Valence-band and resonance-photoemission study of La_2CuO_{4+x} single crystals

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Angle-resolved resonance-photoemission measurements at 15–30 and 100–130 eV photon energy ranges were performed from different principal planes of La₂CuO_{4+x} single crystals. Resonance photoemission near the La-4*d* threshold shows the presence of states in the valence band associated with La within the energy region 2–5.5 eV. At low photon energies near the La-5*p* threshold (16.5 eV) with the normal emission aligned in the (001) direction ($c\perp$ surface), valence-band spectra display nonmonotonic photon energy dependence of a 6-eV binding-energy feature, i.e., beyond the main La density of states in the valence band. Along with the absence of such behavior for normal emission from the other principal planes (100) and (010) ($c\parallel$ surface geometry), this fact implies that surface termination effects need to be taken into account to explain these results. The binding energy of the resonant feature and the resonance photon energy are slightly different for photon polarization vector parallel and perpendicular to the Cu-O planes of the crystal. Measurements were also done on another La-based compound, La_{0.7}Sr_{0.3}MnO₃, having similar La-O plane but much smaller *c*-axis parameter. This manganese oxide demonstrates the same nonmonotonic dependence of the 6-eV bindingenergy feature, but in a wider photon energy region. On the basis of this comparison, it is tentatively suggested that the intensity modulation is governed not only by the core-level threshold, but may carry information of bulk Brillouin zones as well. [S0163-1829(97)05938-9]

I. INTRODUCTION

Photoelectron spectroscopy (PES) has provided invaluable experimental information on the electronic structure of high-temperature superconductors (HTSC's).¹ Experimentally, there have been great improvements in energy resolution in angular-resolved photoelectron spectroscopy (ARPES) Ref. 2 and photoemission data reveal very direct information about the electronic states and their dispersions near the Fermi level (E_f) . However, one should recall that PES and ARPES are surface-sensitive techniques, and the escape depth of photoelectrons is of the order of 5-20 Å depending on the kinetic energy, which is about the size of the unit cell of most superconducting cuprates. This implies that the observed energy distribution curves are related to electrons which are in the outermost cell of the crystal. The importance of a surface-derived electronic band has been demonstrated for cleaved single crystals of the YBa₂Cu₃O₇ compound³ by ARPES, and for Bi₂Sr₂CuO₆ by local density approximation (LDA) calculations.⁴

One of the benefits of studying La_2CuO_{4+x} is that this compound is one of the simplest among the HTSC materials and it can be easily and reversibly doped with oxygen, leading to superconductivity with a critical temperature as high as 55 K.⁵ Band-structure calculations^{6,7} of La_2CuO_4 predict few, if any, La states below E_F in the valence band (VB). In Ref. 6 the La-5*d* band edge is 1 eV above the Fermi level and this band merges into the La-4*f* band about 3 eV above E_F . According to Ref. 7, the valence band consists of a 17-band complex formed primarily of O-2*p* and Cu-3*d* states, though the presence of La states below E_F has been found down to 5.5 eV binding energy (BE). The La-5*p* bands are localized (16 eV below E_F) and the main conclusion from theoretical elaborations implies little contribution from La atoms to the valence band. However, resonance photoemission experiments show^{8,9} a La contribution to the valence band in a wide energy region. To clarify this question we performed angle-dependent resonance photoemission measurements in the 15–30 and 100–130 eV photon energy ranges from different principal planes of La₂CuO_{4+x} single crystals. From this, we conclude the presence of states associated with La over the entire valence band and also that surface termination effects need to be taken into account to explain the present experimental results.

