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Magnetic properties and cation ordering in two synthetic bornite samples, $Cu_5(Fe, Mn)S_4$

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Abstract

The magnetic properties of a synthetic bornite, Cu_5FeS_4, and of a Mn-bearing synthetic bornite were investigated using Superconducting Quantum Interference Device (SQUID) magnetometry and room temperature X-band Electron Paramagnetic Resonance (EPR) spectroscopy. Samples were synthesised from the elements using conventional dry methods. Chemical and phase compositions of the samples were confirmed by means of Electron Probe Micro-Analysis (EPMA) and by powder X-Ray Diffraction (XRD).

Experimental results, interpreted using spectral simulations, highlight the superexchange nature of ionic interactions between paramagnetic centres and the role played by partial intervalence charge transfer between the Fe(III) and Cu(I) species in natural and synthetic bornite. The cation distribution in synthetic samples was shown to be different from the natural sample, in spite of the close similarity in chemical composition and structure.

Key words: bornite; intervalence charge transfer; EPR spectroscopy; SQUID magnetometry; EPMA; Mn(II).

Introduction

The distribution of metal cations in sulphides can provide valuable information on their thermodynamic properties and conditions of formation. This information is also of paramount importance for determining the potential for technological applications of these materials. Synthetic analogues, obtained under laboratory conditions, but with chemical compositions and structures comparable with natural phases, can exhibit very different cation distributions (Danti et al., 2001) compared with minerals. The latter have commonly formed in low-temperature hydrothermal environments and have equilibrated for long times.

In this study, the cation distribution and the nature of the magnetic interactions between paramagnetic Fe(III) ions in bornite have been investigated by a EPR and SQUID magnetometry study, carried out on two synthetic analogues, and compared with the magnetic behaviour of natural bornite (Borgheresi et al., 2007).

Summary of the current structural and crystal chemical knowledge of bornite

Natural bornite ("low bornite") crystallises in the orthorhombic space group *Pbca*, the cell parameters being $a = 10.950(1)$, $b = 21.862(2)$ and $c = 10.950(1)$ Å (Koto and Morimoto, 1975). A high temperature cubic polymorph, stable above 230 °C, and a further cubic polymorph, stable between 230 and 150 °C have been described (Koto and Morimoto, 1975). The formation of "low bornite" entails an ordering of vacancies and metal ions in the sulphur framework to form two different subcells: an antifluorite-type and a sphalerite-type sub-cell (Pierce and Buseck, 1978; Grguric et al., 1998).

Cu and Fe were found to occupy specific cation sites, although their attribution has been the subject of debate in the literature (Koto and Morimoto, 1975; Jagadeesh et al., 1981; Collins et al., 1981; Li et al., 1994; Pattrick et al., 2004; Ding et al., 2005; Borgheresi et al., 2007). Structural investigations (performed through both X-ray and neutron diffraction) have ascertained that the two Fe ions per unit cell are confined in the antifluorite subcells (Collins et al., 1981; Grguric et al., 1998; Ding et al., 2005). Further spectroscopic and magnetic characterisation has shown that the Fe ions are located in the M4 and M5 sites (Collins et al., 1981; Ding et al., 2005; Borgheresi et al., 2007).

Experimental

Two different samples were synthesized: a synthetic analogue of bornite, Cu_5FeS_4, and a Mn-bearing bornite. The Mn-doped synthetic analogue was chosen to explore homonuclear and heteronuclear clustering features in this structure, thanks to the fact that Mn(II) and Fe(III) have both an external d^5 electronic configuration.

