O ls Core-Level Positions of Bi$_2$Sr$_2$CaCu$_2$O$_{8-x}$ by O K$_x$ X-Ray Emission

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Z. Naturforsch. 44a, 780–784 (1989); received July 6, 1989

The measured O K$_x$ X-ray emission spectrum of the high-T$_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8-x}$, is compared with a spectrum based on local density band structure calculations. By taking also into account the shape of the measured O ls X-ray photoelectron spectrum an energy level diagram for the O ls core-level binding energies of the three different oxygen sites is constructed. The O ls binding energy in the Bi$_2$O$_2$-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$_2$Sr$_2$CaCu$_2$O$_{10-x}$) it is possible to produce single-phase samples of the 80 K phase with the composition Bi$_2$Sr$_2$CaCu$_2$O$_{8-x}$. In contrast to the YBa$_2$Cu$_3$O$_{6.5}$ type superconductors the structure of Bi$_2$Sr$_2$CaCu$_2$O$_{6-x}$ consists besides the perovskite-like CuO$_2$-layers also of rock-salt type Bi$_2$O$_2$- 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$_x$ 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 ls 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$_x$ spectrum which we have investigated arises from transitions from the oxygen valence band to the three different O ls core-levels. Because of the selection rules the O 2p density of states is probed.

3. Experimental

The Bi$_2$Sr$_2$CaCu$_2$O$_{8-x}$ single crystals were prepared from high purity powders of SrCO$_3$, Bi$_2$O$_3$, 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...
(≥ 99.99%) recrystallized crucible of A12O3 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 × 2 × 0.1 mm³ and 3 × 2 × 1 mm³ 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 suppression of Te in the crystals. The critical temperature Te 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 clinohlore crystal (resolution Δλ/λ < 1.5 × 10⁻³; λOKa = 23.62 Å). The spectrometer was calibrated with the O Ka main peak of SiO₂ to be at 526.0 eV [9].

The positions of the three partial O Ka-spectra lie nearly at the same energy. Addition 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 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 Is X-ray photoelectron spectra in [14] to [20] which all show nearly symmetrical peaks with a FWHM of about 2 eV. Since the O Is spectra directly show the core-level binding energies, we have modelled that O Is spectrum which would result from the core-level positions of the three partial spectra would be identical to that in Fig. 1a except a slightly (≥ 0.1 eV) broader peak and a less distinct low-energy shoulder.

The comparison of the experimental O Ka-spectrum of Bi₂Sr₂CaCu₂O₈₋ₓ with the calculated local density spectrum (full line in Fig. 1a) 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 Bi₂Sr₂CaCu₂O₈₋ₓ there are three crystallographically different oxygen sites, namely O(1) in the CuO₂-planes, O(2) in the Bi₂O₂-planes, and O(3) in the SrO-planes. The calculation [8] yielded for these three different O Is core-level binding energies as given in Table 1 and presented graphically in Figure 3a. Besides the differences of the core-level binding energies this table also contains the reference energies E₀ (see [7]) of the calculated spectra.

The positions of the three partial O Ka spectra in Fig. 1a 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.

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A further demand for a readjustment of the calculated [7, 8] core-level positions comes from the O Is X-ray photoelectron spectra in [14] to [20] which all show nearly symmetrical peaks with a FWHM of about 2 eV. Since the O Is spectra directly show the core-level binding energies, we have modelled that O Is 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[Oi] of the three Gaussians were taken according to the atomic ratio of the different oxygen sites, i.e.


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) Is level. This asymmetry is not observed in the experimental spectrum (+++ in Fig. 2) as was already mentioned in [18].

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

<table>
<thead>
<tr>
<th>Core-level configuration (see insets in Figs. 1a–f)</th>
<th>BE(O(2))</th>
<th>BE(O(3))</th>
<th>$E_0$ in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) as calc. in [7, 8]</td>
<td>1.57</td>
<td>0.51</td>
<td>528.6</td>
</tr>
<tr>
<td>b)</td>
<td>0.00</td>
<td>0.00</td>
<td>528.8</td>
</tr>
<tr>
<td>c)</td>
<td>-0.50</td>
<td>0.50</td>
<td>529.2</td>
</tr>
<tr>
<td>d)</td>
<td>0.50</td>
<td>-0.50</td>
<td>528.3</td>
</tr>
<tr>
<td>e)</td>
<td>-0.51</td>
<td>-0.51</td>
<td>528.5</td>
</tr>
<tr>
<td>f)</td>
<td>0.51</td>
<td>0.51</td>
<td>528.9</td>
</tr>
</tbody>
</table>

The resulting O K$_\alpha$ spectrum from the symmetrical core-level configurations are shown in Figs. 1c 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 shown in the insets of Figs. 1b–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$_\alpha$ X-ray emission spectra according to these core-level configurations and compare the resulting total spectra with the experimental one. Figures 1b–f show representative O K$_\alpha$ spectra for each of the five core-level configurations.

In Fig. 1b we have assumed identical core-levels. In this case the O K$_\alpha$ spectrum shows three peaks and resembles closely the calculated HeI 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$_\alpha$ spectrum from the symmetrical core-level configurations are shown in Figs. 1c 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.

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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
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$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ 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$_2$Sr$_2$CaCu$_2$O$_{8-\delta}$ spectrum at about 528 eV which arises from the Ca K$_{\beta}$ 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$_{\alpha}$ spectra [7] are in a relatively good agreement with the experimental O K$_{\alpha}$ 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].

Acknowledgements

We would like to thank H. Jaeger for providing us with the polycrystalline sample. We gratefully acknowledge the discussions with J. Redinger from the Technische Universität Wien.