O 1s Core-Level Positions of $Bi_2Sr_2CaCu_2O_{8-x}$ by O K_α X-Ray Emission

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The measured O K_α X-ray emission spectrum of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8-x}$ is compared with a spectrum based on local density band structure calculations. By taking also into account the shape of the measured O 1s X-ray photoelectron spectrum an energy level diagram for the O 1s core-level binding energies of the three different oxygen sites is constructed. The O 1s binding energy in the Bi_2O_2-layers is found to be about the same as that one in the SrO-layers, whereas the binding energy in the CuO_2-layers is lower by about 0.5 eV.

1. Introduction

Soon after the discovery of superconductivity below 20 K in the Bi-Sr-Cu-O system [1] higher critical temperatures at about 80 K and 110 K have been achieved by adding Ca to the system [2–5]. These two critical temperatures in the Bi-Sr-Ca-Cu-O system are due to two different phases. While it has proven difficult to prepare single-phase samples of the 110 K phase ($Bi_2Sr_2Ca_2Cu_3O_{10-x}$) it is possible to produce single-phase samples of the 80 K phase with the composition $Bi_2Sr_2CaCu_2O_{8-x}$. In contrast to the $YBa_2Cu_3O_{7-\delta}$ type superconductors the structure of $Bi_2Sr_2CaCu_2O_{8-x}$ consists besides the perovskite-like CuO_2-layers also of rock-salt type Bi_2O_2- and SrO-layers [3, 5, 6]. This leads to three inequivalent oxygen sites in this compound.

In the present work we investigate these oxygen sites by comparing our experimental O K_α X-ray emission spectrum to the one calculated by Marksteiner et al. [7]. The spectrum in [7] is based on the electronic structure obtained from local density calculations by Massidda et al. [8]. By this comparison an energy level diagram for the three different O 1s core-levels was constructed.

2. X-Ray Emission Spectroscopy

Besides ultraviolet and X-ray photoelectron spectroscopy (UPS, XPS), X-ray emission spectroscopy (XES) is a powerful method for studying the electronic structure of occupied states. X-ray spectra resulting from electronic transitions between the valence band and a core-level are called emission bands, those resulting from electronic transitions between two core-levels are called emission lines. In either case there is an electronic transition between *two* energetic states at *one* atomic site. Since the transition takes place between two states X-ray emission is governed by strong electric dipole selection rules. Thus with valence band XES, valence electrons of different symmetries and different atomic sites can be probed separately. In this respect, XES is superior to UPS and XPS. A further advantage of XES is the larger sampling depth compared to that one with UPS or XPS. Therefore, X-ray emission spectra are much less surface sensitive than photoelectron spectra and are representative of the bulk material.

The O K_α spectrum which we have investigated arises from transitions from the oxygen valence band to the three different O 1s core-levels. Because of the selection rules the O 2p density of states is probed.

3. Experimental

The $Bi_2Sr_2CaCu_2O_{8-x}$ single crystals were prepared from high purity powders of $SrCO_3$, Bi_2O_3, CaO, and CuO (all of them 99.999% purity). These powders were mixed in appropriate proportions, homogenized by ball milling and pressed at 4 to 6 kbar into 20 g pellets with 20 mm diameter. The pellets were sintered at 800 °C for 12 h. As suitable container for the succeeding flux melting a high purity

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($\geq$99.99%) recrystallized crucible of Al_2O_3 was used. Depending on the final composition after flux melting for 1 h at 1150 °C the temperature was held for 6 h at 1050 °C and 960 °C, respectively, and then slowly cooled down to room temperature with cooling rates of 3 to 50 °C/h.

Black plate-like single crystals with typical dimensions between $8 \times 2 \times 0.1$ mm^3 and $3 \times 2 \times 1$ mm^3 have been successfully isolated. On such single crystals the transition to superconductivity was determined by four point electrical resistivity measurements using calibrated platinum resistors. The DC currents were kept between 5 µA and 10 mA in order to avoid any possible supression of T_c in the crystals. The critical temperature $T_{c,\text{zero}}$ of such flux grown single crystals without post annealing was between 77 K and 78 K.

The spectrum was recorded with an electron microprobe (JEOL JXA-733) operated at 10 kV. The focusing linear spectrometer was equipped with a clinochlore crystal (resolution $\Delta\lambda/\lambda < 1.5 \times 10^{-3}$; $\lambda_{\text{OK}_\alpha} = 23.62$ Å). The spectrometer was calibrated with the O K_α main peak of SiO_2 to be at 526.0 eV [9].