II. EXPERIMENT

The La₂CuO_{4+x} single crystals used in the present work were either grown by the floating-zone method (FZM) in the URN-2-ZM experimental setup¹⁰ under oxygen pressures of 4 and 30 atm at a crystallization rate of about 0.5 mm/h or by the molten-solution (MS) method.¹¹ Crystals grown by the FZM displayed superconductivity with T_c (onset)=40 K without any extra oxygenation. According to the hightemperature magnetic susceptibility, these crystals showed a peak at 230-250 K, giving evidence for the presence of long-range antiferromagnetic order. It implies that the crystals are phase separated at low temperatures and lattice parameters evaluated by x-ray diffraction¹² correspond to an excess oxygen content of x = 0.03 - 0.04, i.e., inside the socalled miscibility gap.¹³ To get dielectric reference samples, the as-grown crystals were annealed in an inert atmosphere at 700 °C for 5–10 h. Crystals grown by the molten-solution method, on the other hand, demonstrated good dielectric

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properties ($T_N = 270$ K) without any traces of superconductivity. To get a superconducting response from these crystals, they were put in an electrochemical cell at elevated temperatures in order to introduce excess oxygen. The maximum oxygen index after this treatment did not exceed x = 0.03, thus placing the crystals inside the miscibility gap as well. The above numbers of excess oxygen content should be considered as estimations since the absolute oxygen concentration is very difficult to establish on this scale. The crystal size was up to $4 \times 4 \times 4$ mm³, which enabled us to make two successive cleavages along [001] and [*hk*0] symmetrical planes on the same crystal.

To minimize surface contamination the samples were cleaved in situ, at liquid-nitrogen temperature. The base pressure was in the low 10^{-10} Torr range for all measurements. The crystals were glued with a conducting silver epoxy to the sample holders, and metal sticks were glued on top of the crystals. The fresh surface was obtained by cleaving the crystals using a wobble stick to apply a force to the metal stick. Unlike the case of Bi₂Sr₂CaCu₂O₈ where the crystal cleaves between the two adjacent Bi-O planes connected by weak van der Waals bonds, the cleavage plane for La_2CuO_{4+x} is very uncertain. All surfaces obtained by cleavage were rather irregular, indicating that there is no natural cleavage plane for La_2CuO_{4+x} . This means that the cleavage inevitably leads to the breaking of strong ionic or covalent bonds between layers and thus a rearrangement of the electronic charge on the surface can be expected.

The measurements were performed at beamlines 52 and 22 at the MAX synchrotron radiation laboratory in Lund, Sweden. Beamline 22 is equipped with a modified Zeiss SX-700 plane grating monochromator covering the photon energy range of about 20-1000 eV. A hemispherical electron energy analyzer (200-mm mean radius) with a multichannel detector system was used to record the photoemission spectra. For the normal emission geometry the incidence angle was 40°. Beamline 52 is equipped with a 1-m normalincidence monochromator working in the photon energy range 10-30 eV and a Vacuum Generators ADES 500 spectrometer. To investigate the polarization dependence, photoemission spectra were recorded at two angles of incidence, 30° and 70° , with respect to the sample normal. Changing the incidence angle from 30° to 70° increases the *E*-vector component perpendicular to the crystal surface. All spectra were recorded at liquid-nitrogen temperature and calibrated using a Ta reference spectrum. X-ray-absorption spectra were recorded with a channel plate in the total yield mode.

III. RESULTS

All photoemission spectra showed a good reproducibility independent of the growth technique of the crystals. No Fermi edge was observed for the oxygen-doped samples which may be due to the phase-separation process or some excess oxygen depletion in ultrahigh vacuum. Thus we cannot distinguish between crystals neither with different oxygen contents nor with growth techniques and will mainly concentrate upon anisotropy effects. However, it should be mentioned that there is a clear difference in oxygen *K*-edge x-ray-absorption spectra for dielectric and superconducting



FIG. 1. X-ray-absorption spectrum (total yield) for La₂CuO_{4+x} near the La-4*d* threshold. The marked peaks in the spectrum correspond to three intermediate states that can be reached by an electric-dipole absorption ${}^{3}P_{1}$, ${}^{3}D_{1}$, and ${}^{1}P_{1}$.

compositions, but this point will not be discussed in the present paper.