These samples are labelled S1 and S2, respectively. Bornite powders were synthesised according to a two step procedure (Berger and Bucur, 1996). Initially, binary sulphides (Cu_2S and FeS_2) were synthesised from the elements. Then these binary compounds were mixed in stoichiometric proportions with elemental Cu to synthesise bornite, according to reaction (1)

$$2Cu_2S + FeS_2 + Cu \Rightarrow Cu_5FeS_4 \qquad (1)$$

The Mn-bearing bornite was synthesised by adding elemental Cu and elemental Mn (in a very small amount) in the second run. Both runs were carried out in silica vials under vacuum, following the standard dry synthesis procedure (Scott, 1974). Details of these runs are as follows: during the first step, target temperatures of 450 and 105 °C for FeS_2 and Cu_2S, respectively, ramp speed 1 °C/min, total dwell time in temperature 5 hours, cooling in air; during the second step, target temperature of 700 °C, ramp speed 2 °C/min, total dwell time at temperature 48 hours; successively, temperature decrease at 1.6 °C/min down to 400°C, total dwell time at temperature 24 hours; finally, temperature decrease at 1.6 °C/min down to 150 °C, total dwell time at temperature 24 hours, cooling in air.

Phase composition of the products was checked by means of X-ray powder diffraction (XRPD) using a Philips PW 1710-based powder diffractometer equipped with the PC-APD 3.6 Philips software for acquisition and data processing. The diffractometer utilised Co-Kα radiation ($\lambda = 1.79021$ Å) with an Fe filter. Powder patterns were recorded in the range 10-80° 2θ, step size 0.06° 2θ, time per step 0.5 s.

The chemical composition of sample S2 was checked using EPMA. Measurements were carried out at the SEAES (School of Earth, Atmospheric and Environmental Sciences, University of Manchester) using a CAMECA

Table 1. Mean, Minimum, Maximum, Median and Minimum Detection Limits (mdl) wt% values obtained from 14 point analyses by EPMA on sample S2.

S2 composition	Cu (wt%)	Mn (wt%)	Fe (wt%)	S (wt%)	Tot (wt%)
Mean	63.67	0.326	10.62	25.93	100.55
Min	60.70	0.021	10.06	25.66	99.86
Max	64.60	3.717	10.96	26.31	101.26
Median	63.83	0.053	10.66	25.94	100.49
mdl	*0.06*	*0.008*	*0.01*	*0.05*	

SX100 microprobe. Experimental conditions were: 20 kV voltage, 20 nA current, 5 µm diameter for the electron beam. Counting times were optimised to reduce the minimum detection limits of the analysed elements: 40 s for major elements (Cu, S), 80 s for minor elements (Fe, Mn). Detection limits are shown in Table 1 (Ancey et al., 1998). Chalcopyrite, $CuFeS_2$ (for Cu and S), marcasite, FeS_2 for (Fe), alabandite, MnS (for Mn) were used as standards.

Magnetic and spectroscopic investigations were carried out on the as-synthesised powders. Magnetisation measurements were performed in the 1.6-300 K temperature range using a Cryogenic S600 and a MPMS quantum design superconducting quantum interference device (SQUID) magnetometer in the field-cooled (FC) mode at applied fields of 2.0 and 0.1 T. Corrections for molecular diamagnetism, estimated from Pascal's constants, were applied.

Conventional EPR spectroscopy measurements were performed on powders inserted in amorphous silica tubes using a Teflon bag to minimise possible magnetic orientation effects. Data were collected at room temperature using a Bruker ER 200D-SRC spectrometer operating at X-Band (9.5 GHz) interfaced with DS/EPR software to a PC for data acquisition and handling. Operating conditions were 0.05 mT modulation amplitude and 100 KHz modulation frequency. Scan speed was 2.5 mT per second, over a scan range 0 - 1 T.

Refinement of EPR spectral features was performed by means of spectral simulations. The values of magnetic parameters (g-, fine and hyperfine tensor components) and line widths were refined by using the least-squares minimisation software "EPR" (Rockenbauer and Korecz, 1996). This software proceeds from an externally provided initial set of free and fix parameters trhough an iterative optimisation procedure, constrained by the minimisation of the difference between experimental and simulated spectral profiles. Spin Hamiltonian is treated under the second-order perturbation theory approach.

