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## X-ray absorption near-edge structure of CuInSe<sub>2</sub> crystals

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**Abstract.** X-ray absorption near edge structure (XANES) spectra of CuInSe<sub>2</sub> crystals have been measured at the K edges of Cu and Se, the L<sub>1</sub> edge of In and the L<sub>3</sub> edges of all three elements. The spectra are interpreted using the band structure approach and the self-consistent real-space multiple-scattering approach. Angular momentum projected local densities of one-electron states in the conduction band up to 17 eV above the conduction band minimum have been calculated by the LMTO method. Spectral features in the experimental spectra have been correlated with the structures in the partial densities of states. The contribution of the different atomic states to the conduction band is discussed. The core-hole effect in the XANES spectra of CuInSe<sub>2</sub> is evaluated on the basis of the multiple-scattering calculations.

### 1. Introduction

X-ray absorption spectroscopy provides a well established tool for studying both atomic and electronic structure of solid state. It involves XANES (x-ray-absorption near edge structure) and the EXAFS (extended x-ray-absorption fine structure) investigations, covering different energy ranges of excited electrons: below ~50 eV for XANES and beyond this region up to several hundreds of eV for EXAFS.

EXAFS is mostly determined by the local geometry of the absorbing atom, i.e. the distance to and number of atoms in adjacent shells. It corresponds to scattering (usually single-scattering events) of almost free electrons on neighbouring atoms.

XANES is sensitive to both the geometrical arrangement of atoms as well as the local electronic structure. XANES spectra are interpreted in the multiple-scattering approach [1] or alternatively by the band structure description [2]. In many cases XANES can be related to the unoccupied portion of a local electron density of states (LDOS) taken as a ground state density, in spite of the fact that the core hole is created in the transition process. This approach has been found to work for metals and semiconductors (e.g. [2], [3]). Since dipole transitions dominate the x-ray absorption process, excitation of a core state with the orbital angular momentum number  $l$  probes the  $l \pm 1$  components of the conduction band (CB). Thus, XANES investigated on the K (or L<sub>1</sub>) edge of an element probes a density of empty p-like electronic states around the absorbing atom. L<sub>2,3</sub>-edge XANES gives information about s- and d-like local density of states. These rules can be somewhat relaxed depending on the actual site symmetry of the absorbing atom [4]. In tetrahedral site symmetry, p and d orbitals can hybridize. This allows transitions from a 1s core level to bands with almost pure d character due to the small p hybridization.

Copper based ternary compounds with chalcopyrite structure have been the subject of intense studies for at least two decades now. The most important material of this group is CuInSe<sub>2</sub>, one of the best absorbers used in thin film solar cells (over 18% efficiency achieved). The band structure of CuInSe<sub>2</sub> was calculated by Jaffe and Zunger [5, 6]. The x-ray absorption spectra of CuInSe<sub>2</sub> have been reported in a number of papers: EXAFS [7–9] and XANES [10–12]. However, only a few absorption edges have been examined and no comparison to band structure calculations has been made. Among other Cu–III–VI<sub>2</sub> compounds, the prototype of the whole family, chalcopyrite itself—CuFeS<sub>2</sub> [4, 13], CuGaSe<sub>2</sub> [14], CuGaS<sub>2</sub> and some other sulphides [11, 15] have been the subject of XANES investigations.

In this paper we present the XANES spectra for CuInSe<sub>2</sub> crystals representing a complete set of partial local densities of states in the conduction band (s-, p- and d-like LDOS). The theoretical LDOS curves were calculated by the LMTO method. Alternatively, the XANES is calculated within the real-space multiple-scattering approach.

## 2. Experiment

Crystals of CuInSe<sub>2</sub> have been grown by the gradient freeze method from nearly stoichiometric melt with a slight excess of selenium at the Faculty of Physics of Warsaw University of Technology. We measured also x-ray absorption on crystals from other sources obtaining the same results.

