The interplay of the $3d^9$ and $3d^{10}L$ electronic configurations in the copper K-edge XANES spectra of Cu(II) compounds

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A theoretical analysis of the X-ray absorption near-edge structure spectra at the Cu K-edge in several divalent copper [Cu(II)] compounds showing a distorted nearest-neighborhood around copper is presented. The experimental spectra of CuO and KCuF$_3$ have been compared with computations performed in the framework of the multiple-scattering theory. The results show that ab initio single-channel multiple-scattering calculations are not able to reproduce the experimental spectra. On the contrary, the experimental spectra can be accounted for by using two excitation channels and the sudden limit of the multichannel multiple-scattering theory. The comparison between experimental data and computations indicates that both $3d^9$ and $3d^{10}L$ electronic configurations are needed to account for the absorption process in these systems, suggesting that this is the general case for the K-edge XANES of divalent copper compounds.

Keywords: X-ray absorption spectroscopy; XANES; multiple scattering.

1. Introduction

X-ray absorption spectroscopy (XAS) is nowadays one of the most widespread tools used for local structure determinations (Sayers & Bunker, 1988, and references therein; Iwasawa, 1996). Reliable structural parameters such as interatomic distances, coordination numbers etc. are commonly derived from the analysis of the extended X-ray absorption fine-structure (EXAFS) region of the spectrum. The accuracy of these structural determinations has been improved by the development of powerful computer codes (Ankudinov et al., 1998; Joly, 2001; Natoli & Benfatto, 1986).

The study of the near-edge region of the X-ray absorption spectrum (XANES) is now attracting much attention because of its sensitivity to the bonding geometry. Despite the wealth of electronic and structural information of XANES, its usefulness as a structural tool is lower than EXAFS because the computation of XANES and its analysis are not as straightforward as for the EXAFS region. The search for an accurate description of the XANES spectra motivated new studies, from both experimental and theoretical standpoints. Most of these studies have focused on the $3d$ transition metal K-edge XANES spectra in simple systems (Briois et al., 1995; Benfatto et al., 1997; Merkling et al., 2001, 2002; D’Angelo et al., 2002). Theoretical calculations have provided good agreement with the experimental spectra for the divalent Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ ions in aqueous solutions (Benfatto et al., 1997). Surprisingly, calculations fail to reproduce the experimental spectra of divalent copper (Briois et al., 1995). The latter results cast a shadow over the possibility of extending the range of applicability of XANES analysis to complex Cu systems such as living organisms (Ascone et al., 2003).

In recent work (Chaboy et al., 2005), we have reported a systematic theoretical study of the Cu K-edge XANES spectra in several divalent copper compounds showing a square-planar Cu–N arrangement of increasing complexity around the metal atom. The main finding of this work is the need to include both $3d^9$ and $3d^{10}L$ final-state electronic configurations in the presence of the core hole (where $L$ denotes a 2p hole in N from the ligand) in order to reproduce the experimental spectra. The total cross section is obtained as the sum of two absorption channels with a relative weight of 68% ($3d^{10}L$) and 32% ($3d^9$). A similar scheme applied to the study of the Cu K-edge XANES of NdCuO$_4$ (Wu et al., 1996) and of the cupric cation Cu$^{2+}$ in aqueous solution (Chaboy et al., 2006) also yields a relative weight of ~0.7 and ~0.3 for the two absorption channels.

In order to verify the generality of the above results, i.e. to test whether the two absorption channels scheme is characteristic of divalent copper, we have extended our previous research to Cu(II) systems with other ligands and environments. In this way we have performed a systematic theoretical...
study of the Cu K-edge XANES spectra in CuO and KCuF₃. The interpretation of the Cu K-edge XANES spectrum in CuO is linked to renewed interest in the basic physical properties of copper oxides after the discovery of high-T_c superconductors. In particular, to what extent can CuO be described within a one-electron formalism, as the importance of strong electron correlations in CuO was stressed in many studies, is still an open question (Sipr, 1992; Bocharov et al., 2001). On the other hand, the pseudocubic perovskite KCuF₃ has attracted significant interest in recent years regarding the problem of orbital ordering and the study of the interactions between orbital, magnetic and structural ordering in strongly correlated 3d transition metal compounds (Paolasini et al., 2002; Takahashi et al., 2003; Bingelli & Altarelli, 2004).

