THE OXIDATION STATE OF COPPER AND COBALT IN CARROLLITE, CuCo$_2$S$_4$

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ABSTRACT

Using X-ray absorption spectroscopy (XAS) at the Cu $L_{2,3}$ and Co $L_{2,3}$ edges, we demonstrate that the valence state of copper in the thiospinel carrollite (CuCo$_2$S$_4$) is Cu$^+$ with a $d$ count of Cu $d^{9.8}$. The Co has a $d$ count of $d^{6.4}$, so that the highly covalent mineral has an electronic formula of Cu$_{1.2+}$Co$_{2.4+}$(S$_{1.5–}$)$_4$. There is half a hole per atom in the S 3$p$ band (per unit formula); the Co $L_{2,3}$ XAS indicates a covalent low-spin electronic structure. These data dispel the notion of the presence of Cu$^{2+}$ in carrollite.

Keywords: carrollite, oxidation state, $L$-edge, X-ray absorption spectroscopy, thiospinel, low-spin electronic structure.

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INTRODUCTION

Carrollite, CuCo$_2$S$_4$, a thiospinel of the linnaeite group (cubic, $Fd\bar{3}m$), is found in a wide range of mainly hydrothermal mineral deposits, forming an important cobalt ore, such as in the Central African Copper Belt; the main value of cobalt is as a ferroalloy and in other corrosion-resistant materials, but also in recording devices and as a catalyst. Natural samples commonly contain Ni, and a solid solution exists between CuCo$_2$S$_4$ and Cu(Ni,Co)$_2$S$_4$ in which Ni can replace 50% of the Co (Wagner & Cook 1999). Carrollite is a metallic Pauli paramagnet and has a “normal” spinel structure with half the octahedral sites ( )$_{Oh}$ occupied by Co atoms and one eighth of the tetrahedral sites ( )$_{Td}$ occupied by Cu atoms (Hill et al. 1979, Charnock et al. 1990), such that the formula can be represented as (Cu)$_{Td}$[Co$_2$]$_{Oh}$S$_4$. The oxidation states in carrollite are generally shown as Cu$^{2+}$Co$^{3+}$S$_4$$^{2–}$ to comply with charge balance, although experimental evidence suggests that the copper may be Cu$^+$ (see Nakai et al. 1978), and evidence of Cu$^{2+}$ in sulfide minerals is very rare (Pearce et al. 2006). This contradiction has also been highlighted by other investigators (Vaughan & Tossell 1981). The presence of Cu$^+$ has consequences for the oxidation states of the Co and S in carrollite.

Other members of the linnaeite group include linnaeite (Co$_3$S$_4$), siegenite [(Co,Ni)$_3$S$_4$], polydymite (Ni$_3$S$_4$),
violarite (FeNi$_2$S$_4$) and fletcherite [Cu(Co,Ni)$_2$S$_4$]. Defining the oxidation states of metals in carrollite will assist in the understanding of these linnaeite-group phases and the controls on their substitutional series. In particular, it may help explain the substitutions of Ni and Cu for Co in carrollite (Wagner & Cook 1999), and of Cu for Co in fletcherite (Drüppel et al. 2006) that are indicated by detailed chemical analysis. These chemical data also reveal extensive non-stoichiometry in naturally occurring linnaeite-group minerals. The incorporation of the less favored Ni$^{3+}$ and Cu$^{2+}$ is one explanation, although the metallic character of polydymite and linnaeite (Manthiram & Jeong 1999) indicates that a more complex solution is required. It is our purpose in this study to examine and define the oxidation state of Cu and Co in carrollite using metal $L$-edge X-ray absorption spectroscopy (XAS), which is particularly sensitive to the oxidation state of transition metals.

