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Doping dependence of the O 1*s* core-level photoemission in Bi-Sr-Ca-Cu-O superconductors

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The O 1*s* core level of three different Bi-Sr-Ca-Cu-O superconductors has been studied by means of high-resolution x-ray-photoelectron spectroscopy (XPS) and x-ray-absorption spectroscopy (XAS). The O 1*s* XPS spectra could be decomposed into three components that were unambiguously assigned to the emission from the three different oxide layers in the crystal structure. These are, in order of increasing binding energy, Cu-O_2, Sr-O, and Bi-O. Furthermore, the component assigned to the Cu-O_2 layers exhibits a shift which depends on the hole doping as monitored by the XAS spectra. [S0163-1829(96)50822-2]

Since the discovery of Cu-O based high-T_c superconductors[1] (HTSC) photoelectron spectroscopy has been an important tool in the investigation of their electronic structure.[2,3] Several aspects of this field are today generally agreed upon, for instance the divalent nature of copper as revealed by intense satellite structures in the Cu 2*p* spectrum,[2,3] the fact that dispersive valence bands cross the Fermi level,[2] and that strong electron correlation gives rise to a valence band satellite.[4] In contrast to this and despite a large number of reports,[3] no consensus exists on the interpretation of the 1*s* core level photoemission spectrum of oxygen, the other common element besides copper in HTSC. For instance, in the case of $Bi_2Sr_2CaCu_2O_8$ (Bi2212) no agreement has emerged among the assignments of the different components in the O 1*s* spectrum to the three inequivalent oxygen sites in this layered structure (see, for instance, Refs. 5–9). It has even been proposed[5] that an intense additional peak at about 531 eV binding energy (E_b) is of intrinsic nature despite the findings of earlier studies[3] which showed that the O 1*s* spectrum for a clean HTSC should consist of one rather broad peak at about 529 eV E_b.

As is well known HTSC are obtained by doping of an insulating mother compound. The importance of oxygen in this doping process, exemplified by the doping of Bi2212 being dependent on the oxygen content[10] and the creation of holes in O 2*p* states[11] upon doping, calls for further systematic studies in order to achieve a general understanding of the O 1*s* photoemission spectrum.

One important step in this direction was the O 1*s* x-ray-photoemission spectroscopy (XPS) study by Parmigiani *et al.*[12] Due to the high energy resolution ($\Delta E = 0.35$ eV) in their experiment they were able to resolve a low E_b feature and thereby establish that the O 1*s* spectrum consists of at least two components. Furthermore, by changing the surface sensitivity they showed that the low E_b structure is bulk related. In order to be more specific about the identification of these two components, and a proposed third, Parmigiani *et al.* pointed out that further experiments performed at higher energy resolution and/or with less statistical noise were needed.

The importance of reaching a good understanding of the O 1*s* spectrum is evident from its predicted doping dependence. Using a Cu_2O_7 planar cluster, Eskes and Sawatzky[13] calculated the O 1*s* spectrum to consist of a single peak with weak satellites at higher E_b arising from the core-hole valence-hole repulsion. Upon doping with 0.5 hole per Cu site, a doping level comparable to the situation in Bi2212,[10] the calculated O 1*s* photoemission peak is shifted about 0.5 eV towards lower E_b.

In the present work O 1*s* XPS spectra at very high energy resolution ($\Delta E = 0.25$ eV) and with low statistical noise have been measured. Three different HTSC samples, Bi2212, $Bi_2Sr_2CuO_6$ (Bi2201), and $(Bi,Pb)_2Sr_2(Ca,Er)_1Cu_2O_8$ [Bi2212(Ca/Er)], were studied in order to unravel the O 1*s* XPS spectrum and investigate its doping dependence. X-ray-absorption spectroscopy (XAS) at the O *K* edge was also performed since the hole doping of oxygen in HTSC can be

