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X-ray-photoemission-spectroscopy study of the surface deterioration of $Bi_2Sr_2CaCu_2O_8$ and $Bi_{1.7}Pb_{0.3}Sr_2CaCu_2O_8$ single crystals at 26 K

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We examine the time evolution of the O 1*s* core-level and valence-band spectra of high-quality Pb-free and -doped $Bi_2Sr_2CaCu_2O_8$(001) single crystals cleaved at 26 K in ultrahigh vacuum. A component line at 533.5 eV of the O 1*s* spectrum is unambiguously identified as extrinsic and separated by the doublet structure related to the normal-state electronic structure of this compound. Evidence is given of the surface physisorption of carbon monoxide at low temperature (<30 K) that is removed at room temperature without loss of stoichiometric oxygen. The effects of pollution on the valence-band features are monitored and correlated with those of the core spectra. Spectral changes due to electron etching are also addressed.

Recent valence-band photoemission data on $YBa_2Cu_3O_{7-x}$ single crystals cleaved at 26 K in ultrahigh vacuum[1] point to oxygen losses occurring at the vacuum-solid interface as a major source of surface deterioration. The bismuth cuprate $Bi_2Sr_2CaCu_2O_8$ seems relatively more stable in vacuum against oxygen losses at low temperature. However, its cleaving plane, which is believed to be a Bi-O plane,[2] is reported to be nonmetallic from scanning tunneling spectroscopy[3] and high-resolution energy-loss studies[4] only a small part (5%–10%) of the exposed surface being superconductive at $T<T_c$. Standard high-energy spectroscopies probe much deeper into the surface, typically between 5 and 40 Å, but the information is usually averaged over a large surface area. Work done on sintered powders, films, and single crystals of both Y-based[5] and Bi-based[6] oxide superconductors subjected to controlled heating cycles in ultrahigh vacuum and in O_2 atmosphere has shown that it is possible to distinguish from the spectral changes induced by extrinsic contamination of the surface, resulting from exposure to the ambient, and those related to changes in the compositional stoichiometry. In particular, upon annealing at temperatures between 450–500 °C *in vacuo*, the surface barrier for oxygen out-diffusion is overcome and one observes a strong decrease of the O 1*s* component at ~531-eV binding energy and a disappearance of the Cu $2p_{3/2}$ satellite in x-ray-photoemission-spectroscopy (XPS) spectra which basically reflects the reduction of Cu^{2+}-Cu^{+}. The results obtained on samples annealed in vacuum are, however, open to criticism, since the oxygen replenishment of the outermost layer is controlled by the rate of oxygen diffusion from the bulk to the interface and vice versa for oxygen in-diffusion.[7] Thus the exact stoichiometry of the surface layer caused by these processes is difficult to estimate.

