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Saini, N.L.; Venkatesh, S.; Srivastava, P.; Sekhar, B.R.; Garg, K.B.; Tjeng, L.H.; Chen, C.P.; Menovsky, A.A.; Franse, J.J.M.

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## Polarized x-ray absorption spectroscopy study of the symmetry of unoccupied electronic states near the Fermi level in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ system

N L Saini<sup>†</sup>, S Venkatesh<sup>†</sup>, P Srivastava<sup>†</sup>, B R Sekhar<sup>†</sup>, K B Garg<sup>†</sup>,  
L H Tjeng<sup>‡</sup>, C T Chen<sup>‡</sup>, A Menovsky<sup>§</sup> and J J M Franse<sup>§</sup>

<sup>†</sup> Department of Physics, University of Rajasthan, Jaipur, India

<sup>‡</sup> AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ, USA

<sup>§</sup> Natuur En Sterrenkunde, University of Amsterdam, 1000 HE Amsterdam, The Netherlands

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**Abstract.** A study of the electronic states near the Fermi level in high- $T_c$  superconductors, which is so important to understanding the mechanism of superconductivity, has been carried out on well characterized single crystals of superconducting  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  Bi-2212. A large number of polarized x-ray absorption spectra have been recorded with the  $E$  vector parallel to the  $a$ - $b$  plane and perpendicular to it at the Dragon beam line at the Brookhaven Light Source using the fluorescence mode of detection. These bulk spectra of Cu  $L_3$  and O  $K$  are then analysed to obtain the density of the unoccupied Cu  $3d_{z^2}$  and Cu  $3d_{x^2-y^2}$  orbitals from the Cu  $L_3$  spectra and the density of the O  $2p_z$  and O  $2p_{x,y}$  orbitals from the O  $K$  spectra. The results clearly show the presence of O  $2p_z$  orbitals in a substantial amount although the same cannot be said of the  $3d_{z^2}$  orbitals. Tight-binding calculations of the holes are also reported and compared with experimental results.

### 1. Introduction

In order to decipher the mechanism of high- $T_c$  superconductivity in the cuprates it is essential to understand their electronic structure. High-energy spectroscopy techniques, especially polarized x-ray absorption measurements, have been widely used in probing the electronic states near the Fermi level in these rather complex materials [1, 2]. In particular, a number of polarized x-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) studies have been made to obtain valuable information on the symmetry of unoccupied states in the normal state [3–18], and to understand the behaviour of holes in the superconducting state [19, 20]. The  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi-2212) compound has attracted more attention because interpretation in the 1-2-3 system is more complicated due to presence of the two non-equivalent Cu sites and because the surfaces of 1-2-3 compounds are unstable at room temperature under UHV conditions.

The earlier polarized Cu  $L_3$  XAS measurements on BSCCO (2212) have led to the conclusion that the unoccupied Cu 3d states are predominantly of  $3d_{x^2-y^2}$  character with 10–20 wt.% of Cu  $3d_{z^2}$  character. More investigations of the Cu  $L_3$  edge [6, 7, 10, 11, 14, 15] have reported a positive energy shift of about 300–500 meV between the  $E \parallel a, b$  and  $E \parallel c$  polarized spectra, but other studies [9, 12, 16] detect either no shift or a very small relative weight of  $d_{z^2}$  holes with no shift at all. The surface-sensitive total electron yield (TY) mode of detection was used in all the above cases. Later reports using the bulk-sensitive

fluorescence yield (FY) mode [12] showed an almost insignificant intensity for the out-of-plane Cu  $3d_{z^2}$  states. A recent report by Venkatesh *et al* [21] lists the probable reasons for the observed discrepancies in the TY and FY data. Still no satisfactory explanation has been given so far regarding the various contradictory observations reported.

A number of polarized O K edge XAS data have also been published [4, 13–15, 17, 18] which give a conclusive evidence for the presence of a substantial amount of the O  $2p_z$  symmetric holes in the Bi-2212 system. A significant density of  $p_z$  holes has also been established in  $\text{YBa}_2\text{Cu}_3\text{O}_{\approx 7}$  [3, 12] and in the La–Sr–Cu–O [18] system by such studies. There is variation in data from one system collected using the TY and FY techniques and from two different systems using the same technique. Moreover, not only is the significance of the high out-of-plane O  $2p_z$  difficult to understand but also one may want to question whether the observed O  $2p_z$  content directly reflects the coupling of the apical oxygen atoms with the in-plane orbitals. Many models, especially those proposed by Weber [22] and Kamimura [23], depend on the presence of out-of-plane Cu 3d and O 2p orbitals while others such as that of Ohto *et al* [24] report that the presence of these would act against superconductivity.

In view of the above facts, therefore, we have studied high-quality Bi-2212 crystals by the bulk-sensitive polarization-dependent FY x-ray absorption technique. In the present communication, we have focused our attention on both the Cu  $L_3$  and the O K edges in order to extract the electronic structure of  $\text{CuO}_2$  planes relevant to superconductivity.

