

Structural, magnetic, and Mössbauer effect studies of bornite

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Abstract. The results of a combined study of bornite with Mössbauer spectroscopy, X-ray diffraction and DC magnetometry are reported. The orthorhombic crystallographic structure of the mineral is observed at 15 K and 300 K. It exhibits an increase of the orthorhombic distortion with decreasing temperature. Magnetic susceptibility shows a Curie-Weiss like behaviour between 230 K and 380 K corresponding to the effective magnetic moment of $7.2(3) \mu_B$ per formula unit. The material undergoes a transition to an antiferromagnetic-like state at 75 K. Mössbauer spectra at the paramagnetic range are doublets with a small quadrupole splitting and the isomer shift corresponding to a high spin Fe^{3+} state. Upon magnetic ordering, a coexistence of the paramagnetic doublet with a broadened magnetic sextet is observed indicating an inhomogeneous character of the magnetic transition. The hyperfine field of 350 kOe at 4.2 K is much lower than that observed for a high spin Fe^{3+} in oxides (510 kOe) which is attributed to covalence effects and a possible copper contribution to the effective magnetic moment of the compound.

Key words: bornite • hyperfine interactions • magnetic properties • Mössbauer spectroscopy

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Received: 11 July 2012

Accepted: 13 September 2012

Introduction

Bornite, denoted traditionally with stoichiometry Cu_5FeS_4 , is one of the most important copper ores and exhibits intriguing structural, electrical, magnetic, and other physical properties [4, 10]. It crystallizes in the orthorhombic (pseudotetragonal) structure with space group $Pbca$ [5]. Two other cubic polymorphs (space group $Fm\bar{3}m$) of this mineral are known: a high temperature form (H-bornite), above 535 K, and an intermediate temperature form (I-bornite) observed in the 535 to 473 K range. The I-bornite and the low temperature (L-bornite) structures can be described as superstructures of the high temperature cubic structure ($a = 5.5 \text{ \AA}$), where the consecutive superstructures are arising from a progressively increasing ordering of vacancies and metal atoms [3]. In the proposed structural models relative ordering of the Fe and Cu atoms on available sites was neglected though Koto and Moritomo [5] suggested that Fe atoms could be ordered on two from twelve available sites. Bornite was reported to order antiferromagnetically (AF) at $T_N \sim 64 \text{ K}$ [1, 10] with spins parallel or antiparallel to b -axis [6]. From Mössbauer spectroscopy studies performed by Jagadeesh *et al.* [4] the presence of majority high-spin Fe^{3+} with some low-spin Fe^{2+} , with its content changing with temperature below T_N was concluded. In contrast to that, Oak *et al.* [6] have found presence of high-spin Fe^{3+} only and described temperature behaviour of Mössbauer spectra in terms of superparamagnetic relaxation.

A natural polycrystalline bornite from the Polkowice Mine, Poland, with an iron-to-copper ratio of 0.26 (which corresponds to the formula $\text{Cu}_{4.76}\text{Fe}_{1.24}\text{S}_4$) has been studied using powder X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and DC magnetometry in order to shed some light on the problem of possible ordering of the Fe and Cu atoms and the character of the AF state of the compound.

Experimental

A polycrystalline sample of natural bornite has been used for the measurements. Low temperature X-ray diffraction (XRD) powder patterns were collected with an Empyrean PANalytical diffractometer equipped with a closed-cycle Oxford PheniX cryostat using Ni filter and an X'Celerator linear detector (CuK_α radiation). The data were collected at 300 K and 15 K in the angular range $10\text{--}120^\circ$ (2θ) with steps of 0.016° .

The XRD patterns have been analysed using the profile fitting program FullProf [9] based on the Rietveld method. The background intensity was refined with a polynomial and for the line shape a pseudo-Voigt function was used.

The DC susceptibility and magnetization were measured in the temperature range from 2 K up to 400 K and in magnetic fields up to 80 kOe using the vibrating sample magnetometer (VSM) option of the quantum design physical property measurement system (PPMS).

The ^{57}Fe Mössbauer spectroscopy experiments were performed in the transmission geometry using a conventional constant acceleration type spectrometer with a 10 mCi $^{57\text{m}}\text{Co}$ in Rh source moving at room temperature. The sample was mounted in a continuous flow type cryostat for measurements beyond 50 K and in a static helium cryostat for measurement at 4.2 K. The centre shift values (δ) are given relatively to $\alpha\text{-Fe}$ at room temperature. The spectra were analysed with HDISTR software based on a method published in papers [7, 8].