Results

Phase and chemical composition

The XRPD patterns of the synthetic products reveal the presence of a single crystalline phase (Figure 1). All reflections of the experimental

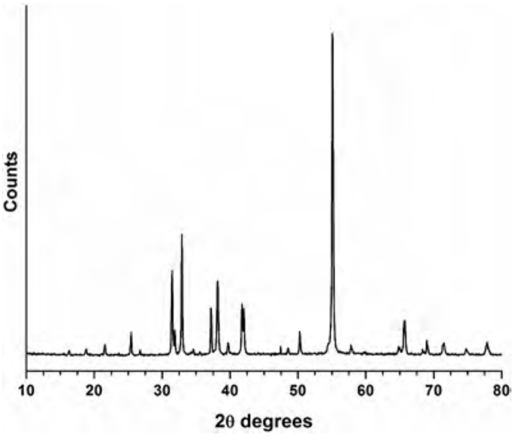

Figure 1. Powder XRD pattern of the S1 sample.

Table 2. Lattice constants of S1, S2 and the natural bornite samples.

Lattice constants (Å)	S1	S2	Nat. bornite[1]
a_0	10.950(6)	10.956(8)	10.950
b_0	21.866(3)	21.861(2)	21.862
c_0	10.956(5)	10.957(8)	10.950

[1] Koto and Morimoto (1975).

patterns can be, in fact, indexed according to the bornite orthorhombic structural model (Koto and Morimoto, 1975). The refined lattice constants are reported in Table 2. On the basis of the analysed patterns, no significant changes of the lattice constants are observed in the data for the synthetic samples by comparison with the natural sample (Koto and Morimoto, 1975).

EPMA investigations, carried out on the S2 sample, allow more detailed insights concerning the incorporation of Mn into the bornite structure. Indeed, results obtained from 14 point analyses carried out on single bornite grains provide substantial evidence of: (a) the stoichiometry of bornite powders, and (b) incorporation of Mn in bornite. Cu, Fe and S wt% data are in excellent agreement with the theoretical composition of a pure bornite (Table 2). The closeness of the mean and median values for these elements, and also the difference between minimum and maximum values, indicate that there is little variation in the chemical content of the powders. By contrast, appreciable variability is observed in the Mn-content. This element, in fact, is found to range from the trace level up to a minor content level (> 3 wt%). Accordingly, in the calculation of the formula, the median value was taken into account. The formula of the S2 sample, calculated from point analyses is: $Cu_{5.01}Mn_{0.05}Fe_{1.03}S_{3.95}$.

EPR spectroscopy

The experimental room temperature EPR spectrum of S1 is shown in Figure 2. A single symmetric line is observed, centred at ~ 340 mT. This line appears broad, with a peak-to-peak width of ~ 100 mT. Moreover, the line does not present any features attributable to the fine structure expected for a d^5 Fe(III) ion. The experimental spectrum of the S1 sample closely resembles that of natural bornite, also shown in Figure 2.

The spectrum of the Mn-bearing (S2) sample is also characterised by a single symmetric signal, but this appears to be due to the superposition of two lines: the first, analogous to the broad line already described; the second, definitely narrower than the first, but also centred at ~ 340 mT. These broad and narrow lines have been tentatively attributed to Fe(III) and Mn(II) ions, respectively, although the narrow line does not show neither the six-line fine multiplet (expected also for the d^5 Mn(II) ions) nor the

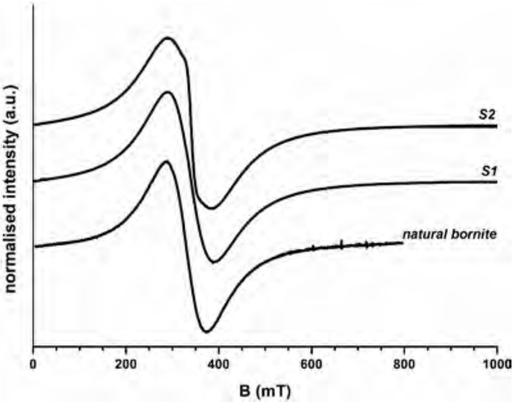

Figure 2. Room temperature X-band EPR spectra of S1 and S2 samples, compared to that of natural specimen (Borgheresi et al., 2007).