In this work we report on core-level photoemission studies of $Bi_2Sr_2CaCu_2O_8$ and $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ single crystals cleaved in ultrahigh vacuum at 26 K in order to preserve the stoichiometry of the sample surface. Of particular interest here is the O 1*s* spectrum for which the controversy concerns whether the higher-binding-energy (BE) component at ~531.0 eV has a structural origin or it is due to surface contamination.[8] To follow surface degradation effects we have also recorded valence-band photoemission spectra just after the cleavage and for increasing times and different sample temperatures. The measurements were performed in a UHV system (1×10^{-10} Torr) using a nonmonochromatized Al$K\alpha$ radiation source with a reduced spot size so that the radiation hit a small area of the cleaved surface. Good quality single crystals of the superconducting 2:2:1:2 phase with $T_c=85$ K were grown by a flux method derived from Morris *et al.*,[9] namely using the eutectic Bi_2O_3-CuO (in 90%–10% proportions) as a solvent of the $Bi_2Sr_2CaCu_2O_8$ constituent oxides. The oxide powders were mixed, put in a platinum crucible, soaked at 900 °C, and cooled to 700 °C at a rate of 0.5 °C h^{-1}. Large aggregates of single crystals of linear size up to 1 cm were obtained and mechanically extracted from the crucible. From such aggregates, single-crystal platelets of average size $7\times5\times2$ mm^3 having crystal orientation perpendicular to the *c* axis were easily cleaved out. A set of Pb-doped single crystals were grown with the same method by adding to the starting mixture a [Pb]/[Bi+Pb] molar ratio equal to 1/3. X-ray diffractograms of such platelets show the crystal to consist of the 2:2:1:2 phase ($c=30.80$ Å). Microprobe measurements have shown that in the crystals the [Pb]/[Bi] atomic ratio is about 0.3/1.7, namely that the Pb content is 0.3 per formula unit of $Bi_2Sr_2CaCu_2O_8$. ac susceptibility measurements (at a frequency of 70 Hz and in a magnetic field of ~1 G rms) indicate a sharp superconducting transition at 90 K, namely 5 K higher than Pb-free crystals. A third set of crystals of reduced grain size, which were tested to have the single 2:2:1:2 phase and to be superconducting below $T_c = 80$ K, were studied to investigate the influence of the crystal size. The samples were mounted with vacuum compatible conducting epoxy onto the copper finger of an Air Products and Chemicals cryotip and were cleaved at 26 K by pulling off the top part of the crystal surface epoxied before the introduction in vacuum. Cleavage of the sample was easy and the terminal (001) surfaces showed large terraces, as seen by optical inspection. For the polycrystalline sample the cleaved surface consisted of highly stepped zones and small flat areas with different orientations. The composition of the background vacuum was carefully checked with a residual gas analyzer. The partial pressures of oxygen and water vapor after baking and cryopumping were in the low 10^{-11} Torr range (not measurable) and the residual CO and N_2 (mass 28) pressure was less than 2×10^{-10} Torr. At temperatures below 75 K for CO_2 and 25 K for CO and hydrocarbons these substances condense onto the cold surface[10] and sublimate when the temperature rises above these equilibrium values at constant pressure. The photoemission spectra were taken for different temperatures after cleaving and no evidence of oxygen loss was measured up to room temperature.

Figure 1 (left panels) displays a series of O 1*s* spectra for the 2:2:1:2 crystals taken after cleavage at $T = 26$ K and at increasing times from the cleave and at room temperature, $T = 300$ K. The spectra consist of two large peaks at BE's of 528.8 ± 0.1 and 531.5 ± 0.2 eV. For some cleaves, the peaks were not resolved and an asymmetric 528.8-eV line was observed. A third small component centered at 533.5 ± 0.2 eV can be identified in the 26-K spectrum after a curve-fitting procedure with Gaussian line shapes. Very similar spectra were measured in the Pb-doped crystals and are not shown here. For the higher BE feature of the O 1*s* core spectrum the prevalent consensus to date is that it has an extrinsic origin due to surface contamination, even if a convincing evidence of this has not been provided. Panels (b) and (c) showing spectra recorded 3 and 5 h after the cleave with the surface maintained at $T = 26$ K indicate clearly that the 533.5-eV peak results from increasing contamination of the exposed surface. The degree of contamination is proportional to the time elapsed from the cleave at a fixed temperature since the increasing exposure results in an increasing thickness of the overlayer. The spectrum (d), taken at $T = 300$ K, is quite similar to the 26-K spectrum (a), apart from a little larger contamination, and does not change with time, indicating that the contaminating species tends to physisorb onto the cold surface. For the lowest pressure attained (5×10^{-11} Torr), no appreciable strength for the 533.5-eV peak was observed to grow overnight on the sample kept at room temperature. Since hydrocarbons are the major residual components in the UHV system, we conclude that carbon monoxide or hydroxides are the most probable source of this structure.

