

Cu $L_{3,2}$ X-ray absorption spectroscopy and the electronic structure of minerals: Spectral variations in non-stoichiometric bornites, Cu_5FeS_4

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ABSTRACT

Synthetic bornites with compositional variations within 2 at% of the stoichiometric formula of Cu_5FeS_4 show dramatic changes in their Cu $L_{2,3}$ absorption spectra, determined using synchrotron radiation. Many of the bornites show L_3 spectra with a strong peak at 932.6 eV and a broader region of intensity in the region 933 eV to 940 eV with specific features at 935.6 eV and 938 eV. However, the intensity of the peak at 932.6 eV varies greatly, and there is a clear correlation between the loss of intensity of this peak and the gain of intensity of the peak at 935.6 eV. EPMA reveals that this change in relative intensities is directly correlated to the excess of valence electrons present in the bornites, calculated the using formal valences of Cu^+ , Fe^{3+} and S^{2-} [The Cu $L_{3,2}$ spectra are typical of Cu(I) sulfides and Fe L_3 edge spectra reveal the Fe to be present as Fe^{3+}]. A simple cluster model can explain this transfer in intensity among the three different peaks. The three peaks in the bornite XAS $2p$ spectrum can be assigned (in order of increasing energy) to the final states $cd^{10}Ls^2$, $cd^{10}s$, and cd^9s^2 ; the transition to an empty s state is possible for all three configurations, $d^{10}Ls \rightarrow cd^{10}Ls^2$, $d^{10} \rightarrow cd^{10}s$, and $d^9s \rightarrow cd^9s^2$. When the amount of excess electrons increases, the holes are filled and the weight of the $d^{10}Ls$ and d^9s configurations will decrease, whereas that of the d^{10} configuration will increase, exactly as observed in the spectra. This study demonstrates the value of metal L -edge spectroscopy, and Cu $L_{2,3}$ spectra in particular, in investigations of minerals with variations in stoichiometry and chemistry; the information derived on electronic structure can be used to explain bonding and other variations in physical and chemical properties of the minerals.