Measurements of x-ray absorption have been carried out at two synchrotron facilities. High energy edges (K edges of Cu, Se and L<sub>1</sub> and L<sub>3</sub> edges of In) were measured at HASYLAB, Hamburg and low energy edges (L<sub>3</sub>/L<sub>2</sub> edges of Cu and Se) at LURE, Orsay. Measurements at HASYLAB were performed in the transmission mode at the A1 station with a four crystal monochromator (energy resolution at 12 keV was about 0.5 eV). Powdered crystals were glued on adhesive tape for this experiment. The total yield method was employed for registration of L<sub>3</sub>/L<sub>2</sub> edges at the SU 22 beamline of the SuperACO storage ring at LURE, equipped with a beryl monochromator. Instrumental energy resolution was 0.35 eV for the Cu L<sub>3</sub> edge and 0.5 eV for Se L<sub>3</sub> edge. Single crystals with carefully prepared surfaces to avoid oxide layers were used for the measurements of low energy edges. Since the crystals were not oriented, no polarization dependence was studied. No differences of the spectra measured on different samples with arbitrary surface orientations have been noted.

## 3. Band structure calculations

The literature on the band structure calculations of CuInSe<sub>2</sub>, including the papers of Jaffe and Zunger [5, 6] fundamental for the subject, does not deal much with the conduction band of this compound, apart from the states near the CB minimum. In the course of the present study we had available calculations of Wei and Zunger [16] encompassing first 7 eV of the CB. Since for the XANES interpretation one needs even higher energy bands we decided to calculate the CB LDOS up to 17 eV, using the linear muffin-tin orbital (LMTO) method [17].

The band structure is calculated for a muffin-tin potential within the atomic sphere approximation (ASA). The calculation is started with geometrical definitions. The space group is  $I\bar{4}2d$  with the lattice parameters  $a = 10.44$  au and  $c = 21.02$  au and the atom positions Cu(0, 0, 0), In(0, 0, 1/2) and Se(0.235, 1/4, 1/8) are assumed. In order to reduce the interstitial region, two empty spheres have been added at the positions E1(1/2, 0, 0) and E2(1/4, 0.235, 1/8). The Wigner–Seitz radii for the atomic and empty spheres are the

following:  $R_{\text{Cu}} = 2.60$  au,  $R_{\text{In}} = 2.81$  au,  $R_{\text{Se}} = 2.73$  au,  $R_{E1} = 2.73$  au and  $R_{E2} = 2.60$  au. These values satisfy the criterion  $(R_i + R_j)/d(i, j) < 1.15$  ( $R_i + R_j$  are muffin-tin radii around atoms  $i$  and  $j$ , and  $d(i, j)$  is the atom distance), so the sphere overlap does not exceed 15%. The  $l$  expansion is truncated to  $l = 2$  in the copper, sulphur and empty spheres and to  $l = 3$  in the indium spheres. It seems to be a reasonable choice for energies not exceeding 1 Rydberg above the CB minimum. The potential has been generated self-consistently for the unit cell containing 16 muffin-tin non-equivalent spheres (two Cu, two In, four Se and eight empty spheres). After full convergence of the band structure has been obtained, the density of occupied and empty states was calculated with the tetrahedra method. The total number of  $k$  points is 65 536 and the number of tetrahedra 393 216, and use of the symmetry has been made to reduce the calculation to the irreducible wedge of the Brillouin zone. Finally, the density of empty states localized on a specific atom and with a given orbital momentum (LDOS) has been calculated.

