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Unoccupied states of pyrite probed by electron energy-loss spectroscopy (EELS)

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ABSTRACT

Electron energy-loss spectra (EELS) of pyrite (FeS_2) were acquired and include the Fe K, $L_{2,3}$, $M_{2,3}$, and M_1 edges, and the S K, $L_{2,3}$, and L_1 edges. The core-loss edges exhibit a range of shapes and different theories are required to understand the spectra. In the process a clear picture of the conduction-band states as a function of energy above the band gap is obtained. This analysis reveals the extent of mixing of unoccupied states and thus provides an understanding of the limits of interpreting core-loss edges in light of the optical dipole limit. A unified picture of the unoccupied states is obtained by aligning the spectra on a common energy scale relative to the published Bremsstrahlung isochromat spectrum (BIS) and with the results of band structure calculations. This alignment allows similarities between the spectra of different atoms to be related to mixing of local conduction-band states. The coincidence of the Fe K and S $L_{2,3}$ spectral features attests to the strong hybridization of the Fe p-S $3d$ states. The main Fe $L_{2,3}$ edges are followed by structures that confirm an Fe-S bond with a substantial degree of mixing between Fe d^6 and d^7 states. The aligned EELS spectra clearly divide the unoccupied states into two regions. The first region is dominated by the intense d-like component of the Fe L_3 edge and p-like components of the S K and L_1 edges. A small pre-peak at the Fe K edge aligned with the Fe $L_{2,3}$ edge peak maximum is indicative of Fe $4p + 3d$ e_g and S $3p$ mixing. Similarly, the pre-peak to the S $L_{2,3}$ edge arises from transitions to states with mixed S $s + p +$ Fe $3d$ e_g character.