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A comparative X-ray absorption near-edge structure study of bornite, Cu_5FeS_4, and chalcopyrite, $CuFeS_2$

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Abstract

High resolution Fe L-, Cu L-, S L-edge and O K-edge X-ray absorption near-edge structure (XANES) spectra of synthetic bornite and the samples oxidized in air and leached in a ferric chloride solution have been recorded and compared with the spectra of chalcopyrite. The pre-edge shoulder in the Cu L-edge spectrum of bornite and the strong leading peak in the spectrum of chalcopyrite were attributed to the electron transitions to the minor density of unoccupied Cu 3d states, and the post-edge features were related to the states of s- and p-type. The Fe L-edge XANES showed the presence of predominant Fe^{2+} for chalcopyrite, and some quantity of Fe^{2+} for bornite cannot be excluded despite XPS and Mössbauer spectroscopy had previously detected only Cu^{+} and Fe^{3+} species in both minerals. The Cu L- and S L-edge spectra of bornite considerably modify and become similar to those of chalcopyrite after the oxidative leaching that produces the heavily metal-depleted surface layers, and the Fe L-edge XANES shows only a slightly increased contribution of Fe^{2+}. The multiparticle configurations involving Fe^{2+} and Cu^{2+} or holes at S atoms may play a role in the L-spectra.

Keywords: Bornite; Chalcopyrite; Copper $L_{2,3}$; Iron $L_{2,3}$; Sulphur $L_{2,3}$; Oxygen K XANES

1. Introduction

Knowledge of the electronic structure and surface characteristics of ternary sulphides of copper and iron, chalcopyrite, $CuFeS_2$, and bornite, Cu_5FeS_4, is important for their applications as major copper minerals and in materials science. Chalcopyrite has a double zinc blend unit cell, in which Cu and Fe atoms are in the tetrahedral interstices of a sulphur framework, so sulphur atoms are four-coordinated too [1]. Bornite exists in three polymorphic forms related by superstructuring [1–3]. The high-temperature polymorph consists of a random distribution of six Cu and Fe atoms and two cationic vacancies in the eight tetrahedral sites of a cubic close-packed S sublattice. The intermediate and low polymorphs are characterized by progressing cation ordering and vacancy clustering, with metal atoms being somewhat displaced from the centers of the sulphur tetrahedra [2]. The highest occupied orbitals in chalcopyrite are antibonding Cu 3d–S 3p ones in so-called fundamental gap, and the Fe 3d levels of t_2 symmetry lie between that levels and S 3p nonbonding set, both with considerable admixture of the Fe 3d orbitals [4–12]. The electronic structure of bornite was poorly examined and understood [1,3]. Mössbauer spectroscopy and XPS show that oxidation states of Cu and Fe are 1+ and 3+, respectively, both in chalcopyrite and bornite [1,13]. However, Cu L- and Fe K- and L-edge X-ray absorption near-edge structure (XANES) spectra of chalcopyrite imply that

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some share of copper and iron to be divalent [7]. Moreover, Todd et al. [14], having recently studied intrinsic and oxidized surfaces of chalcopyrite using X-ray absorption and emission spectroscopy, have claimed that the Cu L- and Fe L-edge XANES support a $Cu^{2+}Fe^{2+}S_2$ composition. XANES is concerned with the electronic transitions from atomic core levels to unoccupied states and provides data on the densities of states at the conduction bands along with some other information [15,16]. In particular, the $L_{2,3}$-edge spectra describe, in line with the dipole selection rule $\Delta l = \pm 1$, the transitions from $2p_{3/2,1/2}$ orbitals to empty orbitals having d and s character [14–19]. The S K- [8,10,20], S L- [8,21], Cu K- [8,20], Cu L- [14,17–21], Fe K- [8] and Fe L-edge XANES [14,21] of chalcopyrite were reported in the literature. Only several Cu L-edge spectra of bornite, which differed from each other, were previously published [17,22–24]. Schmidt et al. [22] pointed out that the heating of tetragonal bornite to 300 °C and the cubic polymorph formation entailed disappearance of a small pre-edge absorption peak and some modification of the post-edge features. Recently van der Laan et al. have established [23,24] that the Cu L-edge spectra, first of all, a leading maximum strongly depend on the bornite composition within a narrow nonstoichiometric range of 2 at.%. The authors ascribed the leading peak to the transitions to a final state configuration $d^{10}\underline{L}s^2$ with a hole in the sulphur ligand band (denoted as $\underline{L}$). They also arrived at conclusion that the hole-ligand initial state $d^{10}\underline{L}s$ has lower energy than the d^{10} configuration.

