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A photoelectron spectroscopy and x-ray absorption study of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ single crystal with adsorbed Cs: on the origin of the states affected by electron doping and evidence for spatially resolved electron doping

S Söderholm[†], M Qvarford[‡], H Bernhoff[†], J N Andersen[‡], E Lundgren[‡],
R Nyholm[‡], U O Karlsson[†], I Lindau[‡] and S A Flodström[†]

[†] Department of Physics, Materials Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

[‡] Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Sölvegatan 14, S-223 62 Lund, Sweden

Received 5 October 1995

Abstract. The influence of electron doping, via deposition of small amounts of Cs, on the electronic structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been studied by high-resolution photoelectron spectroscopy (PES) and x-ray absorption spectroscopy (XAS), utilizing synchrotron radiation. The changes in the electronic structure were monitored by PES of the valence band and of the O 1s, Bi 4f, Bi 5d, Ca 2p and Sr 3d core levels, and by XAS at the O 1s, Cu 2p and Ca 2p edges.

The experimental data suggest that the loss of the Fermi edge and the loss of spectral intensity down to about 2 eV below the Fermi level, and the substantial loss of spectral intensity of the pre-edge structure in the O 1s XAS spectrum are mainly due to annihilation of states with O 2p character in the Cu–O layer. It is evident from bulk- and surface-sensitive XAS spectra that the electron doping by Cs affects the electronic structure more strongly close to the surface. This implies that the doping occurs locally and that the charge transfer between the different layers in the unit cell is not uniform. Thus it seems possible to alter the electronic properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ locally through spatially resolved electron doping.

When larger amounts of Cs are deposited, a chemical reaction occurs which causes a disruption of the Bi–O layer. This deposition regime is characterized by the presence of caesium oxide and reduced (metallic) Bi.

1. Introduction

During recent years, it has been accepted that the electronic structure of so-called high-temperature (or high- T_c) superconductors (HTS) can be understood only by taking strong electron–electron correlations into account. It has also been established that these materials must be doped in order to be conducting, i.e. there exists an undoped insulating mother compound for every HTS system, e.g. La_2CuO_4 for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. However, several important questions remain open, for instance: is a Fermi-liquid description of the doped compounds valid, how should the doping-induced states be described, and to which atoms and sites are the states affected by doping related? Several previous photoemission studies have focused on the geometrical and electronic structure of the interface between the superconductor and a metallic overlayer, thereby treating questions of importance for

the utilization of HTS in different applications. See, for instance, [1, 2, 3]. However, by applying a perturbation on the superconductor, i.e. an adsorbate/overlayer, additional fundamental information about the electronic structure of the superconductor system can be obtained, e.g. on questions related to the doping. The doping of HTS has in most cases been studied by changing the number of holes by annealing in different atmospheres and by changing the stoichiometry of the samples; for instance in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ electrons can be added through substitution of Ca with elements having a formal valency of 3+ instead of 2+ [4, 5, 6, 7].

In the present study, the interaction between $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and Cs is reported. The changes of the electronic structure induced by the deposition of Cs onto the surface of the superconductor were studied via photoelectron spectroscopy of the valence band and several selected core levels, and by x-ray absorption spectroscopy on the O 1s, Cu 2p and Ca 2p edges. By electron doping with Cs the electronic structure at the Fermi level, E_F , could be altered with a limited probability of diffusion of the dopant into the superconductor.

2. Experimental details

The photoemission and x-ray absorption experiments were performed at beamline 22 at the synchrotron radiation facility MAX-lab in Lund, Sweden. The main parts of the beamline are a modified SX-700-type monochromator and an experimental chamber with a hemispherical electron energy analyser with a mean radius of 200 mm [8, 9]. The energy resolution was 0.1 eV at a photon energy of 100 eV and 0.5 eV at 600 eV in the photoemission experiments, and the photon energy resolution was 0.2 (Ca 2p), 0.3 (O 1s) and 0.8 eV (Cu 2p) eV in the x-ray absorption measurements. The absorption was determined both in the total-electron-yield and in the partial-yield mode, the latter being more surface sensitive. The binding energy scale was obtained from measurements of the Fermi edge of a reference sample, and the photon energy scale for the x-ray absorption measurements from measurements of the difference in kinetic energy of the Au 4f photoemission spectrum obtained with first- and second-order radiation. The base pressure in the experimental chamber was in the low 10^{-10} Torr range. The single-crystal samples used in the present study were grown with a directional solidification method, and have a sharp superconducting transition with its onset at 90 K [10]. The crystals were cleaved *in situ* and had mirror-like surfaces. The quality of the single-crystal surface was checked with LEED. It is well established that cleavage causes the surface to be a Bi–O layer [11]. Cs was evaporated onto the surface from a SAES Getter source.

