

Electron-spectroscopy investigation of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ single-crystal cleaved surfaces

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This paper presents spectroscopic investigations of the normal-state properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ single crystals. Ultraviolet photoemission and electron energy loss data are consistent with the filling in of the charge transfer gap upon doping due to spectral weight transfer mechanisms. The modifications occurring in the surface electronic properties after exposure to pure O_2 and after the deposition of one monolayer of bismuth are studied and discussed.

I. INTRODUCTION

After the discovery of the copper-oxide-based high-temperature superconductors (HTSC's), a great deal of work has been done to study the electronic structure of these systems, in attempt to understand the pairing mechanisms leading to high- T_c superconductivity.¹ Many of these studies have been carried out using surface-sensitive spectroscopies in spite of the fact that the surfaces of these materials may not be representative of the bulk. As is well known, HTSC's have very unstable surfaces after cleaving, scraping, or polishing. In particular, the surface oxygen stoichiometry could be very different from the bulk stoichiometry.

The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (Bi2212) high-temperature superconductor has been recognized to be, among the copper oxide-based HTSC's, one of the more stable compounds,^{2,3} and even at room temperature the cleavage surfaces are not affected by segregation phenomena or oxygen depletion. For this reason, the Bi2212 HTSC's family is often used as a representative system to study the electronic structure of HTSC's. Since the Bi2212 materials cleave between two adjacent Bi-O planes, the character of the Bi-O states is closely linked with the intrinsic surface properties.^{4,5}

An earlier paper reported a careful x-ray photoemission study (XPS) of Bi2212 single crystals with different oxygen contents. It has been shown that annealing the crystals at different oxygen partial pressures leads to different superconducting temperatures.^{6,7} These systems have been studied in detail by Shen and co-workers⁸ and an effort was made to understand the chemical-physical behavior of the Bi-O cleavage planes.⁹ However, several aspects of the nature of these planes and their influence

on the superconducting properties are still obscure.

Recently, the properties and reactivity of Bi-O planes have been studied by several groups. Some metal/ $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ interfaces have been investigated¹⁰ and they are still a matter of experiment. The stability and reactivity of Bi-O planes are quite important both for fundamental studies on the superconducting mechanisms of these compounds and for technological purposes.

The aim of this paper is to present an ultraviolet photoelectron spectroscopy (UPS) and an electron energy-loss (EEL) spectroscopy study of the oxidation and reduction of the cleavage lanes of Bi2212 single crystals, as-grown ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$) and annealed in 12 atm of pure O_2 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$). The crystal annealed in 12 atm of O_2 shows a lower critical temperature and a more metallic character with respect to the as-grown crystal. The cleaved surfaces have been studied, at room temperature and in ultrahigh vacuum conditions (UHV), freshly cleaved, after exposure to pure O_2 , and after the deposition of one monolayer (ML) of bismuth. Significant differences were observed in the lower-energy electronic structure between the two Bi2212 crystals and further changes take place after oxygen exposure or bismuth deposition. In particular, the extraoxygen oxygen atoms on the surface of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ seem to oxidize the Bi overlayer leading to a Bi-O plane deficient of oxygen and an electron doping of the system. The modified electronic properties are similar to those of the as-grown crystal surface. On the other hand, the EEL spectra of the as-grown crystal are quite sensitive to O_2 exposure, and after 100 Langmuirs (L) they resemble those of the oxygen-annealed sample. This seems to confirm the important role played by the stoichiometry of the Bi-O lay-

ers in determining the normal-state properties and the superconducting behavior of these materials.

II. EXPERIMENTAL

The growth and characterization of the Bi2212 crystals are reported in Ref. 7. In these compounds, by increasing the oxygen content, the density of states at the Fermi level increases, while the transition temperature decreases. In the present experiment we studied as-grown Bi2212 crystals, exhibiting a Meissner transition onset at 89 K and crystals annealed at 12 atm of O_2 with a transition temperature of 80 K. The crystals were cleaved at room temperature, following the procedure reported in Ref. 6, in a vacuum better than 3×10^{-10} mbar.

