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Valence-band states in $Bi_2(Ca,Sr,La)_3Cu_2O_8$

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We have used photoemission spectroscopy to examine the symmetry of the occupied states of the valence band for the La-doped superconductor $Bi_2(Ca,Sr,La)_3Cu_2O_8$. While the oxygen states near the bottom of the 7-eV-wide valence band exhibit predominantly O $2p_z$ symmetry, the states at the top of the valence band extending to the Fermi level are found to have primarily O $2p_x$ and O $2p_y$ character. We have also examined anomalous intensity enhancements in the valence-band features for photon energies near 18 eV. These enhancements, which occur at photon energies ranging from 15.8 to 18.0 eV for the different valence-band features, are not consistent with either simple final-state effects or direct O $2s$ transitions to unoccupied O $2p$ states.

To date there have been several spectroscopic studies of the $Bi_2CaSr_2Cu_2O_8$ superconductor and related compounds.[1-4] A general picture of the electronic structure of this compound has emerged. However, the picture is not complete. There are still many details of the electronic structure that have not been studied and controversies surround the interpretation of previous work. X-ray-absorption spectroscopy[5] (XAS) and electron-energy-loss spectroscopy[6] (EELS) have been used to find the symmetries and chemical nature of the unoccupied states. However, the symmetries of the occupied part of the valence band have not yet been determined. This paper describes angle-resolved photoemission spectroscopy (ARPES) experiments that are the first determination of the symmetries of the states in the valence band. The highly polarized nature of synchrotron radiation enabled us to study these symmetries. In particular, the symmetry selection rules that govern the states probed in normal emission, angle-resolve-photoemission enable us to locate the O $2p$ states of different symmetry. During the course of our measurements we noticed that different features in the valence band showed an intensity enhancement for particular photon energies from 15 to 18 eV. Many groups have noticed that the intensity at the Fermi level exhibits a large enhancement for photon energies around 18 eV. There has been some argument as to the interpretation of this effect. We examine all of the valence-band features and we find the exact photon energy location of the enhancement for each feature.

Single crystals of $Bi_2(Cu,Sr,La)_3Cu_2O_8$ were used in our experiment. The La dopant substitutes mainly on the Sr sites, as discussed in a previous paper.[7] Microprobe studies give an overall composition of $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$. The preparation of these crystals is described in an earlier paper.[8] The crystals showed superconductivity at 91 K, as measured by magnetic susceptibility. The angle-resolved photoemission experiments ($\pm 2°$ angular resolution) were performed on beam line III-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The VG ADES400 chamber had a base pressure of 2×10^{-10} Torr. The total energy resolution in the available-photon-energy range, 10–40 eV, was about 0.3 eV. The samples were transferred into the chamber with a load-lock system. The samples of dimensions about $8\times5\times1$ mm^3 were cleaved in ultrahigh vacuum.

An energy-dispersion curve (EDC) of the $Bi_2(Ca,Sr,La)_3Cu_2O_8$ sample at a photon energy of 17.25 eV exhibits six main peaks in the valence band as shown in Fig. 1. These peaks are labeled A through F, with A nearest the Fermi level and F at the largest binding energy. The shape and positions of these peaks are similar to those found by Takahashi *et al.* for undoped $Bi_2CaSr_2Cu_2O_8$ at a photon energy of 18 eV.[1] Because of the similarity of our valence-band spectrum to published results for the valence-band spectrum from undoped sam-

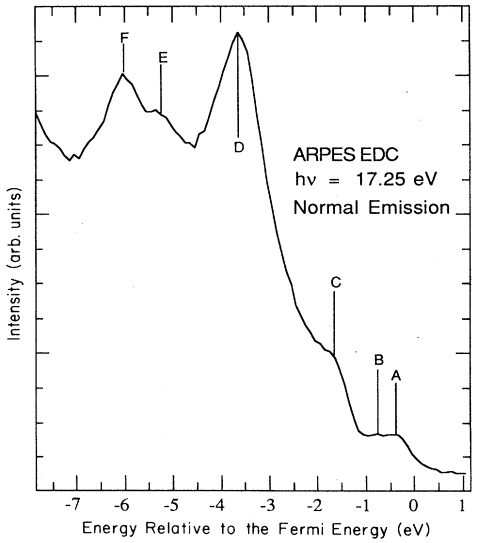

FIG. 1. An ARPES EDC taken at normal emission using 17.25-eV radiation. This EDC shows six main features labeled A–F.

ples and the relatively small amount of La dopant in our sample, we expect that the detailed behavior of the valence band, i.e., the polarization dependence and resonances, for our sample is representative of the undoped sample.

