

Resonant XPS study of the pyrite valence band with implications for molecular orbital contributions

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ABSTRACT

High-quality valence band X-ray photoelectron spectroscopy (XPS) of vacuum-fractured pyrite (FeS₂) was performed using photons from a high resolution undulator beamline. The spectra, collected at photon energies ranging from 50 to 65 eV, span the Fe 3*p* ionization threshold and reveal the nature of both final state and surface state contributions to the valence band. The lower valence band (1.5 to 10 eV binding energy) reflects primarily S 3*p*-like direct emission final state contributions. In contrast, the upper valence band (0 to 1.5 eV binding energy) incorporates both a ligand to metal charge transfer and a Fe 3*d* direct emission final state contribution, the latter perhaps derived in part from surface Fe atoms (a surface chemical state contribution). The results imply that calculations of the pyrite density of states, based on ground state configuration, and without consideration of final state contributions, should reflect closely the XPS valence band structure; this is confirmed by comparison of calculation and collected spectra.

Although generally similar to low resolution valence band spectra previously collected, these high resolution spectra show little resonant enhancement of any valence bands above the Fe 3*p* threshold. The important implication concerns the state of Fe 3*d*_{2g} orbitals; the weakness of the direct emission final state (Fe 3*d*⁵⁺) contribution and strength of the charge transfer final state contribution to the valence band is explained if Fe 3*d*_{2g}-derived orbitals are mixed with S valence orbitals, a possibility predicted by recent theoretical considerations (Eyert et al. 1998). Direct emission final state contributions are, however, observed in the upper valence band (0.40 to 1.3 eV binding energy) and some of the signal may result from surface Fe 3*d* non-bonding orbitals produced by fracture of the mineral.