## 4. Results and discussion

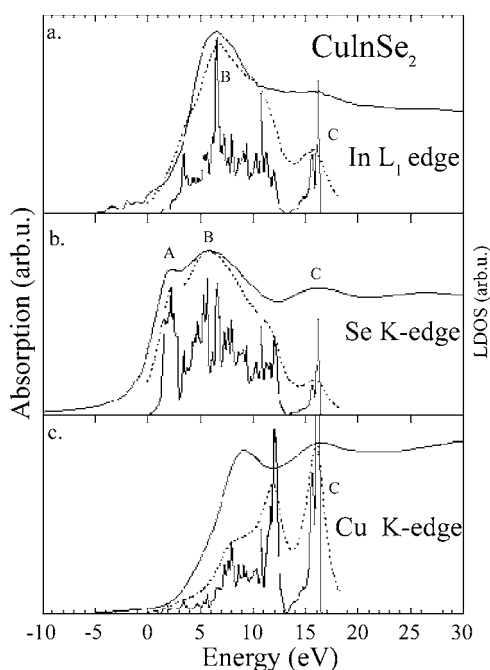
### 4.1. Band structure approach

An extrapolated pre-edge background has been subtracted from the measured x-ray absorption and the spectra have been normalized to a unit edge jump. On the energy axis, the experimental spectra have been aligned with the theoretical LDOS curves to give the best overall match. The origin of the energy scale is at zero energy of the LDOS plot and coincides with the Fermi energy. The LDOS curves are presented as the raw data and as Gaussian broadened plots. The broadening parameter used in the procedure had the values: 1.65 eV (Cu), 2.25 eV (Se) and 2.7 eV (In) for the **p** LDOS, and 0.63 eV (Cu), 2.2 eV (Se) and 2.55 (In) for the weighted **s + d** LDOS. These values are close to the core-hole lifetime broadening for appropriate edges given in [18], apart from the In  $L_1$  edge parameter, which is 5 eV according to [18]. Broadening of the indium p-like LDOS with such a parameter smears out all details of the plot including those corresponding to the features observed in the experimental  $L_1$  edge.

*4.1.1.  $L_1$  edge of In and K edges of Se and Cu.* Figure 1 shows the  $L_1$  edge of In and the K edges of Se and Cu in  $\text{CuInSe}_2$ , compared to the local p-like densities of states in the CB. The absolute positions of the edges taken at the inflection points of the rising part of the spectra are: 4239 eV for the  $L_1$  edge of In, 12 653 eV for the Se K edge and 8979 eV for the K edge of Cu.

The positions of the main resonances in the indium  $L_1$  and selenium K spectra are in agreement with the broadened LDOS plots. The theoretical curves do not reproduce the absorption plateau above 12 eV. The reason is a limited basis set of the LMTO calculation.

The main maximum of the indium  $L_1$  spectrum corresponds to a strong maximum at 6.5 eV in the In p-like LDOS (peak B). It coincides with analogous maxima in the Se p-like and d-like LDOS (see also figure 2) and is assigned to hybridized In(p) + Se(p, d) states. The first maximum of the K-edge spectrum of selenium coincides with a strong maximum in the Se p-like LDOS at 2.2 eV (feature A) that has its equivalents in LDOS of In (s-like) and Cu (d-like). The structure corresponds to hybridized In(s) + Se(p) states with some admixture of Cu d states. This is a manifestation of the anti-bonding counterpart of the In–Se bonding states located 6 eV below the valence band maximum [5]. This confirms that the bottom of the conduction band in  $\text{CuInSe}_2$  is built mainly from In s states with a significant amount of Se p-like states [5]. Copper p-like states can be found at higher energies (>3 eV) in the CB.



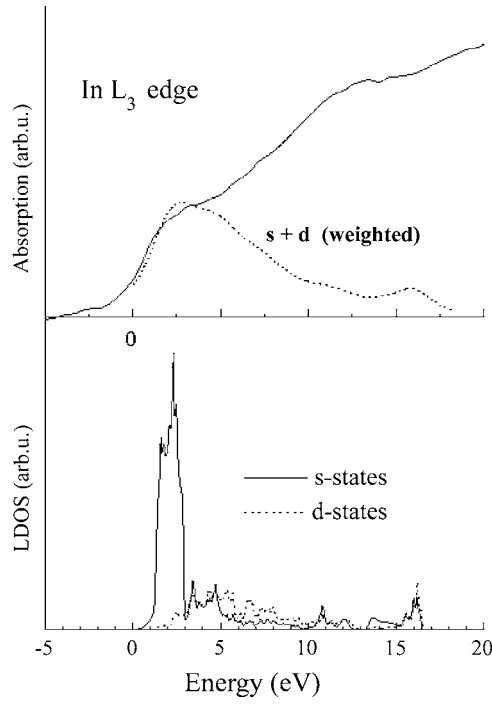
**Figure 1.** X-ray absorption  $L_1$  edge of In and K edges of Se and Cu and the p-like LDOS curves: the raw data (thin solid line) and the broadened LDOS (dashed line).

Our LMTO calculations do not reproduce the K edge of Cu properly. The first strong maximum in LDOS has too high an energy as compared to the main maximum in the experimental curve. The most likely reason for this is the neglect of core-hole effects in the LDOS calculation. We will return to this point while discussing the multiple-scattering approach.

Common for all three p-like spectra (figure 1) but present also in the Se  $L_3$  edge (figure 2) is a maximum at  $\sim 16$  eV correlated with strong features (C) in the corresponding LDOS curves.