Utilizing the high degree of polarization of the synchrotron radiation, we studied the dependence of the valence-band features on the polarization of the electric field of the incident light. Figure 2(a) shows EDC's at three different incidence angles at a photon energy of 18 eV. This figure shows several interesting effects. First, we note that the overall amount of emission is smaller the larger the incidence angle. Thus, we will only discuss changes in the peak heights with respect to the main valence band. The features near the Fermi levels *A*, *B*, and *C* (see Fig. 1) show a marked increase in intensity for smaller incidence angles, while the higher binding-energy peak *F* has a larger intensity for larger incidence angles. Figure 2(b) shows the same spectra but at a photon energy of 17.25 eV. This figure is included because it shows feature *E*, which does not appear in the 18-eV spectrum. We note that feature *E* is also larger for smaller incidence angles, as features *A*, *B*, and *C*.

From the polarization dependence, the symmetries of the valence-band states can be determined by referring to group-theoretical arguments. It has been shown that for a surface with fourfold symmetry the final state that is probed in photoemission at normal emission has the full symmetry of the crystal surface.[9,10] By symmetry, the integrand for the matrix element for the optical transition, $\langle \Psi_i | H_{\text{dipole}} | \Psi_f \rangle$, must be invariant under all symmetry operations. Thus, the observed initial state must have the same symmetry as the dipole operator for the optical transition. The dipole operator is proportional to the $e\mathbf{E}\cdot\mathbf{r}$ and has the symmetry of the electric field vector of the incident radiation, and the 2:1:2:2 material has a tetragonal structure with a superimposed superstructure along the *b* axis. Thus the cleavage face, the *a*-*b* plane, has very nearly fourfold symmetry. With some reservations as to the effect of the *b*-axis superstructure, the *a*-*b* plane probed in our photoemission has C_{4v} symmetry.[11] Thus, for incident light with an electric field parallel to the surface, the allowed initial states must have Δ_5 symmetry, while for the electric field vector along the surface normal, the initial state must have Δ_1 symmetry.[9,10] With this interpretation we assign peaks *A*, *B*, *C*, and *E* to initial states with Δ_5 symmetry and peak *F* to Δ_1 symmetry. We can also discuss these symmetries in terms of atomic orbitals. Band-structure calculations show that the valence band is composed of Cu, Bi, and O related states.[12,13] We rule out large effects from Bi states in our valence-band spectra because band calculations indicate a low Bi density of states (DOS) in the valence band and the Bi cross section is very small at these low photon energies. The O $2p_x$ and O $2p_y$ states and the Cu $3d_{xz}$ and Cu $3d_{yz}$ states all transform according to Δ_5 symmetry.[11] On the other hand, the O $2p_z$ and Cu $3d_{3z^2-r^2}$ states have Δ_1 symmetry. Since the Cy $3d_{xz}$, Cu $3d_{xy}$, and Cu $3d_{yz}$ states are expected to lie deeper than the Cu $3d_{3z^2-r^2}$ and Cu $3d_{x^2-y^2}$ states, we expect peaks *A*, *B*, and *C* to originate mainly form O $2p_{x,y}$ states, while peak *F* arises primarily from O $2p_z$ levels.[14] Therefore, we conclude that the 7-eV-wide valence band, as recorded in normal emission photoemission spectroscopy, has O $2p_z$ character near its bottom and O $2p_{x,y}$ character near the Fermi level.

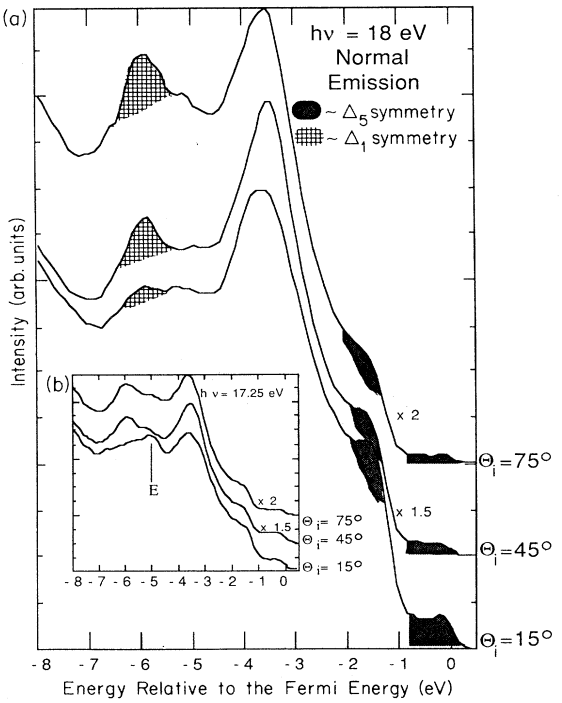

FIG. 2. Polarization-dependent EDC's for (a) 18-eV and (b) 17.25-eV radiation. The 17.25-eV spectrum is included to show feature *E* which only appears for low photon energies. The spectra are normalized to the height of the main valence-band feature, peak *D*.