**METHODOLOGY**

Analysis of the $L_{2,3}$ X-ray absorption spectroscopy (XAS) of 3$d$ transition metal compounds is known to be an excellent tool for providing oxidation state and site symmetry (van der Laan & Thole 1991, van der Laan & Kirkman 1992, Grioni et al. 1989, Pattrick et al. 1993). The $L_{2,3}$ edge absorption spectra are dominated by transitions from core 2$p$ to unoccupied 3$d$ states and, in the presence of a strong electrostatic interaction between core and valence electrons, the large 2$p$ spin-orbit splits the spectrum up into an $L_3$ (2$p_{3/2}$) and $L_2$ (2$p_{1/2}$) structure. The spectra reflect the local electronic structure of the transition-metal atom, so that the oxidation states can generally be derived by spectral analysis, multiplet structure calculations and fingerprinting. In this paper, the $L$-edge spectra of Cu and Co from carrollite (containing only 0.6 wt% Ni) were collected.

**EXPERIMENTAL**

The samples used in this study were taken from large monomineralic crystals of carrollite from Katanga, Democratic Republic of Congo, and chalcopyrite from Palabora, Republic of South Africa. Sample purity was confirmed by X-ray-diffraction analysis, and the composition was established by electron-probe microanalysis. The Cu and Co $L_{2,3}$-edge absorption spectra were measured on the Magnetic Spectroscopy beamline 1.1 of the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory. The beamline was equipped with a spherical grating monochromator set to an energy resolution of 500 meV in the region of interest. The photon energy was referenced to the Cu $L_3$ peak of chalcopyrite, CuFe$_5$S$_4$, assuming a photon energy of 932.5 eV for the main absorption peak (Pearce et al. 2006). The finely powdered samples were mounted on conducting tape on an aluminum plate in a vacuum chamber ($10^{-7}$ torr) within 10 min after grinding. The absorption signal was collected in total electron yield (TEY) mode and normalized to the flux of incident X-rays. At the energy of the Cu $L$-edge, the penetration depth of the X-rays is ~50 Å (>13 atomic layers), thus if oxidation of the surface atoms is present, it can be seen as a small but significant contribution to the spectra.

**RESULTS AND DISCUSSION**

The XAS spectra are presented in Figures 1 and 2. In the Cu $L_{2,3}$ spectrum (Fig. 1), the first peak is located at 932.0 eV (marked as A) followed by a broader structure at 937–941 eV (B). There is also a small feature visible as a low-energy shoulder on the main $L_3$ peak at 929.5 eV (C). All these features are mirrored with lower intensity and larger broadening in the $L_2$ edge at 947–960 eV. The Co $L_{2,3}$ spectrum (Fig. 2) reveals the main Co $L_3$ absorption peak at 777.5 eV (marked as D) and the Co $L_2$ peak at 792.2 eV (G). The spectrum also shows satellites at 782.3 eV (E) and ~783.6 eV (F), with mirroring features in the $L_2$ spectrum commencing at 797.0 eV (H).

Analysis of the Cu $L$-edge XAS sulfide spectra, in general, reveals the “d count” to be intermediate between $d^9$ and $d^{10}$, although these covalent copper compounds can be divided into those nominally monovalent and those nominally divalent (van der Laan et al. 1992, Pearce et al. 2006), which display clearly very different spectral characteristics. Divalent compounds, such as CuO, have a single sharp $L_3$ peak at an energy of 931 eV, corresponding to the $3d^9 \rightarrow 2p^6 3d^{10}$ transition, whereas monovalent compounds have intensities at higher energies owing to $2p \rightarrow 4s$ transitions combined with 3$d$–4$s$ hybridization (Grioni et al. 1989, van der Laan et al. 1992, Pearce et al. 2006). The cross-sections of the monovalent Cu spectral peaks are ~25 times lower than those of the divalent Cu spectral peaks (Pattrick et al. 1993), so that a small Cu$^{2+}$ component in monovalent minerals should be easily visible. The Cu $L$-edge spectrum of carrollite (Fig. 1) has all the characteristics of a monovalent sulfide, $d^{10}$ with some $d^9$ character, and is mixed with ligand $d^{10}L_6$ character (Grioni et al. 1992). The similarity of the carrollite spectrum to that of the monovalent Cu sulfide chalcopyrite (nominally Cu$^{2+}$Fe$^{3+}$S$_2$) is striking (Fig. 1). For carrollite, as in other monovalent Cu sulfides, there is some 3$d$ hole density on the Cu atom, and the true $d$ count is estimated to be ~9.8. The shoulder (C) may represent a very small component of Cu$^{2+}$ (<1% of total Cu); minor surface oxidation could explain this.

