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Resonant inverse photoemission of $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ and $YBa_2Cu_3O_{7-x}$, unoccupied oxygen states, and plasmons

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Inverse photoemission studies of the unoccupied states of $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$, with and without 10% Pb substitution for Bi, show a low density of states within 2 eV of the Fermi level and broad structures at 4, 9.6, and 12.6 eV that are associated with Bi 6*p*, Ca 3*d*, and Sr 4*d* empty-state bands. Plasmon losses are observed via their radiative decay at photon energies of 15 and 21.2 eV. Resonant inverse photoemission, using incident electron energies that excite O 2*s* shallow core levels, enhances emission from the unoccupied O 2*p* levels. Resonance results for $YBa_2Cu_3O_{7-x}$ and $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ show similar oxygen distributions near E_F.

The recent discovery of the Bi-Ca-Sr-Cu-O 2:1:2:2 and 2:2:2:3 high-T_c superconductors[1-2] was rapidly followed by one-electron band calculations. These offered insight into the role of the Cu-O and Bi-O planes,[3-7] and photoemission experiments showed correlation effects to be important.[8-12] Despite the many similarities between the Bi systems and the 2:1:4 and 1:2:3 superconductors, interesting differences have involved the emission of states near the Fermi level and the details of the O bonding configurations.[8] In this paper, we use energy-dependent inverse photoemission to examine the unoccupied electronic states in Bi-Ca-Sr-Cu-O, with and without Pb substitution for Bi. Resonant studies with electron excitation of O 2*s*-2*p* transitions, followed by radiative decay of the core holes, make it possible to highlight the O empty-state features, and these are compared with analogous results for $YBa_2Cu_3O_{7-x}$.

The experiments were performed in a four-chamber ultrahigh vacuum system described in detail elsewhere.[13] The spectrometer is optimized for angle-resolved inverse photoemission studies at ultraviolet energies of 10–44 eV. It contains an $f/3.5$ grating and position sensitive detector, the wavelength window of which is determined by the grating setting. A Pierce-type electron gun from Kimball Physics produces a collimated 1-mm×5-mm electron beam. The total energy resolution of the spectrometer is 0.3–0.6 eV, depending on photon energy.

$Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ samples were prepared from a melt of CaO, SrO, Bi_2O_3, and CuO powder, turned out onto a cooled copper plate, and then annealed in O_2 at 780 °C. These samples exhibited transition temperatures of 80–85 K. Pb-doped samples were prepared by carbonate coprecipitation from nitrate solutions, followed by calcination at 830 °C, pressing into a pellet, and sintering at 860 °C. They had a midpoint transition temperature of 81 K. The $YBa_2Cu_3O_{7-x}$ samples were prepared from a fine stoichiometric powder obtained from Rhone-Poulenc. A 12-h stepwise heating schedule in O_2 finally reached a maximum temperature of 950 °C. The melt was cooled over a 19-h period. Parallel studies of both materials using x-ray photoemission showed the samples to be of high quality and spectral integrity, as discussed elsewhere.[8] Samples were fractured *in situ* at a pressure of 1×10^{-10} Torr immediately before the measurements were undertaken.

In Fig. 1 we show representative photon distribution curves (PDC's) for initial electron energies E_i, where E_i is referenced to the Fermi level E_F. The spectra are normalized to incident electron dose. The spectrum for $E_i=20$ eV was taken immediately after cleaving and was repeated at regular intervals to assess effects of low-energy electron bombardment and chemisorption of ambient gases.[14,15] After ~6 h of measurements, a new structure appeared 1.8 eV above E_F with full width at half maximum (FWHM) of 2 eV. Since exposure of a freshly cleaved surface to oxygen revealed similar structure, we attribute it to chemisorption rather than electron-induced surface degradation. Inverse photoemission studies of $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-x}$ showed similar surface effects.[14,15] The spectra presented here were acquired within ~6 h of cleaving and showed excellent sample to sample reproducibility. Equivalent results were obtained for samples where Pb was substituted for up to 10% of the Bi.

