Unoccupied electronic states of CuO: An oxygen 1s x-ray-absorption spectroscopy investigation

M. Grioni
Research Institute of Materials, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands and Laboratoire pour l'Utilisation du Rayonnement Electromagnetique, Bâtiment 209D, Universite de Paris–Sud, F-91405 Orsay CEDEX, France

M. T. Czyzyk, F. M. F. de Groot, and J. C. Fuggle
Research Institute of Materials, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

B. E. Watts
Department of Physics, Clarendon Laboratory, Oxford University, Oxford OX1 3PU, United Kingdom
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In this article we compare the experimental O 1s x-ray-absorption (XAS) spectrum of CuO with the results of an augmented-localized-spherical-wave (ALSW) calculation with an extended basis set. By extending the basis set in the calculation, we obtain a good overall agreement between experiment and the O 2p unoccupied density of states. Discrepancies in the predicted energy position and intensity of the sharp leading feature in the XAS spectrum are briefly discussed in terms of the core-hole potential, self-energies, and hybridization.

I. INTRODUCTION

Copper monoxide, CuO, has interesting physical and structural properties. It is an antiferromagnetic semiconductor [$E_{gap}=1.4$ eV, $T_{Néel}=230$ K (Refs. 1–4)] where copper atoms are arranged in a characteristic square-planar coordination with oxygen atoms. This local coordination, which it shares with compounds of the class $YBa_2Cu_3O_{7-x}$, together with the fact that reliable, single-crystal samples can be prepared, now makes CuO particularly attractive as a model system to investigate the electronic structure of the recently discovered Cu-based high-T_c superconductors.

CuO itself has been extensively studied with high-energy spectroscopies,[5–14] and the presence of intense satellites at the Cu 2p core lines and in the valence-band x-ray photoemission spectroscopy (XPS),[7] ultraviolet photoemission spectroscopy (UPS),[8] and resonant photoemission[9] spectra, as well as Auger spectra,[14] have all been recognized as manifestations of strong electron correlation within the narrow d band. On the basis of spectroscopic results, the Cu d electron count in CuO was estimated to be 9.4,[13,15] in contrast to the value of 9.0 which is expected in a purely ionic model.

By contrast to the experimental situation, computations of the CuO band structure are only just becoming available, because of difficulties intrinsic to the description of the open d-shell configuration of Cu II, and to the rather complicated crystal structure. As a consequence of the strong correlation effects, theoretical work relating to high-energy spectroscopy and the electronic structure of CuO has generally utilized the Anderson impurity model,[16–19] but it is clearly desirable to contrast the experimental data with *ab initio* calculations that do not require adjustable parameters. Recently, one of us (M.T.C.) has performed band-structure calculations for both CuO and Cu_2O.[20] The results of these calculations have been compared with UPS, XPS, and bremsstrahlung isochromat spectroscopy (BIS) measurements in Ref. 21. Here we address the problem of the unoccupied states in CuO and we compare those results with the experimental O 1s XAS spectrum.

XAS spectra are related to the site and symmetry-selected density of states (DOS). The O 1s spectral data is particularly useful because it is closely related to the partial density of empty O 2p states at the oxygen site and these states are believed to be crucial to superconductivity in the new high-T_c superconductors.[22,23] Moreover, comparison of the calculated DOS with the O 1s XAS to high energies above E_F, is a good test of the extensions introduced in the computational scheme (see below). Finally, discrepancies between experiment and the predictions of one-particle theory can help to identify the effects of electron correlation in this system. The Cu $L_{2,3}$ edges are not considered here because, as we have shown in Ref. 24, they are dominated by excitonic effects which, at this stage, are not included in the calculation.

II. EXPERIMENTAL

The experiment was carried out at the Berliner Elektronenspeicherring-Gesellschaft Für Synchrotronstrahlung m.b.H. (BESSY) storage ring. Synchrotron radiation was monochromatized by the SX-700 plane grating monochromator[25] and spectra were collected in the total electron yield mode in an ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-9} torr. The experimental broadening could be closely simulated with a Lorentzian of 0.6 eV full width at half maximum.[25] Contamination of the optics was checked by collecting total yield spectra of a clean copper sample in the same spectral region, and it was found to contribute a broad and

shallow feature (3% of total throughout) with negligible effects on the measured O 1*s* spectra. The CuO sample was a single crystal with a surface of approximately 3×3 mm^2 grown in Oxford. A clean surface was prepared *in situ* by filing with an Al_2O_3 scraper. Comparison of the measured spectra with the O 1*s* spectrum of Al_2O_3 confirmed *a posteriori* the absence of contamination from the scraper.

