Arsenic clustering in arsenian pyrite: A combined photoemission and theoretical modeling study

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Abstract

Arsenian pyrite is known to have a strong association with gold in most auriferous refractory deposits, and thus understanding the chemical speciation of arsenic in localized environments in arsenian pyrite provides an important basis for determining its reactivity and mobility. However, arsenic is fast-oxidizing among elements in the Fe-As-S system and hence it may exist in various chemical states, which renders it difficult to establish arsenic nature under pristine conditions, particularly in arsenian pyrite. Herein, arsenian pyrite samples were analyzed on a synchrotron soft X-ray spectroscopy beamline under ultrahigh vacuum conditions, and As-3d as well as S-2p spectra were collected. A comparison between the spectrum of bulk As-3d in the samples with its bulk counterpart in arsenopyrite revealed a 0.6 eV shift toward lower binding energies. This observation was similar to loellingite (FeAs2), where the binding energy shift was attributed to high electron density on As of the As-As dimer. Formation of As clusters resulting in comparable binding energy shifts was also proposed from the spectroscopic studies. The experiments were complemented by a series of first-principles calculations simulating four experimentally observed pyrite surfaces where surficial S atoms were randomly substituted by As. As such, six arsenian pyrite crystal surfaces were modeled, two of which constituted surficial As clusters replacing both S and Fe atoms. The surfaces were geometrically optimized, and surface energies were calculated along with the corresponding electronic structure providing a detailed distribution of partial charges for surficial atoms obtained from Löwdin population analysis. The calculated partial charges of atoms located at the surface arsenian pyrite indicated that while the electron density on the As atom of As-S dimers in arsenian pyrite is less negative than the As in bulk arsenopyrite, it is more negative for the As atom of As-As dimers, which were only seen in the surficial As clusters. This validated the description of As presence in arsenian pyrite as local clusters inducing localized lattice strain due to increased bond distances. Our findings offer a good background for future studies into the reactive sites in arsenian pyrite and how that compares with associated minerals, arsenopyrite, and pyrite.

Keywords: X-ray photoelectron spectroscopy, density functional theory, pyrite, arsenian pyrite

Introduction

The most abundant metal sulfide on the surface of Earth, including terrestrial and marine sediments, is pyrite (FeS2). The pyrite space group is Pa3, where two interpenetrating FCC structures form a halite structure. The corners of the cube and face centers are occupied by Fe atoms and sulfur dimers oriented along the <111> direction and are located in the middle of the 12 edges as well as in the cube center. Consequently, each unit cell consists of four formula units of FeS2 and each Fe is surrounded by six S as nearest neighbors forming a distorted octahedron. The bonding is described by d2sp3 hybridization of Fe valence orbitals while each S is tetrahedrally coordinated by three Fe and its dimer partner (Murphy and Strongin 2009).

A broad range of potential applications has been attributed to pyrite. For example, it is a semiconductor with a band gap of ~0.95 eV, which is suited to photovoltaic cells and an optical absorption coefficient on the order of 105 cm−1 (much higher than that of materials like GaAs). Nevertheless, it has a very low open-circuit voltage, which results in the low efficiency of pyrite photoelectrochemical cells (Sun et al. 2011).

On the other hand, valuable sulfide ores often contain pyrite and it is well established that pyrite surface reactivity is instrumental in processes that rely heavily on their physico-chemical properties for separation and extraction (Hu Yuehua et al. 2009). However, pyrite is known to have poor cleavage and while the most observed cleavage direction of pyrite is (100), other cleavages comprising (021), (111), and (110) have also been detected (Murphy and Strongin 2009). Such surfaces can be studied by either X-ray photoelectron spectroscopy (XPS) or ab initio simulations (von Oertzen et al. 2005). Pyrite with As content above about 1 wt% As is called arsenian pyrite (Stepanov et al. 2021; Wells and Mullens 1973) and has been found to concentrate valuable metals such as gold (Arehart et al. 1993; Cook and Chryssoulis 1990). In such mineralogical occurrence, a positive correlation between gold and arsenic, supported by sampling from different geological settings, is observed (Palenik et al. 2004). Using first-principle and Monte Carlo calculations, Reich and Becker proposed (Reich and Becker 2006; Reich et al. 2005) up to 6 wt% arsenic substitution in pyrite, beyond which exsolution occurred with formation of...