demonstrate that only one component is intrinsic to the $Bi_2CaSr_2Cu_2O_8$ superconductor. Even though the oxygen sites in the $Bi_2CaSr_2Cu_2O_8$ are not equal, the chemical shifts of O 1*s* core level are smaller than the experimental resolution of ~ 1 eV, consistent with the theoretical calculation by Redinger *et al.* on the other high-T_c superconductors.[18] Because of the similarity of the different oxygen sites in $Bi_2CaSr_2Cu_2O_8$ and $YBa_2Cu_3O_7$ as revealed by their crystal structures, we suggest that only the lower binding energy component is intrinsic for $YBa_2Cu_3O_7$. It is clear that the O 1*s* core level does not have a strong satellite structure as the Cu 2*p* core level does. There have been suggestions that the Coulomb interaction among the oxygen 2*p* electrons, U_{pp}, is about 5 eV,[19] not too much smaller than U_{dd}, the Coulomb interaction among the Cu 3*d* electrons. The fact that we observed satellites in the Cu 2*p* core level while we did not see satellites in the O 1*s* core level cannot be explained within the context of the configuration interaction (CI) model, but it may be understood if one takes into account the difference between the unrenormalized oxygen and copper bandwidth. Since no strong satellite structure is observed in the O 1*s* core level, which is consistent with the bandlike nature of the oxygen 2*p* states, it seems unlikely that a clear oxygen two-hole satellite will be observed in the valence-band spectra.

To summarize, UPS and XPS experiments have been performed on well characterized single-crystal surfaces of $Bi_2CaSr_2Cu_2O_8$ superconductor. The results are consistent with previous results from polycrystalline samples, which support earlier interpretations based on the polycrystalline samples. Cu satellite structures were observed both in the core-level and valence-band spectra, revealing

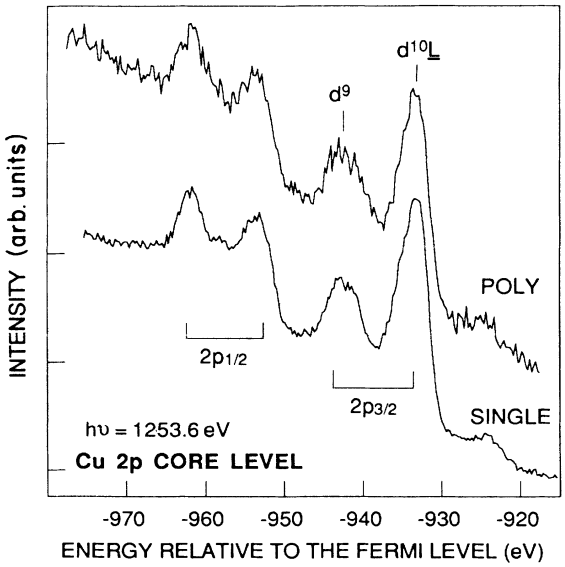

FIG. 3. Cu 2*p* core-level spectra from a single-crystalline and a polycrystalline $Bi_2CaSr_2Cu_2O_8$ sample.

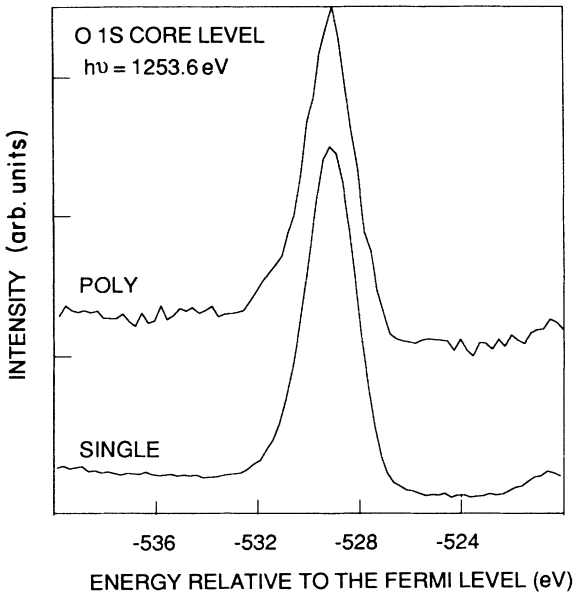

FIG. 4. O 1*s* core-level spectrum from single-crystalline and polycrystalline $Bi_2CaSr_2Cu_2O_8$ samples.

the strongly correlated nature of the $3d$ electrons. For the complicated O $1s$ core-level data, our result clearly indicates that only one peak is intrinsic to the $Bi_2CaSr_2Cu_2O_8$ superconductor. This result demonstrates that the difference of the binding energy of the oxygen ions at the different sites in the superconductor is small. Unlike the Cu core levels, the O $1s$ core level does not have strong satellite structures, which we suggest, is due to the bandlike nature of the oxygen $2p$ states.

We would like to thank D. Dessau for his help in our experiment. Two of the authors would like to thank AT&T (D.B.M.), and the Alfred P. Sloan Foundation and the National Science Foundation (A.K.) for support. 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, Air Force Contract No. AFOSR-87-0389 and Joint Services Electronics Program Contract No. DAAG 29-85-K-0048.