Our results for the oxygen states are in agreement with studies of the unoccupied states of Bi-Ca-Sr-Cu-O. Himpsel *et al.* have performed inverse photoemission and x-ray absorption experiments of the unoccupied states near the Fermi level and conclude that the holes have more than 95% O $2p_{x,y}$ character.[5] Nücker *et al.* have studied the unoccupied states using electron-energy-loss spectroscopy, and also find mainly O $2p_{x,y}$ holes.[6] Nücker *et al.* also probed the empty Cu 3*d* states. They find that the empty Cu 3*d* states are predominantly of $3d_{x^2-y^2}$ symmetry. It is important to note that we cannot compare our data to this result since the $3d_{x^2-y^2}$ states have $\Delta_{2'}$ symmetry which cannot be probed at normal emission.

By recording photoemission spectra at different photon energies, we observed clear intensity enhancements of the different valence-band features. These enhancements are obvious as shown in the EDC's of Fig. 3(a). To find the exact location of each enhancement, we performed constant-initial state (CIS) measurements. In a CIS measurements the photon energy and the analyzer are scanned simultaneously so that one always observes a state with the same binding energy. These CIS curves are shown in Fig. 3(b). The CIS measurements show that peak *A* has an enhancement centered at a photon energy

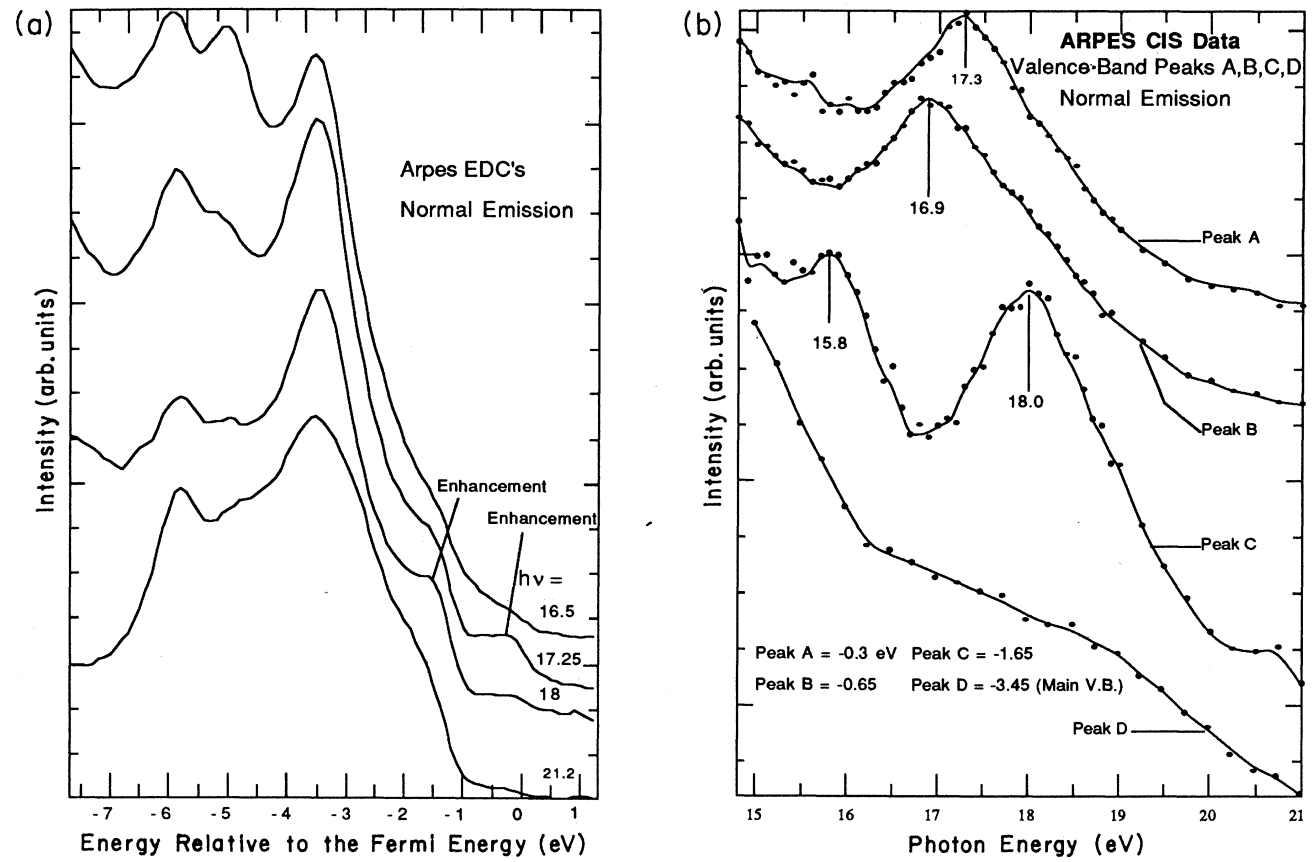

FIG. 3. (a) EDC's at various photon energies that show the resonance effect for peaks *A*, *B*, and *C*. (b) CIS curves for features *A*, *B*, *C*, and *D* in the EDC's. These curves show the exact photon energy locations of the resonance effects shown in (a).

of 17.3 eV while peak *B* shows a similar enhancement centered at 16.9 eV. Peak *C* has two features in its CIS spectrum, at 15.8 and 18.0 eV. The main valence-band peak, *D*, shows a small loss of intensity at 16.3 eV, while peaks *E* and *F* (not shown) have no features in their CIS spectra.

Takahashi *et al.* have reported an enhancement in the intensity of the states near the Fermi level at an energy of 18 eV in undoped Bi-Ca-Sr-Cu-O in both photoemission and inverse photoemission.[1,15,16] Takahashi *et al.* measured EDC's near the Fermi level at photon energies of 16, 18, and 20 eV, and found that of these three spectra, the largest intensity at the Fermi level occurs at a photon energy of 18 eV. We also find more emission near the Fermi level at 18 eV than at either 16 or 20 eV, but because we performed CIS experiments we are able to more accurately find the center of this resonance. In addition, we examined all of the valence-band peaks, while previous studies have concentrated on just the states nearest the Fermi level.

In discussing the enhanced intensity near the Fermi level, Takahashi *et al.* proposed that a resonance related to the oxygen $2s \rightarrow 2p$ absorption edge was responsible for the effect. This interpretation was partly based on the assignment of the -18-eV peak to the O $2s$ states and the -20-eV peak to the Sr $4p$ states. However, some authors have claimed that the O $2s$ core level be at -20 eV and the Sr $4p$ at -18-eV.[3,4] Clearly, this alternative assignment would rule out an oxygen resonance at 18-eV photon energy.