The valence-band spectra displayed some time dependence. Typically, changes first became noticeable after a period of about 5-6 h. Hereafter we describe data taken in the time interval after the surface preparation for which no changes occurred. First we present data on resonance photoemission near the La-4d threshold to clarify the presence and energy range of La states in the valence band. The measurements were performed at beamline 22. The absorption spectrum for the La 4d-4f transition is shown in Fig. 1 and was used to select appropriate photon energies for the resonance photoemission spectra. The peaks in the absorption spectrum are due to the three intermediate states of the configuration $4d^94f^1$ that can be reached by an electric-dipole absorption, ${}^{3}P_{1}$, ${}^{3}D_{1}$, and ${}^{1}P_{1}$. According to calculations, 14 all the line strength goes into the ${}^{1}S_{0} - {}^{1}P_{1}$ transition that results in the strong absorption peak at 117 eV. The on-resonance photoemission spectra were taken at this photon energy. The corresponding off-resonance curves were taken at 113 and 130 eV. Figure 2 shows such normal emission data taken from two different surface planes. As seen in this figure, there is a slightly different behavior of the energy distribution curves for $c \parallel$ surface [Fig. 2(a)] and $c \perp$ surface [Fig. 2(b)] experimental geometries ($c\perp$ surface geometry means that the crystal c axis is directed parallel to the surface normal). However, the main conclusion that can be inferred from the data is the presence of states in the valence band associated with La within the energy region 2-5.5 eV for both geometries.

Next, we consider valence-band photoemission spectra re-



FIG. 2. On-resonance (117 eV) and off-resonance (113 and 130 eV) valence-band spectra at the La-4d-4f threshold for $c\parallel$ surface (a) and for $c\perp$ surface (b) sample orientations. The peaks at 9.5 and 12.5 eV binding energy are due to the Cu- d^8 satellite structures. The spectra are normalized to the photon flux.

corded with low photon energies, 14-25 eV, taken at beamline 52. Selected (photon energies 15-20 eV) normalemission spectra from the different cleavages of the same crystal are shown in Fig. 3 for $c\parallel$ surface (a) and $c\perp$ surface (b). The resonating feature at a binding energy of 6 eV withmaximum intensity at a photon energy (E_{ph}) of 17 eV seen at the $c\perp$ surface sample orientation [Fig. 3(b)] is strongly diminished for the $c\parallel$ surface spectra [Fig. 3(a)]. The intensity



FIG. 3. Selected normal-emission (30° incidence) valence-band spectra for $c\parallel$ surface (a) and $c\perp$ surface (b) sample orientations taken from the same crystal. All spectra are normalized to the photon flux.



FIG. 4. Normal-emission spectra of La_2CuO_{4+x} in the 19–26 eV photon energy energy region for the $c\perp$ surface sample orientation.



FIG. 5. Emission-angle dependence of the resonance feature $E_b = 6 \text{ eV}$ at $h\nu = 17 \text{ eV}$. The curves are normalized at the intensity at 3.4 eV BE. The changing of emission angle affects only the resonance feature.

modulation of the 6-eV BE feature is not finished at $E_{\rm ph}=19$ eV; another modulation is seen at higher photon energies. This effect is seen in Fig. 4 which shows normal emission valence-band spectra of La₂CuO_{4+x} for the $c\perp$ surface sample orientation in the photon energy region 19–26 eV. There is a slight intensity modulation at 6 eV BE in this photon energy region with maximum intensity around 23–24 eV.

The emission angle dependence of this resonance for $E_{\rm ph}=17~{\rm eV}$ is presented in Fig. 5. The enhanced 6-eV peak for normal emission (0°) decreases in intensity when the emission angle increases. Since the cleaved surface is irregular, we do expect increasing emission from the $c\parallel$ surface plane when going off the normal emission at the $c\perp$ surface geometry. Thus, the angle dependence in Fig. 5 in the present case of an irregular surface may just reflect a smooth transition between the two principal geometries.