[1]Goran Wendin, Invited paper presented at the *Fourteenth International Conference on X-ray and Inner-Shell Process, 1987* [J. Phys. (Paris) Colloq. **48**, C9-1157 (1987)], and references therein.

[2]R. L. Kurtz, in *Thin Film Processing and Characterization of High Temperature Superconductors,* edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman, AIP Conf. Proc. No. 165 (American Institute of Physics, New York, 1988), p. 222, and references therein.

[3]M. Onellion, M. Tang, Y. Chang, G. Margaritondo, J. M. Tarascon, P. A. Morris, W. A. Bonner, and N. G. Stoffel, Phys. Rev. B **38**, 881 (1988).

[4]Z.-X. Shen, P.A.P. Lindberg, I. Lindau, W. E. Spicer, C. B. Eom, and T. H. Geballe, Phys. Rev. B **38**, 7152 (1988).

[5]P.A.P. Lindberg, Z.-X. Shen, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, Appl. Phys. Lett. (to be published).

[6]Z.-X. Shen, P. A. P. Lindberg, P. Soukiassian, C. B. Eom, I. Lindau, and T. H. Geballe, Phys. Rev. B (to be published).

[7]L. C. Davis, Phys. Rev. B **25**, 2912 (1982).

[8]M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **26**, 669 (1982).

[9]J. Ghijsen, L. H. Tjeng. J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzky (unpublished).

[10]Z.-X. Shen, J. W. Allen, J.-J. Yeh, J.-S. Kang, W. Ellis, W. E. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, Phys. Rev. B **36**, 8414 (1987).

[11]Y. Dai, A. Manthiram, A. Campion, and J. B. Goodenough, Phys. Rev. B **38**, 5091 (1988).

[12]T. Gourieux, G. Krill, M. Maurer, M. F. Ravet, A. Menny, H. Tolentino, and A. Fontaine, Phys. Rev. B **37**, 7516 (1988).

[13]W. K. Ford, C. T. Chen, J. Anderson, J. Kwo, S. H. Liou, M. Hong, G. V. Rubenacker, and J. E. Drumheller, Phys. Rev. B **37**, 7924 (1988).

[14]J. A. Yarmoff, D. R. Clarks, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[15]A. G. Schrott, S. I. Park, and C. C. Tsuei (unpublished).

[16]T. Takahashi, F. Maeda, H. Katayama-Yoshida, Y. Okabe, T. Suzuki, A. Fujimori, S. Hosiya, S. Shamoto, and M. Sato, Phys. Rev. B **37**, 9788 (1988).

[17]D. D. Sarma, K. Sreedhar, P. Ganguly, and C. N. R. Rao, Phys. Rev. B **36**, 2371 (1987).

[18]J. Redinger, J. Yu, A. J. Freeman, and P. Weinberger, Phys. Lett. A **124**, 463 (1987).

[19]D. van der Marel, J. val Elp, G. A. Sawatzky, and D. Heitmann, Phys. Rev. B **37**, 5136 (1988).

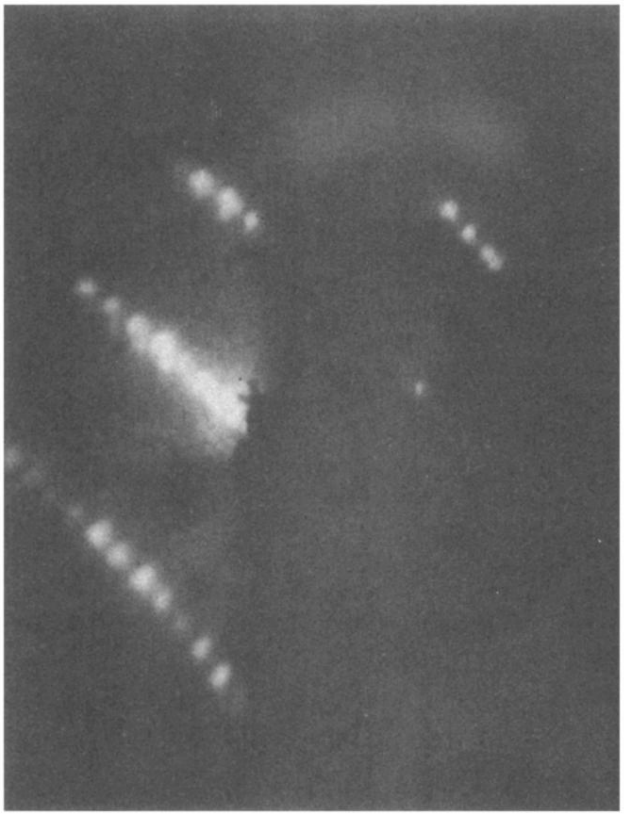

FIG. 1. Low-energy electron diffraction (LEED) pattern from a single-crystal $Bi_2CaSr_2Cu_2O_8$ superconductor recorded at a beam energy of 45 eV and 24 h after cleaving.