## 2. Experimental details

The single-crystal samples were prepared by the travelling-solvent floating method in a mirror furnace with two ellipsoidal reflections using a 750 W halogen lamp. Details of the preparation and characterization have been given elsewhere [25].

The XAS measurements were performed on the AT&T Bell Laboratory's Dragon beam line at NSLS, Brookhaven National Laboratory. Bulk-sensitive (about 2500 Å probing depth) FY spectra were recorded using a high-sensitivity seven-element Ge array detector. To achieve complete polarization geometry and to eliminate optical path variations, an azimuthal rotation method was used which has been discussed elsewhere in detail [18].

## 3. Results and discussion

### 3.1. Cu $L_{2,3}$ XAS measurements

Figures 1 and 2 show the spectra measured at different angles from the normal incidence on crystal A and crystal B respectively. The angle  $0^\circ$  represents the case when  $\mathbf{E} \perp \mathbf{c}$  and  $80^\circ$  the case when  $\mathbf{E}$  is nearly parallel to the  $c$  axis. The dipole transition  $2p \rightarrow 3d$  for the white line (WL) thus probes the unoccupied  $3d_{x^2-y^2}$  orbitals when  $\mathbf{E} \perp \mathbf{c}$  and the  $3d_{3z^2-r^2}$  orbitals when  $\mathbf{E} \parallel \mathbf{c}$ . The zero of the energy scale is taken at the peak of the  $L_3$  WL which occurs at around 931.5 eV in the  $\mathbf{E} \perp \mathbf{c}$  spectrum.

The Cu  $L_3$  absorption spectra for the  $\mathbf{E} \parallel \mathbf{c}$  orientation show a very small intensity ( $\sim 2$ –4%) of the WL as compared to that for the  $\mathbf{E} \perp \mathbf{c}$  polarization. This means that there are no unoccupied  $3d_{z^2}$  orbitals in the system and all 3d unoccupied states must therefore have  $3d_{x^2-y^2}$  symmetry alone. This is in agreement with the case of the La–Sr–Cu–O system reported earlier by Chen *et al* [18] but is in disagreement with the spectra measured earlier in TY mode [6, 7, 10, 11, 14, 15] which all not only show a 10–20% intensity for the  $\mathbf{E} \parallel \mathbf{c}$  case but also report a shift of 300–500 meV for the WL peak towards the lower energy as

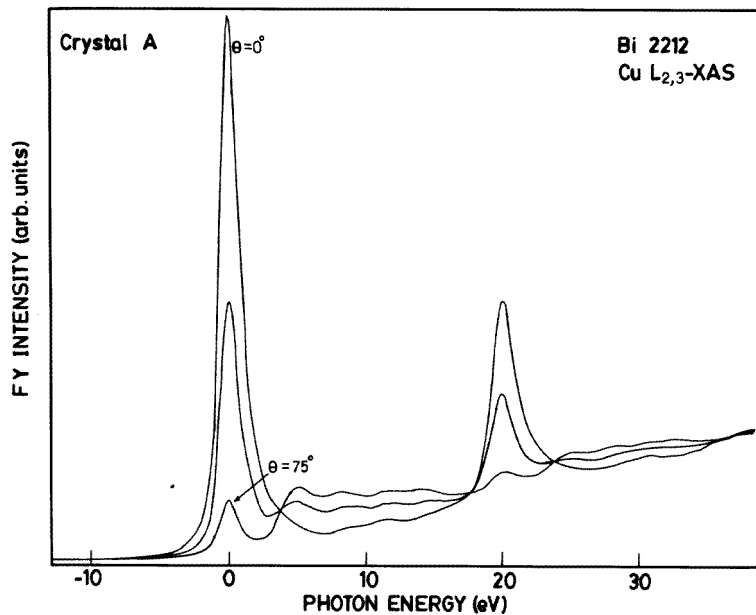


Figure 1. Cu  $L_{2,3}$  edges of a Bi-2212 single crystal measured at various angles of incidence.