4. Results and Discussion

Figure 1 a shows the O K_α spectrum of a randomly oriented $Bi_2Sr_2CaCu_2O_{8-x}$ single crystal (+ + + +). The main peak at 525.6 eV is accompanied by a small shoulder on the low energy side at about 523 eV. Although the shape of the O K_α-spectrum of $Bi_2Sr_2CaCu_2O_{8-x}$ is similar to that of $YBa_2Cu_3O_{7-\delta}$ in [10] and [11], the asymmetry produced by the shoulder is less pronounced than in the one of $YBa_2Cu_3O_{7-\delta}$. In this context we note that in [12] and [13] the shoulder in the O K_α-spectrum of $YBa_2Cu_3O_{7-\delta}$ is much smaller. However, this could be due to the resolution or to the quality of samples. The O K_α-spectrum of a sintered polycrystalline $Bi_2Sr_2CaCu_2O_{8-x}$-sample was almost identical to that in Fig. 1 a except a slightly ($\approx$0.1 eV) broader peak and a less distinct low-energy shoulder.

The comparison of the experimental O K_α-spectrum of $Bi_2Sr_2CaCu_2O_{8-x}$ with the calculated local density spectrum (full line in Fig. 1 a) from [7] reveals that the main peak in the experimental spectrum is considerably broader than in the calculated one. This discrepancy is not due to the experimental resolution. Furthermore the peak-to-shoulder intensity ratio is considerably lower with the experimental spectrum. In the following we will discuss these differences between theory and experiment and use them to improve the core-level positions which were reported in [7].

In $Bi_2Sr_2CaCu_2O_{8-x}$ there are three crystallographically different oxygen sites, namely O(1) in the CuO_2-planes, O(2) in the Bi_2O_2-planes, and O(3) in the SrO-planes. The calculation [8] yielded for these three sites different O 1s core-level binding energies as given in Table 1 and presented graphically in Figure 3 a. Besides the differences of the core-level binding energies this table also contains the reference energies E_0 (see [7]) of the calculated spectra.

The positions of the three partial O K_α spectra in Fig. 1 a result from these binding energies. Addition of the three partial spectra yields the calculated total spectrum which is rather narrow since the main peaks of the three partial spectra lie nearly at the same energy.

In the following we will describe our procedure to achieve a better agreement between theory and experiment. It is obvious that a change of the core-level positions relative to each other will result in a shift of the partial spectra and thus will affect the shape of the total spectrum. Therefore it should be possible to achieve a better agreement between experiment and theory by changing the core-level positions.

A further demand for a readjustment of the calculated [7, 8] core-level positions comes from the O 1s X-ray photoelectron spectra in [14] to [20] which all show nearly symmetrical peaks with a FWHM of about 2 eV. Since the O 1s spectra directly show the core-level binding energies, we have modelled that O 1s spectrum which would result from the core-level positions of [7] and [8] (see Table 1) by simply adding three Gaussians with a FWHM of 1.5 eV. The intensities $I\,[O(i)]$ of the three Gaussians were taken according to the atomic ratio of the different oxygen sites, i.e.

$$I\,[O(1)] : I\,[O(2)] : I\,[O(3)] = 2:1:1\,.$$

The resulting "model-spectrum" as presented in Fig. 2 (full line) shows a pronounced asymmetry due to the high binding-energy contribution of the O(2) 1s level. This asymmetry is not observed in the experimental spectrum (+ + + + in Fig. 2) as was already mentioned in [18].

A symmetrical O 1s spectrum as observed experimentally can roughly be obtained with the five different configurations of the three oxygen core-levels