3. Results

In the present case, the growth of the Cs overlayer was monitored by measuring the intensity of the Cs 5p peaks and the Bi $5d_{3/2}$ peak; see figure 1. The Cs 5p intensity increased almost linearly with evaporation time, indicating a rather uniform adsorption rate. The Bi $5d_{3/2}$ intensity decreased rapidly up to an evaporation time of about two minutes, after which the intensity decreased slowly with longer evaporation times. The change of the rate of decrease for Bi $5d_{3/2}$ at around two minutes indicates a change of the Cs growth mode. It is well established that it is very difficult to obtain overlayers of Cs thicker than one monolayer through evaporation onto a substrate at room temperature. However, the possibility of depositing large amounts of Cs can arise through the chemical reactivity of Cs—in the present case for instance caesium oxide, which exists in many stoichiometries [12]—and

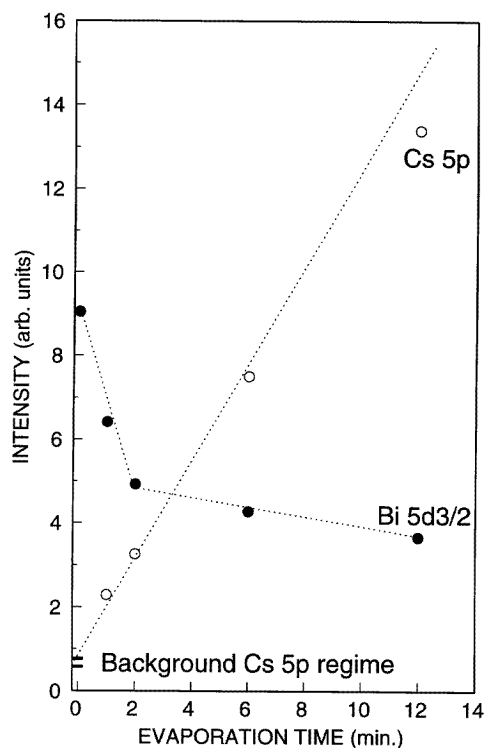


Figure 1. The intensity of the Bi 5d_{3/2} and the Cs 5p peaks as a function of Cs evaporation time. The dotted lines are guides to the eye.

caesium alloys can be formed. Thus, a quantitative measure of the amount of deposited Cs cannot be obtained; however, the data in figure 1 suggest that the deposition may be divided into two regimes; one below and one above approximately two minutes' deposition.

In the photoemission spectra shown in figure 2 several features are evident, the most prominent being the valence band and the Bi 5d core levels at a binding energy relative to the Fermi level (E_b) of about 26 eV and, after deposition of Cs, the Cs 5p level at 12 eV. The spectrum of the clean crystal contains several weak features: the broad structure centred at around 12 eV is assigned to the Cu d⁸ satellite [13, 14, 15] and there is probably also a contribution from Bi 6s in this energy region [16]; the weak peak at 18 eV is attributed to Sr 4p; the broad peak around 21 eV to O 2s; and the peak at 23 eV to Ca 3p [17].

After a deposition time of one minute, the spin-orbit-split Cs 5p peak was clearly visible, and the shallow superconductor core-level peaks were shifted about 0.3 eV towards a higher E_b ; see figure 2. The shift was most evident for the Bi 5d level. The magnitudes of the shifts of the other levels were difficult to determine since these peaks were rather broad. When the deposition time was increased to two minutes, a shoulder appeared on the low-binding-energy side of the Bi 5d_{5/2} peak. At the highest coverage, after twelve minutes' deposition, a peak at 23(3) eV was clearly visible and the shoulder on the low-binding-energy side of Bi 5d_{5/2} was further pronounced. This shoulder consists of several features, as indicated by the lines in figure 2. The main part of this shoulder is attributed to Cs 5s ($E_b \approx 25$ eV). The structures denoted A and B are due to shifted Bi 5d peaks. When the deposition time was increased from two to six minutes the shape of the valence band showed signs of formation of caesium oxide, which gave rise to the peaks with binding energies of approximately 2.5, 4 and 5.5 eV [12]. The rest of the changes appearing in the valence band region will be discussed below.

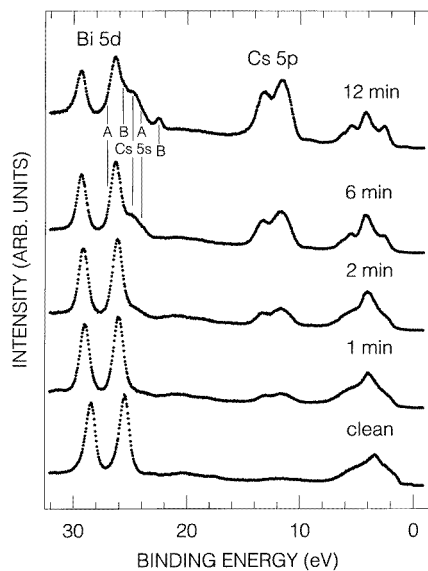


Figure 2. Photoemission spectra of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs deposition for 1, 2, 6 and 12 min, excited with 100 eV photons. The marked binding energies A and B indicate shifted Bi 5d components, identified with the aid of corresponding Bi 4f spectra; see figure 3. The spectra are normalized to the same height.