The results of the Cu K-edge XANES calculations are discussed by showing the improvements obtained by using self-consistent field (SCF) methods to describe the final state of the photoabsorption process. Moreover, the relative weighting of the different electronic configurations involved is also discussed. Our results point out that the need to include a weighting of the different electronic configurations involved is of the photoabsorption process. Moreover, the relative self-consistent field (SCF) methods to describe the final state discussed by showing the improvements obtained by using Cu–N compounds. On the contrary, they suggest it is the Cu

The local structure of Cu in CuO consists of four O atoms in a quasi-planar structure, with interatomic Cu—O distances \( R_1 = 1.95 \) Å and \( R_2 = 1.96 \) Å (Sipr, 1992). These four atoms form a distorted pyramid with two apical O atoms at \( R_3 = 2.78 \) Å from Cu. *Ab initio* single-channel multiple-scattering computations of the Cu K-edge of CuO were performed for different cluster sizes around the photoabsorbing Cu atom and by using different treatments of the exchange-correlation potential (ECP) (Chaboy et al., 2005; Natoli et al., 2003).

Starting from the simplest square-planar Cu–O arrangement, further coordination shells are included to build up a cluster of 51 atoms, i.e. covering contributions from atoms located within the first 5 Å around Cu. The addition of further shells does not produce major changes.

The cluster potential was approximated by a set of spherically averaged muffin-tin potentials built by following the standard Mattheis prescription (Mattheis, 1964). The radii of the muffin-tin potentials centered on the atomic sites were determined following Norman’s criterion and by imposing a 10% overlapping factor (Norman, 1974). The Coulomb part of each atomic potential was generated using charge densities for neutral atoms obtained from the tabulated atomic wavefunctions of Clementi & Roetti (1974). The final-state potential was built according to the screened \( Z + 1 \) approximation (Lee & Beni, 1977) and by adding an appropriate exchange and correlation potential.

Fig. 1 reports a comparison of the experimental CuO spectrum with that of the theoretical computation obtained by using the screened \( Z + 1 \) approximation and complex Hedé-Lundqvist ECP for the construction of the final-state potential. The Cu K-edge experimental spectrum of CuO shows different absorption features: (i) a step-like peak (A) at the raising edge; (ii) a main absorption line composed of up to three contributions (\( B \simeq 8.6 \) eV; \( C \simeq 13.5 \) eV; \( D \simeq 17 \) eV); (iii) a split (\( E \simeq 27 \) eV; \( F \simeq 33 \) eV) feature at the high-energy side of the main line; and finally (iv) a deep minimum (\( G \simeq 43 \) eV) and a broad positive resonance (\( H \simeq 65 \) eV) at higher energies. The single-channel theoretical calculations do not reproduce the experimental spectral shape of CuO, independently of the ECP used for the calculation. The calculation reproduces the step-like feature A and a single main line whose energy position and width resemble those of the spectral feature B. By contrast both C and D structures, at the main peak, and feature F, in the high-energy region, are not accounted for by the calculation. Moreover, the calculated G and H spectral features fall short of the experimental ones. The comparison is not improved by changing the constant parameter \( \Gamma_C \) used for the convolution of the theoretical spectrum to account for the core-hole lifetime and the experimental resolution.

The disagreement between the theoretical calculations and the experimental spectrum is not due either to structural effects or to a bad choice of the interstitial potential. Indeed, as shown in Fig. 1(b), no significant modification of the narrow single-peak spectral profile is obtained by (i) increasing the size of the cluster (from 51 to 135 atoms) to include contributions from atoms located within the first 7.1 Å around Cu; and (ii) by imposing different (1%, 10% and 20%) overlapping factors of the muffin-tin spheres to modify *ad hoc* their scattering power, and in a second instance to decrease the volume of the interstitial region (Natoli et al., 2003). At this
point it is instructive to compare the width of the main Cu K-edge absorption line for the systems under study with that of the tetramminecopper(II) aqueous solution (Chaboy et al., 2005). As shown in Fig. 2, this width is similar in the considered cases, and twice that of the K-edge XANES spectra of different divalent transition metals (Fe, Co, Ni) in aqueous solution (Benfatto et al., 1997). This result suggests the need to include two different excitation channels, as in the case of tetramminecopper(II) (Chaboy et al., 2005), to account for the Cu K-edge XANES spectra of the selected Cu(II) compounds.