The freshly cleaved surface structure was tested *in situ* by low-energy electron diffraction (LEED). Very sharp LEED patterns were observed, as expected for these crystals.⁹ LEED observations, carried out during the experiment to test possible surface segregation, disruption, or disordering, showed very stable and sharp diffraction patterns.

UPS spectra were excited by a He discharge lamp ($h\nu=21.2$ eV) and analyzed by a double-pass cylindrical mirror analyzer (CMA), with an energy resolution better than 200 meV. Resolution and Fermi edge (E_F) position were determined by measuring the valence-band top edge of a freshly evaporated gold film.

EEL spectra were taken in reflection geometry with a primary beam energy of 200 eV, using the electron gun coaxial to the CMA. In this case the resolution was limited by the beam energy spread and amounted to about 0.5–0.6 eV. The spectra have been normalized to the same intensity of the quasielastic peak.

Oxygen exposures were performed in the sample preparation chamber under UHV conditions, with a partial oxygen pressure of 1.7×10^{-8} mbar. Bismuth was deposited by thermal evaporation of pure Bi shots contained in a resistively heated quartz crucible, while the Bi2212 sample was maintained at room temperature. The deposition rate was controlled by a thickness monitor.

III. RESULTS AND DISCUSSION

A. UPS

Figure 1(a) reports the UPS spectra of the freshly cleaved crystals after background subtraction. In the spectrum of the oxygen-annealed crystal, five features can be detected quite clearly at binding energies (BE's) of 1.4, 2.7, 3.4, 5.8, and ~ 9 eV, respectively, and denoted as A to E. In the region within 1 eV below E_F the spectral intensity is very low (about 5% of the maximum), but a clear metallic edge (Fig. 1, inset) is visible, also in the stoichiometric compound (as-grown crystal). Therefore, the as-grown Bi2212 contains an intrinsic carrier concentration (holes) which does not come from the oxygen overstoichiometry.

The feature at 9 eV is the so-called "dirty" peak in the cuprate superconductors. Usually believed to be a contamination peak¹¹ it is, most probably, a feature connect-

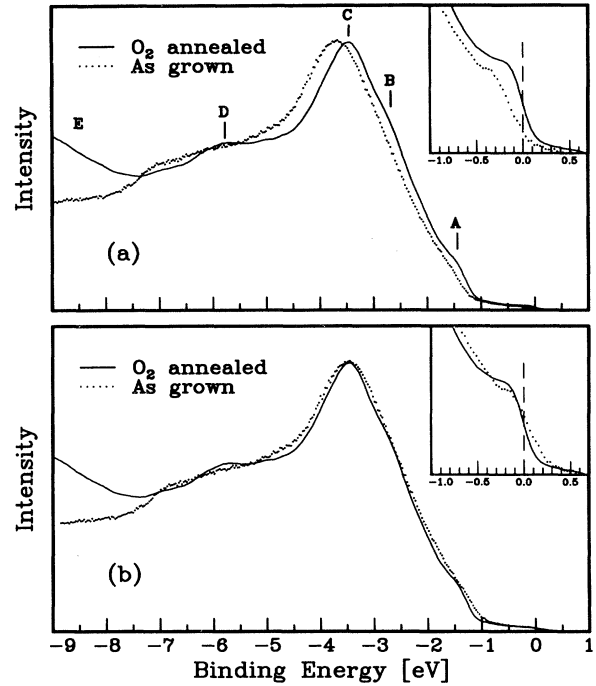


FIG. 1. (a) UPS spectra of the two Bi2212 samples freshly cleaved. (b) The as-grown Bi2212' spectrum has been shifted 200 meV toward lower BE's in order to center the main feature C of the two spectra. In each figure the inset shows the region near the Fermi level.

ed to oxygen disorder on the surface. In fact this feature, as it appears only in the oxygen-annealed sample, should be due to the oxygen atoms interstitially placed between two Bi-O planes, before cleavage.