III. THEORY

Band-structure calculations were performed in the augmented-localized-spherical-wave (ALSW) method with an extended basis set.[20] In this method, the idea of the most-localized muffin-tin orbitals (LMTO) of Andersen and Jepsen[26] and Andersen *et al.*[27] was adopted for the augmented spherical-wave (ASW) method of Williams *et al.*[28] In order to describe the XAS spectra in the energy range higher than the first few electronvolts above the absorption edge, we found it necessary to go beyond the minimal basis set (one SW per *l* quantum value and site) employed by the standard ASW (or LMTO) method. This basis set was extended by adding (optionally) a second SW per *l* site with the number of nodes in the augmenting function incremented by one with respect to the SW already in use. This process possesses the feature of the energy paneling approach in the linear augmented plane wave (LAPW), LMTO, or ASW methods, but actually without the paneling and without the disadvantages created by that process. The method was reimplemented for vector processing on supercomputers. We used the scalar-relativistic Hamiltonian (spin-orbit interaction not included) and exchange and correlation effects were treated in the local density approximation using the Hedin and Lundqvist parametrization.[29] The self-consistent calculation was carried out including all core electrons.

IV. RESULTS AND DISCUSSION

In Figs. 1 and 2 we show the calculated DOS and its various *l* components projected on the oxygen and copper sites, respectively. Note the different scales of the vertical axes. The most relevant states are the Cu 3*d* and the O 2*p* states, although the Cu 4*s* and 4*p* states should not be neglected. Structures occur in the Cu and in the O partial DOS at the same energies, and this is a good indication that hybridization must play an important role in the CuO. The orbital occupation numbers, obtained by integrating up to E_F the partial DOS's of Figs. 1 and 2, are reported in Table I. In the interpretation of these numbers one should be aware of the fact that the projection is made on atomiclike wave functions. The calculated numbers are somewhat dependent on the actual choice of the atomic radii. Approximately 0.8 electrons per formula unit lie outside the chosen atomic spheres. The results of Table I should be contrasted with the purely ionic configuration Cu $3d^9$ O $2p^6$. The O 2*p* shell, with 4.5 electrons per atom, is clearly not full, and ambiguities in the analysis are insufficient to change the conclusion that CuO is not highly ionic. If we allocate about one half of the "interstitial" electrons to the oxygen, we must still as-

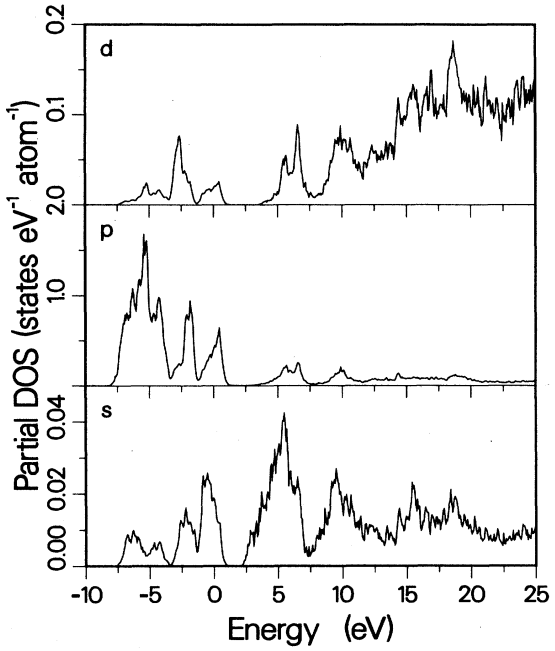

FIG. 1. Calculated partial densities of states at the oxygen site. The zero of the energy is the Fermi level.