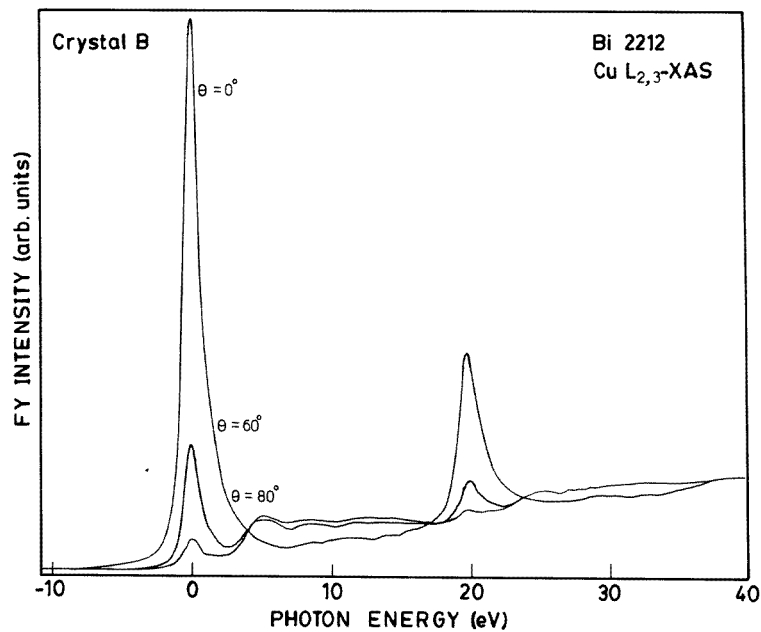


Figure 2. Cu  $L_{2,3}$  edges of a Bi-2212 single crystal measured at  $0^\circ$ ,  $60^\circ$  and  $80^\circ$  angles of incidence.

one goes from  $E \perp c$  to  $E \parallel c$  polarization. Suzuki *et al* [9], on the other hand, do not report observing such a shift in their Cu  $L_3$  spectra measured in TY mode but do report

a 5% intensity in the  $E \parallel c$  polarization. At the same time, Qvarford *et al* [15] report a smaller shift (about 100 meV) for the Bi-2201 crystal also along with a significant intensity in the  $E \parallel c$  polarization. Much earlier, EELS data [12] on Bi-2212 have been reported, showing again a significant intensity in the  $E \parallel c$  polarization.

All the earlier data thus seem to be agreeing on a varying but significant intensity for the Cu  $L_3$  WL in the  $E \parallel c$  polarization while reporting a varying magnitude of its energy shift. As opposed to this, Chen *et al* [18] have reported an intensity of only  $\sim 3\%$ . The present data yield an intensity of about 2–4%. Next, the Cu  $L_3$  WLs for  $E \perp c$  and  $E \parallel c$  for crystal B are resolved into two Gaussians (figure 3) of FWHM about 1.1 eV separated by about 1.2 eV which is of the order of the charge transfer energy ( $\Delta$ ) in the Bi-2212 system. The lower-energy main component  $L_3$  arises from the transition  $3d^9 \rightarrow 2p\ 3d^{10}$  while the doping-induced satellite component  $L'_3$  arises from  $3d^9 \underline{L} \rightarrow 2p3d^{10} \underline{L}$ . Given the larger experimental uncertainties, the  $3d_{z^2}$ -to- $3d_{x^2-y^2}$  intensity ratios for the doping-induced satellite peak  $L'_3$  are estimated to be 3%. The ratio is thus the same as that for the main peak  $L_3$ .

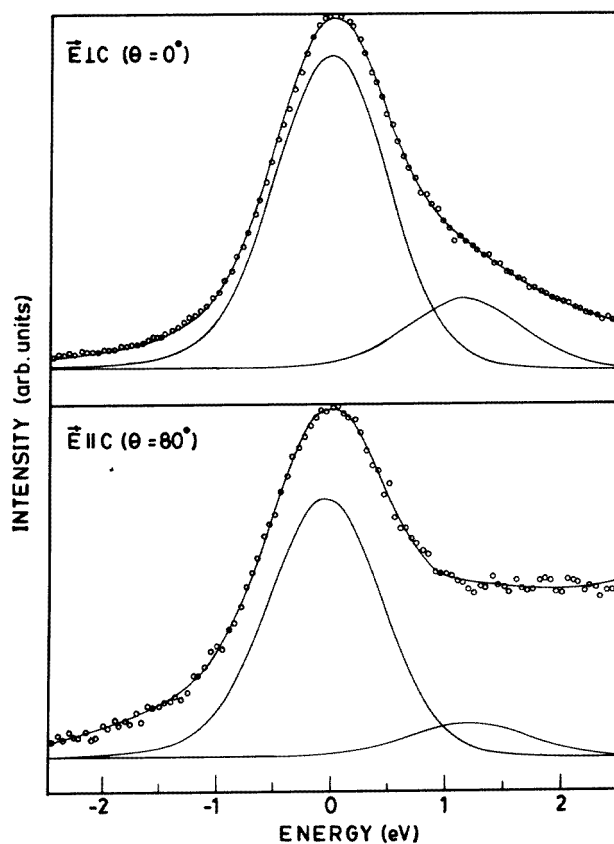


Figure 3. Fitted curves of Cu L edge (a) at  $0^\circ$  and (b) at  $80^\circ$ .