In Fig. 6 we present two spectra taken from the same crystal for the $c\perp$ surface geometry after two successive cleavages. Obviously, the only difference between them is seen in the resonance region. The 6-eV BE feature appeared enhanced only after the second cleavage, while it was completely suppressed after the first one. However, it should be mentioned here that in our measurements for the $c\perp$ surface geometry; the enhanced 6-eV BE feature has been observed in most cases. This example definitely shows that surface conditions are extremely important for the discussed feature and the final result may depend on where in the lattice the cleavage occurs (see below for further discussion).

In Fig. 7 normal-emission spectra of the valence band of



FIG. 6. Normal-emission spectra at $h\nu = 17$ eV for the $c\perp$ surface sample orientation taken from the same crystal after two successive cleavages. The spectra are normalized at the intensity at 3.4 eV BE.

La₂CuO_{4+x} are presented with a 0.25-eV step in photon energies [Fig. 7(a)] and for different orientation of the polarization vector relative to the crystallographic axes [Fig. 7(b)]. Fine structures of the resonating feature can be seen from Fig. 7(a), which shows the presence of a second peak at lower binding energy (5 eV). The most important result can be inferred from Fig. 7(b) where it is clearly seen that the binding energy of the main resonant feature and the resonance photon energy are slightly different (0.3 eV) for photon polarization vector mainly parallel (incidence 30°) and perpendicular (incidence 70°) to the Cu-O planes of the crystal.

Finally, another important piece of information comes from the study of the La-based compound La_{0.7}Sr_{0.3}MnO₃. This compound has quasicubic (rhombohedral) perovskite structure with a much smaller c-axis parameter (5.5 Å), while interatomic distances in the La-O plane are almost the same as in La_2CuO_{4+x} . Selected valence-band spectra of La_{0.7}Sr_{0.3}MnO₃ for the photon energy region 16–26 eV are shown in Fig. 8. A similar nonmonotonic dependence with similar strength is observed, but this resonance is now much more extended in photon energies. Even at $h\nu = 26 \text{ eV}$, the 6-eV BE feature is still detectable, whereas in La_2CuO_{4+x} the first modulation is completely gone already at $h\nu$ = 19 eV [cf. Fig. 3(b)]. To better illustrate the difference between $La_{1-x}Sr_xMnO_3$ and La_2CuO_{4+x} , constant initial state (CIS) plots in the resonance region are shown in Fig. 9 for both compounds.

IV. DISCUSSION

Utilizing the La-4d resonance photoemission process, we are able to distinguish the La partial density of states from the rest of the valence band. Figure 2 shows that La states in



FIG. 7. Valence-band photoelectron spectra of La_2CuO_{4+x} , measured at normal emission in the $c\perp$ surface geometry: (a) spectra with small step in photon energy, incidence angle is 30° and (b) spectra for two incidence angles 30° [solid lines are drawn through the experimental points without smoothing, the same as in Fig. 7(a)] and 70° (experimental points). Vertical lines show constant binding energy peak position (6.3 and 6.0 eV) for the two polarizations.



FIG. 8. Normal-emission spectra of $La_{0.7}Sr_{0.3}MnO_3$ taken in the region around the La-5*p* threshold. The resonance enhancement of the 6-eV BE feature is present up to the highest (26 eV) photon energies used.