Table 3. Refined magnetic parameters (isotropic g-factor and linewidth) for the experimental EPR spectra of S1 and S2.

	S1 Fe(III)	S2 Mn(II)	S2 Fe(III)	natural[1] Fe(III)
Zeeman interaction	2.0108(5)	2.0000(5)	2.0082(5)	2.026
Linewidth (mT)	87.5(2)	17.1(1)	89.9(2)	76.2
%	100	1.5	98.5	100

[1] data from Borgheresi et al. (2007).

characteristic six-line hyperfine multiplet. Simulations of the spectra were performed using the simplest spin Hamiltonian consistent with the observed experimental features, including isotropic Zeeman interaction and isotropic linewidth. The best fit parameters are reported in Table 3.

The experimental EPR spectrum of S1 shows a close similarity to the room temperature spectrum of natural bornite, and can be attributed to magnetically interacting Fe(III) (Borgheresi et al., 2007). Isotropic g-value slightly differ in S1 and natural bornite samples, whereas the width of S1 is larger (+15%) than that of the natural specimen (Table 3). The S2 spectrum was well reproduced by taking into account two different isotropic components (Figure 3). Their width values are clearly distinct (Table 3), whereas only moderate differences in g-values are found. The broader component has a width comparable to that of the S1 sample. The relative weights allow us to see the marked predominance of the broad component with respect to the narrower one.

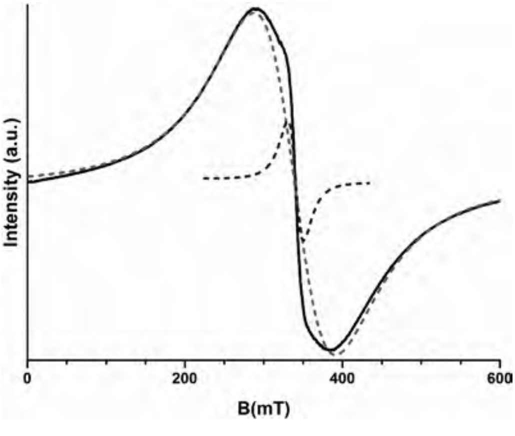

Figure 3. Simulated EPR spectrum of Mn-bearing S2 sample: the two fitting components are shown.

As expected, the linewidth values of the broad component (in S1, S2 and natural bornite) and of the narrow one (in S2) point to different paramagnetic systems, i.e. the broader can be firmly attributed to Fe(III) and the narrower to Mn(II). Moreover, the present spectra confirm that also in synthetic samples paramagnetic cations, i.e. Fe(III) and Mn(II) (when present), are not magnetically diluted.

Magnetic susceptibility

The results of the magnetic susceptibility measurements are shown in Figure 4. Magnetic susceptibility, χ, of both synthetic samples monotonically increases with decreasing temperature. The low values of χ^T at room temperature point to the presence of strong antiferromagnetic (AF) interactions already seen in the high temperature regime. Accordingly, Curie-Weiss modelling of the susceptibility data cannot be performed. Changing in temperature from above to below 65 K, one can observe a change in the behaviour of the susceptibility for both samples (inset of Figure 4). At this critical temperature, T_c, the trend of increasing

