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Anomalous enhancement of $Bi_2Sr_2CaCu_2O_8$ Fermi-level states near the O 2*s* threshold

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Photoemission studies of the (001) face of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ have been performed over the photon energy range 16.5–19 eV. Such spectra have previously been analyzed in terms of O 2*s* resonant photoemission behavior and used to assign O 2*p* character to features close to the Fermi level. We show that these results may be significantly influenced by the presence of Sr 4*p* and O 2*s* core-level peaks created by a small second-order component of the exciting radiation. This could provide an explanation for the anomalous enhancement of states close to the Fermi level recently reported by Wells *et al.*

Despite many spectroscopic studies of the high temperature superconducting oxides,[1] there remain several unresolved controversies surrounding the electronic structure of these materials. One of the main areas of uncertainty is the character of the states near the Fermi level, E_F. The Bi-Sr-Ca-Cu-O superconductors in particular have attracted attention, as a finite density of states (DOS) at E_F is readily observed in photoemission of these materials, whether in ceramic,[2–10] thin film,[11] or single crystal form.[4–6,12–26] This contrasts with the situation for $YBa_2Cu_3O_7$-based systems where a reproducible DOS at E_F has most successfully been obtained by cleaving single crystals of the material below 50 K;[27,28] to date few studies have shown a finite DOS at E_F at room temperature.[29–31]

In principle, resonant photoemission should give an insight into the atomic character of the states at the Fermi level. Earlier work on $Bi_2Sr_2CaCu_2O_8$ (Ref. 17) demonstrated "resonant" enhancement of two Fermi-level features near the O 2*s* threshold which led to their assignment as O 2*p* states. However, in a recent Rapid Communication, Wells *et al.*[12] note that the enhancement of these Fermi-level states, and a third peak at $\sim$1.6 eV below E_F, is anomalous. Here we present photoemission data recorded near the O 2*s* core threshold from $Bi_2Sr_2CaCu_2O_8$(001) which show that this anomalous behavior can be at least partly explained by the presence of monochromator second-order effects.

The single crystals of $Bi_2Sr_2CaCu_2O_8$ used in this work were supplied by SuperconiX Inc. (St. Paul, Minnesota). The crystals were grown from a molten flux employing a proprietary temperature-gas-atmosphere cycle which optimizes the superconducting properties. This growth procedure yields crystals that appear as thin platelets, of face size up to 3×3 mm^2, at the surface of the residual melt. x-ray diffraction of the platelets revealed the presence of the $Bi_2Sr_2CaCu_2O_8$ phase, with *c*-axis orientation.[32] Magnetization measurements showed that the crystals became superconducting at 84 K.

Angle-resolved photoemission measurements employed the VG ADES 400 instrument and low-temperature manipulator on station 6.2 at the SRS, Daresbury Labo-

ratory. Using the low-energy grating in the toroidal grating monochromator on this beam line gives a photon energy range $15 \leq h\nu \leq 55$ eV. The combined (monochromator + analyzer) energy resolution was 0.15 eV, and an analyzer entrance aperture was used to fix the angular resolution at $\pm 2°$ [full width at half maximum (FWHM)]. Contaminant-free surfaces suitable for photoemission measurements were obtained by peeling the sample at room temperature using a tab technique. After removal from the spectrometer, the cleaved surface used in the present study was found to be oriented such that photoemission measurements had been carried out at about 12° from normal emission. Laue back reflection confirmed the crystallinity of the cleaved surface, although some evidence of twinning was detected. Figure 1 shows a photoemission spectrum of $Bi_2Sr_2CaCu_2O_8(001)$, measured at $h\nu = 45$ eV, showing valence and low-lying core levels. The assignment of major features in the spectrum follows earlier work,[5] and will not be commented upon other than to draw attention to the O 2*s* and Sr 4*p* features at ~20 and ~ 17.7 eV binding energy (BE), respectively.[33] Figure 2 shows photoemission spectra of the valence band and the Fermi level regions for photon energies between 16.5 and 19 eV. The majority of the valence band intensity above 1 eV BE originates from strongly hybridized Cu 3*d* and O 2*p* states.[34–36] However, our main interest in the present work is in the features around E_F and on the low BE side of the valence band edge.