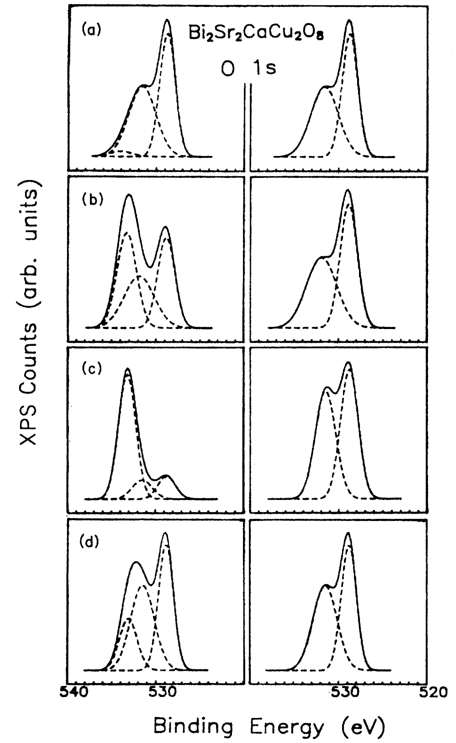

FIG. 1. Left panels: O 1*s* x-ray photoemission spectra of $Bi_2Sr_2CaCu_2O_8$ single crystals after background subtraction and normalization to the 528.8-eV peak for (a) freshly cleaved surface at $T = 26$ K, (b) 3 h after the cleave at $T = 26$ K; (c) 5 h after the cleave at $T = 26$ K; (d) at room temperature. Right panels: corresponding spectra after removal of the 533.5-eV component. The dashed lines are Gaussian fits to the spectra.

Examination of the C 1*s* spectrum did not give evidence of a carbonate structure around −289 eV. The reasons for that are as follows: the lack of chemisorbed $CO_3{}^+$ ions, the larger cross section (nearly 9:1) for O 1*s* relative to C 1*s*, and the small thickness of the deposited overlayer. A CO monolayer requires few hours to form at these pressures if a unit sticking coefficient is assumed. The right panels of Fig. 1 display the O 1*s* spectra after subtraction of the spurious component at 533.5 eV. It is clear that the "clean" spectra are similar, indicating that the adsorbed layer does not alter the surface stoichiometry. Thus the intrinsic O 1*s* line shape consists of a doublet with a high-to-low BE peak area ratio of 1.0 ± 0.1 and energy separation 2.7 ± 0.3 eV. The intensity ratio of the O 1*s* doublet—i.e., the 528.8- and 531.5-eV features—for a clean surface can be estimated from the oxygen structure factor S_0 for a crystal which contains one formula unit per cell.[11] Barring the photoionization cross sections $\sigma(h\nu)$, the photoemitted area ratio from oxygens on the Bi and Sr planes z_i and those on the Cu planes z_j are proportional to

$$S_0 = \sum_i [\exp(-z_i/\lambda_0)] \Big/ \sum_j [\exp(-z_j/\lambda_0)] ,$$

where $\lambda_0 = 19.5$ Å is the electronic mean free length for the photon energy 1486.6 eV. For the (001) surface of a $Bi_2Sr_2CaCu_2O_8$ single crystal, the calculated area ratio is