In the spectrum of the as-grown crystal, features A and B almost vanish, the most intense peak C is broader and shifted by 200 meV towards higher BE's, while feature D completely disappears and a new feature is observed at about 7 eV BE. This spectrum also shows a lower intensity at E_F , as expected from the lower oxygen concentration in the as-grown crystal. This particular difference among Bi2212 crystals with different oxygen contents has already been reported in the literature,¹² but the behavior of the states near E_F as a function of the hole doping and/or oxygen content is still a matter of discussion.^{13,14}

It is well known that the valence band of Bi2212 mainly consists of Cu $3d-O 2p$ states of the Cu-O layers, with some contributions from the Bi $6s-O 2p$ hybridized band as well as Bi $6p-O 2p$ bands of the Bi-O planes and from O $2p$ states of atoms in different crystallographic sites. In particular, for the stoichiometric compound, band theory predicts two distinct kinds of bands contributing to the total density of states (DOS) at E_F .¹⁵ The most relevant one corresponds to a couple of nearly degenerate antibonding Cu $3d_{x^2-y^2}-O 2p_{x,y}$ states dispersing above E_F toward the X point of the Brillouin zone. The second one corresponds to the lowest pair of bands from the Bi-O planes, which disperse downward to the Fermi level away from high symmetry points: one of these two bands just arrives at E_F , from above, while the second one dips

below E_F and hybridizes with the Cu-O bands, thus doping them with additional holes. Since band theory is supposed to give reasonable results for the Bi $6p$ -O $2p$ and Bi $6s$ -O $2p$ bands of the Bi-O planes, which are not affected by strong correlation effects, a contribution to the UPS spectrum near the Fermi level is expected to come from these bands.

Actually, angle-resolved photoemission spectra of both crystals, as well as many others reported in the literature,^{12,16-19} show fairly good agreement with the band theory calculations at least for the bands crossing the Fermi level. The angular resolution of those spectra and the comparison with the calculated band structure allowed some authors to assign the emission at E_F in the spectrum of the oxygen-annealed sample to p bands of the Bi-O surface layer,¹² while in other work there is not evidence for this electron pocket derived from the p bands of the Bi-O layers.^{16,19}

However, it is well accepted that the effects of Coulomb repulsion in the Cu $3d$ band, which are not explicitly considered by band theory, and the $3d$ hole-hole interactions affecting the final state of the photoemission process, induce in the spectra a shift of the valence band centroid of about 2 eV toward higher BE's with respect to the calculated density of states (see Ref. 8 and references therein). These effects explain the indication emerging from experimental data that the Cu $3d$ states are distributed away from E_F (bands C and D in Fig. 1), while the O $2p$ states reveal a rough tendency to be located in the energy region nearest to E_F (features A and B).^{3,20}

In this light, our feeling for the interpretation of the different spectral weight near E_F , in turning from the as-grown crystal to the oxygen-annealed one, is the following.

(a) According to x-ray absorption near-edge spectroscopy (XANES) measurements,²¹ in the stoichiometric compound the formal valence of bismuth is lower than 3^+ ; thus we expect that the photoemission intensity very close to the Fermi level arises also from electrons in the partially filled Bi $6p$ -O $2p$ bands crossing it.

(b) Since some evidence of the presence of additional oxygen near the surface Bi-O layer of a Bi2212 crystal annealed in oxygen was obtained in a previous work,⁶ the extrastochiometric oxygen is supposed to localize near and/or inside the Bi-O planes, probably forming bonds with and further oxidizing the bismuth. In this way the oxygen-annealed system becomes more hole doped than the as-grown crystal and the chemical potential moves down into the valence band, in agreement with the rigid shift of the main valence band features with respect to E_F observed in the UPS spectra of the two samples.