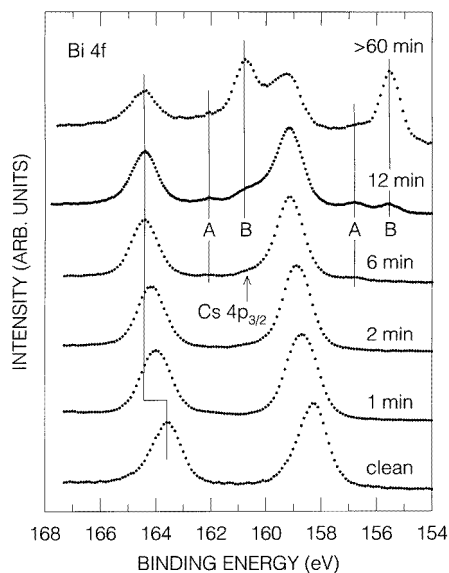


Figure 3. Photoemission spectra of the Bi 4f core level of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs depositions, excited with 400 eV photons. The marked binding energies A and B indicate shifted Bi 4f components. The binding energy of the Cs $4p_{3/2}$ level is also indicated. The spectra are normalized to the same height.

In the photoemission spectra of the Bi 4f core level, figure 3, the additional Bi structures denoted A and B are more clearly seen, due to larger spin-orbit splitting of the Bi 4f level,

5.3 eV, compared to that of the Bi 5d level. The partial overlap of the Cs $4p_{3/2}$ with structure B causes this structure, on the high-binding-energy side of the Bi $4f_{7/2}$ peak, to appear broader than the other shifted Bi 4f peaks. This is most clearly seen in the spectrum recorded after twelve minutes' Cs deposition. The binding energy of the Bi 4f level was 158.3 eV for the clean surface, and shifted towards higher binding energy upon deposition of Cs. The shift saturated at 0.8 eV after about 2–3 min of deposition.

Anticipating the discussion it can be mentioned that the appearance of additional Bi peaks has previously been observed upon the deposition of many different metals, for instance Cu [18, 19], Pb [20], Au [21], Ag [21] and Rb [13], and they have been ascribed to reduced Bi states arising from the disruption of the Bi–O surface. The observed mutual splitting of A and B was 5.3 eV in excellent agreement with the spin–orbit splitting of Bi 4f. The shifts of the two additional doublets (A and B in figure 3) were 2.3 and 3.6 eV towards lower E_b , respectively, relative the main Bi 4f peak at the highest Cs coverages. The shift between A and the main Bi 4f peak was in fair agreement with reported energy shifts between Bi_2O_3 and Bi, falling in the range 2–3 eV [22, 23, 24]. Although these additional structures are not well resolved in the Bi 5d spectra they can be identified with the aid of the Bi 4f spectra. The splitting of structure B could be determined to be about 3 eV, in agreement with the spin–orbit splitting of Bi 5d, and the shift of this doublet was 3.7 eV towards lower binding energy. The shift of A can be estimated to roughly 2.5 eV. The latter shift fell in the range of reported shifts between Bi_2O_3 and Bi, 2–3 eV [22, 23, 24].

The binding energy of Sr 3d was determined to be 131.7 eV for the clean surface. This value increased when Cs was deposited. The observed shift saturated after about 2–3 min of deposition and was 1.3 eV, i.e. slightly larger than the Bi 4f core-level shift.

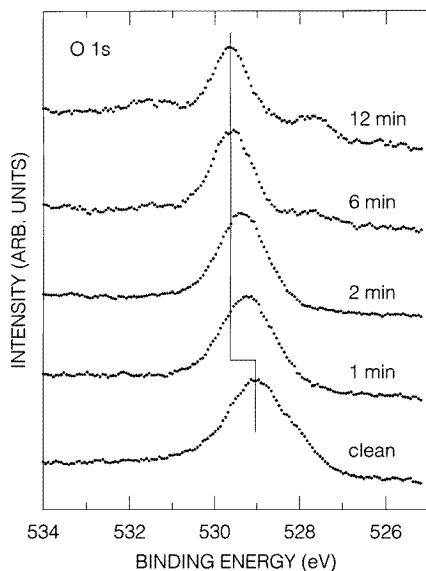


Figure 4. Photoemission spectra of the O 1s core level of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs deposition, excited with 600 eV photons. The spectra are normalized to the same height.

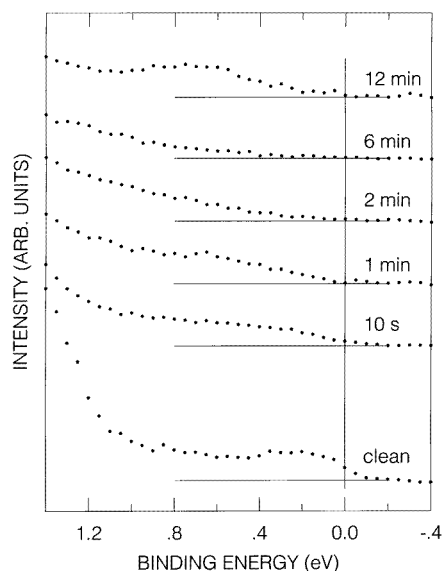


Figure 5. Valence band photoemission spectra of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs deposition for 10 s, and 1, 2, 6 and 12 min, excited with 100 eV photons. The spectra are normalized with respect to the photon flux.