1.03, which agrees with the experiment within 3%. Thus we infer that the assignment of the 528.8- and 531.5-eV peaks to the oxygen states from atoms in the CuO_2 and Bi-Sr lattice planes is correct, in agreement with earlier results[6] and the known values of the O 1*s* binding energies of the main group element and transition-metal oxides,[12] and that the surface oxygen stoichiometry is maintained for good cleaves in ultrahigh vacuum conditions. It is interesting to note that the single crystalline samples exhibiting disoriented or stepped cleavage surfaces show consistently a smaller high BE O 1*s* peak and consequently a smaller (0.7 ± 0.2) intensity ratio at 26 K. Since structural and magnetic characterizations indicated a single phased homogeneous sample with a large superconducting fraction, the result might suggest a larger depletion of oxygen on the terminal BiO plane and/or a reduced collection efficiency for electrons photoemitted from misoriented surface planes. The surface deterioration affects strongly the valence-band photoemission spectra, as shown in Fig. 2(a). The hybridized Cu 3*d* and O 2*p* band, which lies between 1- and 6-eV BE, is modified and clear features are present at about 5, 9, and 13.5 eV in the difference spectrum obtained by subtracting the spectrum of the dirty surface from that of the freshly cleaved one after background removal and normalization to the O 2*s*-Sr 4*p* peak intensity at −19 eV. Such features are not observed, as expected, when the 26 K and the room-temperature valence-band spectra are subtracted [Fig. 2(b)], indicating that these features have a totally extrinsic origin. The adsorbate peaks and their relative intensity are close to those found on scraped $La_xSr_{1-x}CuO_4$ surfaces exposed to 1 L (1 L = 10^{-6} Torr s) of CO_2 or CO and assigned to $1\pi_u + 3\sigma_u$, and $4\sigma_g$ molecular orbitals.[13] The comparison strongly suggests that carbon monoxide physisorption on the surface occurs at low temperature. From the change of the work function with the CO exposure,[13] we expect that a substantial chemisorption of gaseous CO due to background vacuum will begin at a 10-L dose, i.e., after exposure of several days at partial pressures of 10^{-10} Torr, because the sticking coefficient is rather low (3×10^{-4}). However, such exposure time is greatly shortened for the condensed phase. Our experimental conditions are such that a physisorbed layer could develop onto the surface a few hours from the cleave, depending on the base pressure in the chamber. In any case, a direct correlation exists between the O 1*s* peak at 533.5 eV and the multiple structure of the valence-band spectra in the region of the 9-eV feature. Spectral changes induced in the valence band and O 1*s* spectra by surface contamination have been reported in lanthanum oxide ceramics[14] and bismuth oxides crystals,[8(a)] where the growth of a peak at 532 eV and the attendant valence-band changes are attributed to the presence of oxygen states of extrinsic nature. The present study on high-quality single crystals of $Bi_2Sr_2CaCu_2O_8$ allows separation of intrinsic from extrinsic features and indicates that the O 1*s* peak at 531.5 eV is characteristic of these materials. The latter conclusion is supported by other studies[5,6,15] and at variance with studies reporting a single O 1*s* peak [Refs. 1, 8(a), 8(b), 14, and 16].

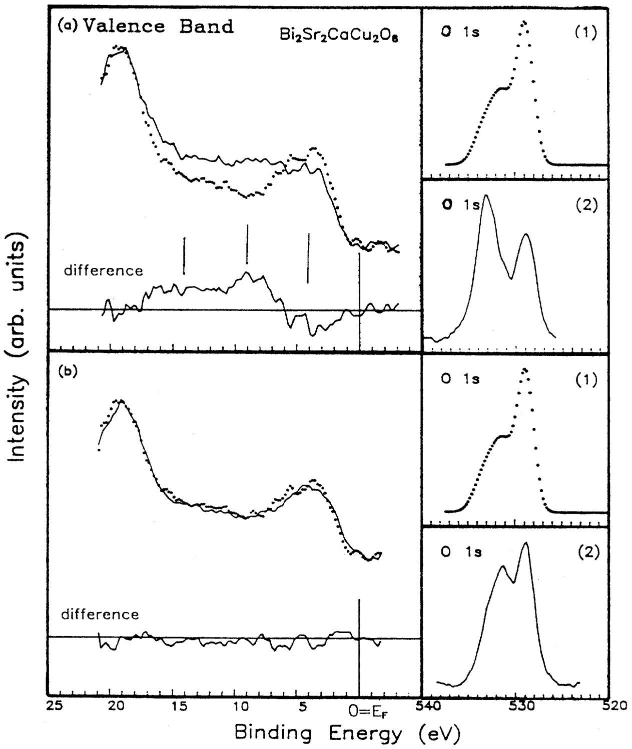

FIG. 2. (a) Valence-band x-ray photoelectron spectra of the freshly cleaved (dotted) and contaminated surface of $Bi_2Sr_2CaCu_2O_8$ single crystal and their difference showing features at about 5, 9, and 13.5 eV. (b) Same as (a) but for surfaces cleaved at 26 K and warmed to 300 K in UHV. Right panels labeled (1) and (2) display the corresponding O 1*s* core-level spectra.