The Co $L_{2,3}$ XAS (Fig. 2) of CuCo$_2$S$_4$ does not resemble the multiplet structure typical of [Co$^{2+}$]$_{10}$, such as for example in CoO or CoFe$_2$O$_4$, which exhibits a very characteristic $L_3$ manifold structure (van der Laan
Neither does the XAS resemble the spectral shape that is typical for [Co$^{3+}$]$_{Oh}$ (van der Laan & Kirkman 1992). However, the Co $L_{2,3}$ XAS of carrollite shows similarities to that derived for cattierite (CoS$_2$) and trogtalite (CoSe$_2$) (Charnock et al. 1996, Muro et al. 1996, 1998). In these dichalcogenide spectra, similar intensities around 5 eV above the main $L_3$ peak were also observed. For comparison, Figure 2 shows the spectrum for CoS$_2$. One can see that the main-peak-to-satellite separation is slightly larger than for CuCo$_2$S$_4$, and the satellite-to-main-peak intensity is slightly lower, with the satellite structure being less pronounced. The satellite features do reflect the covalent character of the $d$ electrons. The main $L_3$ peak corresponds to Co $3d^7 \rightarrow 2p^53d^6$ transitions, whereas the satellites at $\sim$5 eV higher photon energy (peaks $E$ and $F$) correspond to Co $3d^6 \rightarrow 2p^53d^7$ transitions; the shape of the satellite structure changes along the nephelauxetic series (Charnock et al. 1996), although these authors did not include CoPo$_2$ in their study).
to a ground state with Co\textsuperscript{2+} : Co\textsuperscript{3+} ratios of 0.61 : 0.38, the model gives a main-peak-to-satellite separation in energy of \( \sim 5 \) eV and a satellite-to-main-peak intensity ratio of \( \sim 3.4\% \), approximating the experimental spectrum in Figure 2. Thus the satellite structure in carrollite reveals a large mixing of the \( d_7 \) and \( d_6 \) configurations at the Co site, hence a valence state that is between 2+ and 3+.

The absence of a sharp XAS multiplet structure provides evidence for a less localized and more covalent character of the electronic structure of the Co in these sulfide compounds. High-spin and low-spin configurations give distinctly different multiplet structures (see van der Laan & Kirkman 1992). Unfortunately, the disappearance of the multiplet structure due to the covalency makes it impossible to use their distinct signatures at both edges. However, we can make use of a remarkable feature: the \( L_{2,3} \) XAS of CuCo\textsubscript{2}S\textsubscript{4} (Fig. 2) has a branching ratio that is much lower than that of standard high-spin Co compounds, such as CoO and CoFe\textsubscript{2}O\textsubscript{4} (van der Laan et al. 2008). The branching ratio, \( B \), is defined as the total intensity, \( I \), over the \( L_3 \) edge divided by the total intensity over both edges, i.e., \( B = I(L_3)/[I(L_2) + I(L_3)] \). As a general rule, high-spin states give a larger branching ratio than low-spin states, which is due to the selection rule \( \Delta S = 0 \) in the absorption process and the large \( 2p \) spin-orbit interaction of the final state, as explained by Thole & van der Laan (1988). Experimentally, we find \( B \approx 0.82 \) for CoFe\textsubscript{2}O\textsubscript{4}, \( B \approx 0.76 \) for CuCo\textsubscript{2}S\textsubscript{4} and \( B \approx 0.72 \) for CoS\textsubscript{2} (barring any systematic errors). It is well known that Co in CoFe\textsubscript{2}O\textsubscript{4} is high spin, and that Co in CoS\textsubscript{2} is most likely low spin. Thus the low value of the Co \( L_{2,3} \) branching ratio for CuCo\textsubscript{2}S\textsubscript{4} suggests a low-spin configuration, which means that the \( t_{2g} \) level is completely filled, and with 6.6 electrons available, the configuration of the 3\( d \) shell would be \( t_{2g}^{3}e_{g}^{6,6} \). In octahedral site symmetry, the \( e_{g} \) orbitals are directed toward the neighboring atoms, forming the bonding, whereas the \( t_{2g} \) orbitals are directed away from the neighboring atoms, which means that they have lower energy. On the other hand, the exchange interaction between the \( d \) electrons prefers to align the spins parallel. This would lead to a high-spin configuration \( t_{2g}^{3}e_{g}^{2} \), where the \( e_{g} \) states with spins parallel to the \( t_{2g} \) states are filled first, before the \( t_{2g} \) states with antiparallel spin are filled. Thus there is a competition between the crystalline electrostatic field preferring to fill up all the \( t_{2g} \) states and the exchange interaction.

