Polarization dependence of the Cu 2p absorption spectra in $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$

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We have studied the polarization dependence of the Cu 2p absorption spectra in a $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$ single crystal. At normal incidence ($\mathbf{E}\|xy$ plane) we found an intense peak at 932.0 eV, which becomes much weaker and shifts 500 meV toward lower energies at grazing incidence ($\mathbf{E}\|z$ axis). Also, at grazing incidence a structured absorption step appears starting at 935.8 eV. The interpretation of these results is discussed.

I. INTRODUCTION

The electronic properties of high-T_c superconductors represent a key point in the understanding of the peculiar aspects of these materials. These properties have been widely investigated both theoretically and experimentally because the different theories available to explain the pairing mechanism depend heavily on the location and symmetry of the unoccupied states.[1-8] High-energy electron and x-ray spectroscopies have played a prominent role[9] and in particular x-ray absorption spectroscopy (XAS) with polarized light has been widely applied to study the location and symmetry of the unoccupied states in the high-T_c superconductors at both O and Cu sites.[10-13] For instance, it is now well established that the empty states in these materials are mainly located in O $2p_{xy}$ and Cu $3d(x^2-y^2)$ orbitals oriented parallel to the CuO_2 planes.[11-13] In contrast to the origin, properties and relevance of empty states located in Cu $3d(z^2)$ orbitals, oriented along the c axis, are still open questions. The answer to these questions is very important because it would help to decide which theories are more likely to be correct.

Several XAS and electron energy-loss spectroscopy (EELS) experiments have recently shown the presence of this c component in different classes of high-T_c superconductors.[11,14-18] Unfortunately both data and interpretations are not unique. For example, Bianconi *et al.*[14-16] reported an energy shift of the peak corresponding to the c component with respect to the peak related to xy plane transitions, in contrast with EELS measurements of Nücker *et al.*[11]

We have measured the polarization dependence of the Cu 2p absorption spectra in a $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$ single crystal with the aim of clarifying some of the discrepancies mentioned above and to contribute to the discussion in progress. We have paid particular attention to avoiding surface contamination as well as possible experimental artifacts.

II. EXPERIMENTAL DETAILS

The sample was a 5×4-mm^2-wide single crystal, grown as indicated in Ref. 19, which presents a superconducting transition above 80 K as judged from resistance and magnetization measurements. No evidence of a second crystallographic phase was found in either powder or crystal x-ray diffraction studies. The average composition of the $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$ sample corresponds to the 2:2:1:2 phase as judged from energy-dispersive x-ray spectroscopy (EDXS) measurements. Further details are published elsewhere.[20]

The XAS measurements were performed on the SA-22 beamline at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) (Orsay) using the linearly polarized light from the super ACO storage ring.[21] The monochromator was equipped with two beryl $(10\bar{1}0)$ crystals and the instrumental resolution at the Cu edge was about 300 meV. The spectra were collected in the total electron yield mode in a vacuum better than 10^{-9} mbar. The sample was mounted in a rotating feedthrough and measurements were taken at different angles between the c axis and the polarization vector of the light, in the range from $\theta=90°$ (normal incidence, probing mainly unoccupied states in the ab plane) to $\theta=10°$ (grazing incidence, probing mainly unoccupied states along the c axis). The use of a high-precision manipulator and of a reduced lateral beam size (about 200 μm) allowed careful alignment of the sample surface with respect to the beam at any angle, avoiding spill-over effects and spurious contributions from the edges of the sample. In addition, spectra at different angles were collected several times and in random order to check for reproducibility and to avoid systematic errors such as beam-induced damage of the sample or beam instabilities.

To avoid surface contamination the sample was cleaved in a vacuum by pealing off with scotch tape. As an independent test the sample was also analyzed in XPS equipment (spot size 600 μm) using the same cleaving procedure. We measured the O 1s XPS spectra of a freshly cleaved surface in different positions, finding a single peak at 528.2 eV. After 24 h in a vacuum of 5×10^{-10} Torr this peak shifted 400 meV to higher binding energies and a shoulder started to grow around 533 eV. It is worth noting that the spectra of uncleaved surfaces are dominated by the high-binding-energy shoulder. Thus we consider sample cleavage in an ultra-high vacuum (UHV) essential for the success of the experiment.