Comparing the data from the various detection techniques it is natural to ask what could be the reason for the enhanced intensity of the  $E \parallel c$  spectra from the TY mode. A number of factors could contribute to it, such as the lack of perfect polarization in the incident x-ray beam, the surface-sensitiveness of the TY mode coupled with the surface chemistry of the

samples which is different from that of the crystal bulk. The degree of polarization for the TY mode experiments is claimed to be better than 95% and, as reported, the crystals have been repeatedly cleaved in UHV. Moreover, as borne out by ARPES and ARIPES [26, 27] experiments the Bi-2212 crystal surface is known to be very stable in UHV conditions. Pellegrin *et al* [17] have recently indicated how the alignment error of up to  $\pm 5\%$  may also contribute to the overall errors in the measured intensities. They report that a correction may also have to be applied due to lack of proportionality of the measured fluorescence signal to the true absorption coefficient, particularly in the case of the Cu  $L_3$  absorption edge where the true absorption coefficient  $\mu_{tr}$  becomes of the same order as the total absorption coefficient  $\mu_{tot}$  and consequently much greater than the absorption coefficient  $\mu_{rem}$  due to the other atoms in the sample. The intensity of the  $\mathbf{E} \parallel \mathbf{c}$  is thus more or less negligible. Turning to figure 3 this would mean that the two Gaussians in the  $\mathbf{E} \parallel \mathbf{c}$  case would be bereft of any significance. The two Gaussians for the  $\mathbf{E} \perp \mathbf{c}$  signal are, however, significant. The higher of the two Gaussians, as pointed out earlier in this section, would correspond to the dipole transition from the ground state to the  $3d^9 \underline{L}$  state.

More recently, however, Pellegrin *et al* [28] have shown a very substantial intensity for the Cu  $3d_{z^2}$  signal by FY measurements on the  $Tl_2Ba_2Ca_2Cu_3O_{11}$  (Tl-2223) system. This result compels one to think that there may, after all, be no uniformity in the behaviour of the various superconducting cuprates in respect of the relative intensity of the out-of-plane Cu  $3d_{z^2}$  orbitals and that, as suggested by them, the weightage of these orbitals may be of no consequence to their superconducting behaviour.

Also, it is important to pay attention to the step-like structure visible above the WL in the  $\mathbf{E} \parallel \mathbf{c}$  grazing-incidence spectra. It has been ascribed to transitions from  $2p$  to a hybridized  $4s$ ,  $4p$  and  $3d_{z^2}$  state [14]. Bianconi *et al* [10, 11] have ascribed it to a multiple-scattering resonance from the Bi–O band hybridized with the  $CuO_2$  band with d-like symmetry. Flipse *et al* [16] have ascribed it to a composite state of Cu  $3d_{z^2}$ , Cu  $4s$  and O  $2p_z$ . Pellegrin *et al* [17] have also ascribed it to the admixing of the Cu  $3d_{z^2}$  with Cu  $4s$  and Ca  $4p$  states. The presence of this feature in the  $\mathbf{E} \parallel \mathbf{c}$  spectra may constitute an evidence for the non-zero intensity of the  $3d_{z^2}$  orbitals.

### 3.2. O K-edge XAS measurements

Figures 4 and 5 show the normalized polarization-dependent x-ray absorption spectra on the Bi-2212 crystals A and B at the O K edge. The spectra were recorded at various angles to the surface normal in the bulk-sensitive FY mode. The O K-edge spectra are almost similar to those reported from the TY mode [15]. Dipole selection rules imply that, for normal incidence ( $0^\circ$ ), only the states of O  $p_{x,y}$  symmetry will be sampled while, at grazing incidence, only the  $p_z$  orbitals are accessible. The zero of the energy scale in figure 4 has been kept at the pre-edge peak A which appears at about 528.5 eV in the  $\mathbf{E} \perp \mathbf{c}$  spectrum. Peak A is due to the transition from the O  $1s$  levels into the unoccupied O  $2p$  states appearing in the correlation gap with doping holes and has been observed for a number of correlated systems [29]. It has been found that the intensity of this peak is not explicitly dependent on the  $T_c$  of the material but is dependent on the density of the doping holes [30, 31]. The intensity of peak A decreases in going towards the  $\mathbf{E} \parallel \mathbf{c}$  polarization. On extrapolation, the intensity for the  $\mathbf{E} \parallel \mathbf{c}$  case turns out to be about 13% of that for  $\mathbf{E} \perp \mathbf{c}$ , indicating thereby a significant population of holes of  $p_z$  symmetry.