It is immediately apparent that at the higher photon energies represented in Fig. 2, features appear in the spectrum *beyond* the Fermi edge, apparently at negative BE (the position of the Fermi edge was determined using a freshly scraped section of the copper manipulator shroud, which was in electrical contact with the sample). The spectra recorded at 16.5, 17.25, and 18.0 eV are in excellent agreement with the recent spectra of Wells *et al.*[12] However, the smaller photon increments displayed in Fig. 2 allow us to discern the continuous movement of structure through the Fermi energy in our data, as the photon energy is increased. The strongest of

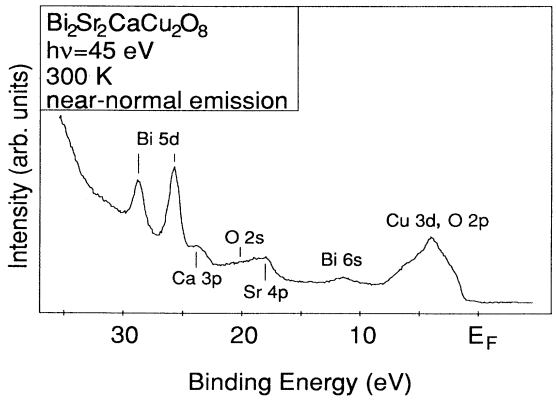

FIG. 1. Photoemission spectra of single crystal $Bi_2Sr_2CaCu_2O_8(001)$, recorded at 300 K and at near normal emission, using 45-eV photon energy.

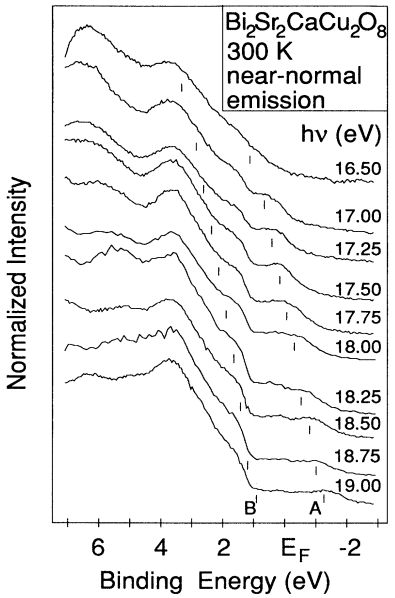

FIG. 2. Photoemission spectra of single crystal $Bi_2Sr_2CaCu_2O_8(001)$ at 300 K, showing the region around E_F and the low-lying valence band states, for photon energies close to the Sr 4*p* and O 2*s* thresholds. The spectra were recorded at near normal emission and have been normalized to the intensity of the incident synchrotron radiation. An additional correction has been included for the 18.25- and 18.75-eV photon-energy spectra, to take account of changes in SRS operation. Tic marks indicate the positions of the peak maxima of the Sr 4*p* (*A*) and O 2*s* (*B*) core-level peaks excited by second-order radiation.

these features (between −2 eV and E_F) is seen to move through the Fermi energy in BE increments equal to the change in photon energy, $\Delta h\nu$, i.e., in increments of $2\Delta h\nu$, when plotted on a kinetic-energy scale. This is a clear indication of a contribution to the monochromator output from second-order radiation. Such a contribution is likely to be significant (~15–25 % of the total flux[37]) at the photon energies used, which are close to the lower limit of the monochromator and correspond to very grazing uv radiation incidence on the monochromator in our system. For each spectrum of Fig. 2, the expected positions of the Sr 4*p* and O 2*s* core level peaks excited by photon energy $2h\nu$ are indicated by tic marks (marked *A* and *B*, respectively). It can be seen that there is a very direct correlation between the expected position of the second-order Sr 4*p* peak (*A*) and the strongest mobile feature of the spectra. It is clear that our results have been influenced by a contribution from the Sr 4*p*, and to a lesser extent the O 2*s* core levels excited by second-order radiation.