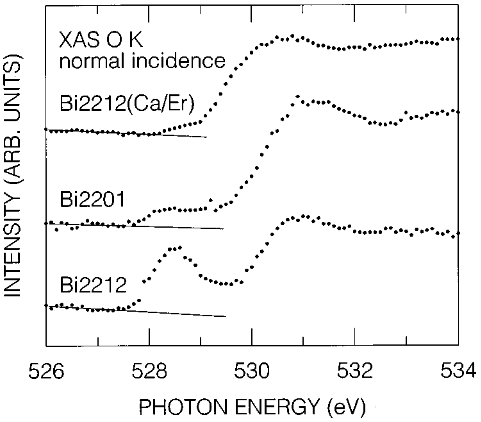

FIG. 1. XAS spectra at the O K edge normalized to the integrated intensity up to 544 eV.

monitored by such measurements.[11,14] The obtained O 1*s* XPS spectra could be decomposed into three components. By varying the surface sensitivity for Bi2212, and thereby the relative photoemission intensity of the different oxide layers, these components were unambiguously assigned to the three different oxygen sites. Furthermore, a doping dependence, which supports the calculation of Eskes and Sawatzky,[13] was found for the component arising from the Cu-O_2 layers.

Monochromatized Al K_α radiation ($h\nu$=1486.6 eV) from a rotating anode was used in the XPS measurements. XPS spectra were recorded by utilizing a large hemispherical electron energy analyzer (360 mm mean radius) with a multichannel detector system.[15] XAS measurements were performed at beamline 22 (Ref. 16) at the MAX National Synchrotron-Radiation Laboratory in Lund, Sweden. The spectra were recorded by detecting the total electron yield using a channeltron and the photon energy resolution was set to 0.3 eV.

The single crystal samples were cleaved *in situ* at a pressure below 1×10^{-10} Torr and were kept at room temperature during cleavage and measurements. The cleaved samples expose a Bi-O surface.[17] The growth methods of the Bi2212 and Bi2201 crystals are described elsewhere.[10,4] The crystal structure of these compounds are similar but with the important difference that Bi2212 has twice as many Cu-O_2 layers in the unit cell as Bi2201.[18] In Bi2212(Ca/Er),[19] the substitution of divalent Ca by trivalent Er is expected to result in a depletion of O 2*p* holes similar to the case of Ca/Y substitution.[11] The onset for superconductivity in Bi2212,[10] Bi2212(Ca/Er), and Bi2201 were determined by magnetic measurements to be around 90, 70, and 18 K, respectively.

O *K* edge XAS spectra of the studied compounds are shown in Fig. 1. The spectra are measured at normal incidence which gives the strongest possible intensity of the prepeak (at about 528.5 eV) due to its polarization dependence.[14,20] The prepeak is clearly more intense in Bi2212 than in the other two samples, reflecting a higher degree of hole doping in Bi2212.[11] In particular, these results confirm the expected influence of the Ca/Er substitution described above.

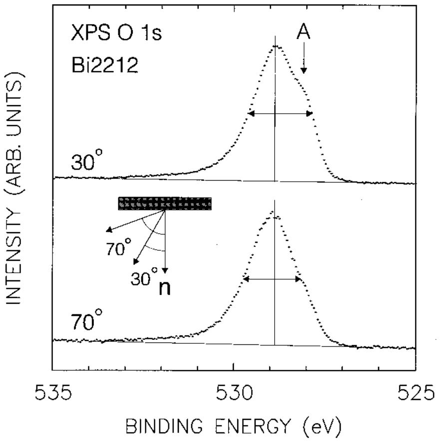

FIG. 2. O 1*s* XPS spectra of Bi2212 measured at different emission angles. The vertical lines are guides to the eye in order to compare differences in intensity on the high and low E_b side of the peak and the horizontal arrows mark the FWHM (see Table I).