There appears to be some polarization-dependent changes in the features above the pre-peak region. For a systematic study of the evolution of intensity and energy positions of these features we have least-squares fitted the O K-edge spectra by Gaussian lineshapes

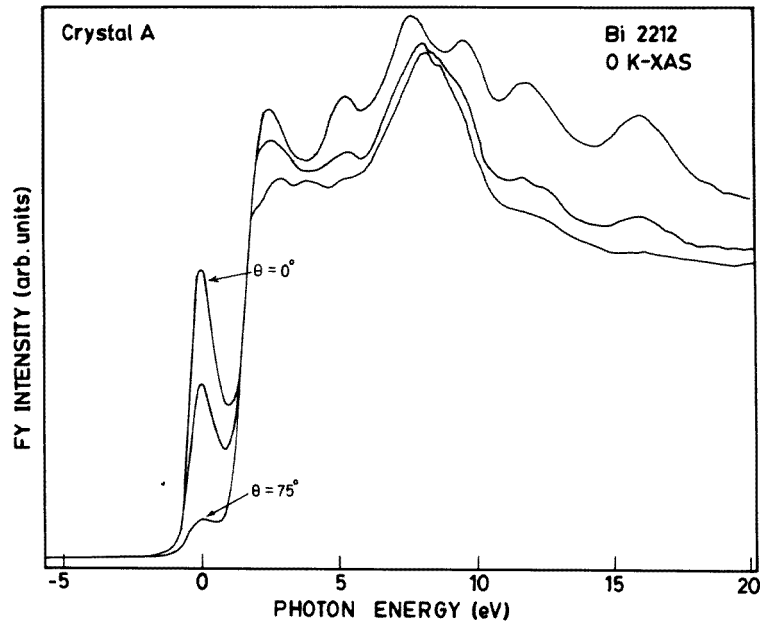


Figure 4. FY spectra of the O K edge on a Bi-2212 single crystal at various angles of incidence.

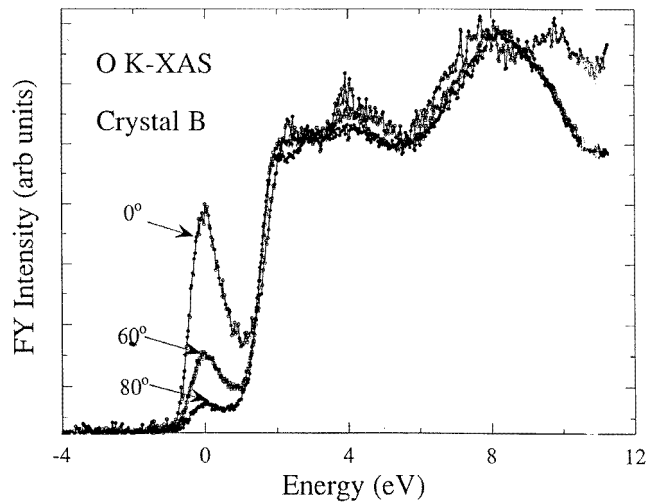
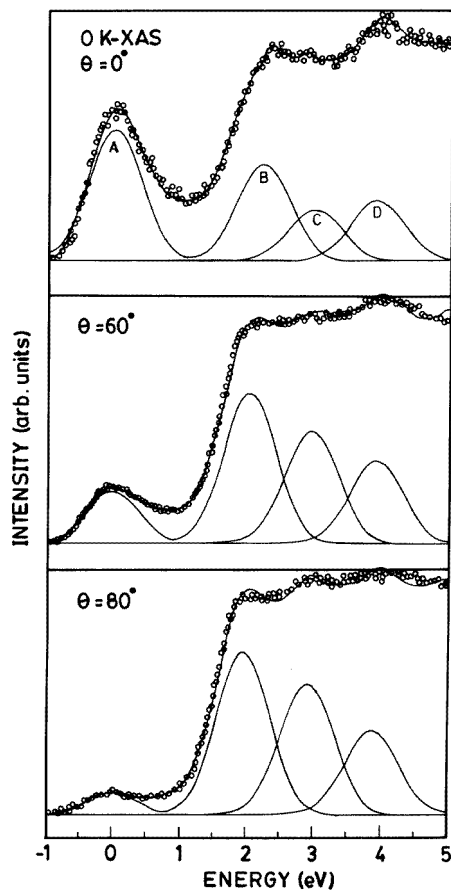


Figure 5. FY spectra of the O K edge on a Bi-2212 single crystal at  $0^\circ$ ,  $60^\circ$  and  $80^\circ$  angles of incidence.

of identical FWHMs (0.9 eV) and backgrounds. Figure 6 shows the three spectra with their fitted components A, B, C and D. Peak A is the same as discussed above. Peak B at about 530.5 eV is associated with the 'upper Hubbard band' and ascribed to the transition  $3d^9 \rightarrow 1s3d^{10}$  of the undoped material [12–15, 18], which is allowed due to the admixture of  $3d^{10} \underline{L}$  with  $3d^9$  in the ground state. The intensity of peak B is thus a measure of covalency of the Cu–O bond in the  $\text{CuO}_2$  layers. There seems to be a small energy shift

(about 250 meV) in peak B with polarization which may be a background effect. Peak C appears at about 531.4 eV, i.e. 2.9 eV above peak A. This peak has been reported to be due to oxygen in the BiO layers [11–13]. A Bi 6p band about 3 eV above the Fermi level is also shown by band-structure calculations [32] and ARPES studies [27] crossing the O 2p band originating from BiO and SrO layers. The assignment of this peak is also supported by the increase in its relative intensity with orientation because Bi-2212 crystals always cleave along the Bi–O plane and, at grazing incidence, the spectra are more surface sensitive. Bianconi *et al* [11] have also been able to reproduce this peak about 3 eV above the Fermi level in their multiple-scattering calculations. The feature D about 4 eV above the pre-peak (532.5 eV) is commonly observed in all cuprate perovskites with CuO<sub>2</sub> layers [8–11]. This may be due to a transition in a band having partial Cu (3d<sub>z<sup>2</sup></sub>) and oxygen character. The intensity of this peak remains more or less constant with orientation, i.e. feature D is polarization independent.



