

## X-RAY PHOTO-ELECTRON AND AUGER ELECTRON SPECTROSCOPY OF OXYGEN IN $\text{La}_2\text{CuO}_4$

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We have measured the XPS and Auger spectra of oxygen in  $\text{La}_2\text{CuO}_4$ . The experimental XPS and Auger data are compared to fully linearized muffin tin orbital (FLMTO) bandstructure calculations of the valence density of states and the core level shifts. An extended version of Sawatzky-Cini theory for the Auger line shape is used to include multiplet structure of the Auger final states for the point symmetries of the two inequivalent oxygen sites. Experimentally no significant anisotropy is found for the planar and apical oxygen 1s core levels nor for the two-hole spectral function as determined with AES, in contrast with bandstructure calculations.

### 1. EXPERIMENTAL DETAILS AND DISCUSSION

The XPS and AES measurements were done in a UHV chamber with a pressure of  $2 \times 10^{-10}$  mbar during operation of the Al  $k_\alpha$  X-ray anode. The electrons were detected with a hemispherical analyser, operated at constant pass energy. The overall resolution for AES was 0.4 eV, for XPS 1.2 eV. Ceramic samples were scraped, exposed to an ozone jet and transported to the analysis chamber without breaking the ultra-high vacuum. Thin films were prepared with the pulsed laser deposition technique and also transported without exposing the samples to air. A more extensive discussion will appear elsewhere<sup>1</sup>. Some traces of the carbon 1s line could still be detected with XPS; this correlated with the shoulder at 531 eV of the oxygen 1s line, as displayed in Fig.1. Apart from this shoulder the O1s line appeared to be featureless within the instrumental accuracy. LMTTO bandstructure calculations of this compound predict a higher binding energy (1.4 eV) of the planar oxygens (O1) relative to the apical oxygens (O2). This relative shift in the calculated core level positions tracks the calculated average energy of the occupied 2p bands projected at the two inequivalent oxygen sites.

In Fig.2 we present the oxygen KLL Auger spectrum. The threshold of this Auger process corresponds to the 1s binding energy of 528.9 eV, which is the zero of energy for the two-hole excitations in the final state. The  $\text{KL}_1\text{L}_1$  peak corresponds to a final state with two 2s-holes in the final state and equals  $E(2s^2) = 47.1 \pm 0.5$  eV. The 2s binding energy was determined with XPS (see Fig 1b) and equals  $E(2s^1) = 21.2$  eV. The difference  $E(2s^2) - 2E(2s^1) = 4.7 \pm 0.5$  eV corresponds to the on-site Coulomb repulsion in the 2s shell.

The  $\text{KL}_1\text{L}_{2,3}$  peaks correspond to one hole in the 2s shell, and one hole in the 2p valence band. Due to the

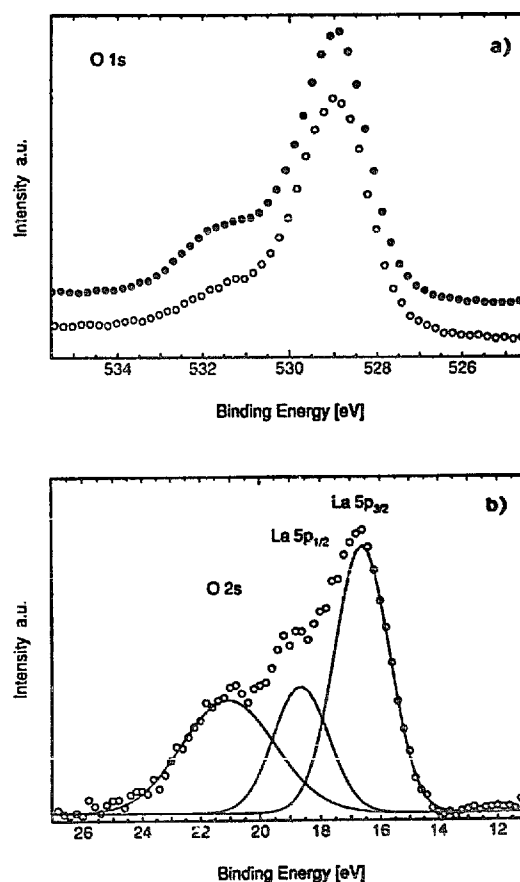


FIGURE 1

(a) XPS spectrum of O 1s. Open circles: Laser ablated film, closed circles: ceramic pellet of  $\text{La}_2\text{CuO}_4$   
(b) XPS spectrum of O 2s, La  $5p_{3/2}$  and La  $5p_{1/2}$ . The solid curves were obtained by fitting three Gaussians.