(c) The increased emission at E_F in the hole-doped system can be caused by the superposition of two effects: first, the shift of the chemical potential inside the valence band toward a region with higher DOS and second, the transfer of spectral weight from the high-energy to the low-energy states. In fact, the shift of the chemical potential and the spectral weight transfer as a function of hole (electron) doping seem to be the major effects of doping in many HTSC's as well as a lot of other strongly

correlated systems.^{13,22} The latter phenomenon is clearly a many-body effect and strongly depends on the doping, as shown by calculations for Hubbard or charge-transfer Hamiltonians.²³

(d) If spectral weight transfer occurs, since it arises from Cu-O states, the emission near E_F in the oxygen-annealed compound is mainly due to Cu-O bands with some contribution from Bi $6s$ -O $2p$ states. In fact, we expect that in the oxygen-enriched crystal only the Cu $3d_{x^2-y^2}$ -O $2p_{x,y}$ bands cross the Fermi level, while the Bi $6p$ derived bands are now empty because of the increased valence of Bi ions, and are placed well above E_F in a more ionic bond with the oxygen atoms.

This scenario receives further support from EEL measurements, as described below, and it agrees with the absence of the Bi $6p$ electron pocket at the Fermi surface in the oxygen-enriched Bi2212, very recently observed by angle-resolved photoemission.^{16,19}

Several indications emerge from the analysis of features A , B , and C , whose behavior can be explained in terms of incorporation of the extrastochiometric oxygen into the Bi2212 lattice. Our spectra show an apparent lack of states at about 3 eV BE and a new shoulder at 1.4 eV passing from the as-grown to the oxygen-annealed sample. Also in the photoemission data of Takahashi *et al.* on $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ [$x=0.6$ and 0.0 (Ref. 24)] and Veenendaal and co-workers on similar compounds [$x=1.0, 0.75, 0.5, 0.3$, and 0.0 (Ref. 13)], there is a band that seems to shift from 2.5–3 eV BE to 1.2–1.5 eV BE, passing from the insulator to the more metallic sample. The origin of this effect is still obscure.

According to the photoemission measurements reported in the literature,^{3,20} we assign feature A to O $2p$ states of the Cu-O planes. This result also agrees with theoretical predictions^{1,15} and with the above-mentioned splitting of the Cu $3d$ and O $2p$ states due to correlation effects. Figure 1(b) compares the two UPS spectra, after a shift of 200 meV towards lower BE's of the as-grown crystal valence band in order to center the main valence-band feature C . We can see that the evidence of structures A and B in the spectrum of the oxygen-annealed sample is probably caused by a band C narrower than in the stoichiometric compound, in which the width of this band masks features A and B . Therefore, the behavior of features A , B , and C can be explained in terms of hole doping of the Cu-O bands, which is likely to change the correlation effect in the Cu $3d$ bands by lowering their filling. This hole doping of the Cu-O planes by Bi-O bands, which is a peculiar characteristic of the Bi2212 system, has been largely investigated with the aim of understanding the role of Bi-O planes in the superconducting mechanism of this compound, and it was found to be sensitive to oxygen stoichiometry:^{7,25} namely, the density of holes per copper site increases with the annealing oxygen partial pressure, as well as the extrastochiometric oxygen content, while the contribution of the Bi-O bands to the hole density in the Cu-O bands decreases.²¹ Thus, the apparent increase of feature A and the changes of feature C in the spectrum of the oxygen-enriched crystal we found should result from a more definite localization of the states from which they derive, allowed by a weak-

ening of the $d-d$ correlation in the Cu-O bands by the hole doping. In the case of feature *C* the consequences of a variation in the correlation strength are more evident because of the higher copper character of this structure with respect to *A*. Angle-resolved photoemission suggests that feature *C* is a composite of several closely spaced bands, whose separation varies inside the Brillouin zone.^{17,24} Therefore, the changes shown by feature *C* between one crystal and the other [Fig. 1(b)] could be due to variations in the distances of the building bands induced by oxygen doping. From the inset of Fig. 1(b) we also observe that the slope at the Fermi level increases with the oxygen (hole) doping and the cutoff is as sharp as the Au reference (not shown) for the oxygen-annealed sample. It is clear that in this region of the spectra there is already spectral weight also in the as-grown compound. Thus, the effect of doping is to change the weight of these states and to shift the chemical potential, in contrast with the formation of midgap states with the pinning of the Fermi level as proposed by others.²⁶

Feature *B* could be part of the described set of bands, getting resolved only when its separation from the others increases. On the other hand, in many photoemission spectra reported in the literature, this feature does not appear as intense as in the spectrum of the oxygen-annealed sample reported here but is frequently unresolved, as for the as-grown crystal. Since the analyzed crystals only differ in the oxygen content, it appears reliable to relate this structure directly to the extrastochiometric oxygen.