Figure 2 shows O 1*s* XPS spectra of Bi2212 measured at different emission angles in order to vary the surface sensitivity. In the more bulk sensitive spectrum (30° emission angle) the low E_b component (marked *A*) is more intense and clearly resolved, i.e., it is a bulk related feature. Furthermore, by inspecting the horizontal arrows which mark the full width at half maximum (FWHM) it is obvious that the more surface sensitive spectrum (70° emission angle) shows an increase in intensity on the high E_b side, demonstrating that a surface related component is present in this region. The shape of the spectra in Fig. 2 suggests also the presence of a third component. Figure 3 compares the O 1*s* spectra for Bi2201 and Bi2212(Ca/Er). These spectra are considerably narrower than the Bi2212 spectrum; the clearly resolved low E_b shoulder seen for Bi2212 is not visible. The correlation between the width of the O 1*s* XPS spectra and the intensity of the prepeak in the O *K* edge XAS spectra strongly suggests that the low E_b feature is associated to the oxide layer influenced by the hole doping.

In all spectra shown in Figs. 2 and 3 the intensity at and above 531 eV is very low, demonstrating the cleanliness of the surfaces. Only for Bi2212(Ca/Er) some small structures are seen in this E_b region which may be related to contami-

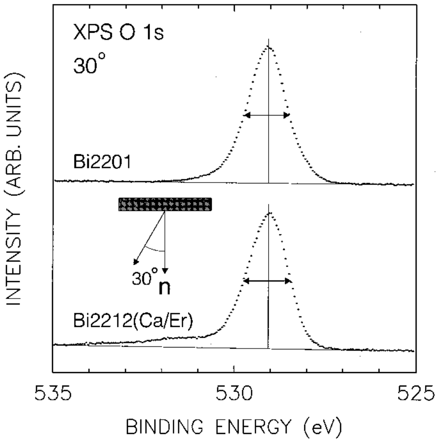

FIG. 3. O 1*s* XPS spectra of Bi2201 and Bi2212(Ca/Er) measured at 30° emission angle. See Fig. 2 for explanations of the vertical lines and arrows.

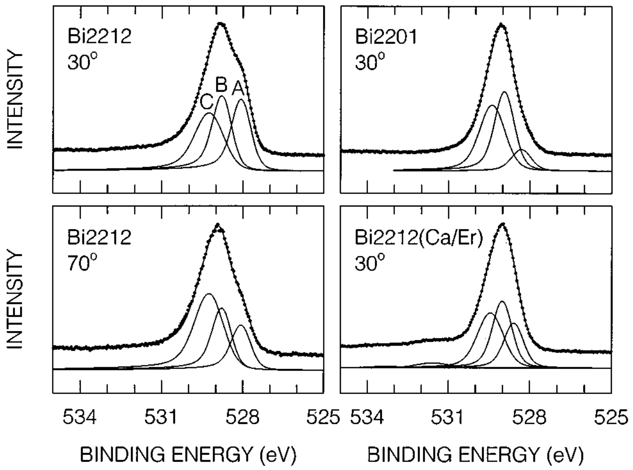

FIG. 4. The result of a curve fitting analysis of the spectra shown in Figs. 2 and 3. The measured spectra are plotted with dots whereas the fitted spectra and their components are plotted with solid lines. See text for details.

nation. It is clear from the Bi2212 spectra measured at different emission angles that the tail extending up to 534 eV E_b is not due to surface contamination. It is believed to be of intrinsic nature, as will be discussed below.