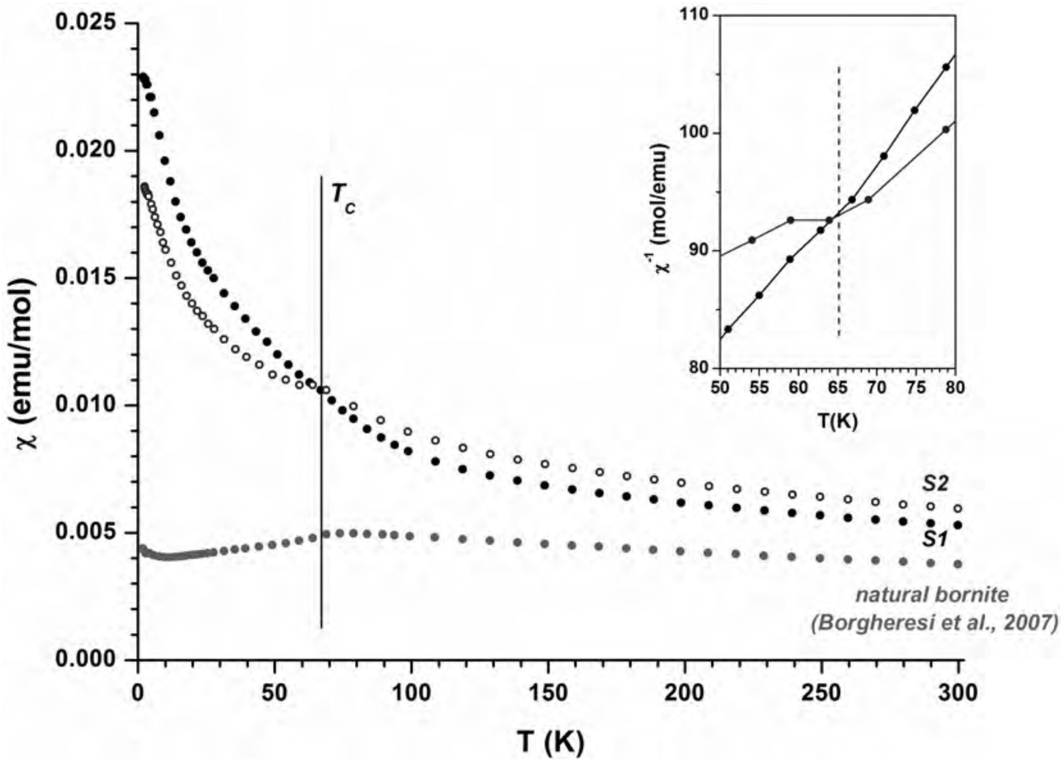

Figure 4. χ^T versus temperature data of S1 and S2 samples compared to data of natural specimen (Borgheresi et al., 2007).

susceptibility is different between S1 and S2. This confirms the existence of extended AF interactions in the samples, that prevent the paramagnetic state persisting at lower temperatures. The strength of the antiferromagnetic coupling among ions, in fact, is apparently no longer balanced by thermal motions when temperature is lowered below T_c. In synthetic samples, however, there is no progressive decrease in magnetic susceptibility with decreasing temperature (Figure 4), as would be expected if a paramagnet transforms to an antiferromagnet. By comparison, this anticipated trend in susceptibility is observed in natural bornite (Figure 4), where a paramagnet to antiferromagnet transition has been described (Collins et al., 1981; Borgheresi et al., 2007). We note that T_c is almost coincident with the Neél temperature of natural bornite. The fact that full magnetic ordering is not achieved points to the lack of a fully ordered array of magnetic moments in the structure of synthetic bornites.

Discussion

The characterisation of the S1 and S2 samples shows that these synthetic products have crystallised with the bornite structure. The chemical compositions of both samples (apart from the small Mn-content in S2) is very close to the theoretical bornite composition. However, this close similarity of S1 and S2 with bornite ends when magnetic properties are taken into account.