Studying the modification induced in the electronic spectra by changing the stoichiometry of the cleavage plane, which is the only Bi-O layer within the sampling depth of UPS and EEL at 200 eV of primary energy,²⁷ we can obtain some more information about the behavior of the extrastochiometric oxygen. In the following, the results of two independent attempts to change the surface Bi-O plane stoichiometry are reported. None of them succeeded in converting the spectra of the two crystals one into the other, but some modification in the expected directions indeed occurred.

First, the effect on the UPS valence band of the deposition of 1 ML of bismuth onto the oxygen-annealed crystal surface is shown (Fig. 2). The leading edge of the spectrum is shifted by 0.3 eV toward higher BE and a clear Fermi edge is no longer observed. The lack of detectable density of states at E_F and the vanished intensity of the spectral feature at 9 eV BE suggest that the Bi overlayer could be oxidized by the disordered oxygen present in the cleavage plane. The spectrum as a whole becomes in some way more similar to that of the as-grown sample: in fact, not only a rigid shift towards higher BE's occurs but, in addition, feature *A* almost disappears and peak *C* broadens. The main spectral features, however, move towards BE higher than those of the as-grown sample. This behavior agrees well with the above description of the valence-band spectra of the freshly cleaved compounds. In fact, the oxidation of the bismuth overlayer results in an electron doping of the system, which reduces the number of holes. From the shift of the main valence features with respect to the Fermi level, it is possible to

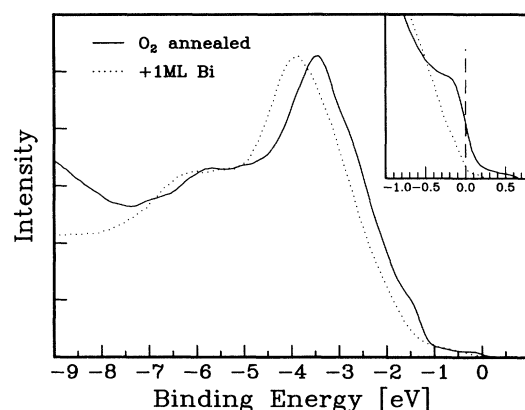


FIG. 2. UPS spectra of the freshly cleaved oxygen-annealed sample and after a deposition of 1 ML of pure bismuth. The inset shows the Fermi level region.

deduce that the actual number of holes in the surface layers is lower than that of the as-grown compound, and a strong reduction of spectral intensity near E_F is observed.

Another way to modify the surface stoichiometry is exposing the sample to pure O_2 . The results of this treatment on the as-grown Bi2212, studied by EEL experiments, are reported below.

B. EEL spectra

The EEL spectra of the two clean samples, in the energy loss region 0–40 eV, are shown in Fig. 3. They are quite similar to each other and agree with the spectra of similar compounds.^{27–29} The EEL spectra of Bi2212 have been largely investigated^{27–29} and the assignments of the main features were made on the basis of the spectral feature dependence on the primary beam energy and by comparison with the EEL spectra of Bi_2CuO_4 ,³⁰ Bi_2O_3 ,²⁸ and other HTSC's.³¹ These assignments, as deduced from the literature, are reported in Table I. In the present work we are more interested in the differences between the spectra of the two kinds of samples investigated. The most interesting one occurs in the energy-loss range 0–3 eV, where the spectrum of the as-grown sam-

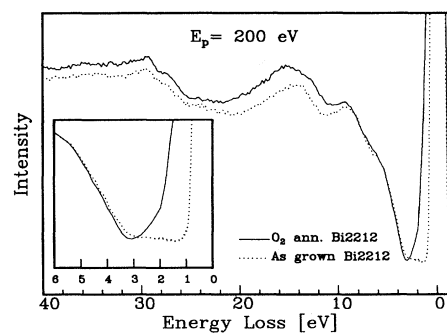


FIG. 3. EEL spectra of the two Bi2212 samples freshly cleaved, at a primary beam energy of 200 eV. The inset shows the differences between the two spectra in the energy-loss region 0–6 eV.