The absolute position of the x-ray absorption edge depends on the charge state of an absorbing atom and is used to determine bond ionicity. Determination of an absolute position requires use of standards. An interesting method of the spectra analysis for the evaluation of the formal valence of Cu was developed for copper compounds by Alp *et al* [19]. It is based on the analysis of the energy moments of Cu K-edge spectra. The authors found correlation of the characteristic energy parameter  $S$  calculated from the two first moments and the Cu valence. Using the same method, we found the  $S$  value to be between 3.2 and 3.5, which corresponds to the formal valence  $\text{Cu}^+$  in agreement with results of Deshpande *et al* [20].

**4.1.2.  $L_3$ -edges: transition probabilities.**  $L_2$  and  $L_3$  edges correspond to transitions from spin-orbit split 2p core states to s- and d-like local densities of unoccupied states. The differences between  $L_2$  and  $L_3$  edges result from the interelectronic Coulomb repulsion and the spin-orbit coupling acting on the orbitals that receive the photoelectron in the final state. These effects are small in  $\text{Cu}^+$ ,  $\text{Se}^{2-}$  and  $\text{In}^{3+}$ , so that the  $L_2$  edge of any of these elements is essentially similar to the  $L_3$  one, except for its intensity, that is reduced by two, in the statistic ratio. Since the  $L_2$  edge appears on the absorption background from  $L_3$  edge transitions, we concentrated on the  $L_3$  edge.



**Figure 2.** L<sub>3</sub> edge of In and the corresponding LDOS curves: s like—solid line and d like—dotted line, the weighted sum of both—dashed line.

The x-ray absorption coefficient due to transitions from a core state  $c = (n, l, j)$  is given in the dipole approximation by the formula [2, 3]

$$\mu(E) = \frac{2(2j+1)\pi^2 e^2 v}{(2l+1)c\hbar\Omega} \left[ \frac{l}{2l-1} f_{c,l-1}(E) + \frac{l+1}{2l+3} f_{c,l+1}(E) \right] \quad (1)$$

where  $\Omega$  is the primitive cell volume,  $v$  is the number of atoms in the primitive cell and

$$f_{c,l} = r_{c,l}^2(E) N_l(E) \quad (2)$$

$r_{c,l}$  is the dipole transition matrix element,  $N_l$  is the partial density of states.

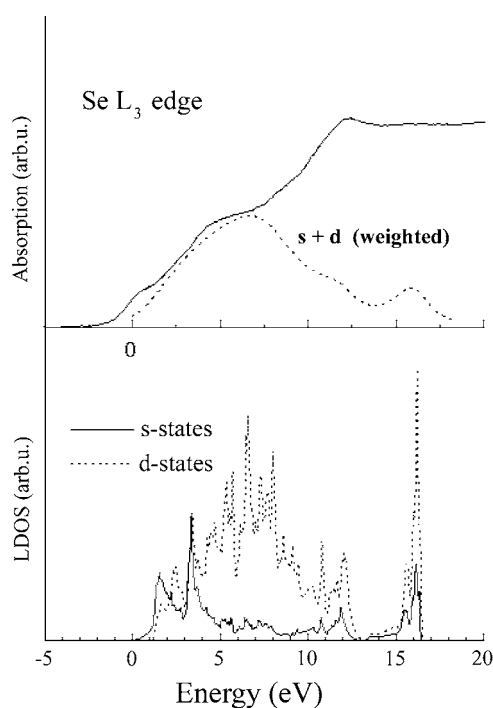
For the L<sub>3</sub> edge we have  $l = 1$  and

$$\mu \propto (r_{10})^2 N_s + \frac{2}{3} (r_{12})^2 N_d \quad (3)$$

where  $N_s$  and  $N_d$  are the partial densities of states (LDOS) for s and d states, respectively.

Transitions to s-like states have smaller dipole matrix element and are usually neglected in L<sub>3</sub>-edge analysis. In order to estimate their contribution to the L<sub>3</sub> spectra, the corrected ratio of the squared radial matrix elements for the  $2p \rightarrow nd$  and  $2p \rightarrow ns$  transitions  $x = 0.4(r_{12}/r_{10})^2$  has been calculated using the Cowan multiplet atom model [21]. It represents the relative contribution of the partial densities of states  $N_d$  and  $N_s$  to the L<sub>3</sub> absorption spectrum. An assumption has been made that the matrix elements are energy independent. The calculation of  $x$  requires a defined electronic configuration of both the initial and final state of an atom which depends on its charge state and consequently the bond ionicity.