![Fig. 2. Co \( L_{2,3} \) X-ray absorption spectra of carrollite, CuCo\textsubscript{2}S\textsubscript{4} (upper curve) and, for comparison, that of CoS\textsubscript{2} (lower curve). The Co \( L_3 \) absorption edge has its main peak at 777.5 eV (\( D \)) and satellites at 782.3 eV (\( E \)) and \( \sim 783.6 \) eV (\( F \)). These structures are mirrored at the Co \( L_2 \) edge with the main peak at 792.2 eV (\( G \)) and satellites at 797.0 eV (\( H \)). The spectra are normalized to the maximum of the \( L_3 \) peak and shifted vertically for clarity.](image-url)
preferring to align the spins, thereby spreading the electrons out over both \(e_g\) and \(t_{2g}\) levels. In the case of the sulfides, (i) the strong covalent character (i.e., large overlap) of the bonding increases the preference of the \(d\) electrons for the non-bonding \(t_{2g}\) states, and (ii) the exchange interaction is usually smaller than in the more ionic oxides, both resulting in a tendency for low spin. Furthermore, any additional electronic charge in a more ionic oxides, both resulting in a tendency for low spin. Since the exchange interaction is usually smaller than in the more ionic oxides, both resulting in a tendency for low spin. More generally, a low-spin covalent electronic structure does also occur in other sulfides, such as CoS

\[\text{L}2,\text{3 XAS of pyrite, FeS}_2\] (Thole & van der Laan 1988), a well-known pyrite structure. Incorporating Cu to the unit formula, the valence distribution in carrollite can be described as Cu1.2\((\text{Co}^{2.4+})_2\text{(S}_{1.5-}\)\(_4\). The value S

\[\text{S}_{1.5-}\] which is a consequence of charge neutrality, means that there is effectively half a hole per atom in the S 3p band. Vaughan & Tossell (1981) predicted a “deficiency of electrons on the S anions”. The presence of holes on the S atoms is supported by the S K-edge XAS spectrum of carrollite (Li et al. 1995), which shows major intensity at the onset of absorption. In addition, the low branching ratio of the \(\text{Cu L}_{2,3}\) XAS of \(\text{CuCo}_2\text{S}_4\) suggests a low-spin configuration \((t_{2g}^6e_g^{0.6})\) (Thole & van der Laan 1988), as for CoS\(_2\) (Muro et al. 1996); both Vaughan & Tossell (1981) and Li et al. (1995) also assumed this to be the case.

**CONCLUSION**

Incorporating Cu \(\text{a}^{0.8}\) into the unit formula, the valence distribution in carrollite can be described as \(\text{Cu}^{1.2}_{1.2}\)(\(\text{Co}^{2.4+}\))\(_2\)\(\text{S}_{1.5-}\). The value \(\text{S}_{1.5-}\), which is a consequence of charge neutrality, means that there is effectively half a hole per atom in the S 3p band. Vaughan & Tossell (1981) predicted a “deficiency of electrons on the S anions”. The presence of holes on the S atoms is supported by the S K-edge XAS spectrum of carrollite (Li et al. 1995), which shows major intensity at the onset of absorption. In addition, the low branching ratio of the \(\text{Co L}_{2,3}\) XAS of \(\text{CuCo}_2\text{S}_4\) suggests a low-spin configuration \((t_{2g}^6e_g^{0.6})\) (Thole & van der Laan 1988), as for CoS\(_2\) (Muro et al. 1996); both Vaughan & Tossell (1981) and Li et al. (1995) also assumed this to be the case.

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