TABLE I. Assignment of the spectral features of the EEL data reported in Fig. 3 as deduced from the literature (see Refs. 27–34). The numbers between parentheses are relative to the as-grown crystal.

| Peaks assignment | Energy position (eV) |
|---|--|
| Hole plasmon | 0.9 |
| (Cu 3d–O 2p)→(Cu 3d–O 2p) ^a | { 2.5 (2.4) 3.5 (3.6) |
| (Bi 6s–O 2p) ^b →Bi 6p _{1/2,3/2} | 5.7 (5.9) |
| (Bi 6s–O 2p)→Bi 6p _{1/2,3/2} | 9.4 (9.6) |
| Surface plasmon | 12.9 (13.4) |
| Volume plasmon+O 2p→O 3sp | 15.0–22.0 |
| O 2s→(Cu 3d–O 2p) ^a | 22.6 (23.0) |
| Bi 5d _{3/2,5/2} →Bi 6p _{1/2,3/2} | { 26.1–27.5 (26.0–27.3) 29.2–31.2 (29.2–31.0) |

^aEmpty states.

^bAntibonding.

ple lacks spectral intensity with respect to the oxygen-annealed sample (see Fig. 3, inset). Three kinds of loss processes contribute to the spectral intensity in the region of interest.

(a) One-particle excitation across the charge-transfer gap from the valence band to the empty states in the higher Hubbard band. It is well known that Bi2212 has a charge-transfer energy of about 2 eV.³² Thus, the above-mentioned excitations are responsible for the spectral intensity around this loss energy and, in particular, they are the origin of the 2.5–2.7 eV feature always present in the EEL spectra of Bi2212.

(b) The free hole plasmon excitation,³³ which occurs at about 0.9 eV in the oxygen-annealed sample.

(c) A continuum of transitions across the Fermi level from the occupied to the unoccupied states in the valence band. These excitations contribute, in particular, to the spectral intensity in the range between the quasielastic peak and 2.5 eV, also broadening the tail of the hole plasmon peak by screening effects.

The shape of the EEL spectrum of the as-grown sample is reminiscent of the charge-transfer gap formation seen in these copper-oxide-based compounds, indicating a flat and low DOS in the valence band just above and below E_F . On the other hand, the filling of this spectral dip in the oxygen-annealed sample suggests an increased DOS at E_F in the latter compound. Considering the small shift of the chemical potential we observe in the UPS spectra of the two compounds, the behavior of the EEL spectra can be ascribed to an effective change in the DOS near the Fermi level due to the spectral weight transfer. As EEL spectra are the convolution of filled and empty states, if in the extrastochiometric material (with respect to the stoichiometric one) a spectral weight transfer occurs from empty states (related to Cu-O bands) far from E_F to states closer to it, we should correspondingly have a reduction of some energy-loss features related to these empty states far from E_F . The tiny feature at ~ 3.6 eV, originating from electronic excitations in the Cu-O layers,²⁹ seems to show this behavior. The inset of Fig. 3 shows, in particular, a reduction of spectral inten-

sity around 3.6 eV in the spectrum of the oxygen-annealed sample, while the feature at ~ 5.7 eV (related to electronic transitions in the Bi-O-derived bands) remains unchanged.

Summarizing, the EEL spectra of the pristine compounds give further indications about the spectral weight transfer occurring in Bi2212 samples, indicating that when the DOS near E_F is reduced the spectral intensity must be redistributed away from E_F .

