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Synchrotron XPS evidence for Fe^{2+}-S and Fe^{3+}-S surface species on pyrite fracture-surfaces, and their 3D electronic states

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ABSTRACT

A X-ray photoelectron Fe $2p_{3/2}$ spectrum of a pristine pyrite fracture surface was collected using synchrotron radiation with the source tuned to 800 eV. Comparison of this highly surface sensitive Fe 2p spectrum with Fe 2p spectra collected by conventional means (1487 eV Al$K\alpha$ source) reveals that the high binding energy tail of the pyrite Fe $2p_{3/2}$ line results primarily from Fe surface state contributions. The three major contributions to the spectrum are interpreted to be: (1) Fe^{2+} resident on bulk sites; (2) Fe^{2+} resident on surfaces, edges and corners; (3) Fe^{3+} surface states produced during fracture by an auto-redox reaction involving Fe and S. The intense main peak is ascribed to the bulk state, whereas the high binding energy tail of the spectrum is composed primarily of Fe^{2+} and Fe^{3+} surface state contributions.

Fe^{2+} on bulk sites is octahedrally coordinated (O_h symmetry). All valence electrons of Fe on bulk sites are paired (diamagnetic) and a singlet photopeak at 707 eV is consequently produced. Fracture produces Fe^{2+} surface states with lower coordination than bulk sites. Fe^{2+} located at surfaces, edges and corners experiences modified Ligand Field Stabilization Energies (LFSE) which results in stabilization of the d_{z^2} orbital and destabilization of the d_{xy} orbital. Promotion of a d_{xy} electron to the d_{z^2} orbital makes surface Fe^{2+} surface states paramagnetic resulting in multiplet splitting of their associated photopeaks. The Fe^{3+} surface state is necessarily paramagnetic and its photoemissions are consequently multiply split.

Analysis of photopeak structures and binding energy splittings of Fe^{2+} and Fe^{3+} surface states demonstrates that they are located at the appropriate binding energies, and span the appropriate energy range, to satisfactorily explain the high binding energy tail on of the Fe $2p_{3/2}$ spectrum.