As with the previous results (Chaboy et al., 2005), we have used SCF potentials for the different electronic configurations used in the calculations: 3d\(^9\) and 3d\(^{10}\)\(L\), where \(L\) denotes a 2p hole in the ligand oxygen atom. The excited final-state potential was calculated by promoting one of the 1s electrons of Cu to the first free energy level of the right symmetry and fixing to one the 1s occupancy during the SCF procedure. The energy of the process is then given by the difference between the total energy of the excited final state and the initial ground state. We have (SCF) stabilized a small \([\text{CuO}_4]^{6-}\) cluster with an outer sphere with a 6+ charge to neutralize the whole cluster. This cluster has been embedded in the larger ones in order to perform the multiple-scattering calculations. Then, the potential of both the absorbing Cu and the four next-neighbor O atoms is SCF, while the potential around the other atoms was built according to Mattheis’ prescription. This procedure has been previously shown to be successful on extended systems (Wu et al., 1996). Both 3d\(^9\) and 3d\(^{10}\)\(L\) configurations give rise to two absorption edges shifted in energy by \(\Delta = 6.1\) eV, close to the values found for other Cu(II) systems (Chaboy et al., 2005, 2006). As shown in Fig. 3, a remarkable agreement is found between the experimental data and the Cu K-edge cross section computed as the sum of both 3d\(^{10}\)\(L\) and 3d\(^9\) contributions with fixed relative weights of 68\% and 32\%, respectively (Chaboy et al., 2005). These factors, close to the values reported by Wu et al. (1996), were fixed throughout this study.

### 3.2. KCuF\(_3\)

The results obtained for CuO suggest that the two absorption channels (3d\(^{10}\)\(L\) and 3d\(^9\)) scheme is a general characteristic of Cu(II) K-edge XANES spectra, the relative weight of both channels being close to the 70:30 ratio. Further confirmation of this result can be obtained by computing the Cu K-edge X-ray absorption of Cu(II) in KCuF\(_3\).

Research into the KCuF\(_3\) compound has recently attracted much attention owing to its links with the development of the resonant elastic X-ray scattering (RXS) technique that has been postulated as an incomparable tool for probing orbital ordering (Paolasini et al., 2002). The theoretical interpretation of the RXS spectra is being developed and several questions still remain open regarding the role of the spin polarization.
The RXS at the Cu K-edge in KCuF₃ derives from a virtual dipolar excitation to the empty 4p states. The resulting RXS amplitude is thus not directly related to the 3d states that exhibit orbital ordering, but to the anisotropy induced in the surrounding 4p states. This indirect dependence makes the interpretation of the RXS results difficult (Takahashi et al., 1998). The distorted CuF₆ octahedron contains two F₁ ions at 1.96 Å from Cu and two pairs of F₂ ions with interatomic Cu—F₂ distances R = 1.88 Å and 2.26 Å, respectively. The Cu K-edge RXS of KCuF₃ is shown in Fig. 5. It is characterized by (i) a shoulder (A) at the threshold; (ii) an asymmetric absorption line showing a main peak (B₁) at ~7 eV above the edge and a second shoulder (B₂) at the high-energy side (~12.5 eV); (iii) a positive peak (C) at ~21 eV above the edge and, finally, (iv) three well defined spectral features, D (~37 eV), E (~52 eV) and F (~72 eV), at high energy. The width of the main absorption line is comparable with that of the previously studied Cu(II) compounds (see Fig. 2), suggesting also the presence of different excitation channels. We have initially calculated the Cu K-edge absorption within a single-channel frame by using both non-SCF Xα and Hedin–Lundqvist potentials for different cluster sizes. The smallest cluster was built by including the first F and K coordination shells around absorbing Cu (Rₓmax = 3.5 Å) (Hidaka et al., 1998). The calculation performed for this cluster, shown in Fig. 5(a), reproduces the peak at the edge and the high-energy features (D to F). However, only a single main peak without trace of both shoulder B₂ and peak C is obtained. Addition of further shells, including atoms located within a maximum interatomic distance of 4.7 Å around copper, reproduces the B₂ peak. Similar results are found by extending the maximum interatomic distance to 5.9 Å and 7.1 Å around copper (see Fig. 5a). However, the calculations fail in reproducing the intensity ratio of both B₁ and B₂ features and in reproducing peak C. The latter result strongly suggests that the omission of peak C in the calculations is not due to a structural effect. Conse-

Figure 3
Comparison of the experimental XANES spectrum at the Cu K-edge in CuO and the theoretical spectrum obtained as the weighted sum of the 3d⁹ (32%) and 3d¹⁰L₉ (68%) contributions (solid line); equal weighting (50%) of both channels (dotted line) and the calculation performed on the single-channel approximation (dashed line). All the calculations have been performed by using the Hedin–Lundqvist ECP and a convolution parameter Γₑ = 1.84 eV (see text for details).