FIG. 9. CIS plots $(6 \pm 0.1 \text{ eV binding energy})$ for La₂CuO_{4+x} and La_{0.7}Sr_{0.3}MnO₃, extracted from sets of photoemission spectra. The background connected with the photon energy cross section dependence is subtracted for clarity. The lines are a guide for the eye.

the valence band are found between 2 and 5.5 eV BE, with the maximum intensity around 3 eV. This finding agrees very well with the theoretical result of Mattheiss.⁷ Let us now discuss the results at low photon energies with the main emphasis given to the nonmonotonic photon energy dependence of the 6-eV BE feature. The assignment of this feature has been controversial.^{9,15} Since the 6-eV BE feature is observed on very different La-based compounds, La₂CuO_{4+x} (Refs. 9, 15, and 16 and this work), La_{0.7}Sr_{0.3}MnO₃ (this work), La_2NiO_{4+x} , and partially oxidized metallic La (Ref. 16), it is very likely to assign this feature to the only common property for all these compounds, La-O bonds. The first attempts to explain the nonmonotonic intensity of the 6-eV BE feature of La₂CuO_{4+x} were based only upon $c\perp$ surface data taken at low photon energies for which it was treated as a bulk resonance feature of hybridized La-5d-O-2p states and related to the presence of empty O-2p states just above E_F (Ref. 15) or hybridized La-5*d*-O-2*p* empty states⁹ to which excitation from the La- $5p_{3/2}$ state (hybridized with O-2s in the first case¹⁵) occurs. It can often be difficult to determine whether a particular peak or other structure in the photoemission spectra originates from the surface or the bulk. The main criterion to be fulfilled for the identification of a surface state concerns its energy position. Surface states lie in a gap in the projection of the bulk band structure onto the two-dimensional surface Brillouin zone. In the present case of La_2CuO_{4+x} , the fact that the resonating feature (BE=6 eV) is situated beyond the main region of La states 2<BE<5.5 eV (as can be inferred from Fig. 2 and bandstructure calculations⁷) directly points to the surface nature of the observed phenomenon. Another test used for the identification of a surface state is the sensitivity of emission intensity to chemisorption of atoms or molecules on the surface. We did not carry out direct experiments on surface chemisorption, but believe that Fig. 6 indirectly proves the surface nature of the feature under discussion. Maximum intensity of the 6-eV BE feature was observed at photon energies close to the La-5p threshold, suggesting that we may have a LaO surface; i.e., cleavage occurs mainly between two adjacent LaO planes in the lattice like it happens in the Bi2212 system between two adjacent BiO planes. The only difference is that the BiO layers in Bi2212 are bound by weak van der Waals bonds, while LaO planes in La_2CuO_{4+r} are bound by strong ionic bonds. This fact makes it possible in particular cases to have a cleavage between CuO and LaO layers in La_2CuO_{4+x} , thus leaving the CuO plane on top and providing a natural explanation of the absence of the resonance feature (Fig. 6, first cleavage).

When a surface state is considered, we do not expect to observe any dispersion with photon energy in the normalemission spectra (only k_{\perp} varies). However, a closer inspection of Fig. 3(b) for La₂CuO_{4+x} and Fig. 8 for La_{0.7}Sr_{0.3}MnO₃ clearly shows pronounced dispersion as the photon energy is lowered. As was shown in Ref. 16, the binding energies of the resonant features and the resonant photon energies are slightly different for photon polarization vector parallel and perpendicular to the Cu-O planes of the La₂CuO_{4+x} crystal. To clarify this point we performed a detailed study of the photon energy and polarization dependence of the 6-eV BE feature (Fig. 7). The first important finding is that there is not only a second resonating feature around 5 eV BE as it was found in Ref. 16, but the main 6-eV feature also shows a fine structure. In the geometry when the E vector is mainly directed parallel to the c axis, the 6-eV BE feature is shifted about 0.3 eV towards lower binding energy. It explains the "shift" of the main feature on going from 18.5 eV down to 16.25 eV [Fig. 7(a)] photon energy. The further "shifting" of this feature as is seen from Fig. 7(b) may be due the fact that the second 5-eV BE feature has a maximum intensity around 16 eV photon energy when the intensity of the main peak already goes down. These experimental data show that nonmonotonic behavior of the intensity around 5-6 eV BE is rather complex and depends on the polarization of the light. In our experimental conditions we always have contributions from both polarizations. Hence different photon energy dependences of the peak intensity for the different polarizations explain the observed binding energy shift. If all arguments about the surface nature of the 6-eV BE feature remain valid for both polarizations, the second 5-eV BE feature might be considered as coming from a bulk transition since there are La states at this binding energy as follows from Fig. 2 and bandstructure calculations.⁷ One can suggest that the above arguments concerning the dispersion of the 6-eV BE feature is applicable to the case of La_{0.7}Sr_{0.3}MnO₃ as well.