In order to extract a more precise interpretation of the O 1*s* XPS spectra presented in Figs. 2 and 3, they have been analyzed by a curve fitting procedure. Previous attempts to use curve fitting analysis have suffered from low energy resolution and/or high statistical noise. With the present O 1*s* XPS spectra for Bi2212 the curve fitting is less arbitrary for two reasons: first, the high energy resolution which results in a resolved shoulder on the low E_b side and an asymmetric profile with a tail at high E_b; secondly, the spectra measured with different surface sensitivity must be fitted with the same line-shape parameters, the only difference being the intensity of the components. Three components were chosen, a number well justified both by inspection of the spectra and the presence of three different oxygen sites in the crystal structures. The tail at high E_b was modeled by the use of the asymmetric Doniach-Šunjić line profile,[21] convoluted with a Gaussian profile, for all components. This is an approximation because at least part of the intensity in this tail can be expected to arise from the predicted weak satellite structures.[13] In the calculated spectrum these satellites resulted in a tail extending up to 534 eV E_b.

The curve fitting results are shown in Fig. 4. The different components are labeled A, B, and C in order of increasing E_b. For Bi2212, the shape of the low E_b shoulder gives a strict constraint on the width of component A. It is possible to use the same width for component B, but the smaller slope on the high E_b side suggests a larger width of component C. Letting C be broader than A and B (Ref. 22) a good fit is achieved, as seen in Fig. 4. There are several possible explanations for the extra broadening of component C. For instance, it could be due to larger disorder in the corresponding crystal layer, to a nonstoichiometric oxygen content, or to a proposed energy loss structure.[6] It could also arise from a larger vibrational broadening, as can be expected for oxygen at the surface. In the fits of the spectra for Bi2201 and Bi2212(Ca/Er) the Gaussian widths of components A and B were kept the same as for Bi2212 but the Gaussian width of component C is slightly smaller than for Bi2212.[22] This does not violate the proposed explanations for the extra broadening of component C. Also, the asymmetry of the Doniach-Šunjić line profile is smaller for Bi2201 and Bi2212(Ca/Er). The results of the analysis of the XPS spectra are summarized in Table I. $I_{A,B,C}$ and $E_{A,B,C}$ are the relative intensities and binding energies of the components A, B, and C, respectively.

Comparing the curve fitting for the Bi2212 spectra measured at different emission angles clearly shows that I_A decreases whereas I_C increases in the more surface sensitive spectrum, in agreement with what was already suggested by the inspection of Fig. 2 above. The crystal structure of Bi2212 consists of a stacking of oxide layers which from the surface of the cleaved crystal to three layers down are Bi-O, Sr-O, and Cu-O_2, respectively. Especially in the measurement performed at 70° emission angle, the major part of the intensity in the XPS spectrum originates from these first layers because of the strong surface sensitivity. These considerations give a straightforward assignment of the different components: A corresponds to Cu-O_2, B to Sr-O, and C to Bi-O.[23] As noted above, Balzarotti *et al.*[5] assigned an intense component at 531.5 eV to the combined emission from the Bi-O and Sr-O layers, an interpretation for which no support is found in the present results. This peak does not exist for a sample which is clean and not heavily oxygenated.[12]

The variation of I_A seen in Table I between the three compounds is consistent with the assignment of component A to the Cu-O_2 layers. For Bi2201 I_A is smaller than for Bi2212, a difference which is understood by considering the short electron escape depth in XPS and the different numbers of Cu-O_2 layers in the unit cell, i.e., in Bi2212 the first and second Cu-O_2 layers are separated only by a Ca layer, whereas in Bi2201 the first Cu-O_2 layer is followed by a sequence of four oxide layers till the second Cu-O_2 layer. I_A for Bi2212(Ca/Er) is nearly the same as for Bi2212, in agreement with their similar crystal structure.

TABLE I. The results of the analysis of the O 1*s* XPS spectra. $I_{A,B,C}$ and $E_{A,B,C}$ are the relative intensities and binding energies of the components A, B, and C, respectively. θ is the emission angle. FWHM are from the raw spectra as marked in Figs. 2 and 3.