Figure 4
Comparison of the experimental Cu K-edge spectrum of KCuF₃ (circles), adapted from Paolasini et al. (2002), and the absorption coefficient obtained from the calculated 4p density of states of Cu by Takahashi et al. (2003) (solid line) and by Bingelli & Altarelli (2004) (dotted line).
Additional peak close to the B2 shoulder, resembling the C configuration, where \( \text{L} \) denotes a hole from a ligand) within the sudden limit of the multichannel multiple-scattering theory. Moreover, the use of self-consistency field potentials for the photoabsorbing Cu and its next-neighboring atoms provides a more realistic charge density than that obtained by using the standard neutral atom approximation.

These results are in agreement with previous findings obtained for NdCuO\(_4\) (Wu et al., 1996), the hydrated Cu\(^{2+}\) complex in aqueous solution (Chaboy et al., 2006) and Cu–N systems (Chaboy et al., 2005) suggesting that the two-channels (3\(d^9\) and 3\(d^{10}\)) scheme is the general case for the K-edge XANES of divalent copper systems. This result appears to be independent of both the local environment around Cu as well as of the nature of the ligand. In addition, it is shown that the energy shift between both absorption channels is sensitive to the nature of the bonded atom (N, O, F). By contrast, the relative weight of both 3\(d^{10}\) and 3\(d^9\) channels is close to the 70:30 ratio in all the studied cases with the exception of KCuF\(_3\), for which the agreement between the two-channels computation and the experimental spectrum is not so straightforward. These results, which could stimulate further theoretical work beyond single-configuration approximations, provide a way to face the study of complex Cu systems, including copper oxides or living organisms, by means of XANES.

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4. Summary and conclusions

We have thoroughly analyzed the Cu K-edge XANES spectra of the Cu(II) compounds CuO and KCuF\(_3\). Detailed theoretical computations of the Cu K-edge spectra have been performed within the multichannel multiple-scattering framework.

The comparison between the experimental data and computations indicates that the experimental spectra can be accounted for by using two electronic configurations (3\(d^9\) and 3\(d^{10}\), \(\text{L}\) being a hole from a ligand) within the sudden limit of the multichannel multiple-scattering theory. Moreover, the use of self-consistency field potentials for the photoabsorbing Cu and its next-neighboring atoms provides a more realistic charge density than that obtained by using the standard neutral atom approximation.

These results are in agreement with previous findings obtained for NdCuO\(_4\) (Wu et al., 1996), the hydrated Cu\(^{2+}\) complex in aqueous solution (Chaboy et al., 2006) and Cu–N systems (Chaboy et al., 2005) suggesting that the two-channels (3\(d^9\) and 3\(d^{10}\)) scheme is the general case for the K-edge XANES of divalent copper systems. This result appears to be independent of both the local environment around Cu as well as of the nature of the ligand. In addition, it is shown that the energy shift between both absorption channels is sensitive to the nature of the bonded atom (N, O, F). By contrast, the relative weight of both 3\(d^{10}\) and 3\(d^9\) channels is close to the 70:30 ratio in all the studied cases with the exception of KCuF\(_3\), for which the agreement between the two-channels computation and the experimental spectrum is not so straightforward. These results, which could stimulate further theoretical work beyond single-configuration approximations, provide a way to face the study of complex Cu systems, including copper oxides or living organisms, by means of XANES.

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Figure 5

(a) Comparison of the experimental Cu K-edge spectrum of KCuF\(_3\) (circles) and the spectra calculated by using a complex Hedin–Lundqvist ECP and different clusters with a maximum distance around Cu of \(R_{\text{max}} = 3.5\) \(\text{Å}\) (dotted line), 4.7 \(\text{Å}\) (dashed line), 5.9 \(\text{Å}\) (solid line) and 7.1 \(\text{Å}\) (dotted-dashed line). (b) Comparison of the experimental spectrum and the theoretical calculations obtained for both 3\(d^9\) (dashed line) and 3\(d^{10}\) (solid line) after applying a 32% and 68% weighting factor. The weighted sum obtained according to the 68:32 (dot-dashed line) and 84:16 (dotted line) ratios is shown (see text for details).
beam-time allocation at the BM29 line (experiment number CH-1192).

References