Results and discussion

The XRD pattern recorded at room temperature shows orthorhombic structure with $Pbca$ space group [5] and unit cell parameters $a = 10.9474(9)$ Å, $b = 21.8699(13)$ Å and $c = 10.9618(7)$ Å. The average apparent crystallite diameter is of $0.20\ \mu\text{m}$. In the Rietveld refinement all positional parameters for 8 sulphur positions (24) and 12 copper/iron positions (36) in unit cell were fitted. As the Fe and Cu metal atoms cannot be distinguished from XRD patterns a weighted scattering factor $(5f_{\text{Cu}} + f_{\text{Fe}})/6$ was assumed for metal positions and additionally, (to reduce the number of refined parameters) common isotropic temperature factors were assumed for all the sulphur and all the metal sites. Measurements performed at 300 K and 15 K show that the structure is preserved in this temperature range and that a , $b/2$ parameters show similar and stronger temperature dependence than the c parameter. Due to this, orthorhombic distortion is considerably increasing with

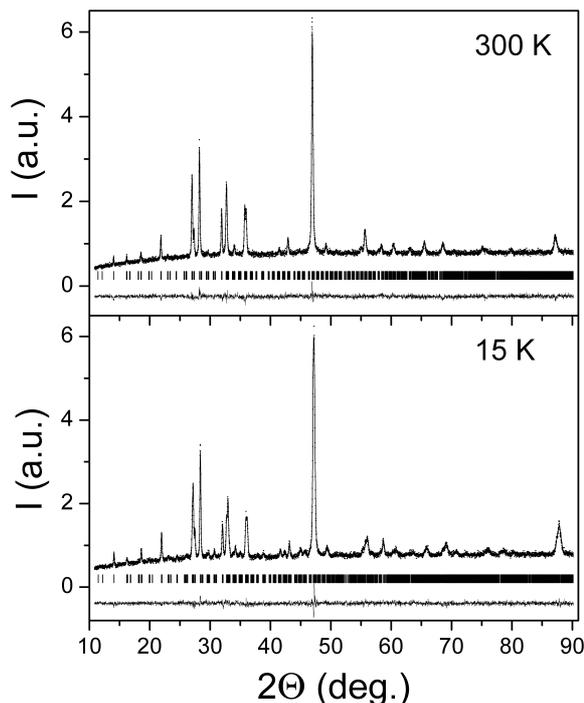


Fig. 1. Rietveld refinement of the XRD patterns for the bornite sample measured at 300 K (upper panel) and 15 K (lower panel). The sets of vertical bars represent the Bragg peak positions of L-bornite (space group $Pbca$) and the lower solid lines represent the difference between experimental and calculated patterns (at the same scale).

decreasing temperature. Additionally, common occupancy factor for all the metal sites was refined and found to be of 95(1)% for XRD pattern at 300 K, indicating that iron excess is accommodated by an off-stoichiometry. As an example, the parts of Rietveld refined XRD patterns measured at 300 K and 15 K are shown in Fig. 1.

In order to determine magnetic ordering temperature the low field ($H = 100$ Oe) zero field cooled (ZFC) and field cooled (FC) DC magnetic susceptibilities (χ) were measured as a function of temperature. Before ZFC measurement, the sample was cooled from 350 K to 3 K at zero applied magnetic field. Figure 2 shows the measured ZFC and FC χ vs. T curves.

Relatively weak irreversibility between the ZFC and FC χ curves (appearing below approximately 125 K) and two peaks at about 75 K and 30 K should be noted.

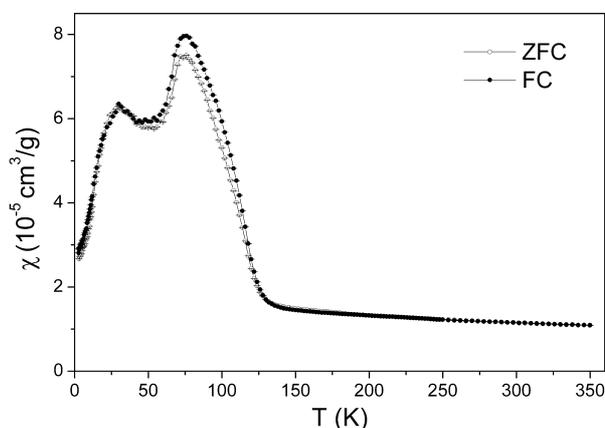


Fig. 2. FC and ZFC DC magnetic susceptibility (χ) for the bornite sample measured as a function of temperature at $H = 100$ Oe.