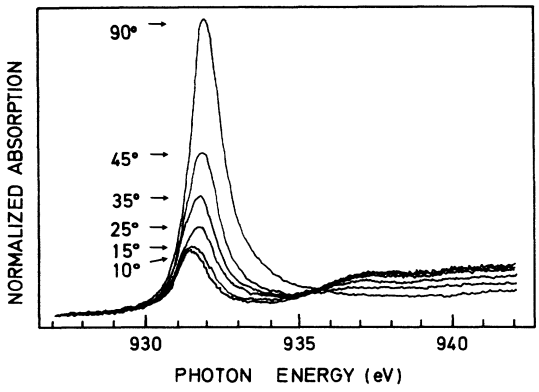

FIG. 1. Polarization-dependent Cu 2p absorption spectra in a $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$ single crystal as a function of the angle θ between the x-ray beam and the surface of the sample. The spectra were normalized to the background below the edge.

III. RESULTS

In Fig. 1 we show the angular dependence of the Cu 2p absorption spectra in $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$. θ denotes the angle between the x-ray beam and the surface of the sample, or equivalently, the angle between the polarization vector of the light and the z axis. The spectra were normalized to the background intensity below the edge with the purpose of comparing the relative intensity of the observed features at different angles. The normal-incidence spectrum ($\mathbf{E}\|xy$ plane) shows a strong peak at 932.0 eV related to transitions of the form $3d^9 \rightarrow 2p^5 3d^{10}$. At grazing incidence ($\mathbf{E}\|z$ axis), this peak becomes much weaker and shifts ~ 500 meV towards lower energies. In addition to the peak, the grazing-incidence spectra also show a steplike feature starting at 935.8 eV.

In Fig. 2 we show the spectra taken at three different angles. In this case the spectra were normalized to the peak intensity for a better comparison of the shape of the peak at different angles and the high-energy step. The full width at half maximum (FWHM) of the peak at normal incidence ($\mathbf{E}\|xy$ plane) is 1.1 eV. As one moves towards grazing-incidence angles this peak starts to broaden, reaching a FWHM of 1.3 eV at 35°. However, a close examination of the shape of the peak at intermediate angles shows that the extra broadening is not uniform, but it is caused by the appearance of a second component at lower energies. Finally at grazing incidence ($\mathbf{E}\|z$ axis), where only the lower-energy z component is present, the FWHM of the peak is 1.1 eV again. We also note that the peak at normal incidence ($\mathbf{E}\|xy$ plane) presents a pronounced asymmetry towards higher energies that is absent in the z-component peak. Finally we call the reader's attention to the rather structured shape of the absorption step, which is more apparent in the spectra taken at grazing incidence ($\mathbf{E}\|z$ axis). In particular we note that this feature, related to higher-energy final states, presents two broad maxima, at 937.6 and 940.7 eV, and is completely polarized along the z axis.

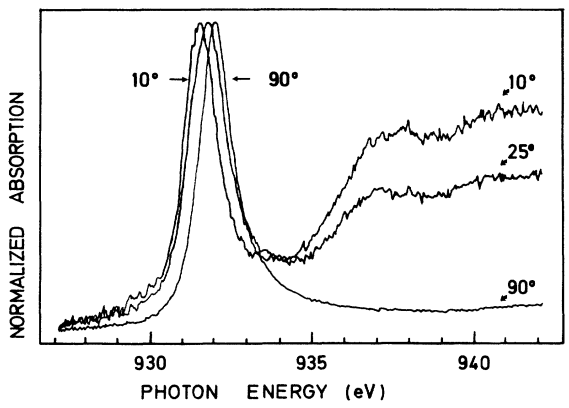

FIG. 2. Cu 2p absorption spectra taken at different angles between the x-ray beam and the surface of the sample; 90°, 25°, and 10°. The spectra were normalized to the peak height.

IV. DISCUSSION

A. Angular dependence of the intensity of the peak and the step

The spectra shown in Fig. 1 were normalized to the background intensity below the edge with the purpose of illustrating the trend in the relative intensity of the peak as a function of the angle of incidence. We note that this normalization procedure is not fully justified. However, we obtain an intensity ratio between the grazing- and normal-incidence peak of 16%, which is in close agreement with the results obtained by Nücker *et al.* for the same material.[11] These authors used EELS, which yields an absolute intensity scale, and reported an intensity ratio of 15%. The observation of strong intensity at normal incidence indicates that most of the Cu holes have $3d(x^2-y^2)$ character. However, the presence of some intensity at grazing incidence suggests that some of the holes at the Cu site are located in $3d(z^2)$ orbitals. Following the same arguments outlined by Nücker *et al.*[11] we note that both Cu $3d(x^2-y^2)$ and $3d(z^2)$ orbitals are reached at normal incidence ($\mathbf{E}\|xy$ plane), with a relative weight of $\frac{1}{2}$ and $\frac{1}{6}$, respectively. On the other hand, only the Cu $3d(z^2)$ orbital is reached at grazing incidence ($\mathbf{E}\|z$ axis), with a relative weight of $\frac{2}{3}$.[22] Taking these facts into account, the intensity of the peak I as a function of the angle θ is given by the following expression:

$$I(\theta) \propto [3I(x^2-y^2)+I(z^2)]\sin^2\theta+4I(z^2)\cos^2\theta \ , \quad (1)$$

where $I(x^2-y^2)$ and $I(z^2)$ are the reduced intensities of the $3d(x^2-y^2)$ and $3d(z^2)$ channels, respectively, which we assume to be proportional to the ground-state hole density in each orbital. Then using Eq. (1) and the relative intensities of the normal- and grazing-incidence peak we estimate that 10% of the holes at the Cu site are located in Cu $3d(z^2)$ orbitals. This estimation is in agreement with the EELS results of Nücker *et al.*[11]

Now we turn our attention to the steplike features observed at higher energies. We note that these features are completely polarized along the z axis, i.e., no step is seen in the spectra taken at normal incidence ($\mathbf{E}\|xy$ plane).

This angular dependence suggests that the step is related to transitions to excited final states polarized along the z axis.

B. Asymmetry of the peak

It is well known that low-energy electron-hole pair creation is the source of divergences and asymmetries in many electronic spectroscopies where the potential experienced by the valence electrons is suddenly changed. In the present case we observe that the peak in the $\mathbf{E}\|xy$ plane spectra, which corresponds to transitions to empty states in Cu $3d(x^2-y^2)$ orbitals, is rather asymmetric. The asymmetry in this case is attributed to the shake-up process in the O $2p_{xy}$ derived band through the hybridization interaction between both orbitals. In contrast, the peak in the $\mathbf{E}\|z$ axis spectra is symmetric because the Cu $3d(z^2)$ orbitals, which are populated in this case, can no longer interact with the O $2p_{xy}$ states. This interpretation of the asymmetry, in terms of shake-up processes in the O $2p_{xy}$ band, was already proposed by Nücer *et al.*[11] to explain the peak asymmetry in the Cu $2p$ absorption spectra of $YBa_2Cu_3O_7$ (where there are O $2p_{xy}$ holes induced by nonstoichiometry) and its absence in the spectra of $YBa_2Cu_3O_6$ (where no O $2p_{xy}$ holes are present).

C. Assignment of the peak

Many high-energy electronic spectroscopies have been used to determine the actual valency of the Cu atoms in the high-T_c superconductors.[9] It is now well established that the lowest-energy charge fluctuation in these materials involves the creation of a ligand hole because the intratomic Cu $3d-3d$ Coulomb interaction is larger than the O $2p-$Cu $3d$ charge-transfer energy.[23–25] Therefore the ground state in these materials is a mixture of $3d^9$ and $3d^{10}\underline{L}$ configurations, where $\underline{L}$ is a ligand hole. In particular, the presence of the $3d^8$ configuration in the ground state of these materials was never observed, within experimental errors, in either XPS or XAS studies.[26] The main peak in the spectra is attributed to transitions from the $3d^9$ initial configuration to a core excitonic $2p^5 3d^{10}$ final state. We note that the $\mathbf{E}\|xy$ plane and the $\mathbf{E}\|z$ axis components of the peak are shifted ~ 500 meV. We will discuss the possible origin of the peak shift below.

