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THE OXIDATION STATE OF COPPER AND COBALT IN CARROLLITE, $CuCo_2S_4$

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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 ($CuCo_2S_4$) 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 $Cu^{1.2+}(Co^{2.4+})_2(S^{1.5-})_4$. 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.

Sommaire

Nous avons utilisé la spectroscopie d'absorption des rayons X (XAS) des seuils Cu $L_{2,3}$ et Co $L_{2,3}$ pour démontrer que la valence du cuivre dans le thiospinelle carrollite ($CuCo_2S_4$) est monovalent, avec un compte des électrons *d* associés de $d^{9.8}$. Le cobalt possède un compte de $d^{6.4}$, de sorte que ce minéral fortement covalent est représenté par la formule électronique $Cu^{1.2+}(Co^{2.4+})_2(S^{1.5-})_4$. Il y a la moitié d'un trou dans la bande S 3*p* par formule unitaire; le spectre XAS $L_{2,3}$ du Co indique qu'il s'agit d'une structure électronique covalente à faible spin. Ces données viennent réfuter la notion de la présence de Cu^{2+} dans la carrollite.

(Traduit par la Rédaction)

Mots-clés: carrollite, taux d'oxydation, seuil *L*, spectroscopie d'absorption des rayons X, thiospinelle, structure électronique à faible spin.

Introduction

Carrollite, $CuCo_2S_4$, a thiospinel of the linnaeite group (cubic, *Fd*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 $CuCo_2S_4$ and $Cu(Ni,Co)_2S_4$ 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 $Cu^{2+}Co_2{}^{3+}S_4{}^{2-}$ 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_3S_4), siegenite [$(Co,Ni_3)S_4)$], polydymite (Ni_3S_4),

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violarite ($FeNi_2S_4$) and fletcherite [$Cu(Co,Ni)_2S_4$)]. 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 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) 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 micro-analysis. 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, $CuFeS_2$, 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 $3d^9 \rightarrow 2p^5 3d^{10}$ 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^9s character, and is mixed with ligand $d^{10}\underline{L}s$ character (Grioni *et al.* 1992). The similarity of the carrollite spectrum to that of the monovalent Cu sulfide chalcopyrite (nominally $Cu^+Fe^{3+}S_2$) 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 $CuCo_2S_4$ does not resemble the multiplet structure typical of $[Co^{2+}]_{Oh}$, such as for example in CoO or $CoFe_2O_4$, which exhibits a very characteristic L_3 manifold structure (van der Laan

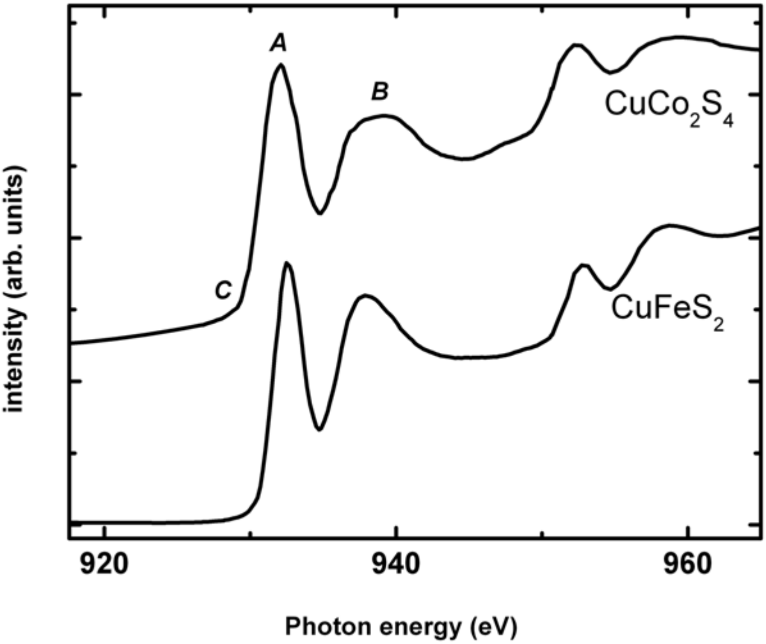

Fig. 1. Cu $L_{2,3}$ X-ray absorption spectra of carrollite, CuCo$_2$S$_4$ (upper curve), and chalcopyrite, CuFeS$_2$ (lower curve). The L_3 absorption edge comprises the sharp peak at 932.0 eV (*A*) and a broader structure at 937–941 eV (*B*); these structures are mirrored in the L_2 edge in the energy range 947–960 eV. A very small shoulder at 929.5 eV (*C*) is the only definable Cu^{2+} component of the spectrum (see text). The spectra are normalized to the maximum of the L_3 peak and shifted vertically for clarity.