The bombardment with Ar^+ ions produces a strong decrease or disappearance of the high-BE peak of the O 1*s* spectrum; this is attributed to disruption of the surface layer caused by the ions.[17] The interaction of 1.5-keV electrons with the surface is less destructive than that with ions but nevertheless not negligible. Figure 3 shows the

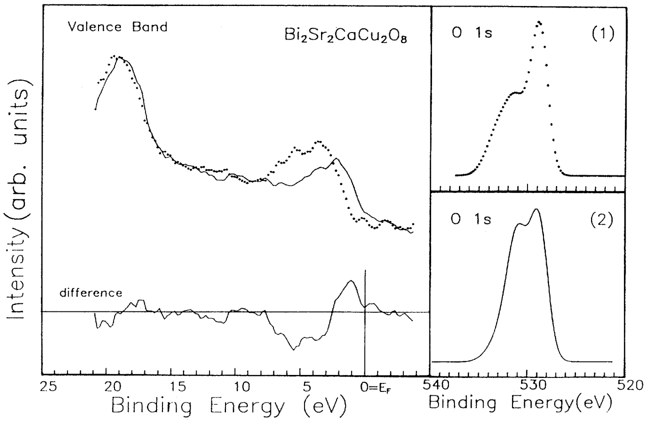

FIG. 3. Valence-band x-ray photoelectron spectra of $Bi_2Sr_2CaCu_2O_8$ single crystal cleaved at 26 K (dotted curve) and after electron etching at 32 K (1.5 keV, 300 μA for 2 h) and their difference curve. The right panels show the corresponding O 1*s* spectra.

modifications induced on the valence-band states of clean surfaces, respectively, by electron etching with a current density of approximately 10 μA/mm^2. During electron bombardment the temperature of the sample raises slightly above 30 K. It is interesting to note that the bombardment is more effective on the metallic CuO planes than on the insulating BiO/SrO planes. The 528.8-eV O 1s core peak is also weakened relative to the 531.5-eV peak and a sizable loss of intensity occurs in the lower part of the valence band, where the partial density of states of the Cu and Bi character is important,[18] with an apparent shift of the entire band to low BE's. It is plausible that the metal-oxygen bond is heavily modified with loss of the superconducting properties of the uppermost crystal layers. Knowing that the copper-oxygen bonding is strongly affected by the oxygen release due to thermal heating,[5] we believe that the electron bombardment induces an oxygen deficiency at the surface of the sample, preferentially on the copper-oxygen planes. In view of these effects, it is advisable to treat electron excitations on high-T_c superconductors with great caution. The other relevant core levels, notably Cu 2p and Sr 3d, have been measured against surface contamination but they hardly show any sign of reaction. For the Cu 2$p_{3/2}$ spectrum, the characteristic main peak at 932.4 eV at its high-binding energy d^9 satellite are unaffected, suggesting that the average Cu valence remains close to 2. Similarly, it is difficult to see changes on the Sr 3d lines consisting of peaks at 131.8 and 134.0 eV, which, otherwise, change their intensity when bulk oxygen is released, as found in studies on thin films.[6]

In conclusion we have observed time-dependent physisorption of carbon monoxide on single crystalline $Bi_2Sr_2CaCu_2O_8$ and $Bi_{1.7}Pb_{0.3}Sr_2CaCu_2O_8$ surfaces cleaved at 26 K. This contamination contributes spectral intensity between 9 and 14 eV below the Fermi level and it is responsible for the extra peak at 533.5 eV in the O 1s spectrum. The physisorbed layer is removed at room temperature and the intrinsic O 1s spectrum is seen to consist of a doublet structure attributed to excitations from oxygen 1s core levels in different environments. No evidence is found of oxygen loss from the surface. The exposed BiO plane is extremely sensitive to external agents, particularly to electron etching, which alter profoundly the stoichiometry of the terminal layer through removal of oxygen from copper and bismuth planes. The surface sensitivity of the metallic CuO_2 planes to electron bombardment is consistent with the picture of a partially conducting surface given by recent microstructural surface studies.[4] Such issues are extremely important to developing methods of surface passivation, to understanding the effects of metallic overlayers,[8(c),19] and for the development of reliable multilayers structures and superlattices.[20]

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