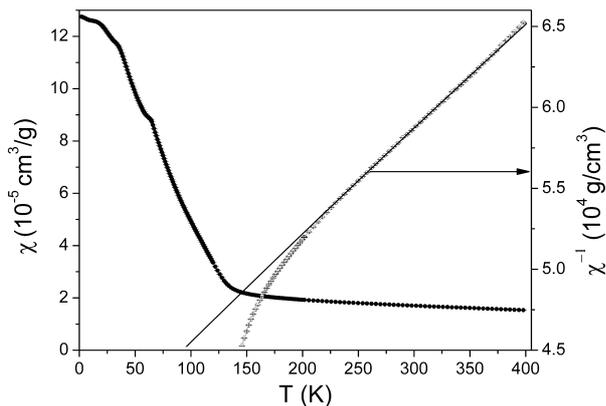


Fig. 3. Temperature dependence of the mass magnetic susceptibility (χ) (left-hand scale) and inverse susceptibility (right-hand scale) for the sample in an external magnetic field of 1 kOe. The continuous straight line represents the fitted (between 225 and 380 K) modified Curie-Weiss law, as explained in the text. Below 225 K and above 380 K, a departure from the modified Curie-Weiss law is observed.

Ascribing the upper one to an antiferromagnetic-paramagnetic transition, the resulting Néel temperature (T_N) equal to 75 K was determined as the mean value of temperatures where the zeros of the $d\chi/dT$ derivative of ZFC and FC curves occur. An additional, less intense peak observed at about 30 K indicates a possible change in the magnetic structure of the compound at lower temperature. The temperature dependencies of χ measured at $H = 1$ kOe and its reciprocal $1/\chi(T)$ are presented in Fig. 3. The paramagnetic range (between 225 K and 380 K) of the $1/\chi(T)$ curve was fitted by a modified Curie-Weiss law in the form (denoted with solid line in Fig. 3): $\chi(T) = \chi_0 + C/(T - \theta_{CW})$, with the temperature independent factor $\chi_0 = 1.5(7) \cdot 10^{-6} \text{ cm}^3/\text{g}$, the Curie constant $C = 1.28(11) \cdot 10^{-2} \text{ K} \cdot \text{cm}^3/\text{g}$ and the paramagnetic Curie-Weiss temperature $\theta_{CW} = -527(35) \text{ K}$. A large negative value of θ_{CW} is indicative for antiferromagnetic interactions. The effective magnetic moment per formula unit $\text{Cu}_{5-x}\text{Fe}_{1+x}\text{S}_4$ was derived from the formula:

$$(1) \quad \mu_{\text{eff}} = \sqrt{\frac{3k_B C M_{fu}}{N_A \mu_B^2}},$$

where: N_A is the Avogadro number, k_B is the Boltzmann constant, μ_B is the Bohr magneton and M_{fu} is the molar mass of the $\text{Cu}_{5-x}\text{Fe}_{1+x}\text{S}_4$ compound. Its experimental

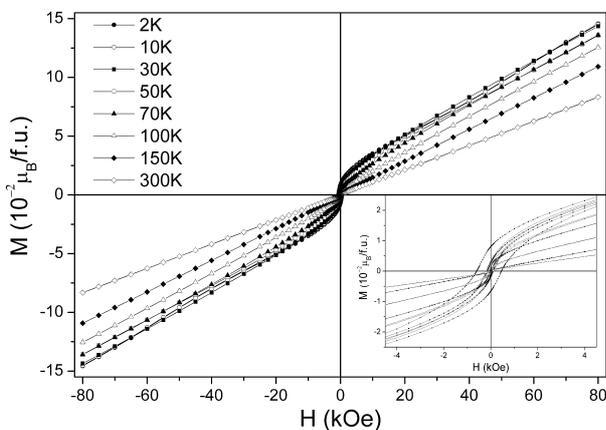


Fig. 4. DC Magnetization (M) as a function of applied magnetic field (H) up to ± 80 kOe at selected temperatures. The inset shows enlarged central part of the plot.

value $\mu_{\text{eff}} = 7.2(3) \mu_B$ is much larger than expected for $x = 0$ and Fe^{3+} ions with spin $S_{\text{Fe}} = 2.5$ ($\mu_{\text{eff}} = 5.92 \mu_B$) and corresponds to $x = 0.24$ value.