The binding energies of O 1s and Ca 2p followed the same trend when Cs was deposited. For the clean surface the binding energy of the main O 1s peak was 528.9 eV and the core-level shift towards higher binding energy saturated at 0.6 eV when the deposition time was about 2–3 min; see figure 4. For Ca 2p these values are 344.8 and 1.3 eV. At the highest Cs coverage, weak peaks are seen on both sides of the O 1s peak. The peak at around $E_b = 527.7$ eV can be assigned to the caesium oxide species since it appears at the coverage at which caesium oxide is seen at in the valence band region. A likely caesium oxide is Cs_2O since the binding energy of O 1s in this oxide is 527.5 eV [25]. The peak at $E_b = 531$ eV has been shown to arise from the presence of a variety of oxides, hydroxides, carbonates, etc [26]. Note that this structure appears concomitantly with the structure due to extrinsic oxygen species in the valence band regime at 9 eV [1].

The valence band spectrum was also affected by the deposition of Cs. The Cs-induced changes were seen even after only short deposition times; see figures 2 and 5, the latter being a magnification of the region around E_F . A reduction of the spectral intensity around the Fermi level and the loss of a sharp Fermi edge are clearly seen at an evaporation time of less than 1–2 min. These changes are seen even for the smallest amount of deposited Cs, i.e. after 10 s of deposition. The centre of gravity of the valence band is shifted by 0.5 eV towards higher E_b . But the onset of the main structure is not shifted to the same extent and the width of the main structure is unaffected. A reduction of spectral intensity on the leading edge is observed when Cs has been deposited for 1 min, i.e. the shoulder in the binding energy regime at 1–4 eV seen in the spectrum of the clean surface has almost disappeared. The centre of gravity remains at the same position until the Cs has been being deposited for more than 2 min, then an additional shift of about 0.3 eV towards higher binding energy occurs. The shape of the valence band was altered at these coverages, due to the presence of caesium oxide, which caused the intensity lost initially in the regime, $E_b \approx 2\text{--}4$ eV, to reappear; however, the intensity at binding energies less than 2.3 eV remained smaller than the intensity of the clean surface, and no intensity was detectable below 0.2 eV.

Figures 6(a) and 6(b) show O 1s x-ray absorption spectra of the clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ surface and of the surface after deposition of Cs, obtained in the partial-yield mode (surface sensitive), and in the total-yield mode (bulk sensitive) respectively. A striking feature in the spectra of the clean surface is a pre-edge structure centred at around 528.3 eV. This energy almost coincides with the binding energy of the main O 1s peak [17, 27, 28, 29]. The onset of the main absorption occurs at 530 eV. These energies and the shape of the spectrum are in agreement with earlier measurements of the O 1s absorption of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ by both x-ray absorption spectroscopy (XAS) [4, 28] and EELS [30].

Focusing on the surface-sensitive spectra where the effects of the deposited Cs are the greatest, it is evident that even after only 10 s of Cs deposition much of the pre-edge structure had disappeared, and after 1 min only a weak shoulder remains. After 2 min of deposition of Cs, no traces of the pre-edge structure were visible. Upon further deposition, the two main structures in the XAS spectrum of the clean surface at around 532 and 536 eV, respectively, became less distinct. At the highest coverage they are not resolved due to the appearance of a third structure at roughly 535 eV. Measurements on several $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ samples, in this and in other experiments, have shown that this additional structure appears concomitantly with the peak at 531 eV in the O 1s photoemission spectrum assigned to extrinsic oxygen species. This was also the case in the present experiment. The bulk-sensitive spectrum was affected in the same manner by Cs deposition, although the changes were not so pronounced. Traces of the pre-edge structure are still seen as a small shoulder after 12 min of deposition.

Figure 7 shows the $\text{Cu } 2p_{3/2}$ x-ray absorption of the clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ surface and

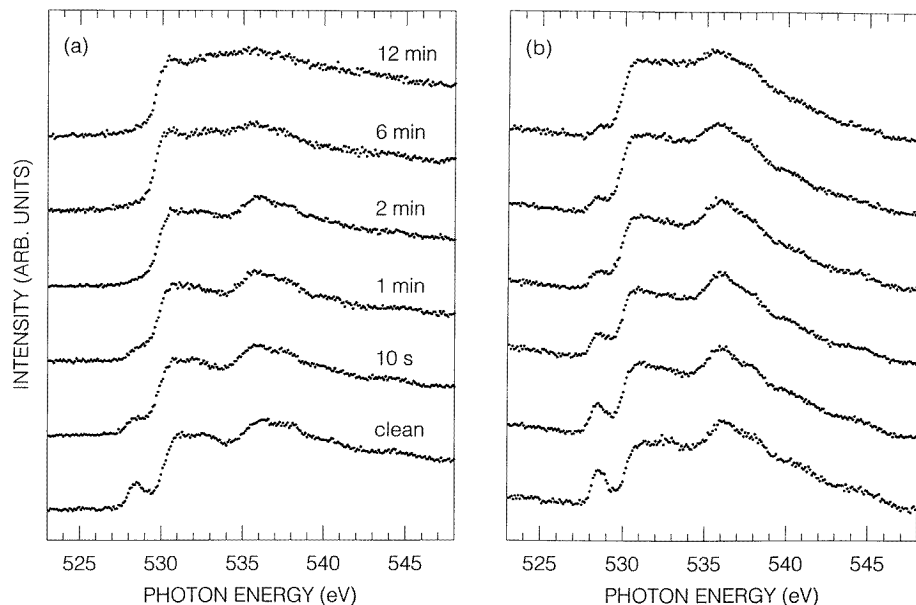


Figure 6. O 1s absorption spectra of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs deposition for 10 s, and 1, 2, 6 and 12 min; (a) surface-sensitive spectra recorded in the partial-yield mode, (b) bulk-sensitive spectra recorded in the total-yield mode. The spectra are normalized to the same height.

of the surface after deposition of different amounts of Cs. The Cu $2p_{3/2}$ absorption occurred at 931.6 eV. At the highest Cs coverages (after 6 and 12 min of deposition) a broad and featureless structure appeared on the high-energy flank of the $2p_{3/2}$ peak. The evolution of this structure was slightly faster in the surface-sensitive spectra.

