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Identification of pyrite valence band contributions using synchrotron-excited X-ray photoelectron spectroscopy

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ABSTRACT

The major contributions to the pyrite valence band have been identified experimentally by monitoring XPS valence band signal intensity as a function of photon (X-ray source) energy. The S-S σ and σ* orbitals are located at about 13 and 16 eV binding energy and are almost exclusively derived from S 3*s*-S 3*s* mixing; there is no experimental evidence for a S 3*p* contribution to these molecular orbital (molecular orbital) values as required for sp^3 hybridization. Fe-S σ (Fe $3d_{eg}$-S $3p_z$ derived) and Fe-S π and π* (Fe $3d_{t2g}$-S $3p_{x,y}$ derived) molecular orbitals are identified at Binding Energies (B.E.) less than 8 eV, and are consistent with energies calculated by Eyert et al. (1998). Fe-S π molecular orbital contributions are located in the valence band between about 1.8 and 3 eV and Fe-S π* molecular orbitals contribute between about 0.7 to 1.5 eV binding energy. Contributions observed at the top of the valence band and concentrated between the Fermi level and about 0.6 eV B.E. may be derived from Fe $3d_{eg}$ (non-bonding) orbitals. The experimental data are consistent with these non-bonding contributions being derived from surface Fe species (Fe electronic surface states), and perhaps represent the Fe $3d_{eg}$ "dangling bonds" produced by rupture of Fe-S σ bonds during fracture. The conformity of spectral assignments based on experimental data with band theoretical calculations (of Eyert et al. 1998, using a basis set appropriate to pyrite) indicates that the essential aspects of the pyrite valence band are understood and energetically quantified. Additional study is required to identify positively