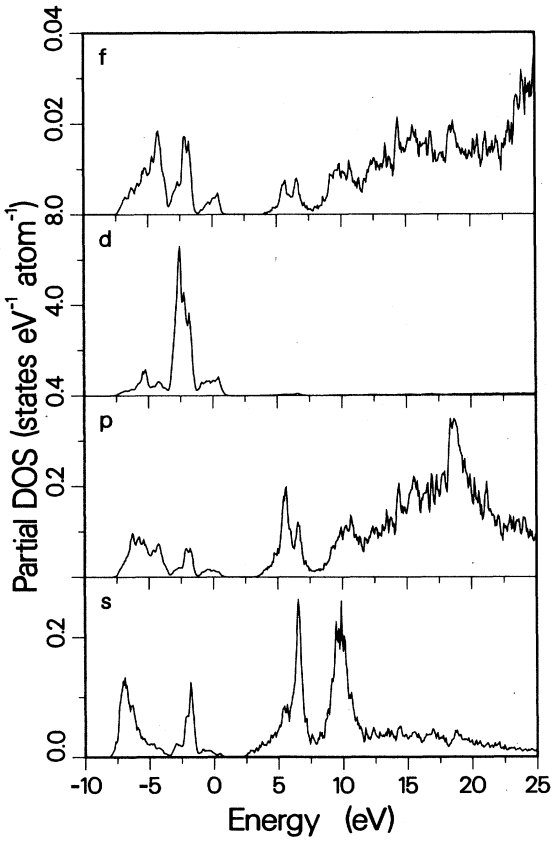

FIG. 2. Calculated partial densities of states at the copper site. The zero of the energy is the Fermi level.

TABLE I. The orbital occupation numbers.

	1 character	Integrated charge to E_F
Cu	s	0.34
	p	0.35
	d	8.95
	f	0.06
	total	9.70
O	s	1.84
	p	4.54
	d	0.13
	total	6.51
Interstitial		0.80

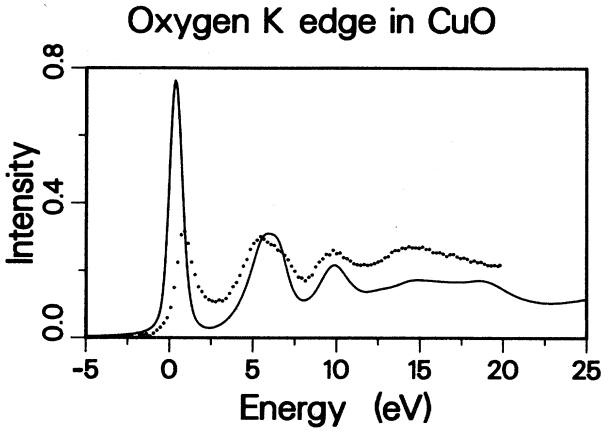

FIG. 3. Experimental (dots) and calculated (solid line) O 1s spectrum. The intensity units are arbitrary.

sume that about 1.1 O 2p states per atom are empty and are spread into states up to 15 eV above E_F. A number of 1.1 empty O states implies less than 50% ionic character, but this is not in disagreement with other indications. For instance, interpretation of core-level spectra of CuO using an Anderson impurity approach, suggests 9.4 d electrons per Cu atom, which implies 0.4 holes per O atom, even before Cu 4s and 4p bands are considered.[15] The low d electron count, and the presence of a total of 0.7 electrons in the Cu 4s and 4p states indicates that hybridization between these states and the Cu d bands is not negligible.

The experimental gap of 1.4 eV does not appear in the calculated DOS, and the Fermi level is straddled by partially filled bands of mixed Cu "d" and O "p" character. This is typical for a local-density approximation (LDA) calculation of transition metal (TM) oxides where the atomic correlations make a significant contribution to the self-energy and are not explicitly treated. The nature of the unoccupied states can be illustrated with the nature of the states in a square-planar CuO_4^{6-} cluster. The lowest-lying unoccupied states can be construed as the solid-state version of the half-filled $b1g$ (x^2-y^2) molecular orbital and therefore represent σ antibonding combinations of Cu "d" and O "p" orbitals. We observe that some "d" character is spread out over a wide energy range above E_F, contributing approximately 0.4 electrons within 15 eV of E_F.