Figure 4 shows the modification occurring in the EEL spectra of the two samples when they were exposed to 100 L of pure O₂ (as-grown sample) or 1 ML of bismuth (oxygen-annealed sample). It is interesting to note the changes in the energy-loss region below 3 eV. When 1 ML of Bi is deposited onto the surface layer of the extrastochiometric material, the EEL spectrum loses spectral intensity in this region, becoming more similar to that of the as-grown material. This behavior is the same observed by UPS and agrees with the idea that the Bi overlayer is oxidized by the extrastochiometric oxygen on the Bi2212 surface, doping the surface layers of the system with electrons. In the same way, exposing the as-grown sample to 100 L of O₂, the EEL spectrum is modified in such a way that it becomes more similar to that of the oxygen-annealed compound. In particular the inset of Fig. 4 shows the evolution of this spectrum, in the energy-loss range 0–6 eV, at different oxygen exposures,

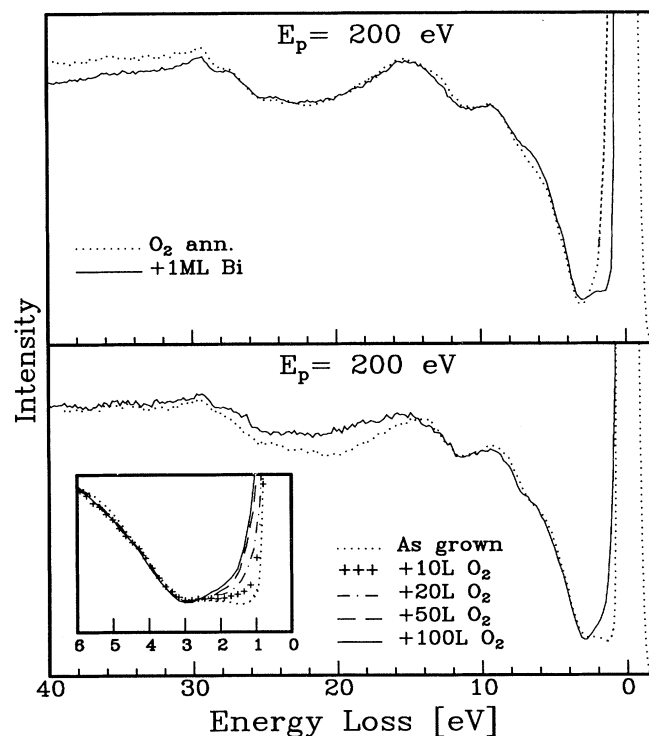


FIG. 4. The top panel compares the EEL, at $E_p=200$ eV, with spectra of the freshly cleaved oxygen-annealed Bi2212 before and after a deposition of 1 ML of bismuth. The bottom panel compares the EEL spectra of the freshly cleaved as-grown Bi2212 before and after an exposure to 100 L of pure O₂. The inset shows the evolution of the as-grown Bi2212 EEL spectrum, in the 0–6 eV region, with subsequent oxygen exposure.

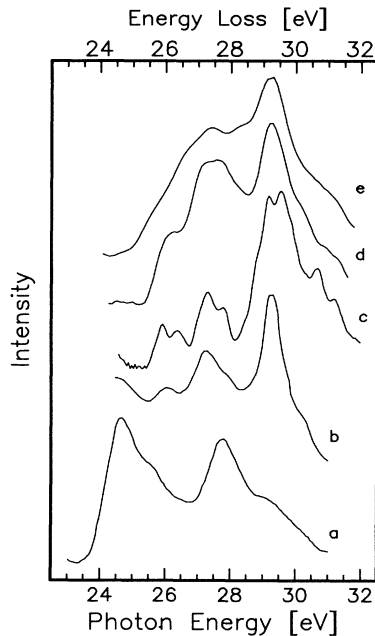


FIG. 5. The CFS spectra (Ref. 34) (bottom scale) of pure bismuth (a) and Bi_2O_3 (b) are compared with the EEL spectra (top scale) of Bi_2CuO_4 (c) (Ref. 35), oxygen-annealed Bi2212 (d), and as-grown Bi2212 (e). The EEL spectra have been shifted by 0.2 eV to lower energies in order to center the main feature with that of the CFS spectrum (b).

providing evidence of the transfer of spectral weight as a function of the hole doping (oxygen exposure) and of the filling of the spectral dip.

