


# Mössbauer study of bornite and chemical bonding in Fe-bearing sulphides

M. Borgheresi<sup>1</sup> · F. Di Benedetto<sup>1,2,3</sup>  · M. Romanelli<sup>1,3</sup> · M. Reissner<sup>4</sup> ·  
W. Lottermoser<sup>5</sup> · R. R. Gainov<sup>6,7</sup> · R. R. Khassanov<sup>6</sup> · G. Tippelt<sup>5</sup> · A. Giaccherini<sup>3,8</sup> ·  
L. Sorace<sup>3,8</sup> · G. Montegrossi<sup>2,3</sup> · R. Wagner<sup>5</sup> · G. Amthauer<sup>5</sup>

Received: 23 March 2017 / Accepted: 4 July 2017  
© Springer-Verlag GmbH Germany 2017

**Abstract** The Mössbauer spectra of a nearly stoichiometric natural bornite,  $\text{Cu}_5\text{FeS}_4$ , specimen were reinvestigated between 295 and 4.2 K. There is no difference between the Néel temperature  $T_N$  as determined by the Mössbauer effect or by the susceptibility measurements ( $T_N = 67.5$  K). No additional paramagnetic doublet can be observed in the low-temperature MS spectra. The valence state of Fe is  $\text{Fe}^{(3-x)+}$  caused by a partial electron transfer from the  $\text{Cu}^+$  ions to the  $\text{Fe}^{3+}$  ions which increases the shielding of the s-electrons by the d-electron density and by this increases the isomer shift to a value intermediate between tetrahedral high-spin  $\text{Fe}^{2+}$  and tetrahedral high-spin  $\text{Fe}^{3+}$ .

**Keywords** Magnetic properties · Bornite · Mössbauer spectroscopy · Chemical bond in sulphides

## Introduction

Bornite,  $\text{Cu}_5\text{FeS}_4$ , is one of the most important copper ore minerals. Besides this aspect, bornite shows special semi-conducting and magnetic properties used in several high-tech materials, such as diluted magnetic semiconductors or thermoelectrics provided that the metal ions are ordered in the structure (Qiu et al. 2014). Therefore, bornite is of potential interest for technological applications.

There are three different polymorphic phases of bornite with superstructure relationships (Koto and Morimoto 1975): a low-, an intermediate- and a high-temperature form. The low bornite is the only naturally occurring phase (Vaughan and Craig 1978).

High bornite is stable above 230 °C, has a cubic structure with space group  $Fm\bar{3}m$  and a cell constant  $a = 5.50$  Å. High bornite crystallizes in the antifluorite structure, where the  $\text{S}^{2-}$  ions occupy the positions of a face-centered cubic Bravais lattice and 5  $\text{Cu}^+$  ions, 1  $\text{Fe}^{3+}$  ion, and 2 vacancies randomly occupy the centers of the 8 tetrahedral voids within that face-centered lattice (Fig. 1a).

With decreasing temperature, cations and vacancies entail order forming first intermediate bornite and finally low-temperature bornite. Their unit cells are multiple of that of high bornite with  $2a_2a_2a$  for intermediate bornite, with partial ordering of cations and vacancies, and  $2a_4a_2a$  for low bornite, with almost complete ordering.

Low bornite is orthorhombic ( $a = 10.950$  Å,  $b = 21.862$  Å,  $c = 10.950$  Å) and belongs to the space group  $Pbca$ . The structure can be described consisting of 2 subcells: one has a sphalerite arrangement, with four metal ions and four vacancies in the eight available tetrahedral sites within a cubic face-centered  $\text{S}^{2-}$  lattice; the other one has again an antifluorite-type structure with all the tetrahedral voids within a cubic face-centered

✉ F. Di Benedetto  
francesco.dibenedetto@unifi.it

<sup>1</sup> Dipartimento di Scienze della Terra, Università di Firenze, Florence, Italy

<sup>2</sup> IGG-CNR, Florence, Italy

<sup>3</sup> INSTM Unit of Florence, Florence, Italy

<sup>4</sup> Institut für Festkörperphysik, TU Wien, Vienna, Austria

<sup>5</sup> Fachbereich Chemie und Physik der Materialien, Universität Salzburg, Salzburg, Austria

<sup>6</sup> Kazan Federal University, Kazan, Russia

<sup>7</sup> Forschungszentrum Jülich, Jülich, Germany

<sup>8</sup> Dipartimento di Chimica U. Schiff, Università di Firenze, Sesto Fiorentino, Italy