The shape of the Cu $2p_{3/2}$ absorption spectrum obtained from the clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ surface is very similar to the spectrum of CuO, i.e. Cu^{2+} [31], the only difference being that the Cu $2p_{3/2}$ spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is slightly asymmetric. This indicates that most of the copper in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is present as Cu^{2+} . The additional intensity occurring on the high-energy side of the absorption line upon Cs deposition can be ascribed to the reduction of Cu. Evidence for this is obtained from a comparison of the shape of the Cu 2p XAS spectra with spectra of compounds containing copper with different valencies [31, 32], and with spectra from an experiment involving Cu deposition on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [19].

The Ca 2p XAS spectra recorded at different Cs coverages show that Ca was also reduced when Cs was deposited; see figure 8. The crystal-field-split structure of the clean surface, consisting of two major peaks each having a weak neighbour on the low-energy side as commonly found for solids containing Ca^{2+} [17, 33], became gradually less distinct upon Cs deposition. It is known that calcium which does not experience a strong crystal field—for instance atomic and metallic Ca—gives rise to a simpler XAS spectrum, with peaks at 348 and 351.4 eV [33]. This suggests that the shape of the spectrum at the highest coverage in figure 8 can be understood as a superposition of spectra from the unaffected bulk and from reduced Ca near the surface.

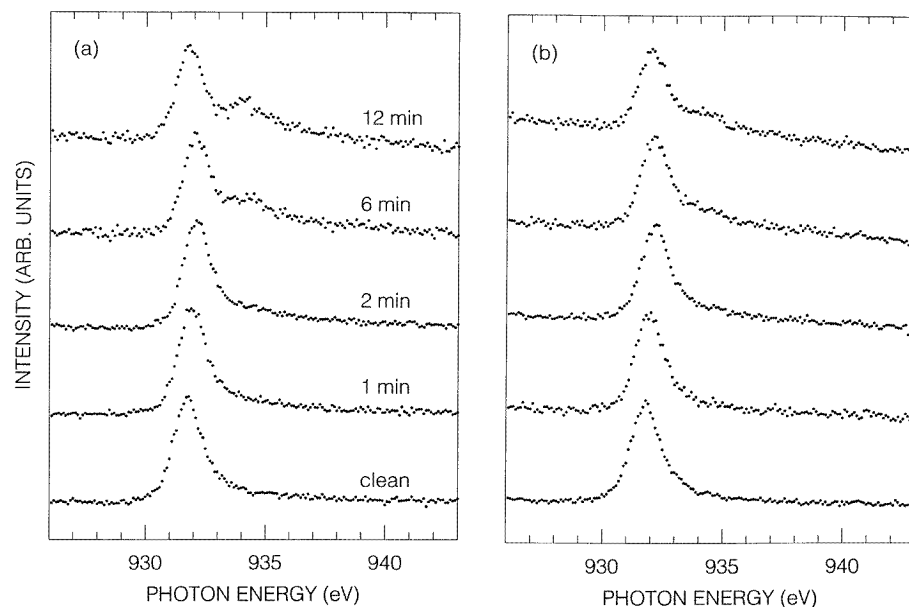


Figure 7. Cu 2p_{3/2} absorption spectra of clean Bi₂Sr₂CaCu₂O₈ and Bi₂Sr₂CaCu₂O₈ after Cs deposition for 1, 2, 6 and 12 min; (a) surface-sensitive spectra recorded in the partial-yield mode, (b) bulk-sensitive spectra recorded in the total-yield mode. The spectra are normalized to the same height.

4. Discussion

The results presented show that when Cs is deposited on Bi₂Sr₂CaCu₂O₈ two different regimes can be identified. (I) A *low-coverage regime*, for up to about two minutes' evaporation time, where the electronic structure of Bi₂Sr₂CaCu₂O₈ is altered but there are no signs of a chemical reaction. Below it will be argued that the observed changes of the electronic structure are due to the addition of electrons to Bi₂Sr₂CaCu₂O₈ and that the changes can be ascribed mainly to the annihilation of states with O 2p character in the Cu–O layer. (II) A *high-coverage regime*, for more than three minutes' evaporation time, where a chemical reaction takes place. This regime is characterized by the presence of reduced bismuth and caesium oxide, which become present through the disruption of the surface of the crystal, i.e. a Bi–O layer. Regime II will be discussed first.