The spectra in Fig. 1 reveal a low density of states from E_F to ~2 eV above E_F. These results are similar to those for the 1:2:3 and 2:1:4 superconductors, although the Fermi level cutoff for the 2:1:2:2 superconductors is more pronounced. (Photoemission studies have also indicated that the Fermi level cutoff was sharper for the 2:2:1:2 superconductor than for the 1:2:3's.[8,12]) We postulate that the ill-defined cutoff for the 1:2:3's is due in part to disorder-induced broadening of the bands that cross the Fermi level since they are derived in part from Cu-O antibonding hy-

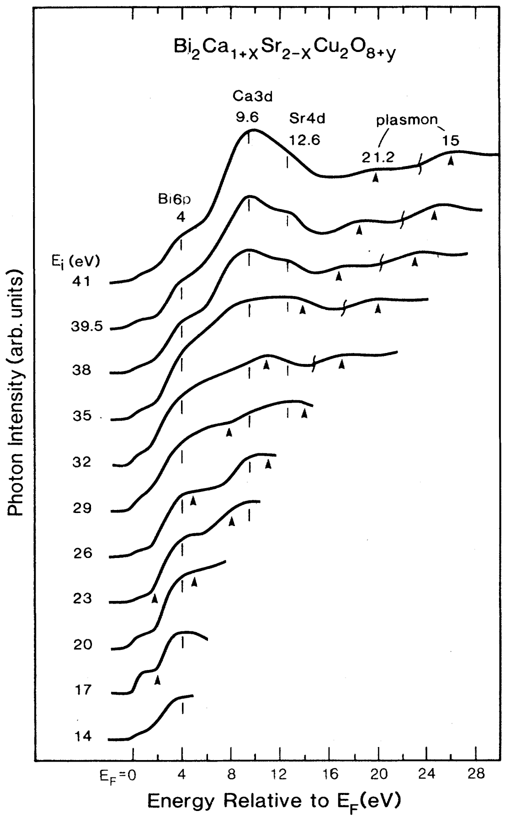

FIG. 1. Inverse photoemission spectra for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ normalized to electron dose with incident electron energy E_i referenced to E_F. Low emission is found from E_F to ~ 2 eV, although the Fermi-level cutoff is sharp, and there is structure at 4, 9.6, and 12.6 eV due to Bi 6*p*, Ca 3*d*, and Sr 4*d* empty states. Features identified with arrows are due to plasmons and appear at constant photon energies of 15 and 21.2 eV. Spectra at high electron energy show a break because of a change in grating setting. Pb substitution for up to 10% of the Bi gave identical results.

brids and the 1:2:3's exhibit disorder in the chain structures. For the 2:1:2:2's, additional bands derived from Bi—O bonds cross E_F.[3-7] From Fig. 1, we can also see structure at ~ 4 eV above E_F that is derived from the higher-lying Bi 6*p* orbitals, as predicted by theory.[3-7] Experimentally, they are ~ 1.5 eV farther from E_F than predicted by all of the ground-state calculations. We will return to the states near E_F in the context of resonant enhancement of the O states.

Figure 1 shows strong emission between 6 and 14 eV above E_F with broad maxima at 9.6 and 12.6 eV. The feature at 9.6 eV is enhanced for $E_i = 38\text{–}41$ eV, and we attribute the enhancement to a giant 3*p*-3*d* dipole resonant transition in Ca. (Results for $Tl_2CaBa_2Cu_2O_8$ show a similar feature.) This empty-state resonance is analogous to that discussed in detail for Sc.[16] The Sr 4*d* levels form a broader band with reduced *p*-*d* enhancement and we associate them with the emission up to 12.6 eV. The fact that these Ca 3*d* and Sr 4*d* levels, which are likely to overlap in energy, appear well above E_F is consistent with the highly ionic character of Ca and Sr in these superconductors. [The centroids of the metallic Ca 3*d* and Sr 4*d* bands lie ~ 6 eV (Ref. 17) and ~ 5 eV (Ref. 18) above E_F.] Analogous effects have been observed for $La_{1.85}Sr_{0.15}CuO_4$ (~ 3.2 eV shift for the La 5*d* and 4*f* levels[14]) and $YBa_2Cu_3O_{7-x}$ (~ 4.7 eV shift for the Y 4*d* and the Ba 5*d* and 4*f* levels[15]).