For copper in CuInSe<sub>2</sub> we assumed charge state Cu<sup>+</sup> and a completely filled 3d shell. The resulting transition probability ratio  $x$  is 1.4.



**Figure 3.**  $L_3$  edge of Se and the corresponding LDOS curves: s like—solid line and d like—dotted line, the weighted sum of both—dashed line.

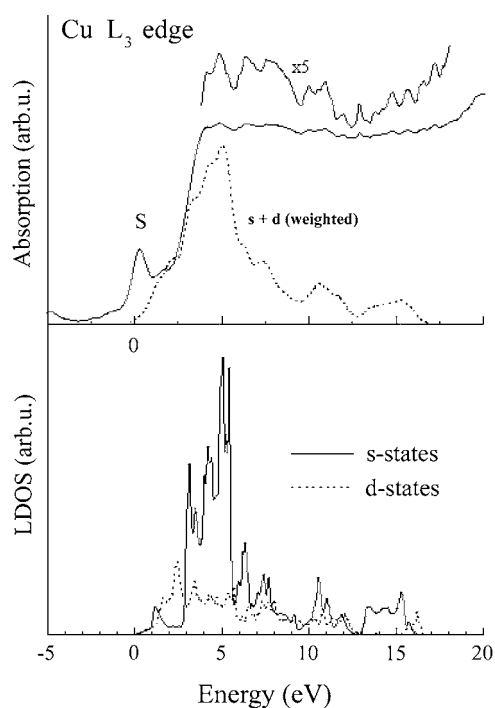
For indium, depending on the assumed charge state (+1, +2, +3), we obtained the  $x$  values 22, 8.8 and 9.2 respectively. This means that for comparable magnitudes of  $N_s$  and  $N_d$ , transitions to s states of In are negligible compared to transitions to d states in any of these charge states. However, for much higher s-like density, which is the case for the In LDOS in the 1–3 eV range, it affects the XANES at the In  $L_3$  edge.

For selenium the  $x$  values are 14.4 and 3.1 for the  $\text{Se}^-$  and  $\text{Se}^{2-}$  charge states respectively. Taking into account that the Se s-like LDOS in  $\text{CuInSe}_2$  does not exceed the d-like one, this means that the former has negligible effect on the XANES at the  $L_3$  edge of Se. Concluding these remarks, we may say that for the  $L_3$  edges in  $\text{CuInSe}_2$  only the Se spectrum is determined almost exclusively by the d-like densities of states. For In and Cu both s- and d-like LDOS influence the absorption curves. The s-like LDOS curves presented in figure 2–4 have been reduced to account for the discussed probability ratios ( $x$ ) taken for the following charge states:  $\text{Cu}^+$ ,  $\text{In}^{3+}$  and  $\text{Se}^{2-}$ .

**4.1.3.  $L_3$  edges: results.** The  $L_3$ -edge spectra of In, Se and Cu compared with the weighted sum of s- and d-like LDOSs are shown in figure 2–4. The raw LDOS data are also presented. The absolute positions of the edges determined from the experiment are 3731 eV for In, 1421 eV for Se and 930 eV for Cu.

The combined LDOS reproduces approximately only the position of the main features of the spectra. It fails to reproduce the absorption step intensity. This is due to limitations of our LMTO calculations.

An absorption rise in the first portion of the In edge and a broad maximum around 2 eV correspond to a strong maximum in the In s-like LDOS (A feature), and are due to the 5s states



**Figure 4.**  $L_3$  edge of Cu and the corresponding LDOS curves: s like—solid line and d like—dotted line, the weighted sum of both—dashed line.

of indium hybridized with Se 4p states. The higher energy features correspond to the d-like bands which exhibit some p–d hybridization and are also hybridized with the Se p–d states.