et al. 2008, Coker *et al*. 2008). Neither does the XAS resemble the spectral shape that is typical for $[\mathrm{Co}^{3+}]_{\mathrm{Oh}}$ (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 structure in both compounds is unlikely to be due to variations in the density of unoccupied *s*-continuum states, because the transition probability to the *s* states is much lower than to the *d* states. The satellite features do reflect the covalent character of the *d* electrons. The main L_3 peak corresponds to Co $3d^7 \rightarrow 2p^5 3d^8$ transitions, whereas the satellites at ~5 eV higher photon energy (peaks *E* and *F*) correspond to Co $3d^6 \rightarrow 2p^5 3d^7$ 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).

The satellite is missing in the multiplet calculation by Charnock *et al*. (1996), who took into account only a single-configuration ground state, Co $3d^7$. The calculated average difference in energy $E(2p^5 3d^7) - E(3d^6)$ is 2.3 eV larger than $E(2p^5 3d^8) - E(3d^7)$ (van der Laan & Kirkman 1992), so that the satellite due to d^6 should be located at higher energy. The energy separation and the ratio in relative intensity of the satellite peaks (*C* and *D*) with respect to the main peak (*A*) can be estimated using a charge-transfer model (van der Laan *et al*. 1981, 1986), which contains as parameters the charge-transfer energy, $\Delta = E(\mathrm{Co}^{3+}) - E(\mathrm{Co}^{2+})$, the transfer integral *T* (representing the mixing matrix element of the Hamiltonian between the $3d^7$ and $3d^6$ configurations), *i.e.,* the energy and the difference in energy between the 3*d*–3*d* and 2*p*–3*d* Coulomb interaction, (*U*–*Q*). In XAS, where the excited core-electron screens the *d* electrons, it is uncommon to have large intensities of satellites at large distances from the main peak. In fact, the only way to obtain sizeable intensities of satellites at a relatively large separation in energy is to have a strong mixing (large *T*) between the two configurations. Taking typical values (Bocquet *et al*. 1992), $\Delta = E(\mathrm{Co}^{3+}) - E(\mathrm{Co}^{2+}) =$ 2.5 eV, $T = 2.5$ eV and $U\text{–}Q = 2$ eV, which correspond

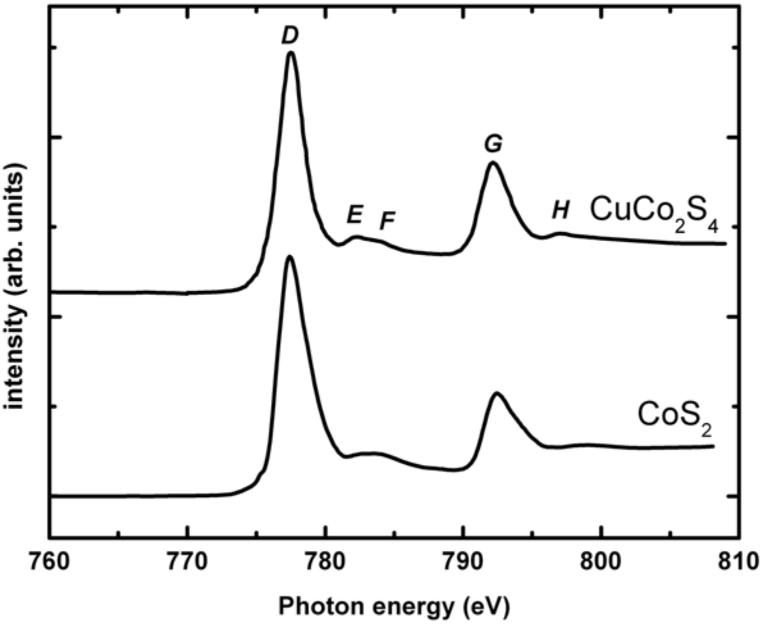

Fig. 2. Co $L_{2,3}$ X-ray absorption spectra of carrollite, $CuCo_2S_4$ (upper curve) and, for comparison, that of CoS_2 (lower curve). The Co L_3 absorption edge has its main peak at 777.5 eV (*D*) and satellites at 782.3 eV (*E*) and ~783.6 eV (*F*). These structures are mirrored at the Co L_2 edge 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.