One explanation of the appearance of shifted Bi 5d and 4f doublets and the large Cs-induced shift, which is consistent with existing experimental data, is the following picture of the disruption of the Bi–O layer and the related reduction of Bi. At low Cs coverages, the deposited Cs donates the 6s electron without affecting the bonds in the Bi–O layer. When the coverage is increased, corresponding to 2–3 min of evaporation time, the Bi–O bonds are broken, Bi is reduced and caesium oxide species are formed. The structure labelled A in figures 2 and 3 is assigned to this metallic Bi. In the next stage, when more Cs is deposited, some of the reduced Bi becomes surrounded by Cs and is further reduced by the deposited Cs, due to the low ionization potential of Cs. Thus the binding energy of these Bi species is further lowered; structure B in figures 2 and 3 is due to these species.

The spectra of the Bi 4f core level show that both structure A and structure B are relatively sharp, and, furthermore structure A has the same binding energy as metallic Bi.

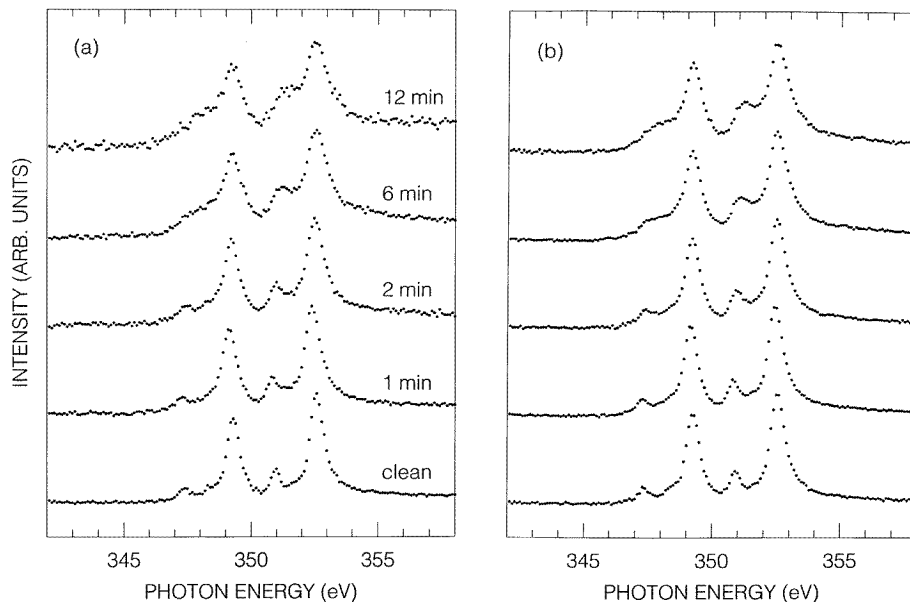


Figure 8. Ca 2p absorption spectra of clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ after Cs deposition for 1, 2, 6 and 12 min; (a) surface-sensitive spectra recorded in the partial-yield mode, (b) bulk-sensitive spectra recorded in the total-yield mode. The spectra are normalized to the same height.

This suggests the Cs-induced disruption of the Bi–O layer results in separate clusters of Bi and Bi which is highly coordinated to Cs, as described above. As Bi and Cs form alloys easily and several Bi–Cs alloys are known [34], it is likely that the latter kind of cluster consists of an alloy. The presence of a Bi–Cs alloy is also supported by the Bi 4f results. Spectra recorded after a deposition time of more than 60 min showed that structure B had grown in intensity and had become the dominant Bi peak while it maintained its sharpness and binding energy. This extended exposure did not result in additional chemically shifted Bi components. These findings suggest that Bi forms an alloy with Cs and that the oxidation state of Bi is independent of the amount of Cs deposited when enough Cs has been deposited to facilitate the formation of an alloy. It should be noted that the binding energy shift of 1.2 eV between A and B, i.e. between metallic Bi and the possible Bi–Cs alloy, is of a comparable magnitude to shifts commonly found for alloys [35].

In several previous studies of different metallic overlayers on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, chemically shifted Bi 5d doublets have appeared as a result of the growth of an overlayer—see, for instance [13, 18, 19, 20, 21, 36]—and have been interpreted in terms of a disruption of the Bi–O layer followed by a reduction of Bi when Cu, Au, or Pb was deposited [19, 20]. A disruption of the Bi–O layer has also been observed when Rb was deposited [13, 36]. The magnitude of the shift of the additional Bi 5d peak was about 3 eV for one monolayer of Rb [13], i.e. comparable to the shift of structure B observed in the Bi 5d spectrum in this study, 3.7 eV.

The lack of additional features in the Sr 3d core-level regime when Cs is deposited indicates that the Sr–O layer is not affected by the disruption of the Bi–O layer, i.e. the Sr–O layer is chemically quite inert. From the binding energy and its shift, no conclusions

about the oxidation state of Sr can be drawn, since the binding energies of the 3d levels in both Sr and SrO are higher than in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [37].

The Ca and Cu XAS spectra together with the photoemission data imply that the reduction of Ca and Cu is associated with a disruption of the Bi–O layer.

The fact that no features which could be assigned to extrinsic oxygen species were detected for evaporation times of up to 2 min indicates that the deposited Cs donates its valence electron and does not react with the superconductor or residual gases in the experimental chamber in any other way at lower coverages. The appearance of extrinsic oxygen species at the highest coverages indicates that Cs present on the surface has reacted with the residual gases in the system, i.e. not all of the deposited Cs has taken part in the formation of the proposed alloy and the formation of caesium oxide occurring when the Bi–O layer is disrupted.

