Modified Surface Layers of Reactive Materials

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Metal sulfides are typical of materials that react rapidly with air to form a modified surface layer. To investigate the formation of such a layer by means of SXPS and NEXAFS spectroscopy, it is first necessary to characterise an unreacted surface, which can be prepared by fracture and subsequent transfer to the end-station analysis chamber while under clean UHV. This can be achieved in the ASRP end-station where both a dual-blade fracture stage and the analysis chamber are attached to a rotary distribution chamber maintained under UHV.

Carrollite, $CuCo_2S_4$, is one example of the sulfides of interest. The formal oxidation states of the constituent elements in carrollite have been controversial for many years, with no consensus between $Cu^{I}Co^{III}Co^{IV}S^{-II}_4$, $Cu^{I}Co^{III}_2S^{-II}_3S^{-I}$ and $Cu^{II}Co^{III}_2S^{-II}_4$. The Cu^{II} description has either been assumed or proposed on the basis of several different experimental measurements on synthetic and natural specimens, including magnetic behaviour, ^{63}Cu and ^{59}Co NMR spectra and X-ray absorption spectra. The XAS evidence (for ground material) consisted of a Cu L_3-edge absorption peak at 930.5 eV, 0.7 eV lower than the corresponding peak for Cu^{II} oxide, and a clear indicator of a Cu $3d^9$ ground state. In contrast, the Cu 2*p* photoelectron spectrum from a fresh surface had displayed no excited final state satellites that are normally associated with Cu^{II}; the $2p_{3/2}$ binding energy was ~932.5 eV which is consistent with Cu^{I}. Also, band calculations had revealed that mainly Co 3*d* and S 3*p* states were present near the Fermi level (E_F). The Cu 3*d* states formed almost fully occupied narrow bands situated well below E_F, indicating Cu^{I} rather than Cu^{II}.

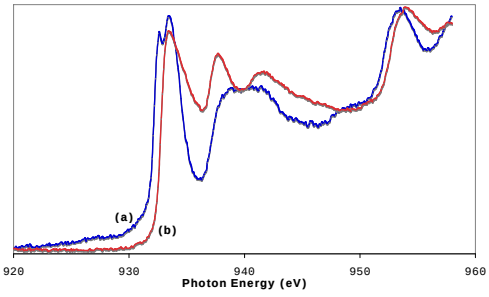

Figure 1. Cu $L_{2,3}$-edge spectrum from: (a) a carrollite surface prepared by fracture under UHV; (b) Cu metal.

The electron yield Cu $L_{2,3}$-edge NEXAFS spectrum of a carrollite surface prepared in the presesnt work by fracture under UHV is shown in Fig. 1 together with the corresponding spectrum for Cu metal. Surprisingly, two components in the leading absorption peak were observed; the first near 932.5 eV and the second near 933.5 eV. No absorption peak was discernible below 931.5 eV, generally considered to be the lower limit for Cu^{I} L_3 absorption, in marked contrast to the peak at 930.5 eV previously reported for ground carrollite. Thus, the subsurface Cu in carrollite was certainly not Cu^{II}; rather, it was most probably Cu^{I}, but the intense absorption peak near 933 eV, and especially the structure in that absorption peak, had not been expected. The previously reported band structure for carrollite had predicted an extremely low density of Cu *d*-states above E_F, therefore a Cu $L_{2,3}$-edge absorption spectrum more like that for chalcocite had been expected. It is pertinent to note that there is only one crystallographic site for Cu in the carrollite unit cell, and that the structure in the leading absorption peak was not attributable to the presence of another Cu sulfide phase in the mineral specimen. Also, there was no evidence that the component near 933.5 eV was due to Cu^{II} that had been photo-reduced to Cu^0.

The Co oxidation state(s) could not be positively identified from the Co $L_{2,3}$-edge spectrum. The spectrum was consistent with Co^{III} but the presence of Co^{IV} could not be excluded. The S 2p spectra provided no evidence for a bulk S^{-I} environment accounting for 25% of the S as might have been expected if carrollite could be represented by $Cu^{I}Co^{III}_2S^{-II}_3S^{-I}$.

Because of the apparent discrepancy between the observed Cu $L_{2,3}$-edge spectrum and the previously reported Cu 3*d* density of states for carrollite, new *ab initio* electronic structure calculations were undertaken. The total density of states calculated using the WIEN2k code was broadly similar to that reported previously, including the position of E_F. The Co 3*d* and S 3*p* partial densities of states were also broadly similar, however, the Cu 3*d* density of states was quite different. The WIEN2k calculations revealed the Cu 3*d* states to extend beyond E_F to result in a low and narrow density immediately above E_F, and an even lower but broader density of Cu 3*d* states between about 1.5 and 2.5 eV above E_F. In both cases, these 3*d* states were mostly t_{2g} rather than e_g, and the density of Cu *s* states in these two regions was very low. The simulated Cu L_3 absorption spectrum based on the densities of states calculated by WIEN2k was consistent with the observed spectrum.

Given that oxidation states in the carrollite bulk of Cu^{I} and S^{-II} were established, but that a definitive oxidation state for the Co could not be ascertained, it can be concluded that carrollite is best represented as $Cu^{I}(Co_2)^{VII}S^{-II}_4$.