Additional structure in Fig. 1 reveals constant photon energy features at $h\nu = 15$ and 21.2 eV, as marked by arrows. (They are best seen at high E_i and their positions are extrapolated to lower E_i, although they are not easily identified.) These features, which have FWHM's of ~ 3 eV, move to the right in Fig. 1 with increasing E_i because the PDC's are aligned at E_F. Analogous structure has been observed for $YBa_2Cu_3O_{7-x}$ at $h\nu = 22.2$ eV. These constant photon energy features reflect the radiative decay of plasmons in the highly anisotropic superconductors. Equally broad radiative losses for plasmons have been ob-

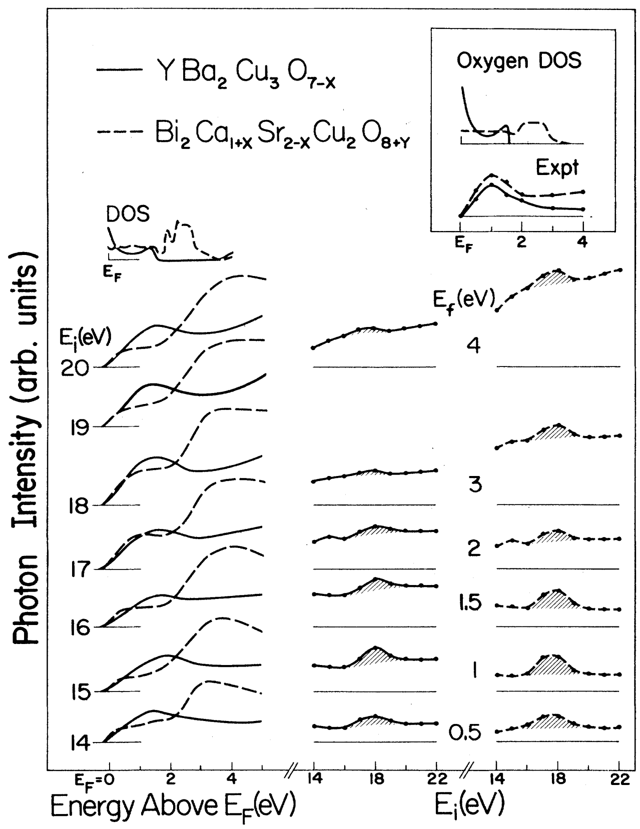

FIG. 2. The left panel shows PDC's for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ (dashed line) and $YBa_2Cu_3O_{7-x}$ (solid line) for $E_i = 14\text{–}20$ eV, normalized to electron dose. Theoretical densities of states at the top left are from Refs. 3 and 25. The right panel displays inverse constant final state (ICFS) spectra derived from the PDC's for states 0.5, 1, 1.5, 2, 3, and 4 eV above E_F. ICFS maxima for $E_i \sim 18$ eV reveal resonant enhancement of oxygen states, and the enhancement varies with energy above E_F. The bottom curves of the inset quantify the enhancement as a function of E_f for $E_i = 18$ eV. The oxygen-derived density of states are shown at the top from Refs. 3 and 25.

served in Sb,[19] Al,[20] GaAs,[21] and graphite.[22] Likewise, electron energy loss studies have revealed losses at ~ 15 and 20 eV for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ (Ref. 11) and at 19.9 and 24.9 eV for $YBa_2Cu_3O_{7-x}$ (Ref. 23).