Regime I is characterized by a loss of spectral intensity in the vicinity of the Fermi level (figure 5), a significant reduction of the intensity of the pre-edge structure in the O 1s XAS spectrum (figure 6), and a shift of the monitored core levels towards higher binding energy (e.g. figures 3 and 4). This behaviour cannot readily be associated with a large-scale disruption of the Bi–O layer, since at these coverages no reduction of Bi was observed (figures 2 and 3).

The observed shift of the core levels towards higher E_b at low Cs coverages (regime I), and to some extent the shift of the centre of gravity of the valence band, can be partially assigned to the shift of the chemical potential due to electron doping by Cs. A shift towards higher energy is in agreement with the addition of electrons to the system. Additional evidence for this is given by studies of the influence of oxygen annealing on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, i.e. hole doping, which gave rise to a shift of the shallow core levels and the valence band towards lower E_b , and a slight increase in the spectral intensity in the vicinity of E_F [3, 38]. The magnitude of the shift of the chemical potential upon hole doping is comparable to that observed for the lowest Cs coverages. Another contribution to the observed shift of the binding energies, which cannot be neglected at high coverages, is Cs-induced changes of the chemical environment of the atoms mainly through the disruption of the Bi–O layer.

Neglecting a downward shift of the absorption features due to electron–hole interaction (excitonic effect), which in most cases has been found to be small for the 1s edge of light elements [39, 40], the unoccupied states with O 2p character giving rise to the pre-edge structure in the O 1s XAS spectrum are located in the vicinity of the Fermi level. The simultaneous loss of these states and of spectral intensity just below E_F indicates that Cs deposition/addition of electrons gives rise to the annihilation of states around the Fermi level and that these states have O 2p character. This observation is in agreement with earlier studies using EELS [30], XAS [28] and resonant inverse photoemission [41, 42]. The results of resonant photoemission experiments are not conclusive on this subject [1, 43, 44, 45, 46].

The O 2p character deduced for the states around E_F sheds some light on the origin of the different components constituting the O 1s photoemission peak. Figure 4 shows that the component of the O 1s spectrum giving rise to the shoulder at $E_b \approx 528$ eV disappeared simultaneously with the states below E_F (figure 5) and the pre-edge structure at 528 eV in the O 1s XAS spectrum (figure 6). This strongly suggests that at least this component of the O 1s spectrum is due to oxygen species/states responsible for the metallic properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

The site of these states can be determined with the aid of an O 1s XPS investigation by Parmigiani *et al* on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [29], and high-resolution O 1s XPS on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$,

$\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and crystals with Ca substituted for with Er [47]. These XPS data show that low-binding-energy component of the O 1s spectrum is associated with the bulk. The low-binding-energy component in the O 1s spectrum can therefore be attributed to oxygen associated with holes in the Cu–O layer and the pre-edge structure in the O 1s XAS spectrum to O 2p holes in the same layer. From the work by Kuiper *et al* [48] the number of holes per oxygen in the crystal can be estimated from the XAS spectra to be 0.1–0.2. The charge transfer between the Bi–O layer and the Cu–O layer must be almost perfect if the holes in the Cu–O layer are solely due to excess oxygen since the amount of excess oxygen is small, about 0.05–0.3 per formula unit, even for oxygen-annealed samples [49, 50, 51], and the excess oxygen is situated in the Bi–O layer [50, 51].

There is also a loss of spectral intensity on the high-binding-energy side of the main O 1s peak, but this loss is not prominent at low coverages; see figure 4. Since the loss of spectral intensity on the high-binding-energy side of the main O 1s photoemission peak first becomes observable after 2 min of deposition and is most clearly seen at the highest coverages (6 and 12 min of deposition), when the Bi–O layer is disrupted, this component of the spectrum can be assigned to oxygen in the Bi–O layer, in agreement with [47]. Only a minor part of the loss of intensity can be due to a loss of asymmetry in the line profiles of the different components when the sample ceases to be metallic, since the sample has ceased to be metallic at lower coverages (≤ 1 min of deposition).

It should be noted that the complete disappearance of the pre-edge structure in the surface-sensitive O 1s XAS spectrum coincides with the onset of the disruption of the Bi–O layer, i.e. the surface. This indicates that the disruption first begins when most of the O 2p holes have been filled. Thus, the filling of the O 2p holes defines a threshold coverage below which it appears possible to change the properties of the superconductor by doping through Cs deposition without destroying the crystal structure. It is not clear whether the reduction of Cu and Ca occurring when the Bi–O layer is disrupted is due to the addition of electrons or to a redistribution of electrons in the system caused by the disruption of the Bi–O layer.

It is evident from the XAS spectra presented (figures 6, 7 and 8) that the influence of the electron doping and the subsequent disruption process affects the electronic structure close to the surface more strongly than in the bulk. This difference implies in regime I, where there is no experimental evidence for a large-scale disruption of the Bi–O layer, that the doping occurs locally and that the exchange of charge between some of the layers is small. Thus, it seems possible to alter locally the properties of the superconductor via spatially resolved electron doping, as in conventional semiconductors.

