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Evolution of local electronic structure in alabandite and niningerite solid solutions [(Mn,Fe)S, (Mg,Mn)S, (Mg,Fe)S] using sulfur *K*- and *L*-edge XANES spectroscopy

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ABSTRACT

Synchrotron radiation S *K*- and *L*-edge X-ray absorption near-edge structure (XANES) spectra are reported for the cubic, rocksalt (B1) structure sulfides niningerite (MgS), alabandite (MnS), and oldhamite (CaS), and for their solid solutions (Mn,Fe)S and (Mg,Mn)S, and S *L*-edge XANES spectra are reported also for (Mg,Fe)S solid solutions. Pre-edge features at the S *K*-edge are attributed to transition of S 1*s* electrons to the lowest available unoccupied S 3*p* σ* antibonding states hybridized with metal 3*d*(e_g) states, and at the S *L*-edge to transition of S 2*p* electrons to unoccupied S 3*s* σ*, 4*s* σ*, and 3*d* antibonding states hybridized with metal 3*d*(e_g) states, and to a lesser extent 3*d*(t_{2g}) states.

The S *K*-edge XANES spectra for the solid solutions show a progressive participation of 3*d* orbitals in metal-S bonding with increase in substitution by Fe in (Mn,Fe)S and (Mg,Fe)S and Mn in (Mg,Mn)S through progressive increase in the area of the pre-edge feature. However, the pre-peak area does not increase linearly in each solid solution series showing that a real change in bulk electronic properties has occurred. Increase in pre-peak area reflects an increase in overall attainability of metal 3*d* states for hybridization with S 3*p* σ* antibonding states as proportionally more metal 3*d* orbitals become available. The S *L*-edge XANES spectra show progressive evolution of pre-edge features at the L_3- and L_2-edges (a_1 and a_2, respectively). Only a_2 is present in the S *L*-edge XANES spectrum of FeS (troilite), and with progressive decrease in Fe content in (Mn,Fe)S and (Mg,Fe)S solid solutions, a_1 first appears, then becomes dominant. Since a_1 is attributed to transition of S 2$p_{3/2}$ electrons to S 3*s* σ* states hybridized with metal 3*d*(e_g) and 3*d*(t_{2g}) states, this appears to represent an increased contribution from metal-S π-bonding. The results show that the size and position of the pre-edge features to the S *K*- and *L*-edges are controlled more by the DOS of hybridized 3*d*(e_g^{β}) and 3*d*(t_{2g}^{β}) states and nearest-neighbor coordination of the metal atoms than by the precise coordination of S and the extended structure of the sulfide.

The full multiple scattering approach has been applied to the calculation of the S *K*-edge XANES spectra of MgS, MnS, and CaS. Results are consistent with experimental XANES spectra, especially for the pre-edge features, which are often neglected in such calculations.