Finally, we would discuss the formal valence state of bismuth atoms in the two Bi2212 samples. Figure 5 compares the electron emission total yield in constant-final-state (CFS) absorption spectroscopy of pure Bi and Bi_2O_3 (Ref. 34) with the structures of the EEL spectra of Bi_2CuO_4 (Ref. 30) and Bi2212 compounds. The 25.5–28.5 eV range of the spectra corresponds to the excitation of the $\text{Bi } 5d_{5/2} \rightarrow \text{Bi } 6p_{1/2,3/2}$ electron transitions, while the region above 28.5 eV involves the Bi 6p final state as coupled with the Bi $5d_{3/2}$ core level. First we note that the CFS spectra of Bi_2O_3 and the EEL spectra of Bi_2CuO_4 , which are Bi^{3+} -based compounds, are very similar. The fingerprint of the 3^+ valence state of the bismuth in these materials is the presence of the strong and narrow peak at about 29.5 eV,³⁴ which indicates a localization of the unoccupied Bi $6p_{1/2}$ state at the Bi sites and the ionic transfer of these electrons from bismuth to oxygen. Also in the case of Bi2212, there is a dominant peak at about 29.5 eV, which means that the formal valence of Bi is close to 3^+ . On the other hand, it is not possible to compare directly the EEL spectra of the Bi2212 with that of Bi_2CuO_4 , in order to extract a value for the valence state

of Bi, because of the superposition of other loss processes in the former compound (mainly related to the more complicated crystal structure, with the presence of Sr and Ca ions) at these energies. However, we can compare the spectra of the two Bi2212 samples, since the spectral intensity at these energies arises from the same loss processes. In Fig. 5 we note that in the as-grown sample the main peak at 29.5 eV broadens and reduces its intensity with respect to the oxygen-annealed sample. This is the expected behavior if there is a reduction of the Bi valence state with a consequent minor localization of the Bi 6p states. Therefore, the formal valence state of Bi ions in the as-grown Bi2212 should be lower than in the oxygen-annealed Bi2212. According to XANES (Ref. 21) measurements the formal valence of bismuth in the stoichiometric Bi2212 is $\sim 2.88^+$, which implies that in our oxygen-enriched compound it is very close (or even equal) to 3^+ .

IV. CONCLUSIONS

We have reported a UPS and EEL spectroscopy study of the electronic structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (as-grown) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (oxygen-annealed) single crystals. The differences already present in the spectra of the two samples and those induced by changing the surface stoichiometry provide evidence of the importance of extrastochiometric oxygen on the normal-state properties of Bi2212 compounds. Our spectra can be explained inside the framework of the spectral weight transfer picture with the chemical potential shifting as a function of doping^{13,22,23} and they do not agree with the midgap state scenario.²⁶ A number of results point toward the breakdown of the single particle approach. In particular, the reduction of the bandwidths (not only near E_F) with doping and the transfer of spectral weight between low-energy and high-energy states can only be explained in terms of many-body interactions.

EEL spectra suggest a different formal valence state of bismuth in the two Bi2212 samples. While in the as-grown material the valence of Bi ions is lower than 3^+ , in the oxygen-annealed one it is very close or equal to 3^+ , which could explain the absence of the Bi-O-derived electron pocket at E_F in the extrastochiometric Bi2212 materials, as suggested by some angle-resolved photoemission data.

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- ³⁵The double structure of the peaks in the EEL spectrum of Bi₂CuO₄ is related to the particular crystal structure of this compound (Ref. 30). In fact, with a primary beam energy of 200 eV, at these loss energies we probe Bi atoms at different depths. While the atoms in the bulk are surrounded by six oxygen atoms, the surface bismuth lacks some oxygen atoms on its top. Therefore, a different effect related to a different surrounding polarization is expected in the EEL structures of these atoms.