**Figure 6.** O K-edge spectra with their fitted components.

It is still unclear whether some of the oxygen holes with  $p_z$  symmetry are, in accordance with the theoretical models that involve  $d_{z^2}$  holes, situated in the CuO<sub>2</sub> planes or the  $p_z$  holes predominantly belong to the apex oxygen atom [23]. There is also evidence quoted against this argument [24, 34] which claims that these, if present, would suppress superconductivity.



One possibility is that the holes in the BiO plane may be of  $p_z$  symmetry and contribute some intensity to the pre-peak as a small density of states at  $E_F$  by the BiO plane as predicted by band-structure calculations [32] and ARPES studies [26]. Another report [35] in the case of the 1-2-3 system indicates an increase in the weight of the O  $2p_{x,y}$  orbital but no change in the weight of the O  $2p_z$  orbital when these go from the normal to the superconducting state. This would then be in contradiction to the theoretical predictions such as those in [24, 34]. Another question related to these is whether these predominantly arise from the apical oxygen atom and whether any increase in the number of holes at the apical O sites are detrimental to superconductivity. Pellegrin *et al* [17] have supported such a conclusion on the basis of the lower value for O  $2p_z$  that they observe in the Bi-2212 system as compared to that in the La-Sr-Cu-O system which has a lower  $T_c$ . However, there is evidence from ARUPS [26] measurements that the Bi-O plane may also be contributing to the density of states at  $E_F$  and hence to superconductivity. Some of the  $p_z$  orbitals may be arising from the O in these planes.

### 3.3. Tight-binding calculations for the holes

Tight-binding calculations have been attempted on both the La<sub>2</sub>CuO<sub>4</sub> (La-214) and the Bi-2212 systems using the Slater-Koster formulation [33] to see whether the experimental observations can be reproduced from these. The calculations have been performed for a cluster of square lattices. In case of the La-214 system the Cu is bonded with O in octahedral symmetry. Eighteen basic sets have (inter atomic matrix elements) been used for La-214. On the other hand, 15 basic sets are required for the Bi-2212 system where we have only one apical oxygen atom in the Cu-O pyramid. The interaction parameters (sps, pps, ppp, pds and pdp) are approximated by the (distance)<sup>-2</sup> and (distance)<sup>-3.5</sup> law [33]. The values are consistent with the earlier reports on La-214 system. The eigenvalues for d and p states ( $e_p$  and  $e_d$ ) were taken from the earlier reports. However, the position of the Cu 4s states is still uncertain (we have used the values reported in x-ray absorption studies). These input parameters were fed into the computer program for the one electron band structure calculations developed by Tjeng [36].

The calculations show a small presence of out-of-plane symmetry holes in La-214 and Bi-2212 systems which is in agreement with the experimental findings. We have varied the hole density by the addition and removal of electrons in both the systems, and changes in the band structure are observed. The change in symmetry of the Cu 3d and O 2p holes is also monitored. Figure 7 shows the change in the ratio of out-of-plane to in-plane d and p orbitals for the La-214 and Bi-2212 systems with respect to the addition of holes per Cu site. The results indicate a small increase in the  $d_{3z^2-r^2}$ -to- $d_{x^2-y^2}$  ratio with hole density which is in agreement with the earlier band-structure calculations [35] under the presence of strong local correlations but are in disagreement with experiment [33]. On the other hand, the  $p_z$ -to- $p_{x,y}$  ratio appears to be almost invariable. At the optimum doping ( $\sim 0.2$  holes/Cu site) we estimate  $\sim 3$ – $4\%$   $d_{z^2}$  holes corresponding to  $5$ – $8\%$   $p_z$  symmetry holes in the two systems with slightly higher values of  $p_z$  holes in the La-214 system as expected due to the presence of octahedral geometry instead of tetrahedral geometry of Cu-O cluster in the Bi-2212 system.

