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 2p₁/₂ 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 3d 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 As⁺⁺ (formal oxidation state) in both loellingite and arsenopyrite.

The presence of an intense Fe 2p₁/₂ 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 2p₁/₂ spectrum. This set of peaks is derived from Fe surface species. As for pyrite surfaces, Fe surface sites are of C₄ᵥ symmetry due to loss of a ligand during fracture. The symmetry stabilizes the dₛ 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 Fe⁺⁺⁺ 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 3d 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.

INTRODUCTION

Discussions have ensued since the mid 1960s over the oxidation state and electronic structure of iron and arsenic in loellingite and the nature of the interactions controlling its structure. Early investigators (Pearson 1965; Hullinger and Mooser 1965; Nickel 1968) argued that the structural differences between loellingite, arsenopyrite, and marcasite resulted from metal-metal interactions parallel to the c crystallographic axis and that Fe was tetravalent in loellingite, trivalent in arsenopyrite, and divalent in marcasite. This was thought to be associated with substitution of S for As (Pearson 1965; Nickel 1968).

Goodenough (1972) criticized these arguments and instead proposed a markedly different ligand field splitting of the Fe 3d orbitals into three groups, two of which differed slightly in energy (t₂g orbitals), and a third group of high energy orbitals resulting from metal-metal interaction parallel to the c axis. He concluded that distortions in arsenopyrite and loellingite relative to marcasite result from metal-anion interactions, not metal-metal interactions. He still assumed, however, that the formal oxidation state of iron was different in each of the three minerals.

Vaughan and Craig (1978) contested the differing Fe oxidation state in these minerals providing evidence from Mössbauer measurements that indicated the presence of Fe⁺⁺ in each mineral. Tossell et al. (1981) and Tossell (1983, 1984) also supported the presence of Fe⁺⁺ through molecular orbital calculations and stressed the role of ligand-ligand interactions as a control on structure. Extended Hückel calculations of Wijeyesekera and Hoffman (1983) did not, however, support these proposals.

A goal of this study is to document (for the first time) the contributions to the Fe 2p₁/₂ and As 3d spectra of loellingite in an attempt to determine the chemical state properties of Fe and As within the bulk and at the surface of the mineral. A second goal is to provide experimental XPS evidence for the oxidation states of Fe and As in loellingite, as this information should help to resolve previous, conflicting interpretations concerning the chemical states of Fe and As in marcasite, arsenopyrite, and loellingite, and to be used to confirm preliminary observations of Fe and As surface species on loellingite. To this end, a pristine loellingite fracture surface was analyzed with an X-ray Photoelectron Spectrometer (XPS) and core-level Fe 2p₁/₂ and As 3d photoelectron spectra were collected.

EXPERIMENTAL ASPECTS

Sample preparation

The loellingite sample, collected from the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey, was obtained from the Mineralogical Research Company. A single, elongate lath of loellingite was cut from the massive sample. The lath was

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