to a ground state with Co^{2+} : Co^{3+} ratios of 0.61 : 0.38, the model gives a main-peak-to-satellite separation in energy of ~5 eV and a satellite-to-main-peak intensity ratio of ~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 $CuCo_2S_4$ (Fig. 2) has a branching ratio that is much lower than that of standard high-spin Co compounds, such as CoO and $CoFe_2O_4$ (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 2*p* spin-orbit interaction of the final state, as explained by Thole & van der Laan (1988). Experimentally, we find $B \approx 0.82$ for $CoFe_2O_4$, $B \approx 0.76$ for $CuCo_2S_4$ and $B \approx 0.72$ for CoS_2 (barring any systematic errors). It is well known that Co in $CoFe_2O_4$ is high spin, and that Co in CoS_2 is most likely low spin. Thus the low value of the Co $L_{2,3}$ branching ratio for $CuCo_2S_4$ 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 $t_{2g}{}^{6}e_{g}{}^{0.6}$. 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 $t_{2g}{}^{3.6}e_{g}{}^{2}$, 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 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 low-spin configuration $t_{2g}{}^6e_g{}^{0.6}$ has to go into the high-energy e_g state, giving no gain in exchange interaction since the t_{2g} level is full with net zero spin. This means that reducing the amount of *d* electrons, *i.e.*, going from 2+ toward 3+ valence state, in the case of a low-spin state, can lead to an energy benefit. The above arguments support a low-spin covalent electronic character of $CuCo_2S_4$, as evidenced by $L_{2,3}$ edge XAS.

More generally, a low-spin covalent electronic structure does also occur in other sulfides, such as CoS_2 (Muro *et al.* 1996). Interestingly, the Fe $L_{2,3}$ XAS of pyrite, FeS_2 (Thole & van der Laan 1988), a well-known low-spin covalent compound, also shows a very similar spectral shape as the Co $L_{2,3}$ XAS of carrollite, namely a low branching ratio and the presence of a low-intensity satellite structure at ~5 eV above the main peak.

CONCLUSION

Incorporating Cu $d^{9.8}$ into the unit formula, the valence distribution in carrollite can be described as $Cu^{1.2+}(Co^{2.4+})_2(S^{1.5-})_4$. The value $S^{1.5-}$, which is a consequence of charge neutrality, means that there is effectively half a hole per atom in the S 3*p* 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 Co $L_{3,2}$ XAS of $CuCo_2S_4$ 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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REFERENCES

BOCQUET, A.E., MIZOKAWA, T., SAITOH, T., NAMATAME, H. & FUJIMORI, A. (1992): Electronic structure of 3*d*-transition-metal compounds by analysis of the 2*p* core-level photoemission spectra. *Phys. Rev. B* **46**, 3771-3784.

CHARNOCK, J.M., GARNER, C.D., PATTRICK, R.A.D. & VAUGHAN, D.J. (1990): An EXAFS study of thiospinel minerals. *Am. Mineral.* **75**, 247-255.

CHARNOCK, J.M., HENDERSON, C.M.B., MOSSELMANS, J.F.W. & PATTRICK, R.A.D. (1996): 3d transition metal L-edge X-ray absorption studies of the dichalcogenides of Fe, Co and Ni. *Phys. Chem. Minerals* **23**, 403-408.

COKER, V.S., PEARCE, C.I., PATTRICK, R.A.D., VAN DER LAAN, G., TELLING, N.D., CHARNOCK, J., ARENHOLZ, E. & LLOYD, J.R. (2008): Probing the site occupancies of Co-, Ni-, and Mn-substituted biogenic magnetite using XAS and XMCD. *Am. Mineral.* **93**, 1119-1132.

DRŰPPEL, K., WAGNER, T. & BOYCE, A.J. (2006): Evolution of sulfide mineralization in ferrocarbonatite, Swartbooisdrif, northwestern Namibia: constraints from mineral compostions and sulfur isotopes. *Can. Mineral.* **44**, 877-894.

GRIONI, M., GOEDKOOP, J.B., SCHOORL, R., DE GROOT, F.M.F., FUGGLE, J.C., SCHÄFERS, F., KOCH, E.E., ROSSI, G., ESTEVA, J.-M. & KARNATAK, R.C. (1989): Studies of copper valence states with Cu L_3 x-ray absorption spectroscopy. *Phys. Rev. B* **39**, 1541-1545.

GRIONI, M., VAN ACKER, J.F., CZYZYK, M.T. & FUGGLE, J.C. (1992): Unoccupied electronic structure and core-hole effects in the x-ray-absorption spectra of Cu_2O. *Phys. Rev. B, Condensed Matter and Materials Phys.* **45**, 3309-3318.

HILL, R.J., CRAIG, J.R. & GIBBS, G.V. (1979): Systematics of the spinel structure type. *Phys. Chem. Minerals* **4**, 317-339.