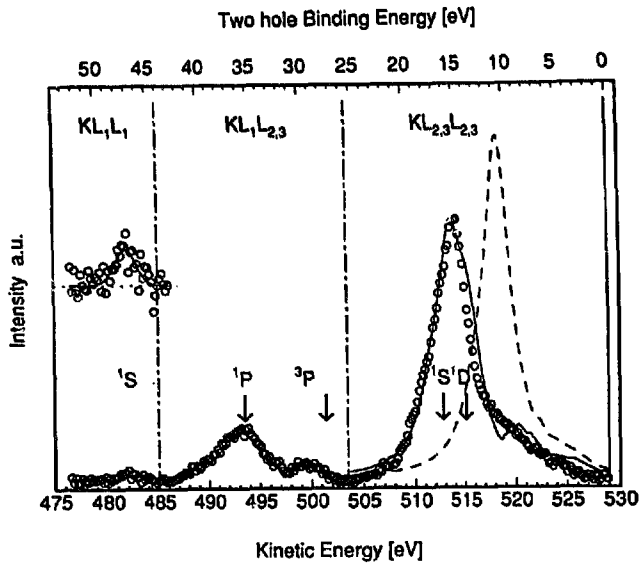


FIGURE 2

Open circles: Experimental oxygen KLL Auger spectrum. Arrows indicate the positions of optically determined  $p^4$  states. The  $1P$  position was adjusted to the Auger spectrum, the other positions were shifted accordingly. Top left: Expanded view of the  $KL_1L_1$  line with a fitted gaussian (solid curve). Righthand side: Theoretical Auger lineshape for the planar (solid) and apical (dashed) oxygen atoms.

Coulomb-exchange interactions one observes two peaks, which are splitt-off from the valence bands, rather than just the oxygen 2p local density of states. In principle we expect some mixing to occur with delocalized valence band states, which will be subject of future research.

The  $KL_{2,3}L_{2,3}$  peak corresponds to two holes in the 2p valence bands occupying the same oxygen site. The line shape can be calculated with a generalized Cini-Sawatzky<sup>2</sup> expression which incorporates crystal field effects and multiplet splitting, starting from the symmetry (*i.e.*  $p_x$ ,  $p_y$  and  $p_z$ ), and site projected DOS. The former was calculated with the FLMTO method<sup>3</sup>. The parameters used are (1) the on-site Coulomb-exchange repulsion  $U$ , and (2) the Slater integral  $F^2$  which determines the multiplet splitting ( $^3P$  (not observed),  $^1D$  and  $^1S$  for a  $p^4$  configuration).  $F^2$  was fixed at the experimental atomic value of 6.2 eV, and  $U(^1D)=F^0+F^2/25$  was used as a fit parameter. A good fit was obtained for the planar oxygens with  $U(^1D)=6.25$  eV (the solid curve in Fig.2). This value of  $U$  is not too far from what we find for the  $2s^2$  Coulomb repulsion, which is an encouraging result. If we calculate the Auger line shape for the apical oxygens with the same method and the same  $U$ , we obtain the dashed curve which is consid-

erably shifted from the experimental curve. Obviously this is not a very satisfactory fit. In a recent paper on Sr and Ba doped  $La_2CuO_4$  Bar-Deroma *et al.* considered the possibility that there is an anisotropy in  $U^4$ . This, however, requires a rather high value of  $U(^1D)$  for the apical oxygens. A possibility that is consistent both with the observed absence of a difference in core level binding energies for the two types of oxygen and the absence of a splitting of the Auger lines, would be that in the bandstructure calculations the difference in the positions of the valence band at the two inequivalent oxygen sites of the calculated densities of states is over-estimated. An occupied density of states at the apical oxygens that has its centroid shifted toward higher binding energy by  $\pm 1.7$  eV would account for the observed differences. As the core level energies track the occupied 2p DOS this would probably also remove the core-level anisotropy obtained in the bandstructure calculations. A remedy could be a relative shift of the background potential at the oxygen sites.

## 2. CONCLUSIONS

We studied XPS and Auger spectra of oxygen in  $La_2CuO_4$  ceramic and laser ablated samples. From the observed absence of a difference in binding energy of the 1s level for the O1 and O2 oxygen sites, as well as from an analysis of the oxygen  $KL_{2,3}L_{2,3}$  Auger lines, we conclude that there is an inconsistency when comparing these results to fully fledged LMTD bandstructure calculations of the same compound. A remedy is proposed that would remove the inconsistency.

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