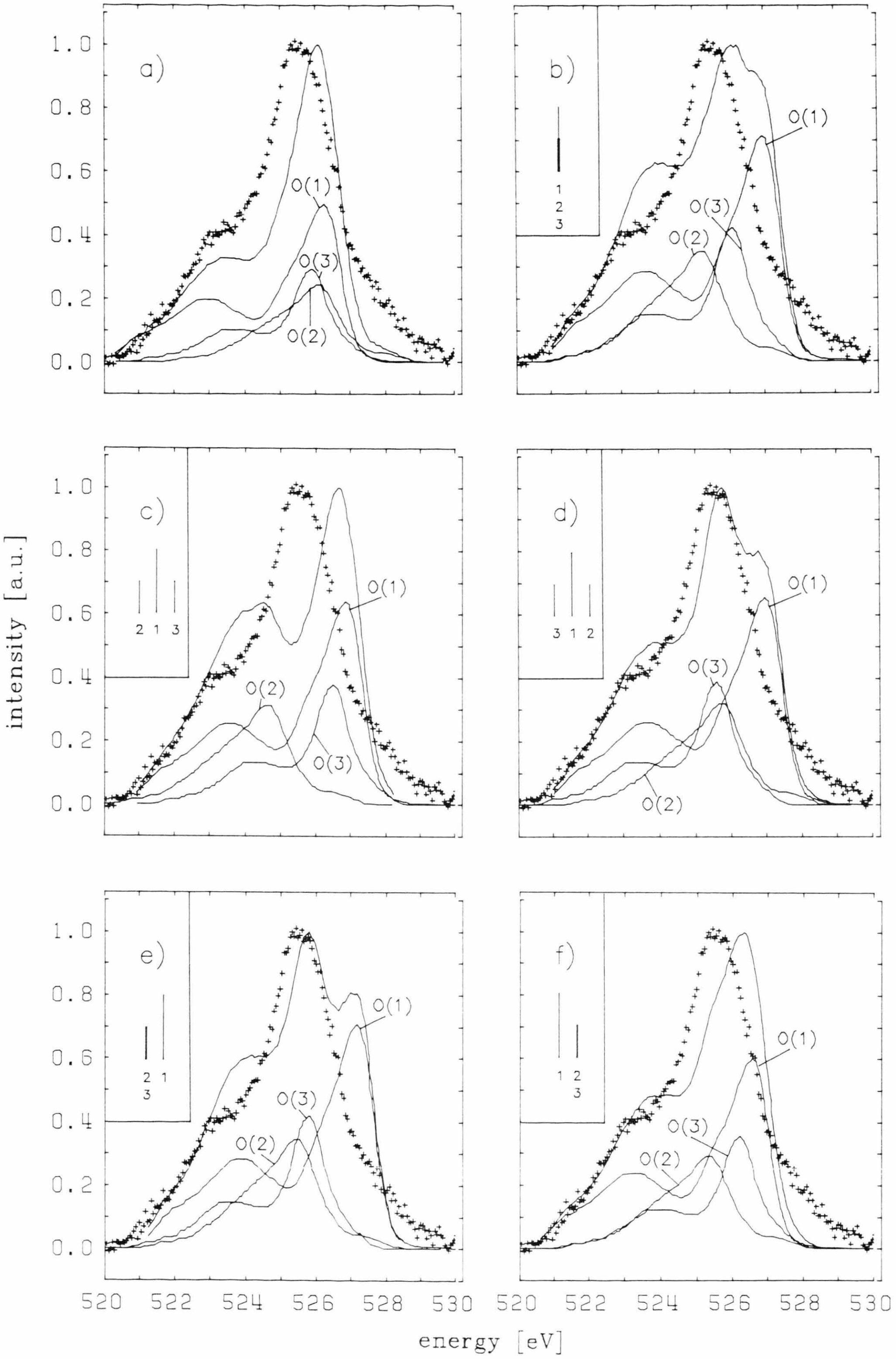
a)
b)
c)
d)
e)
f)
O(1)
O(2)
O(3)
1
2
3
2 1 3
3 1 2
2 1
3
1 2
3
1.0
0.8
0.6
0.4
0.2
0.0
intensity [a.u.]
520
522
524
526
528
530
energy [eV]

Table 1. Differences of the O 1s core-level binding energies (BE) in the theoretical spectra of Figure 1. E_0 is the position of the reference energy of the calculated spectra (see [7]) within the energy scale of the experimental spectrum.

Core-level constellation (see insets in Figs. 1 a–f)	BE(O(2))– BE(O(1)) in eV	BE(O(3))– BE(O(1)) in eV	E_0 in eV
a) as calc. in [7, 8]	1.57	0.51	528.6
b)	0.00	0.00	528.8
c)	−0.50	0.50	529.2
d)	0.50	−0.50	528.3
e)	−0.51	−0.51	528.5
f)	0.51	0.51	528.9

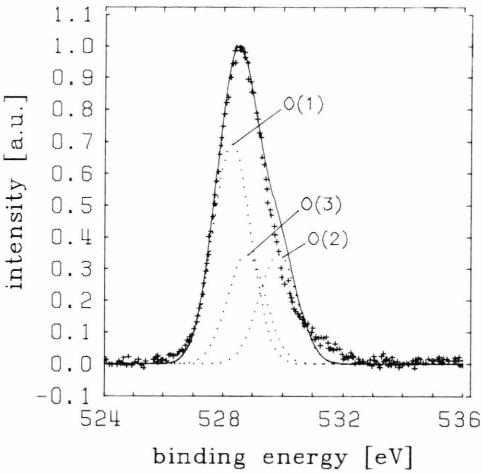

Fig. 2. $Bi_2Sr_2CaCu_2O_{8-x}$: O 1s XPS spectrum. (+ + + +): as measured in [18]. (——): as calculated with one Gaussian (· · · ·) for each core-level.

shown in the insets of Figs. 1 b–f. While it is not possible to decide with the O 1s XPS-spectrum which configuration proves right, it is possible to arrange the partial O K_α X-ray emission spectra according to these core-level configurations and compare the resulting total spectra with the experimental one. Figures 1 b–f show representative O K_α spectra for each of the five core-level configurations.