Above the first unoccupied band with its mixture of Cu d and O p character, we observe a gap of 1.5 eV both in the O and Cu DOS. Above this gap the calculation yields two structures: A centered at 6 eV and B at around 10 eV, which would be equivalent to the $2a_{1g}$ and $3e_u$ molecular orbitals (MO's) for the CuO_4^{6-} cluster. We notice that, unlike their MO counterpart, both A and B have mixed 4s, 4p, and 3d character at the Cu site, and mixed p and d character at the oxygen site. Above 10 eV the electronic states have mostly O p-d and Cu s-p character.

The experimental O 1s XAS is compared with the calculated O 2p DOS in Fig. 3. The calculated O 2p DOS has been broadened with a $0.3+0.10(E-E_F)$ eV Lorentzian and a Gaussian broadening of 0.5 eV to account for the core-hole lifetime and the experimental resolution, and the two curves have been aligned to give the best overall match. There is a good general agreement between the XAS spectrum and the calculated O p DOS, which predicts a sharp leading peak A, and the occurrence of the following structures B and C at 6 and 10 eV, and of the shoulder at 14 eV in the experimental spectrum. It is interesting to notice in particular that the overall shape of the XAS spectrum is well reproduced by the calculated O p DOS, without the need to introduce extra (excitonic) peaks, as was suggested in Ref. 11. Such good agreement could not be achieved without the extension of the basis set described above.

There are, however, some discrepancies that concern, in particular, peak A, which is misplaced by approximately 0.5 eV and whose calculated intensity with respect to the higher-energy structures is about 1.8 times larger than the experimental value. Also, the calculation does not reproduce well the asymmetry of peak B and the decrease of intensity above 15 eV.

Differences between the experimental O 1s XAS spectrum and the calculated O 2p DOS can be attributed to a combination of the core-hole potential and single-particle matrix elements (i.e., the cross section per empty state). The most direct way to estimate the importance of the core-hole potential is to compare XAS and BIS, where no core holes are present. The BIS spectrum, calculated on the basis of the same DOS's of Figs. 1 and 2, was shown in Ref. 21 to give an excellent fit to the experimental data, *except* for a shift of the leading peak of the same magnitude as that observed in the XAS spectrum. We may then argue that the introduction of core-hole effects in our model could possibly improve the quality of the fit to the experimental XAS spectrum but that it would not remove the discrepancy between the measured and the predicted width of the gap between A and B. We rather attribute the observed shift to the one-particle treatment of exchange and correlation in our calculations. Similar effects are quite common in comparison of the calculated DOS with spectra of transition-metal compounds, and have been observed for occupied[11,30–32] and empty states.[33,34] Only a complete evaluation of self-energy

corrections could reconcile theory and experiment over this point.

The relative intensity of the various features in the calculated XAS spectrum will almost certainly be affected by the presence of the core-hole potential. In the absence of a calculation, and by analogy with results on related systems,[35] we can speculate that the effect of the core hole will be a shift towards E_F of spectral weight in the O 1s spectrum. In fact, some empty O p states could be pulled below the Fermi level. This would reduce the predicted intensity of peak A and possibly enhance the asymmetry of peak B. Moreover, single-particle matrix-elements effects could further modify intensities in the calculated spectrum.[36] However, there are reasons to believe that relative weight of O p character in peak A is dependent on its energy with respect to the O 2p centroid and the shift of its position due to atomic correlation effects on the Cu site (this is the leading term in the self-energy) has an indirect effect on the O 2p weight. Overestimation of the p-d hybridization in the final state may then be the cause of the excessive intensity in peak A in the calculated spectrum of Fig. 2.

V. CONCLUDING REMARKS

We have used a combination of O 1s spectra and computed density of states to study the distribution of empty O p character in the unoccupied states of CuO. We note that there is interesting structure in the unoccupied states up to at least 15 eV above E_F, and this necessitates extension of the ALSW basis set before satisfactory comparison between theory and experiment is possible. For states more than 5 eV above E_F there is a good agreement between the broadened partial DOS and the observed XAS spectrum, both with respect to peak positions, and their general shape. There are about 1.1 O 2p electron states per O atom in the region up to 15 eV above E_F, which indicates a large covalent component in bonding in CuO. Both the O 1s XAS and the calculated DOS show a peak close to E_F, but the precise energy and position of the peak are not well reproduced by the computations because the Cu 3d-3d atomic correlation contribution to the self-energy is not fully treated.

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