

XPS evidence for Fe and As oxidation states and electronic states in loellingite (FeAs₂)

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ABSTRACT

This first X-ray Photoelectron Spectroscopy (XPS) study of loellingite (FeAs₂) reveals a strong Fe 2*p*_{3/2} singlet peak at 707.0 eV signifying that fully coordinated Fe of the bulk phase has the same oxidation state of bulk Fe in marcasite, arsenopyrite, and pyrite. The As 3*d* peak of loellingite (41.1 eV) demonstrates that As atoms of As dimers in loellingite have the same oxidation state as As atoms of As-S dimers in arsenopyrite. These XPS data consequently corroborate previous Mössbauer studies and confirm theoretical considerations; Fe of loellingite, arsenopyrite, and marcasite is divalent (formally) rather than being trivalent (arsenopyrite) or tetravalent (loellingite). Arsenic is present as As¹⁻ (formal oxidation state) in both loellingite and arsenopyrite.

The presence of an intense Fe 2*p*_{3/2} singlet peak for loellingite, rather than a multiplet set of peaks, demonstrates that all valence electrons of Fe in the bulk phase are paired; loellingite is a diamagnetic material thus resolving issues related to magnetic studies of the mineral. A multiplet set of peaks explains the weak high binding energy tail of the Fe 2*p*_{3/2} spectrum. This set of peaks is derived from Fe surface species. As for pyrite surfaces, Fe surface sites are of C_{4v} symmetry due to loss of a ligand during fracture. The symmetry stabilizes the *d*_{z²} orbital leading to an intermediate spin state with unpaired electrons in Fe valence orbitals and a multiplet set of peaks. A second, weak set of multiplet peaks, probably representing Fe³⁺ bonded to As are also present, suggesting that a minor proportion of surface Fe²⁺ and arsenic undergo an auto-redox reaction in response to fracture.

The As 3*d* spectrum includes two spin-orbit-split doublets. One doublet represents As of As-As dimers located within the bulk phase (fully coordinated). The second is located at somewhat greater binding energy than the bulk contribution and may represent a surface polymeric As contribution.