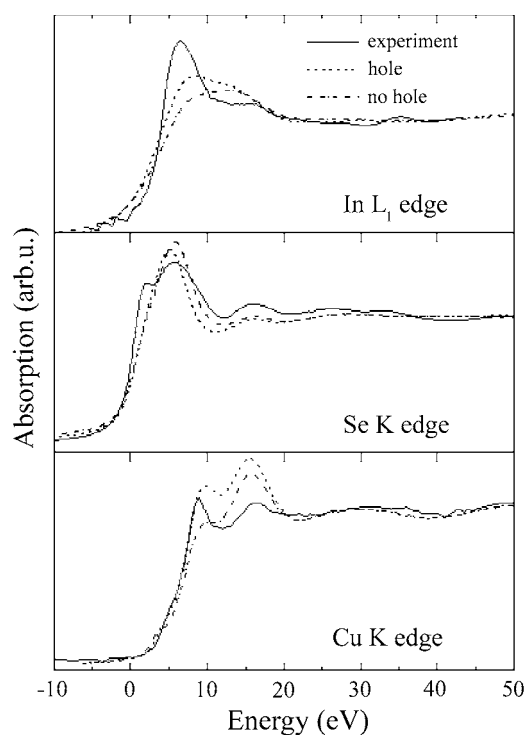
The  $L_3$  edge of Se (figure 3) reflects the contribution of the selenium 4d density of states to the CB.

The  $L_3$  edge of Cu is presented in figure 4. We consider the first peak (S) observed in the pre-edge region to be a spurious feature due to traces of CuO on the surface of a  $\text{CuInSe}_2$  crystal. It corresponds to transitions to the unfilled 3d states and has a very large oscillator strength, so even a small amount of CuO results in a visible spectral feature in XANES. Its magnitude changes from sample to sample. The  $L_3$ -edge spectrum of copper is determined by the s- and d-like densities of states. The admixture of Cu 3d states to the conduction band is the result of 3d–4s hybridization as suggested by Grioni *et al* [12]. The absorption rise at the  $L_3$  edge is due to the d states hybridized with the anti-bonding In–Se orbital. The spectral features in the 3 to 6 eV range are mostly due to the copper 4s-state LDOS that dominates here even after the reduction by the relevant transition probability ratio.

#### 4.2. Real-space multiple-scattering approach

Theoretical calculations of the XANES spectra within the real-space multiple-scattering approach have been performed using an *ab initio* FEFF8 code [1]. The approach is based on a cluster calculation of the single-particle Green function. The scattering potentials are calculated self-consistently in the muffin-tin approximation. The Hedin–Lundquist exchange correlation potential was used. Coordinates of 231 atoms in the cluster were given as input data. A full multiple-scattering calculation was carried out for clusters containing up to 87 atoms (seven





**Figure 5.** Comparison of the RSMS calculated spectra with a core hole (dashed line) and without a core hole (dotted line) for the  $L_1$  edge of In and K edges of Se and Cu.

shells). The XANES calculations were performed either with a relaxed and screened core hole in a final state or with no core hole included. A comparison of the calculated XANES curves and the experimental data for the 'p-like' edges is shown in figure 5. Though FEEF8 calculation reproduces quite well global features of the spectra, there are still discrepancies between the theoretical and experimental XANES in the low energy range. It fails to reproduce the right amplitude ratio and especially it underestimates the first maximum intensity. The possible source of discrepancies seems to lie in non-muffin-tin effects found also in the XANES of  $\text{CuGaSe}_2$  [14]. The core-hole potential affects the spectra in the first 20 eV. This is most important for the Cu K edge (figure 5(c)) and produces only minor changes for the Se K edge and In  $L_1$  edge.

## 5. Conclusions

We have reported XANES spectra for  $\text{CuInSe}_2$  at the K edges of Se and Cu, the  $L_1$  edge of In and the  $L_3$  edges of In, Se and Cu. The corresponding conduction band local densities of states have been calculated using the LMTO-ASA method. Fairly good agreement between theoretical and experimental results has been found for the In  $L_1$  edge and Se K edge. In the  $L_3$  spectra, only positions of the low energy features can be correlated with the weighted sum of s- and d-like LDOSs. A comparison of theoretical and experimental results indicates a significant contribution of the s-like final states to the XANES at the  $L_3$  edges of Cu and In.

The calculations of the XANES by the RSMS method show that the core-hole potential modifies significantly the calculated spectra only in the case of the copper K edge. That effect

can account for the observed discrepancies between the XANES at the Cu K edge and the Cu p-like LDOS.

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