Fig. 1. $Bi_2Sr_2CaCu_2O_{8-x}$: measured O K_α spectrum (+ + + +) compared to theoretical spectra (——) based on the calculated partial spectra for the three oxygen sites from [7]. The position of the partial spectra is determined by the O 1s core-level binding energy. a) O 1s core-level binding energy as calculated in [7] and [8]. b)–f) The insets show qualitatively the different O 1s core-level configurations which determine the shape of the total spectra.

In Fig. 1 b we have assumed identical core-levels. In this case the O K_α spectrum shows three peaks and resembles closely the calculated He I UPS spectrum [7] which maps mainly the O 2p density of states. This arises because UPS does not involve core-level transitions. Therefore the positions of the partial spectra do not reflect different core-level binding energies. Since there is no agreement at all with our experimental spectrum, identical core-level binding energies can be excluded.

The resulting O K_α spectrum from the symmetrical core-level configurations are shown in Figs. 1 c and d. In the first case (c) the low-energy shoulder turns into a strong peak and in the second case (d) there is again a three peak structure due to the large peak-separation between the O(1)-peak and the two other peaks (O(2) and O(3)). Therefore both symmetrical core-level configurations (c) and (d) can be excluded, too.

The core-level configuration (f) in Fig. 1f was achieved by shifting only the O(2) partial spectrum by 1.06 eV to the O(3) core-level keeping fixed the calculated energy difference of 0.51 eV between the O(1) and the O(3) core-level as shown in Figure 3f. In configuration (e) (Fig. 1e) we adopted the energy difference of 0.51 eV from configuration (f) between the O(1)- and the two other core-levels. Again the three peak structure resulting from configuration (e) does not fit the experimental spectrum at all.

In conclusion of the present discussion we note that in Fig. 1 configuration (f) comes closest to a good agreement between experiment and theory. With this configuration a width of the main peak comparable to the experimental one and a good agreement with the

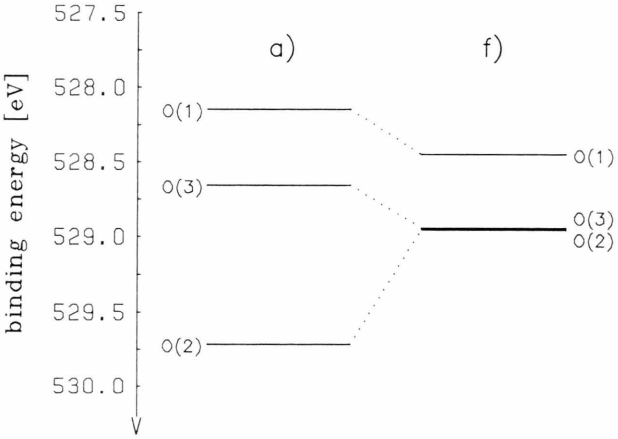

Fig. 3. O 1s energy level diagram. The absolute energy scale was calibrated to match the O 1s peak positions from [14] to [20]. a) As calculated in [7] and [8] (see Fig. 1 a). f) As obtained by the "best fit" from Fig. 1 f.

experimental peak-to-shoulder intensity ratio was achieved. In Fig. 3 we show the change in the core-level energy diagram from the calculated values of [7] and [8] to the values suggested from the "best fit" in Fig. 1f. In configuration (f) the reference energy E_0 (see [7]) had to be raised by 0.3 eV. Nevertheless, Fig. 1f shows still some differences between theory and experiment especially due to the large separation between the main peak and the peak which constitutes the low-energy shoulder. This discrepancy seems to be inherent to spectra based on local density calculations because we have shown in a foregoing publication [10] that with La_2CuO_4 and $YBa_2Cu_3O_{7-\delta}$ the calculated spectra also come out too broad. For this reason a perfect agreement between the calculations and the experiment could not be expected and therefore the core-level positions in Fig. 3 are subject to error-bars of about 0.2 eV. Furthermore, the fitting did not account for the high-energy tail in the experimental $Bi_2Sr_2CaCu_2O_{8-x}$ spectrum at about 528 eV which arises from the Ca $K_{\alpha_{1,L}}$ lines reflected in seventh order. On the other hand this structure may contain a satellite due to multiply ionized core-levels (shake-off) or valence electrons excited to an unoccupied level (shake-up). In order to clear up this question there is a need of threshold-excited X-ray emission measurements which can be performed on a synchrotron facility.

5. Conclusions

We have shown that the calculated partial O K_α spectra [7] are in a relatively good agreement with the experimental O K_α XES and O 1s XPS spectrum only when the O(2) core-level binding energy is reduced by about 1 eV. This is an indication that either the Bi–O-bonds are more ionic or the Bi–O-bond-length is smaller than assumed in [8].

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