An earlier paper by Takahashi *et al.*[17] concluded that the enhancement of two weak features within 1 eV of the Fermi energy near a photon energy of 18 eV was attributable to O 2*s* resonance effects. More recently Wells *et al.*,[12] using constant initial state (CIS) spectroscopy with a small photon-energy step, came to a rather different conclusion. The latter data show that the two

peaks close to the Fermi edge have intensity maxima at different photon energies: 17.3 eV for the 0.3 eV BE feature (peak *A* in Ref. 12); and 16.9 eV for the 0.65 eV BE feature (peak *B* in Ref. 12). These results are not consistent with an O 2*s*-related resonance, and photoemission final-state effects have been proposed as a possible origin.[12] However, the behavior observed is precisely that expected on the basis of our interpretation of spectra in Fig. 2, which strongly suggests that this anomalous effect is an experimental artifact, arising from a second-order–derived Sr 4*p* peak. The additional resonance-type behavior observed by Wells *et al.*,[12] that of a 1.6 eV BE feature (peak *C* in Ref. 12), has two maxima, at photon energies of 15.8 and 18.0 eV. The difference between these two energies coincides almost exactly with the binding energy difference between the Sr 4*p* and O 2*s* core levels of 2.3 eV, and the absolute values are in line with those expected from the data in Fig. 2. This suggests that the behavior of peak *C* in the CIS spectra[12] may be similarly influenced by second-order effects. This being the case, the two features closer to E_F (*A* and *B* in Ref. 12) would also be expected to show an increase in intensity at ca. 19.6 and 19.2 eV photon energies, respectively. At these energies a second-order derived O 2*s* feature would move through the kinetic-energy window. The lack of these features in the CIS spectra[12] could be explained on the basis of the limited range of the Seya-Namioka monochromator used in Ref. 12. The transmission of this monochromator should be decreasing rapidly close to 38–40 eV, the appropriate energy range for any second-order O 2*s* effects which might contribute to the intensities of peaks *A* and *B* in the CIS spectra (Ref. 12). However, the CIS scan for the 3.45-eV BE feature (peak *D* in Ref. 12) does not obviously behave anomalously at around 16.2 eV, the photon-energy position expected for the second-order O 2*s* feature. This may be masked by the greater intensity of peak *D* compared to the features closer to E_F, but this result does confuse the issue regarding second-order versus true resonance enhancement.

We do not intend to imply that the observation of some type of resonance enhancement of the Bi-Sr-Ca-Cu-O features close to the Fermi energy is invalid,[12,17] as studies of the empty states above E_F by inverse photoemission,[38,40] soft-x-ray absorption[41,42] and electron energy loss[43] spectroscopies tend towards the same result. Dispersion of structure through the Fermi level as a function of emission angle at a fixed photon energy, observed by several authors[17,18,24–26] clearly cannot be explained by the effect of second-order light. Moreover, the proportion of second-order radiation present will obviously depend on the monochromator employed. However, we believe that *anomalous* intensity enhancement as a function of photon energy of the type observed by Wells *et al.*[12] may reflect results influenced by this experimental artifact. It is also the case that a marked intensity enhancement at 18 eV photon energy has not been observed in all studies.[31]

In conclusion, we have observed that our measurements of the $Bi_2Sr_2CaCu_2O_8$ Fermi-level states near the O 2*s* threshold are influenced by a component of second-order radiation in the incident photon flux. We suggest that this may offer an explanation for the anomalous enhancement of Fermi-level states at the same photon energies.[12] We further suggest that photoemission experiments near the O 2*s* threshold should be repeated using a monochromator with a negligible second-order contribution. This would provide a definitive test for O 2*s* resonance effects.

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