The calculations thus do not show conformity with the two significant experimental facts: firstly the O  $2p_z$ -to-O  $2p_{x,y}$  ratio is much higher than the Cu  $3d_{z^2}$ -to-Cu  $3d_{x^2-y^2}$  ratio, and secondly the above ratios are doping independent. It appears that a tight-binding calculation involving the O 2p and Cu 3d, both in-plane and out-of-plane, orbitals but excluding the Cu 4s orbitals may not reproduce the observed high O  $2p_z$  content without

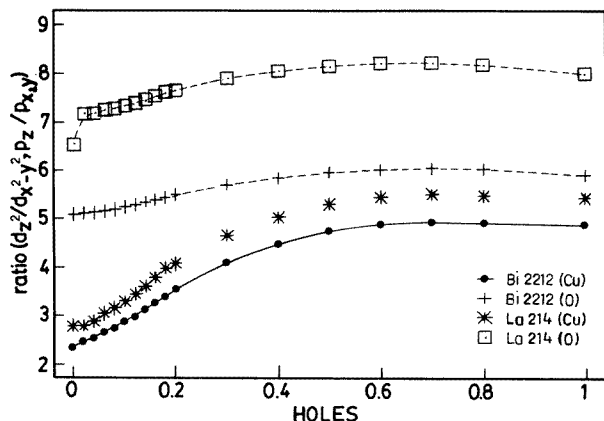


Figure 7. Ratio of out-of-plane to in-plane d and p orbitals for the La214 and Bi-2212 systems.

having an even higher Cu  $3d_{z^2}$  content. Including a hole from the in-plane orbitals in the apical O  $2p_z$  via the Cu  $3d_{z^2}$  we shall always end up producing more holes on the Cu  $3d_{z^2}$  than on the apical O  $2p_z$ . Also, the direct in-plane O  $2p_{x,y}$ -apical O  $2p_z$  coupling is too weak to induce a large number of holes in the latter.

#### 4. Conclusions

In summary, it can be clearly stated that the weightage of the vacant Cu  $3d_{z^2}$  orbitals in the Bi-2212 system is insignificant. The much higher weightage observed in the TY mode is, amongst others, probably due to the surface-sensitiveness of that technique. It is, however, still a moot point why the surface O  $2p$  states are not similarly affected. The observed difference in the weightage of the Cu  $3d_{z^2}$  orbitals is not due to the non-proportionality of the absorption coefficient to the FY signal. The well pronounced structure beyond the main excitonic line is, as predicted by Grioni *et al* [37] and Mei and Stollhoff [38], due to strong hybridization of Cu  $3d$  with Cu  $4s$ ,  $4p$  states and their weight may be as much as 20% of the total number of Cu  $3d$  out-of-plane orbitals.

The tight binding calculations (one electron approximation) appears to reproduce the amount of  $d_{z^2}$  holes in the Bi-2212 system. However, as discussed above, the corresponding  $p_z$  holes differ in experiment and the calculations. This may be understood due to strong correlation effects operative in these systems. In fact, it has been stressed in a recent report [39] that orbital polarization should be treated equally with spin polarization and charge density, for strongly interacting systems like high temperature superconductors.

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#### References

- [1] Al Shamma F and Fuggle J C 1990 *Physica C* **169** 325
- [2] Lindberg P A P, Shen Z X, Spicer W E and Lindau I 1990 *Surf. Sci. Rep.* **11** 1