From the polarization data mentioned above, we believe that the initial states corresponding to peaks *A*, *B*, and *C* are of primarily oxygen character. However, our data does not support the possibility of a simple oxygen resonance near 17–18 eV. Since the photon energies at which these resonances occur are different for different peaks in the valence band, the enhancements cannot be due to a conventional photoemission resonance which occurs at a photon energy that corresponds to the simple energy difference between the initial and final states involved in the optical absorption.

Another explanation that has been proposed is that the enhancement is caused by a peak in the final-state DOS.[15] Using this interpretation, one would always see the enhancement at the same final-state energy. However, these enhancements do not occur at a constant final-state energy. Consider the states nearest the Fermi level, peaks *A* and *B*. Peak *B*, which has a higher binding-energy than peak *A*, shows an enhancement at a lower photon energy than peak *A*. Thus, these peaks have final-state energies of approximately 17 eV (*A*) and 16.2 eV (*B*). It is important to mention that an enhancement at the Fermi level

for energies near 18 eV also occurs in angle-integrated photoemission spectra (not shown). Thus, if the enhancements are due to a final-state effect, it appears to have a three-dimensional nature.

It is difficult to conceive of a single mechanism that would cause the recorded pattern of enhancements in the superconductor spectrum. It is possible that either the appearance of two closely spaced core levels, the O 2*s* and Sr 4*p* states, or electron-electron correlations may alter the normal photoemission resonance process and produce these effects. Also, we may be seeing the results of a complex, **k**-dependent final-state band effect. These ideas are purely speculative and we do not propose a detailed process. The enhancement that is seen may be a superposition of several mechanisms. Whatever the proper explanation, this data should shed some light on the current discussion of the nature of the enhancements seen in the low-energy spectra of the Bi-based superconductors.

We have examined the polarization dependence of the photoemission spectra of the Bi-related superconductors. We find that states with Δ_5 symmetry, which tend to lie in the planes, dominate the emission near the Fermi level, while states of Δ_1 symmetry, which are oriented along the *c* axis, appear at higher binding energies, in agreement with the results of previous XAS and EELS experiments. We have also investigated the photon-energy-dependent enhancements of the valence-band features. We find that the different peaks in the EDC show enhancements for different photon energies. We are led to rule out two proposed explanations for these features. Our data are not consistent with either a traditional absorption edge-intermediated resonance or the existence of a simple peak in the unoccupied density of states.

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