IO-03   **Mon. 16. 06., 12^{10}-12^{30}**

X-ray absorption near-edge structure spectroscopy of bornite, Cu$_5$FeS$_4$

A. Rudkowski[1]*, T. Strączek[1], A. Czajka[1], D.A. Zając[1], Ł. Gondek[1], J. Przewoźnik[1], D. Rybicki[1], Cz. Kapusta[1] and A. Piestrzyński[2]

[1]*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Solid State Physics, al. A. Mickiewicza 30, 30-059 Kraków, Poland*
[2]*AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental protection, al. A. Mickiewicza 30, 30-059 Kraków, Poland*

Keywords: bornite, XANES, synchrotron radiation

*e-mail: rudkowski.andrzej@gmail.com

Bornite (Cu$_5$FeS$_4$) is one of the most important copper ores. Depending on temperature, three polymorphs of it are known to exist [1, 2]. Above 535 K bornite is cubic (space group *Fm3m*, a = 5.50 Å) with antifluorite structure. It has six Cu and one Fe atoms and two cationic vacancies distributed randomly in the eight tetrahedral sites of a cubic close-packed S sublattice. This high-temperature form transforms on cooling to metastable structure with doubling the unit cell (a = 10.94 Å). Finally, on cooling below 473K, the low-temperature stable form is obtained. This is the only phase that occurs naturally. The transition from the metastable to the low-temperature form involves the ordering of the Cu and Fe atoms among the S atom tetrahedra. The low-temperature stable form is orthorhombic (space group *Pbca*, $a = 10.95$ Å, $b = 21.86$ Å, $c = 10.95$ Å). The unit cell contains 16 Cu$_5$FeS$_4$ units.

A complex study of bornite structure and its physical properties was carried out on a natural polycrystalline bornite from the Polkowice Mine in Poland with the composition of Cu$_{4.76}$Fe$_{1.24}$S$_4$. X-ray diffraction studies [3] on this sample showed orthorhombic structure with *Pbca* space group and unit cell parameters $a = 10.9474(9)$ Å, $b = 21.8699(13)$ Å, $c = 10.9618$ Å.

The basic building blocks (10 atoms of Cu, 2 atoms of Fe and atoms of 8 S – all symmetrically inequivalent) are presented in Fig. 1 for temperatures 15 K and 300 K respectively.
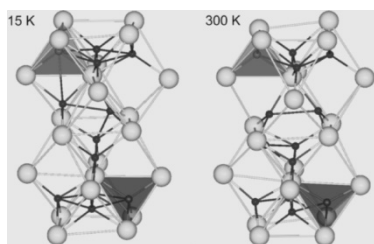

Figure 1. The basic building block of low-temperature bornite. Yellow, blue and red circles are respectively S, Cu and Fe atoms

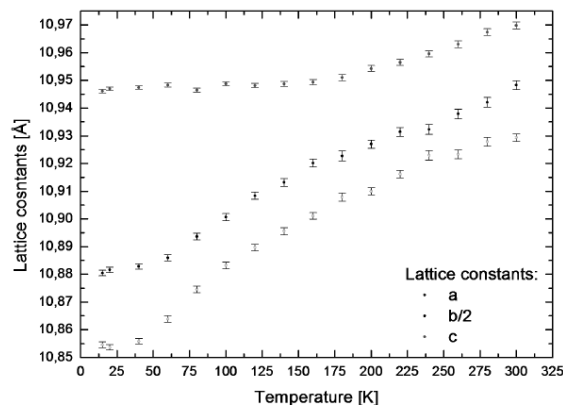In Fig. 2 the temperature dependence of the lattice constants is shown.

Figure 2. Temperature dependence of lattice constants of bornite.

An increase of orthorhombic distortion on decreasing temperature is pronounced.

Electrical transport measurements versus temperature indicate that bornite exhibits behaviour characteristic of semiconductor, Fig. 3.
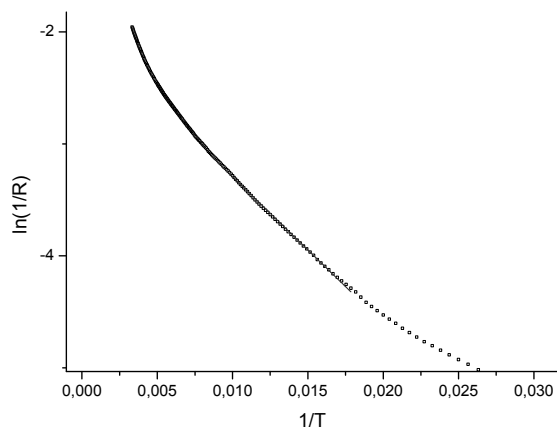

Figure 3. The dependence of logarithm of electrical conduction (reciprocal resistance) on the reciprocal temperature.

Measurements of resistance in the temperature range 2 K – 400 K were carried out, from which energy gap value was determined as equal to 0.3 eV. Significant magnetoresistance effect was also observed, corresponding to a decrease of the electrical resistance caused by the application of magnetic field.