The DC magnetization (M) vs. H isotherms for selected temperatures between 2 K and room temperature are shown in Fig. 4. At temperatures higher than 100 K the normal paramagnetic linear M vs. H behaviour is observed. For lower temperatures, nonlinear and hysteretic behaviour is observed indicating the appearance of a magnetic ordering in this temperature range. For example, the mutual crossing of the $M(H)$ curves for T equal to 2 and 30 K indicate the existence of a nontrivial antiferromagnetic ordering in this compound. One should also note a remarkable coercive field of about 600 Oe for the $M(H)$ loop at 2 K which progressively decreases with increasing temperature and reaches zero value for $T > 150$ K (see inset in Fig. 4).

The representative Mössbauer spectra are shown in Fig. 5. Above T_N , the spectra can be fitted by a single quadrupole doublet. The hyperfine parameters at room temperature amount to respectively: centre shift $\delta = 0.377(1) \text{ mm/s}$ and quadrupole splitting $\Delta = 0.218(1) \text{ mm/s}$ (where

$$(2) \quad \Delta = \frac{eQV_{ZZ}}{2} \left(1 + \frac{\eta^2}{3} \right)^{1/2},$$

e is the elementary charge, Q is the quadrupole moment of the ^{57}Fe nucleus in the excited state, V_{ZZ} is the principal component of the electric field gradient tensor and η is the asymmetry parameter). Non-zero Δ has its origin in a very low local symmetry (general positions in $Pbca$ group) of the Fe/Cu atoms which locate inside distorted tetrahedrons formed by the S atoms. The same value of the quadrupole splitting was reported previously [2, 6]. A zero value of the quadrupole splitting reported in [4] could be related to a different stoichiometry of bornite used in that study and a possible higher symmetry of iron environments in that material.

The sharp six-line spectrum with only slightly broadened lines was measured in the antiferromagnetic (AF) state at 4.2 K. It was fitted with a single magnetic

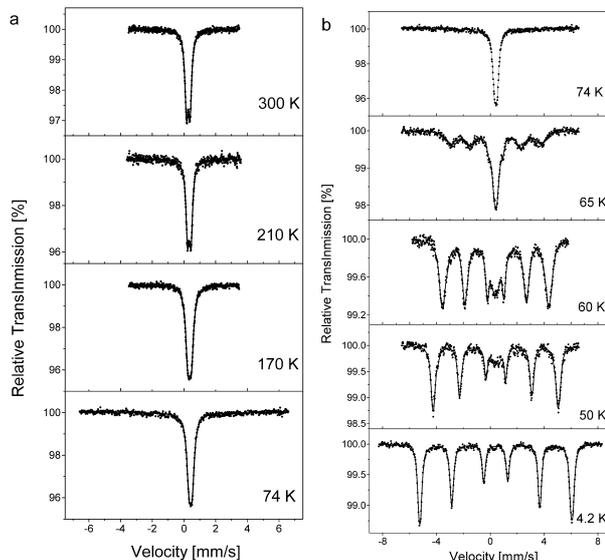


Fig. 5. ^{57}Fe Mössbauer spectra of bornite at selected temperatures. Solid lines denote the best fits.

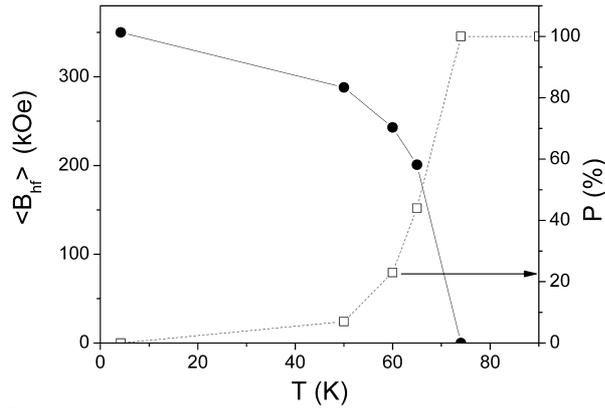


Fig. 6. Temperature dependence of the mean hyperfine field $\langle B_{\text{hf}} \rangle$ in the AF phase (full circles) and of the paramagnetic fraction P (open squares) obtained from Mössbauer spectra. Dotted line and solid lines are guides for eye.