D. Assignment of the step

We do not fully understand, at the moment, which are the transitions that give rise to the steplike feature in the spectra taken at grazing incidence ($\mathbf{E}\|z$ axis). In particular transitions to unoccupied Cu $4s$ orbitals cannot be the origin of the step because they are much weaker.[11] In addition such transitions should be also observed in the $\mathbf{E}\|xy$ plane spectra, which is in contrast with the complete polarization along the z axis observed experimentally. Therefore the step is most likely caused by transitions to excited states that are polarized along the z axis. We note that the Cu $3d(z^2)$ orbitals, which are probed in this case, can hybridize with Cu $4p_z$ orbitals located in out-of-plane Cu sites.[27] Therefore we suggest that the main peak in the grazing-incidence spectra ($\mathbf{E}\|z$ axis) should be regarded as transitions to combinations of mostly on-site $3d(z^2)$ character, whereas the step would correspond to transitions to combinations with mostly out-of-plane $4p_z$ character. In contrast, at normal incidence ($\mathbf{E}\|xy$ plane) the spectra show no step because the Cu $3d(x^2-y^2)$ orbitals are hybridized with O $2p_{xy}$ orbitals and the combinations with mostly O $2p$ character are already fully occupied. This assignment, in terms of transitions to low-lying combinations with mostly out-of-plane Cu $4p_z$ character gives the correct angular dependence for the step. It is also worth noting that angular dependent Cu $1s$ absorption studies showed that the $4p_z$ orbitals are below the $4p_{xy}$ states.[29] The same effect is also seen in the angular dependent Cu $1s$ absorption spectra in the different La_2CuO_4 compound.[30] As stated above, we are not completely confident with this interpretation, which should be regarded as tentative. However, we point out that this fact does not invalidate our experimental findings.

E. Origin of the shift in the main peak

The energy shift of the main peak with angle represents a real puzzle because the core excitonic $2p^5 3d^{10}$ final state should be the same regardless of the orientation of the hole that is filled in. Bianconi *et al.*[31] related this shift to the difference in energy between the Cu $3d(x^2-y^2)$ and $3d(z^2)$ holes in the initial state.[31] However, these components (at 932.0 and 931.5 eV) are actually below the Cu $2p$ binding energy measured by XPS (932.6 eV) due to the strong Cu $2p-3d$ potential in the final state. In addition, interaction between the $2p^5 3d^{10}$ and excited configurations in the final state can induce further shifts. Therefore a simple comparison between the peak shift and the position of the unoccupied levels in the unperturbed ground state is not yet justified. In particular we suggest that interaction in the final state with the excited configuration of mostly out-of-plane Cu $4p_z$ character can also contribute to the peak shift in the grazing-incidence spectra ($\mathbf{E}\|z$ axis) and should be included in any quantitative analysis.

V. CONCLUDING REMARKS

In summary, we have investigated the angular dependence of the Cu $2p$ absorption spectra in a $(Bi_{0.84}Pb_{0.16})_2Sr_2CaCu_2O_8$ single crystal. At normal incidence ($\mathbf{E}\|xy$ plane) the spectra shows an intense peak at 932.0 eV, this peak corresponds to core-excitonic transitions of the form $3d^9 \rightarrow 2p^5 3d^{10}$. At grazing incidence ($\mathbf{E}\|z$ axis) the spectra show a much weaker peak shifted ~ 500 meV towards lower energies. The spectra at intermediate angles present a broader peak, which is a combination of the normal and grazing-incidence components. Since the $\mathbf{E}\|xy$ plane peak is more intense than the $\mathbf{E}\|z$ one we conclude that most of the holes at the Cu site are located in $3d(x^2-y^2)$ orbitals. However, we estimate using the intensity ratio between the normal- and grazing-incidence peaks that the holes have 10% of $3d(z^2)$ character. The $\mathbf{E}\|xy$ plane peak, which corre-

sponds to transitions to empty states in Cu $3d(x^2-y^2)$ orbitals, is rather asymmetric due to shake up in the O $2p_{xy}$ derived band. In contrast, the $\mathbf{E}\|z$ axis peak is symmetric because, in this case, the Cu $3d(z^2)$ orbital can no longer interact with the O $2p_{xy}$ band. The origin of the peak shift represents a real puzzle and should not yet be directly interpreted as differences in energy in the initial state. In addition to the main peak, the $\mathbf{E}\|z$ axis spectra show also a rather structured feature starting at 935.8 eV. This steplike edge is completely polarized along the z axis. We do not fully understand which kind of transitions give rise to this step, but we have postulated that it might correspond to transitions to Cu $3d(z^2)$ orbitals that are mixed in with out-of-plane Cu $4p_z$ states.

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[27]This hybridization can be important in this compound. In particular, the distance between both CuO_2 planes is 3.3 Å (from Ref. 28), by comparison the interatomic distance in Cu is 2.4 Å. The hybridization with out-of-plane Cu $3d(z^2)$ orbitals is neglected because, is this case, the hopping integral is much smaller. Finally hydridization with O $2p_z$ orbitals located in the SrO layers is also possible, but in this case, the combinations with mostly O $2p_z$ character are already occupied.

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