We believe that this set of experimental data implies a necessity of considering surface effects on the electronic structure of at least some HTSC's. It is clear that the atomic and orbital character of the surface state depends strongly on the actual cleavage plane. In the present case of La_2CuO_{4+x} , the plane $c\perp$ surface is distinguished by the fact that the doping related charge transfer occurs along the c axis and the creation of a surface between any layers along this direction should lead to a rearrangement of the electronic charge and thus to a change of the surface electronic structure compared to that of the bulk. As far as the other copper oxides are concerned, the importance of surface termination effects has been demonstrated for YBa₂Cu₃O₇ experimentally³ and theoretically by Calandra et al.,^{17,18} who have found distinct changes between the surface density of states (DOS) and the bulk DOS for several crystal terminations. A first-principles determination of surface effects on the electronic structure of Bi₂Sr₂CuO₆ within the LDA has been done by Rodriguez et al. $^{\overline{4}}$

Discussing the nature of the photon energy dependence of a surface state, it should be remembered that surface states can have very different characters, depending on their localization near the surface. Free electrons in metals form surface states which are determined by the boundary conditions at the surface where Bloch-like evanescent functions are matched.¹⁹ These states usually extend several atomic layers into the solid. On the other hand, much more localized d-like surface states have atomiclike wave functions which have no extension into the solid and are essentially localized on surface atoms. Examples of surface states of the first kind are states on fcc Cu(111) and Al(100) which have been seen in ARPES through rather wide photon energy regions.^{20,21} The main experimental result in these works was that there is a nonmonotonic (oscillating) behavior of the photoelectric cross section of the surface states which was supported by a general spectral decomposition theory presented in Ref. 20. This theory describes the observed intensity behavior and predicts the universality of such behavior for all surface states of this type. According to the theory,²⁰ a surface state Ψ_s of parallel momentum k_{\parallel} and energy E_s can be expanded in bulk states φ_n in the *n*th band: $\Psi_s(E_s, k_{\parallel})$ $=\sum_{n} \alpha_n(k_{\perp}) \varphi_n(k_{\perp})$. The emission intensity at $h\nu$ is given by the expression $I_s(h\nu) \sim |\Sigma \alpha_n(k_\perp) M_b(n)|^2 \sim f\{\cos(k_\perp a)\},\$ where M is the matrix element and a the lattice parameter. The energy conservation condition $E(k_{\perp}) - E_s = h\nu$ is fulfilled. Hence I_s is oscillatory in $h\nu$ since in general $\alpha_n(k_{\perp})$ is a peaked function of k_{\perp} . This reasoning gives a natural explanation for the sharpness as a function of photon energy of the discussed resonance in La_2CuO_{4+x} (Fig. 9). Since the unit cell of La_2CuO_{4+x} in the *c* direction is extremely large $(5.3 \times 5.3 \times 13.15 \text{ Å})$, one needs only a small step in the k_{\perp} value (and energy, respectively) to cross over the zone in the z direction. In the framework of the spectral decomposition theory, we should also expect nonmonotonic dependence of the respective surface-state intensities every time when the next zone boundary is crossed. In the case of La_2CuO_{4+x} , the resonance is extremely sharp in photon energy and peaked at $E_{ph} = 17 \text{ eV}$. Hence the photon energy region for the second intensity modulation can be evaluated. With the given lattice constant (c = 13 Å) and using the free-electronlike empty-state model, one gets for the second symmetrical point a photon energy in the region 22-25 eV depending on the value of the inner potential. It agrees well with our experimental data (Fig. 4) where the second intensity modulation can be observed around 23 eV.