LI, DIEN, BANCROFT, G.M., KASRAI, M., FLEET, M.E., FENG, XINGHONG & KIM, TAN (1995): S *K*-edge and *L*-edge X-ray absorption spectroscopy of metal sulfides and sulfates: applications in mineralogy and geochemistry. *Can. Mineral.* **33**, 949-960.

MANTHIRAM, A. & JEONG, J.U. (1999): Ambient temperature synthesis of spinel Ni_3S_4: an itinerant electron ferrimagnet. *J. Solid State Chem.* **147**, 679-681.

MURO, T., KIMURA, A., IWASAKI, T., UEDA, S., IMADA, S., MATSUSHITA, T., SEKIYAMA, A., SUSAKI, T., MAMIYA, K., HARADA, T., KANOMATA, T. & SUGA, S. (1998): Resonance and high-resolution photoemission study of CoS_2. *J. Electron Spectrosc. Relat. Phenom.* **88–91**, 361-364.

MURO, T., SHISHIDOU, T., ODA, F., FUKAWA, T., YAMADA, H., KIMURA, A., IMADA, S., SUGA, S., PARK, S. Y., MIYAHARA, T. & SATO, K. (1996): Magnetic circular dichroism of the S 2*p*, Co 2*p*, and Co 3*p* core absorption and orbital angular momentum of the Co 3*d* state in low-spin CoS_2. *Phys. Rev. B* **53**, 7055-7058.

NAKAI, I., SUGITANI, Y., NAGASHIMA, K. & NIWA, Y. (1978): X-ray photoelectron spectroscopic study of copper minerals. *J. Inorg. Nucl. Chem.* **40**, 789-791.

PATTRICK, R.A.D., VAN DER LAAN, G., VAUGHAN, D.J. & HENDERSON, C.M.B. (1993): Oxidation state and electronic configuration determination of copper in tetrahedrite group minerals by *L*-edge X-ray absorption spectroscopy. *Phys. Chem. Minerals* **20**, 395-401.

PEARCE, C.I., PATTRICK, R.A.D., VAUGHAN, D.J., HENDERSON, C.M.B. & VAN DER LAAN, G. (2006): Copper oxidation state in chalcopyrite: mixed Cu d^9 and d^{10} characteristics. *Geochim. Cosmochim. Acta* **70**, 4635-4642.

THOLE, B.T. & VAN DER LAAN, G. (1988): Branching ratio in X-ray absorption spectroscopy. *Phys. Rev. B* **38**, 3158-3171.

VAN DER LAAN, G., ARENHOLZ, E., CHOPDEKAR, R.V. & SUZUKI, Y. (2008): Influence of crystal field on anisotropic X-ray magnetic linear dichroism at the Co^{2+} $L_{2,3}$ edges. *Phys. Rev. B* **77**, 064407-1/11.

VAN DER LAAN, G. & KIRKMAN, I.W. (1992): The 2*p* absorption spectra of 3*d* transition metal compounds in tetrahedral and octahedral symmetry. *J. Phys.: Condens. Matter* **4**, 4189-4204.

VAN DER LAAN, G., PATTRICK, R.A.D., VAUGHAN, D.J. & HENDERSON, C.M.B. (1992): Determination of the valence state in copper compounds using Cu $L_{2,3}$ absorption spectroscopy. *J. Phys. Chem. Solids* **53**, 1185-1190.

VAN DER LAAN, G. & THOLE, B.T. (1991): Strong magnetic X-ray dichroism in 2*p* absorption spectra of 3*d* transition-metal ions. *Phys. Rev. B* **43**, 13401-13411.

VAN DER LAAN, G., WESTRA, C., HAAS, C. & SAWATZKY, G.A. (1981): Satellite structure in photoelectron and Auger spectra of copper dihalides. *Phys. Rev. B* **23**, 4369-4380.

VAN DER LAAN, G., ZAANEN, J., SAWATZKY, G.A., KARNATAK, R. & ESTEVA, J.-M. (1986): Comparison of X-ray absorption with X-ray photoemission of nickel dihalides and NiO. *Phys. Rev. B* **33**, 4253-4263.

VAUGHAN, D.J. & TOSSELL, J.A. (1981): Electronic structure of thiospinel minerals; results from MO calculations. *Am. Mineral.* **66**, 1250-1253.

WAGNER, T. & COOK, N.J. (1999): Carrollite and related minerals of the linnaeite group: solid solutions and nomenclature in the light of new data from the Siegerland District, Germany. *Can. Mineral.* **37**, 545-558.

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