The main result from this study concerns the magnetic susceptibilities of the synthetic samples, which are different from that of natural bornite. A lack of magnetic ordering at low temperature in the synthetic powders is found. The onset of coupling among two set of ions ordered in different sublattices (as experimentally observed for natural bornite, Collins et al., 1981; Borgheresi et al., 2007) progressively reduces the bulk magnetisation with falling temperature. This is not seen for synthetic samples: their susceptibility data show a large paramagnetic contribution even below T_c. The transition from above to below T_c is, in fact, sluggish in samples S1 and S2. The magnetic behaviour of S1 and S2 can be ascribed to the lack of compensation of the coupling of spin magnetisations, which arises from a non ordered distribution of paramagnetic centres. Collective effects in coupling among Fe(III) ions can contribute to the sluggish transition of bulk susceptibility, as already observed in other sulphides with randomly distributed paramagnetic centres (Di Benedetto et al., 2005). Within this framework, a possible interpretation could involve the simultaneous occurrence of two magnetically different phases, i.e. an ordered one, similar to the natural sample, and a fully random one. However, the facts that S1 and S2 are monophasic along with the EPR results point to the uniqueness of the magnetic phase. According to the susceptibility data, therefore, Fe and Cu can be considered randomly distributed over the available cation sites, although precise information about the degree of disorder is not available.

The second important insight is provided by the EPR spectrum of the Mn-bearing S2 sample. The presence of an additional EPR spectrum due to Mn ions (even at very low concentrations) allows us to investigate the prevailing nature of magnetic interactions among the paramagnetic ions. The main feature of a typical Mn(II) EPR spectrum, i.e. the presence of hyperfine sextet, is absent in the experimental spectrum of S2. This absence is explained by a narrowing exchange process (Spalek et al., 1986; Weil et al., 1994). Accordingly, the isotropic contact hyperfine splitting is averaged out, and the six hyperfine lines collapse into a single line, as already observed for e.g. sphalerite (Bernardini et al., 2004). Thus, the superexchange interaction claimed by Furdyna (1988) to explain the magnetism of Diluted Magnetic Semiconductors is operating also in the case of Mn ions in S2 bornite.

On this basis, the origin of the broad Fe(III) signal seen in S1 and S2, and also in the natural specimen, can be reconsidered. Borgheresi et al. (2007) discussed the nature of the spin-spin interaction producing the large line width value in the Fe(III) EPR spectrum of natural bornite (Table 3). These authors, ruling out a possible attribution to dipolar or isotropic exchange coupling, invoked the anisotropic part of the exchange interaction. Moreover, they suggested that a partial spin delocalisation from Fe to neighbouring Cu ions could occur.

The identification of the prevailing exchange nature of the spin-spin interaction, obtained through doping with Mn(II) impurities, confirms the attribution proposed by Borgheresi et al. (2007) for natural bornite, and it is also valid in the case of sample S1. On the other hand, the Fe(III) signal in the two spectra has a g-value (Table 3) different from that of a free electron ($g_e = 2.0023$). Indeed, g-values different from g_e are unexpected for a d^5 system, one having a $^6A_1$ ground state in tetrahedral coordination, and where admixture with excited states is spin forbidden so that their contribution to the g-value is almost negligible (e.g., as in the case of the Mn(II) line, Table 3). In contrast, increase of g-values can be inferred assuming a partial electron transfer from diamagnetic Cu(I) ions to neighbouring Fe(III) ions. This transfer has to be assumed to be faster than characteristic times for X-band EPR spectroscopy (i.e. 10^{-10} s). With this assumption, the original features of the Fe(III) spectrum are not retained, and a line broadening coupled to a shift of the resonant field is observed (Weil et al., 1994). In this case, therefore, the occurrence of a partial intervalence exchange between Fe(III) and Cu(I) (Borgheresi et al., 2007) appears confirmed.

In conclusion, a comparative analysis of the EPR and SQUID data for these bornites allows us to state that:

1) the superexchange nature of the ionic interactions between paramagnetic centres in bornite has been demonstrated;

2) partial intervalence charge transfer between Fe(III) and Cu(I) in natural and synthetic bornite samples has been experimentally confirmed.

In addition, the cation distributions in natural and synthetic samples appears to be different, even for corresponding chemical compositions and structures.

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References

Ancey M., Bastenaire F. and Tixier R. (1980) - Microanalysis and Scanning Electron Microscopy Summer School (St. Martin d'Hères, 38041 France), 330 p. Les Editions de Physique, Orsay, France.

Berger R. and Bucur R.V. (1996) - Potentiometric measurements of copper diffusion in polycrystalline chalcocite, chalcopyrite and bornite. *Solid State Ionics*, 89(3-4), 269-278.