component assuming a small static Gaussian distribution of the magnetic hyperfine field (B_{hf}). The mean value of $\langle B_{\text{hf}} \rangle = 350$ kOe and $\delta = 0.530(2)$ mm/s were obtained. The spectral lines of the sextet broaden and a paramagnetic doublet with increasing relative contribution appears in the spectra at temperatures in the range $50 \text{ K} \leq T \leq 65 \text{ K}$ (Fig. 5). No relaxational effects could be accounted for in the fitting of the spectra near T_N . Consequently, two components – the magnetic one with static Gaussian distribution of the magnetic hyperfine field and the non-magnetic one were fitted to the spectra in this temperature range. The obtained mean values of $\langle B_{\text{hf}} \rangle$ for the magnetic phase and the contribution of the paramagnetic phase (PM) to the spectrum are shown in Fig. 6 as a function of temperature.

For $T > 50 \text{ K}$, rapidly growing contribution of the PM phase (open squares) to the spectra and a fast decrease of $\langle B_{\text{hf}} \rangle$ for AF phase (full circles) are observed. The measured spectra were also analysed to get the mean centre shift $\langle \delta \rangle$. Its temperature dependence was modelled by expression $\langle \delta \rangle = \delta_0 + \delta_{\text{SOD}}(T)$, where the second-order Doppler shift contribution $\delta_{\text{SOD}}(T)$ is expressed by the formula:

$$(3) \quad \delta_{\text{SOD}} = -\frac{9k_{\text{B}}T}{2m_{\text{Fe}}c} \left(\frac{T}{\theta_{\text{D}}} \right)^3 \int_0^{\frac{\theta_{\text{D}}}{T}} \frac{x^3 dx}{(e^x - 1)}$$

(with: θ_{D} is the Debye characteristic temperature, k_{B} is the Boltzmann's constant and m_{Fe} is the mass of the ^{57}Fe nucleus). This formula fitted well the experimental $\langle \delta \rangle$ points in the 300 K to 4.2 K range, and the Debye characteristic temperature equal to 286(25) K was obtained.

Summary

X-ray diffraction measurements performed on the bornite material at temperatures 15 K and 300 K reveal a single-phase with orthorhombic structure (space group $Pbca$). The distortion of the unit cell is larger at a lower temperature.

Magnetic susceptibility exhibits a Curie-Weiss like behaviour between 230 K and 380 K corresponding to the effective magnetic moment of 7.2(3) μ_{B} per formula unit. It corresponds to 5.9(3) μ_{B} per Fe atom. The material undergoes a transition to an antiferromagnetic-like

state at 75 K. Hysteresis loops measured in the fields up to 80 kOe reveal a behaviour characteristic of an antiferromagnet with a coercive field of 600 Oe at 2 K, decreasing to zero above T_N .

Mössbauer spectroscopy measurements performed at temperatures between 4.2 K and 300 K prove the magnetically ordered state in the compound below the T_N deduced from DC magnetization measurements. Above T_N , the spectra could be fitted by a single quadrupole doublet. At 4.2 K, a six-line spectrum for the AFM magnetic state is observed with some broadening of the lines and a trace of the paramagnetic doublet. At the intermediate temperatures ($50 \text{ K} \leq T < T_N$) further line broadening and a gradual increase of the intensity of the paramagnetic doublet is noted. It reveals 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 much lower than that for a high spin Fe^{3+} in oxides (510 kOe). The effect is attributed to Fe-S covalency and a possible copper contribution to the effective magnetic moment of the compound.

Structural, magnetic and Mössbauer spectroscopy study of the $\text{Cu}_{4.76}\text{Fe}_{1.24}\text{S}_4$ natural bornite presented in this paper reveal a well ordered crystal structure with an antiferromagnetic ground state.

Acknowledgment. A support of the Polish Ministry of Science and Higher Education is gratefully acknowledged.

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