The discussed decomposition theory also explains the different width of the CIS curves for $La_{0.7}Sr_{0.3}MnO_3$ and La_2CuO_{4+x} (Fig. 9). Due to the different sizes of the Brillouin zones (c = 13.13 Å for La_2CuO_{4+x} and c = 5.5 Å for $La_{0.7}Sr_{0.3}MnO_3$), one could expect a more extended (in photon energy) feature for the manganate compound.

A quite different approach must be considered when we treat a surface state as strongly localized. In this case one can speak of a photoemission resonance though details of the treatment can be different. In semiconducting GaP (110) (Ref. 22) and GaAs(110)* (Ref. 23), enhanced electron emission has been interpreted as being due to an additional direct recombination process involving filled and empty surface states²² or exitonlike bound states.²³ The resonance feature could also be considered in much more general terms as having an atomic origin as is done, i.e., for the 5p-5d transition for metallic²⁴ tungsten which is found to behave very similar to atomic tungsten.²⁵ However, applying this approach we are left with the problem of describing the second intensity modulation in La_2CuO_{4+x} (Fig. 4) and the different width of the CIS curves (Fig. 9) for La_2CuO_{4+x} and $La_{0.7}Sr_{0.3}MnO_3$.

One can envision one way to get around this problem. Two different languages have been used in describing two extreme cases of localized and delocalized surface states. It can be suggested that the localization of a surface state has an intermediate strength. In this case, the intensity modulation of a surface state would be governed by respective corelevel threshold, La-5p in our case, and carry information about bulk Brillouin zones as well, as discussed above. In other words, we suggest that the intensity modulation can be described as a superposition of two mechanisms: resonant photoemission and band-structure effects. This is possibly seen even in simple metals like Cu and Al. For these metals, surface-state intensities have their maximums just near the corresponding core-level thresholds. For Cu (111) the surface state S_3 has a maximum at 74 eV photon energy²⁰ (the Cu-3p threshold is 74.5 eV) and for Al (100) the surfacestate intensity in the first Brillouin zone is peaked at 72 eV photon energy²¹ (the Al-2*p* threshold is 72 eV). It may be argued that it is only a coincidence that symmetry points in Cu and Al have the same energies as the corresponding core levels, but the fact that both cited intensity profiles have asymmetrical shapes can hardly be expected from the theory discussed above²⁰ for delocalized surface states.

V. CONCLUSIONS

By resonance photoemission spectroscopy performed on cleaved La_2CuO_{4+x} single crystals we found the presence of bulk La states in the valence band over the region 2-5.5 eV and strong evidence for the existence of surface-derived La-O electronic bands for the $c\perp$ surface plane. We assign a feature at BE=6 eV, resonating at the La-5p threshold as coming from a La-O surface state, while a second resonating feature (BE=5 eV) that has maximum intensity at $E \parallel c$ light polarization might be connected with a bulk transition. The very narrow interval of photon energies where the 6-eV BE feature is observed is due to the small size of the Brillouin zone along the c direction in La₂CuO_{4+x}. We conclude that surface-termination effects need to be considered when treating the photoemission data on cuprates which have no natural cleavage plane. To reconcile the fact that the surface state resonates at the La-5p threshold and has features connected with the bulk Brillouin zone (second intensity modulation and very narrow interval of photon energies where it is observed as compared to the other La-based compounds), we tentatively describe this surface state as having an intermediate strength of localization. As a consequence, a new approach should be elaborated to describe nonmonotonic photon energy dependence of the surface-state intensity. The necessity of such an approach may be found for surface states on simple metals.

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