Bernardini G.P., Borgheresi M., Cipriani C., Di Benedetto F. and Romanelli M. (2004) - Mn distribution in sphalerite: an EPR study. *Physics and Chemistry of Minerals*, 31, 80-84.

Borgheresi M., Di Benedetto F., Caneschi A., Pratesi G., Romanelli M. and Sorace L. (2007) - An EPR and SQUID magnetometry study of bornite. *Physics and Chemistry of Minerals*, 34, 609-619.

Collins M.F., Longworth G. and Townsend M.G. (1981) - Magnetic structure of bornite, Cu_5FeS_4. *Canadian Journal of Physics,* 59, 535-539.

Danti C., Bente K., Doering Th., Bernardini G.P. and Cipriani C. (2001) - The aikinite-bismuthinite isoseries: a minerochemical study. *Neues Jahrbuch für Mineralogie Monatshefte,* 221-234.

Di Benedetto F., Bernardini G.P., Cipriani C., Emiliani C., Gatteschi D. and Romanelli M. (2005) - The distribution of Cu(II) and the magnetic properties of the synthetic analogue of tetrahedrite: $Cu_{12}Sb_4S_{13}$. *Physics and Chemistry of Minerals*, 32, 155-164.

Ding Y., Veblen D.R. and Prewitt C. (2005) - Possible Fe-Cu ordering schemes in the *2a* superstructure of bornite (Cu_5FeS_4). *American Mineralogist*, 90, 1265-1269.

Furdyna J.K. (1988) - Diluted magnetic semiconductors. *Journal of Applied Physics,* 64, R29-R64.

Grguric B.A., Putnis A. and Harrison R.J. (1998) - An investigation of the phase transitions in bornite (Cu_5FeS_4) using neutron diffraction and differential scanning calorimetry. *American Mineralogist*, 83, 1231-1239.

Jagadeesh M.S., Nagarathna H.M., Montano P.A. and Seera M.S. (1981) - Magnetic and Mössbauer studies of phase transitions and mixed valences in bornite ($Cu_{4.5}Fe_{1.2}S_{4.7}$). *Physical Review*, B23, 2350-2356.

Koto K. and Morimoto N. (1975) - Superstructure investigation of bornite, Cu_5FeS_4, by the modified partial Patterson function. *Acta Crystallographica* B31, 2268-2273.

Li D., Bancroft G.M., Kasrai M., Fleet M.E. Feng X.H., Yang B.X. and Tan K.H. (1994) - S K- and L-edge XANES and electronic structure of some copper sulfide minerals. *Physics and Chemistry of Minerals*, 21, 317-324.

Pattrick R.A.D., Van der Laan G., Charnock J.M. and Grguric B.A. (2004) - Cu L3 X-ray absorption spectroscopy and electronic structure of minerals: Spectral variations in non-stoichiometric bornites, Cu_5FeS_4. *American Mineralogist*, 89, 541-546.

Pierce L. and Buseck P.R. (1978) - Superstructuring in the bornite-digenite series: a high-resolution electron microscopy study. *American Mineralogist*, 63, 1-16.

Rockenbauer A. and Korecz L. (1996) - Automatic computer simulations of ESR spectra. *Applied Magnetic Resonance,* 10, 29-43.

Scott S.D. (1974) - Experimental methods in sulfide synthesis. In: Sulfide mineralogy, P.H. Ribbe (ed.) *Reviews in Mineralogy*, 1, Mineralogical Society of America, Washington.

Spalek J., Lewicki A., Tarnawski Z., Furdyna J.K., Galazka R.R. and Obuszko Z. (1986) - Magnetic susceptibility of semimagnetic semiconductors: the high temperature regime and the role of superexchange. *Physical Review,* B33(5), 3407-3418.

Weil J.A., Bolton J.R. and Wertz J.E. (1994) - Electron Paramagnetic Resonance. John Wiley & Sons, New York.

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