We have also examined the effects of the substitution of up to 10% Pb for Bi in the 2:1:2:2 structure. Spectroscopically, there are minimal differences for Pb-doped and undoped $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$, with several cleaves of both types revealing almost identical line shapes. Likewise, x-ray photoemission studies showed no changes in the valence bands or the O 1s and Cu 2p core levels, with differences in the Ca 2p core levels that probably reflect Ca-Sr sublattice disorder.[8]

The results of Fig. 1 show a clear enhancement of emission near the Fermi level for $E_i \cong 18$ eV. To examine this enhancement in more detail, we display PDC's in the left panel of Fig. 2 for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ (dashed lines) and $YBa_2Cu_3O_{7-x}$ (solid lines) for $E_i = 14-20$ eV. (We note that preliminary results for the Tl superconductor also display an 18-eV resonance, as expected.) Intensity normalization has been done according to electron dose, but there is no unique way of showing their relative yields. Negligible contributions for plasmon emission appear in this energy range. (The probability of electron energy loss via plasmon scattering is very small at threshold.[24]) From these spectra, the emission at E_F appears clearly sharper for the 2:1:2:2's when compared to the 1:2:3's, as noted above (resolution 0.3 eV). Further differences are observed above E_F. Indeed, the spectra for Bi_2Ca_{1+x}-$Sr_{2-x}Cu_2O_{8+y}$ show constant emission to ~ 2 eV while there is a broad peak at ~ 1.4 eV for $YBa_2Cu_3O_{7-x}$. Comparison with the one-electron densities of states[3,25] shown in the top left panel of Fig. 2 reveals reasonable agreement for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ leading up to the Bi 6p-derived empty levels. For $YBa_2Cu_3O_{7-x}$, the broad spectral feature at ~ 1.4 eV probably represents the predicted DOS feature at 1.4 eV, corresponding to the maxima in the antibonding Cu—O hybrid bonds.

The two right panels of Fig. 2 show inverse constant-final-state energy (ICFS) spectra obtained by determining the emission intensity at final-state energies E_f from the normalized PDC's. The final-state energies are indicated next to each curve for both $YBa_2Cu_3O_{7-x}$ (left) and $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$ (right). The horizontal lines represent the zero emission levels. No significant contribution is observed from plasmon emission in this energy range. Spectral enhancement is evident for both superconductors between E_F and +4 eV when E_i sweeps through ~ 18 eV (shaded regions, FWHM ~ 2 eV). Enhancement is not seen at E_F, perhaps because low emission makes identification difficult. The increase cannot be associated with a fixed photon channel, so luminescence and plasmon decay can be ruled out.

We associate the enhancement at $E_i \sim 18$ eV with electron excitation of O 2s core electrons. This $2s \rightarrow 2p$ excitation is followed by radiative decay of the core hole, $O(2s^1 2p^6) \rightarrow O(2s^2 2p^5) + h\nu$. This new channel couples with continuum inverse photoemission decay channels to lead to resonant emission. Significantly, the very recent photoemission results of Takahashi *et al.*[9] showed an increase in electron emission for O-derived states near E_F for photon energies ~ 18 eV. Although they did not discuss the point, this led to coupling that involved direct excitation and the super Coster Kronig decay process,[26] $h\nu + O(2s^2 2p^5) \rightarrow O(2s^1 2p^6) \rightarrow O(2s^2 2p^4) + e^-$. Since photoemission shows the O 2s core-level emission as a broad feature at 20 eV,[27] we associate the difference in energy (2 eV) with intermediate O 2p screening states for the O 2s core hole, lowered in energy by Coulomb interaction with that core hole.

The inset of Fig. 2 shows the shaded area as a function of E_f for incident electron energies centered at 18 eV (lower curves). We propose that these curves represent the distribution of O 2p holes, as suggested by Takahashi *et al.*[9] and Nucker *et al.*[28] It has been proposed that these O 2p holes form Cooper pairs and, therefore, lead to superconductivity. These states are peaked at ~ 1 eV, whereas oxygen 1s electron excitation into empty states shows these states centered near E_F.

In conclusion, we have used inverse and resonant-inverse photoemission to examine the distribution of empty states for $Bi_2Ca_{1+x}Sr_{2-x}Cu_2O_{8+y}$, showing the empty Ca and Sr d bands and the Bi 5p bands (~ 1.5 eV farther from E_F than predicted). Comparison with YBa_2Cu_3-O_{7-x} reveals a sharper Fermi-level cutoff for the former, in agreement with photoemission, and we suggest that the difference is related to disorder in the lattice of the 1:2:3. The O 2s-2p resonant transition shows a peak in the O 2p holes centered at ~ 1 eV above E_F.

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