The magnetic susceptibility measurements [3,4] indicate, that bornite undergoes antiferromagnetic-paramagnetic transition at the Neèl temperature T_N equal to 75 K. Mössbauer spectroscopy measurements [3] prove the magnetically ordered state in the compound below the T_N. They also revealed an inhomogeneous character of the transition and the occurrence of the AFM-PM phase segregation below T_N. The hyperfine field of 350 kOe, observed at 4.2 K, is higher than that for a spin Fe^{3+} in oxides (510 kOe). That effect may be attributed to Fe-S covalency and a possible copper

contribution to the effective magnetic moment of the compound. Zero field NMR measurements were also carried out. The measured NMR spectrum was very broad due to presence of several Cu lattice sites and significant quadrupole splitting. The transferred hyperfine field on Cu is in the range of 10-30 kOe. [5]

X-ray absorption near-edge structure (XANES) measurements have been carried out in the Helmholtz-Zentrum Berlin at a bending magnet beamline of the synchrotron radiation storage ring BESSY II. The Cu $L_{2,3}$- and Fe $L_{2,3}$- edge spectra were recorded in the total electron yield (TEY) and partial fluorescence yield (PFY) modes at room temperature. The spectra are presented in Figs. 3,4. The L_2 and L_3 absorption edges of Cu and Fe are associated respectively with electron transitions from the $2p_{1/2}$ and $2p_{3/2}$ core orbitals to the 3d bands.

The XANES spectra have also been preliminary computed using FEFF8.4 software package [6,7] – self-consistent real space multiple-scattering code for simultaneous calculations of x-ray absorption spectra and electronic structure. For data elaboration and analysis, Athena and Artemis [8,9] programs were used.

In Fig. 4 XANES spectra of iron L_2 and L_3 edges of bornite are presented. Electron binding energies amounts to 706.8 eV and 719.9 eV, respectively. The red solid line corresponds to experimental data recorded at the synchrotron, whereas blue dashed line corresponds to numerically calculated spectra.

The unit cell of bornite consist of two inequivalent Fe atoms. Thus, the calculations were performed for each of the two atomic sites individually and the final result was taken as a linear combination of them.
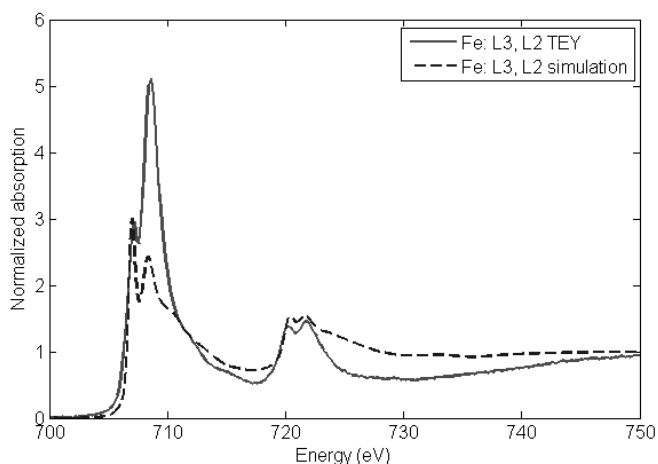

Figure 4: Experimental (red line) and preliminary calculated (blue dashed line) XANES spectra of Fe L_2 and L_3 edges in bornite.

In Fig. 5 XANES spectra of copper L_2 and L_3 edges of bornite are presented. Electron binding energies are equal to 932.7 eV and 952.3 eV respectively. As on previous picture, red line indicate values of absorption measured experimentally, while dashed blue shows calculated spectra. As the unit cell contains 10 inequivalent Cu atoms, calculations were made for each one and final result was obtained by averaging the individual results.
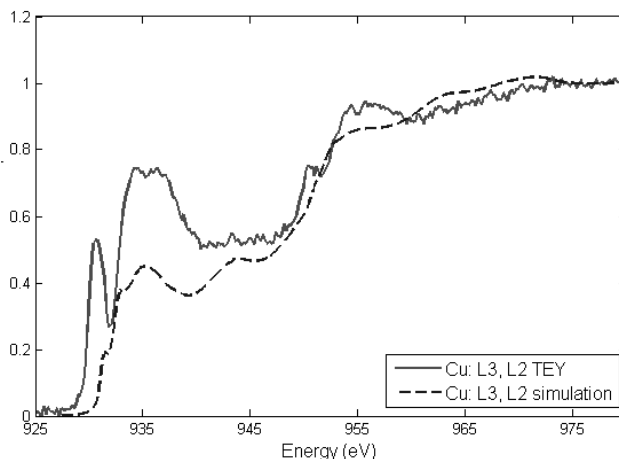

Figure 5: Experimental (red line) and preliminary calculated (blue dashed line) XANES spectra of Cu L_2 and L_3 edges in bornite.

The calculated spectra resemble well the experimental ones for iron edges. For both edges a double peak structure appearing in the experiment is reproduced in calculations. For copper the agreement is less satisfactory and a strong L_3 pre-edge peak in the experimental data corresponds to a shoulder in calculations.

The results obtained are discussed and compared to the electronic structure calculations and conclusions on modifications of band structure with variation of stoichiometry, intermixing and doping are drawn.

[1] N. Morimoto, G. Kullerud *Am. Mineral* **46** (1961) 1270.
[2] K. Koto, N. Morimoto, *Acta Crystsllogr.* **31** (1875) 2268.
[3] J. Przewoźnik, J. Żukrowski, Ł.Gondek, K.Gąska, A. Lemański, C. Kapusta, A. Piestrzyński, *Nukleonika* **58** (2013) 43.
[4] M. Brogheresi, F. Di Benedetoo, A. Caneschi, G. Pratesi, M. Romanelli, L. Sorace, *Phys Chem Minerals* **34** (2007) 609.
[5] D. Rybicki et al., unpublished
[6] A. L. Ankudinov, A. I. Nesvizhskii, J. J. Rehr, *Phys. Rev. B* **67** (2003) 115120.
[7] M.S. Moreno, K. Jorissen, J.J. Rehr, *Micron* **38** (2007) 1.
[8] B. Ravel, M. Newville, *J. Synchrotron Rad.* **12** (2005) 537.
[9] M. Newville, *J. Synchrotron Rad.* **8** (2001) 322.