- [3] Bianconi A, De Santis M, Di Cicco A, Flank A M, Fontaine A, Lagarde P, Katayama Yoshida H, Kotani A and Marcelli A 1988 *Phys. Rev. B* **38** 7196
- [4] Himpsel F J, Chandrashekar G V, McLean A B and Shafer M W 1988 *Phys. Rev. B* **38** 11 946
- [5] Krol A, Lin C S, Ming Z H, Sher C J, Kao Y H, Chen C T, Sette F, Ma Y, Smith G C, Zhu Y Z and Shaw D T 1990 *Phys. Rev. B* **42** 2635
- [6] Bianconi A, Castrucci P, Fabrizi A, Pompa M, Flank A M, Lagarde P, Katayama-Yoshida H and Calestani G 1990 *Earlier and Recent Aspects of Superconductivity (Springer Series in Solid State Sciences 90)* (Berlin: Springer) p 407
- [7] Abbate M, Sacchi M, Wnuk J J, Schreurs L W M, Wang Y S, Lof R and Fuggle J C 1990 *Phys. Rev. B* **42** 7914
- [8] Pompa M, Castrucci P, Li C, Udron D, Flank A M, Lagarde P, Katayama-Yoshida H, Della Longa S and Bianconi A 1991 *Physica C* **184** 102  
Pompa M, Li C, Bianconi A, Congiu Castellano A, Della Longa S, Flank A M, Lagarde P and Udron D 1991 *Physica C* **184** 51  
Li C, Pompa M, Della Longa S and Bianconi A 1991 *Physica C* **178** 421
- [9] Suzuki S, Takahashi T, Kusunoki T, Morikawa T, Sato S, Katayama-Yoshida H, Yamanaka A, Minami F and Takekawa S 1991 *Phys. Rev. B* **44** 5381
- [10] Bianconi A, Della Longa S, Li C, Pompa M, Congiu-Castellano A, Udron D, Flank A M and Lagarde P 1991 *Phys. Rev. B* **44** 10 126
- [11] Bianconi A, Li C, Della Longa S and Pompa M 1992 *Phys. Rev. B* **45** 4989
- [12] Nucker N, Romberg H, Xi X X, Fink J, Gengenheimer B and Zhao Z X 1989 *Phys. Rev. B* **39** 6619
- [13] Kuiper P, Grioni M, Sawatzky G A, Mitzi D B, Kapitunik A, Santaniello A, de Padova P and Thiry P 1989 *Physica C* **157** 260
- [14] Garg K B, Saini N L, Merrien N, Studer F, Durcok S and Tourillon G 1993 *Solid State Commun.* **85** 447
- [15] Qvarford M, Saini N L, Andersen J N, Nyholm R, Lundgren E, Lindau I, van Acker J F, Leonyak L, Soderholm S and Flodstrom S A 1993 *Physica C* **214** 119
- [16] Flipse C F J, van der Laan G, Thole B T and Myhra S 1993 *Z. Phys. B* **90** 89
- [17] Pellegrin E et al 1993 *Phys. Rev. B* **47** 3354
- [18] Chen C T, Tjeng L H, Kwo J, Kao H L, Rudolf P, Sette F and Fleming R M 1992 *Phys. Rev. Lett.* **68** 2543
- [19] Saini N L, Law D S-L, Pudney P, Garg K B, Menovsky A A and Franse J M 1995 *Phys. Rev. B* **52** 6219
- [20] Saini N L, Law D S-L, Pudney P, Srivastava P, Menovsky A, Franse J J M, Ohkubo H, Akinaga M, Studer F and Garg K B 1995 *Physica C* **251** 7
- [21] Venkatesh S, Srivastava P, Saini N L, Garg K B, Studer F, Ruyter A, Menovsky A, Ohkubo H and Akinaga M 1995 *Phys. Status Solidi* **192** 115
- [22] Weber W 1988 *Z. Phys. B* **70** 323  
Jarrel M, Krishnamurthy H R and Cox D L 1988 *Phys. Rev. B* **38** 4584  
Cox D L, Jarrel M, Jayaprakash C, Krishnamurthy H R and Deisz J 1989 *Phys. Rev. Lett.* **62** 2188
- [23] Kamimura H 1987 *Japan. J. Appl. Phys.* **26** 6627
- [24] Ohto Y, Tohyama T and Maekawa S 1991 *Phys. Rev. B* **43** 2968
- [25] Menken M J V, Winkelman A J M and Menovsky A 1991 *J. Crystal Growth* **113** 9
- [26] Takahashi T, Matsuyama H, Katayama-Yoshida H, Okabe Y, Hosoya S, Seki K, Fujimoto H, Sato M and Inokuchi H 1988 *Nature* **334** 691  
Olson C G, Liu R, Lynch D W, List R S, Arko A J, Veal B W, Chang Y C, Jiang P Z and Paulikas A P 1990 *Phys. Rev. B* **42** 381  
Manzke R, Buslaps T, Claessen R and Fink J 1989 *Europhys. Lett.* **9** 477  
Manzke R, Buslaps T, Claessen R, Skibowski M and Fink J 1990 *Phys. Scr.* **41** 579
- [27] Watanabe T, Takahashi T, Suzuki S, Katayama-Yoshida H and Minami F 1991 *Physica C* **176** 274
- [28] Pellegrin E, Nucker N, Fink J, Simmons C T, Kaindl G, Bernhard J, Renk K F, Kumm G and Winzer K 1993 *Phys. Rev. B* **48** 10 520
- [29] Kuiper P 1990 *PhD Thesis* University of Groningen
- [30] Romberg H, Alexander M, Nucker N, Aldemann P and Fink J 1990 *Phys. Rev. B* **42** 8768
- [31] Chen C T et al 1991 *Phys. Rev. Lett.* **66** 104
- [32] Massidda S, Yu J and Freeman A J 1988 *Physica C* **152** 251  
Krakauer H and Pickett W E 1988 *Phys. Rev. Lett.* **60** 251  
Hybersten M S and Mattheiss L F 1988 *Phys. Rev. Lett.* **60** 1661
- [33] Harrison W A 1980 *Electronic Structure and* (New York: Dover)
- [34] Di Casto C, Feiner L F and Grilli M 1991 *Phys. Rev. Lett.* **66** 3209
- [35] Hirai Y, Waki I, Momose A, Fukazawa T, Aida T, Takagi K and Hirano T 1992 *Phys. Rev. B* **45** 2573

- [36] Tjeng L H Private communication
- [37] Grioni M *et al* 1989 *Phys. Rev. B* **39** 1541
- [38] Mei C-J and Stollhoff G 1991 *Phys. Rev. B* **43** 3065
- [39] Liechtenstein A I, Anisimov V I and Zaanen J 1995 *Phys. Rev. B* **52** 5467