The influence of the hole concentration on the electronic structure has been studied by Matsuyama *et al* [4], by Mante *et al* [5] and by van Veenendaal *et al* [6, 7] by varying the ratio between Ca and Y in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$, i.e. by bulk doping. The replacement of Ca with Y which corresponds to a decrease of the hole concentration, i.e. to the addition of electrons, caused a gradual loss of intensity in the vicinity of the Fermi level and a disappearance of the Fermi edge when x was about 0.5, and the pre-edge structure in the O 1s XAS spectrum had almost disappeared at the same degree of doping. (Note that XAS was not performed by van Veenendaal *et al*.) The O 1s XAS spectra presented for $x = 0.5$ are very similar to those in figure 6 with an evaporation time of 10 s and 1 min partial yield (total yield 12 min). Valence spectra recorded by these authors for $x = 0.5$ are also very similar to those with an evaporation time of 10 s and 1 min in figures 2 and 5. Both Mante *et al* and van Veenendaal *et al* observe a shift of the centre of gravity of the valence band, by about 0.5 eV, upon doping. The shift towards higher binding energy increases continuously with increasing x . This comparison lends further support to the conclusion

that changes of the electronic structure in regime I are due to the addition of electrons when small amounts of Cs are deposited on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

The observed changes of the electronic structure when Ca is substituted for with Y, i.e. electrons are added to the system, are discussed by Matsuyama *et al* [4], Mante *et al* [5] and van Veenendaal *et al* [6, 7] within the framework of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and other HTS being classified as doped charge-transfer insulators, according to the phase diagram of Zaanen, Sawatsky and Allen [52]. As there is a consensus on this point, the main question today is as regards the nature of the states in the charge-transfer gap which give rise to the metallic properties of the ‘doped’ compound. Existing models can be roughly divided into two groups: (1) bandgap states which are due to ‘impurities/dopants’ forming a band in the charge-transfer gap, by analogy with doped semiconductors, which give rise to a finite density of states at E_F (the ‘doping’-induced states can partially overlap the valence band); and (2) bandgap states which are so-called split-off states formed through the interaction between a hole in an O 2p orbital and a hole in a Cu 3d orbital. This gives rise to triplet and singlet states, the latter being split off from the valence band. Such states are predicted to pre-exist in the insulator. The split-off singlet states give rise to a narrow band-like state into which the Fermi level moves upon doping. (For further details, see [4, 5, 6, 7, 53, 54, 55].)

The experimental data in the present work do not give unambiguous support for any of these models. The valence band spectra show that a loss of spectral intensity at E_F is accompanied by a shift of the main valence band towards higher binding energy and the almost complete disappearance of a shoulder on the low-binding-energy side of the main valence band, which is seen in the spectrum of the clean surface. This is not readily understood in the ‘impurity’ picture, but the loss of the pre-edge structure in the XAS spectrum is in agreement with an ‘impurity’ picture, i.e. states are annihilated by the electron doping. Although the loss of spectral intensity at E_F , the reduction of the shoulder on the low-binding-energy side of the main valence band, roughly between binding energies of 1 and 4 eV, and the shift of the valence band can be explained in the model based on split-off states, the lack of spectral intensity from the split-off states in the insulating regime is an argument against this model.

Thus, none of these models are in complete agreement with the experimental data. The same conclusion was reached by Mante *et al* [5], but Matsuyama *et al* [4] suggest that the electronic states at the Fermi level are ‘impurity states’. Van Veenendaal *et al* [6, 7] do not support this interpretation and argue that many-body effects must be taken into account in order to understand the experimental data. Thus, the present study and the previous studies strongly suggest that further developments of theoretical models are necessary.

5. Summary

The influence of added electrons, i.e. the removal of hole states, on the electronic structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been studied by depositing Cs on the surface of single crystals. The deposition of Cs caused the core levels studied, O 1s, Bi 4f and 5d, Sr 3d and Ca 2p, to shift to higher energies. The shift saturated at about 1 eV higher binding energy when Cs had been deposited for 2–3 min. At this coverage, the Bi–O layer was disrupted and features in the Bi core-level spectra assigned to reduced (metallic) Bi appear. The disruption is associated with the formation of caesium oxide. At higher coverages, a second even more shifted (4 eV) Bi core-level peak appears, which is assigned to reduced Bi highly coordinated to Cs. The observed loss of spectral intensity, in this regime, on the high-binding-energy side of the O 1s core level, suggests that this component is associated with the Bi–O layer.

The deposition of small amounts of Cs caused the spectral intensity to vanish in the vicinity of the Fermi level and reduced the spectral intensity down to 4 eV below the Fermi level. X-ray absorption experiments show that a pre-edge structure in the O 1s absorption spectrum decreases significantly for the same small depositions. These structures are assigned to states with O 2p character in the Cu–O layer. Concomitantly the low-binding-energy component of the O 1s photoemission spectrum decreases in intensity. These observations show that the electronic structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is strongly affected by small amounts of deposited Cs, i.e. the addition of electrons to the system. Bi core-level data indicate that the observed changes of the electronic structure are not related to a large-scale disruption of the Bi–O layer.

The present study indicates that it can be possible to alter locally the properties of the superconductor via spatially resolved doping.

Acknowledgments

The authors wish to thank Dr Z-X Shen, Stanford University, for providing the crystals used in this study. The financial support from the Swedish Natural Science Research Council and the Swedish Research Council for Engineering Sciences is gratefully acknowledged.

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