Sample	θ	FWHM (eV)	I_A (%)	E_A (eV)	I_B (%)	E_B (eV)	I_C (%)	E_C (eV)
Bi2212	30°	1.78	32	528.04	33	528.76	35	529.21
Bi2212	70°	1.64	21	528.04	29	528.76	50	529.21
Bi2201	30°	1.28	12	528.30	43	528.93	45	529.37
Bi2212(Ca/Er)	30°	1.31	25	528.58	37	529.00	39	529.44

In the discussion above of the XPS spectra in Figs. 2 and 3 it was suggested that component A is related to the layer being hole doped. The intensity variations of this component made it possible to assign it to the Cu-O_2 layers, i.e., the layers expected to be hole doped in HTSC. Evidently, this assignment supports that a doping dependence should be present for component A. The curve fitting results in Table I together with the XAS spectra in Fig. 1 reveal a doping dependence consisting of a decrease of E_A relative to E_B and E_C upon increased hole doping. The XAS results show a clear prepeak structure for Bi2201 which is stronger than for Bi2212(Ca/Er) despite the larger number of Cu-O_2 layers in the unit cell of the latter compound. The Cu-O_2 layer of Bi2201 is thus rather highly doped and therefore the difference between E_A and E_B is nearly the same as for Bi2212. The very low intensity of the O K edge prepeak for Bi2212(Ca/Er), i.e., a low hole doping, is accompanied by a clear increase of E_A as compared to the other two compounds. The doping dependent shift of the Cu-O_2 component agrees with the theoretical results by Eskes and Sawatzky[13] and is supported by the O 1*s* XPS study by Nagoshi *et al.*[9] of polycrystalline $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ ($n=1,2,3$) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$. However, Nagoshi *et al.* gave a reversed assignment of components B and C. It should also be noted that there is no support in the present data for the claim of Leiro *et al.*[24] that the intense low E_b shoulder in O 1*s* spectra of Bi2212 to a large extent originates from oxygen bound to lead in the Bi-O surface layer in lead-substituted samples. Indeed, the spectrum for our lead containing Bi2212(Ca/Er) sample does not show any intense low E_b shoulder.

In conclusion, high resolution O 1*s* XPS spectra in combination with O K edge XAS spectra of three different Bi-Sr-Ca-Cu-O superconductors have made it possible to obtain a consistent interpretation of the O 1*s* XPS spectra in terms of three different components which, in order of increasing E_b, are assigned to the Cu-O_2, Sr-O, and Bi-O layers, respectively. The component arising from the Cu-O_2 layers shifts towards lower E_b relative to the other components upon increased hole doping. The shift of the Cu-O_2 component as a function of doping has two important implications. First, it shows that not only XAS at the O K edge, but also high resolution XPS of the O 1*s* core level can be used to study the doping of HTSC. Secondly, it stresses that it is not sufficient to be guided by measured E_b from simple oxides to interpret the O 1*s* spectra of HTSC, as has been attempted earlier.[8]

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[19] The Bi2212(Ca/Er) crystals were grown by a slow cooling method from a melt with initial composition 4 $BiO_{1.5}$ +3 $SrCO_3$+3 CaO+4 CuO with 10% of the CaO content substituted by $ErO_{1.5}$ and 10% of the $BiO_{1.5}$ content substituted by PbO. The initial mixture was heated in an alumina crucible up to 1000 °C with a rate of 4 °C/h, then cooled down with the same rate to 400 °C and then quenched to RT. The single crystals grown were characterized by x-ray diffraction and microprobe compositional analysis. The Ca/Er and Bi/Pb ratios were near 11/3 and 12/1, respectively.

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[22] The Lorentzian (L) and Gaussian (G) widths used are (in eV): Bi2212 A and B: $L=0.21$, $G=0.7$; C: $L=0.21$, $G=1.1$. Bi2201 A and B: $L=0.25$, $G=0.7$; C: $L=0.25$, $G=0.95$. Bi2212(Ca/Er) A and B: $L=0.24$, $G=0.7$; C: $L=0.24$, $G=0.97$.

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