In the current work we report Cu L-, S L- and Fe L-edge XANES of bornite and essentially metal-deficient surface layers formed at this material by the oxidative leaching in comparison with the spectra of chalcopyrite [21]. The objective of the research was to clarify the electronic structures of bornite and chalcopyrite, and of their oxidized surfaces. In order to avoid troubles with the presence of admixtures in the bornite mineral samples available to us, synthetic compound of Cu_5FeS_4 composition in the low polymorph form, akin to naturally occurring mineral, was used. The near-edge features in the spectra of these minerals were qualitatively explained using a combination of the one-electron molecular orbital model and the atomic multiplet approach [16,23,24].

2. Experimental

Bornite crystals were obtained using a routine of hydrothermal thermogradient synthesis [25]. The synthesis was performed employing an autoclave equipped with a floating 50 cm^3 beaker of passivated Ti in a 10% NH_4Cl solution at 500 °C and pressure of 100 MPa during 10 days, following quenching at the rate of ∼5 °C/s in cold water flow. The bornite crystals were obtained as joint 2–3 mm grains, which were applied as approximately 2 mm × 4 mm × 5 mm wafer. XRD examination showed the orthorhombic crystalline structure (low-temperature polymorph) of the crystals and absence of other crystalline phases. The wafers were abraded at silicon carbide paper, cleaned with a wet filter paper and transferred into a vacuum chamber of a spectrometer or etched in aqueous 1 M HCl + 0.4 M $FeCl_3$ solution at 50 °C for 1 h and then rinsed with distilled water before the transfer. The unreacted samples were additionally abraded with a steel file in the vacuum. Natural polycrystalline n-type chalcopyrite $CuFeS_2$ described in detail elsewhere [21] was treated in the same way. X-ray absorption spectra were collected using facilities of the Russian–German Laboratory [26] at a bending magnet beamline at the synchrotron radiation storage ring BESSY II (Berlin, Germany). The Cu $L_{2,3}$-, Fe $L_{2,3}$-, S $L_{2,3}$- and O K-edge spectra were recorded in the total electron yield (TEY) mode at room temperature, the step width was 0.05 eV; the analyzer chamber pressure was in the range of 10^{-9} Pa. The estimated monochromator resolution was better than 0.1 eV, the transmission of the monochromator was accounted for by measuring the TEY of Au foil. The X-ray spot size on the specimen was about 0.2 mm. The energy scales were referred to gaseous Ne K-edge absorption.

3. Results and discussion

The Cu L_3-edge XANES of the vacuum-abraded bornite (Fig. 1, 1) shows a small shoulder A at 932.2 eV and closely resemble those reported in Ref. [23] for the bornite samples containing a big “electron excess” N = at.% Cu + 3 at.% Fe–2 at.% S. For the bornite sample abraded in air and somewhat oxidized, all the maxima are shifted by 0.6 eV toward higher energies with indiscernible changes in their intensities. The notably distinct spectrum of chalcopyrite has rather strong peak A while the peak B is either small or shifted to a higher energy. The oxidative leaching of bornite in the ferric chloride solution results in considerable growing of the feature A at 932.0 eV. Furthermore, it becomes evident that

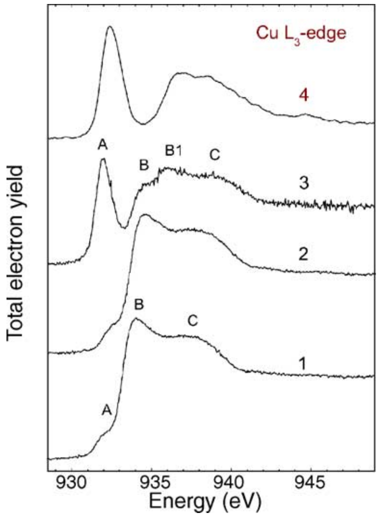

Fig. 1. The Cu L_3-edge XANES of (1) bornite abraded in vacuum, (2) abraded in air, (3) leached in 1 M HCl + 0.4 M $FeCl_3$ at 50 °C for 1 h, and (4) chalcopyrite abraded in vacuum.