Application of ^{57}Fe Mössbauer spectroscopy as a tool for mining exploration of bornite (Cu$_5$FeS$_4$) copper ore

**R. R. Gainov · F. G. Vagizov · V. A. Golovanevskiy ·
V. A. Ksenofontov · G. Klingelhöfer · V. V. Klekovkina ·
T. G. Shumilova · I. N. Pen'kov**

Abstract Nuclear resonance methods, including Mössbauer spectroscopy, are considered as unique techniques suitable for remote on-line mineralogical analysis. The employment of these methods provides potentially significant commercial benefits for mining industry. As applied to copper sulfide ores, Mössbauer spectroscopy method is suitable for the analysis noted. Bornite (formally Cu$_5$FeS$_4$) is a significant part of copper ore and identification of its properties is important for economic exploitation of commercial copper ore deposits. A series of natural bornite samples was studied by ^{57}Fe Mössbauer spectroscopy. Two aspects were considered: reexamination of ^{57}Fe Mössbauer properties of natural bornite samples and their stability irrespective of origin and potential use of miniaturized Mössbauer spectrometers MIMOS II for in-situ bornite identification. The results obtained show a number

R. R. Gainov (✉) · F. G. Vagizov · V. V. Klekovkina
Institute of Physics, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia
e-mail: g_ramil@mail.ru

R. R. Gainov · V. A. Ksenofontov · G. Klingelhöfer
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Staudingerweg 9, 55099 Mainz, Germany

F. G. Vagizov
Department of Physics, Texas A&M University, College Station, TX 77843-4242, USA

V. A. Golovanevskiy
Western Australian School of Mines, Curtin University of Technology, Kent str. Bentley,
GPO Box U1987, Perth, WA 6845, Australia

T. G. Shumilova
Institute of Geology of the Komi Scientific Center, Ural Branch of the Russian Academy of Science, Pervomayskaya str. 54, 167982 Syktyvkar, Russia

I. N. Pen'kov
Institute of Geology and Oil-and-Gas Technologies, Kazan Federal University, Kremlevskaya str. 4/5, 420111 Kazan, Russia

of potential benefits of introducing the available portative Mössbauer equipment into the mining industry for express mineralogical analysis. In addition, results of some preliminary ^{63,65}Cu nuclear quadrupole resonance (NQR) studies of bornite are reported and their merits with Mössbauer techniques for bornite detection discussed.

Keywords Mössbauer spectroscopy · NQR · Bornite · Cu_5FeS_4 · Mining industry

1 Introduction

Bornite has 3 polymorph phases and one of them exists in nature as mineral at T < 423 K [1]. Bornite (Cu_5FeS_4) and chalcopyrite ($CuFeS_2$) together form the most economically important components of copper ore [2]. On the one hand, a more efficient exploration of this ore, which necessitates the implementation of remote and real-time bulk mineralogical analysis, is very important for mining industry worldwide at the present time. Two spectroscopy methods are considered as perspective tools for copper mining industry: Mössbauer (sometimes referred to as nuclear gamma resonance) [3] and nuclear quadrupole resonance (NQR) techniques [4–6]. Both Mössbauer and NQR instrumentations are microscopic methods, however the corresponding effects are observed primarily for different nuclei-probes. For instance, Mössbauer technique is suitable for Fe-bearing compounds, whereas NQR is mainly appropriate for Cu-bearing minerals [7]. Notably, ^{57}Fe-Mössbauer and ^{63,65}Cu-NQR properties of bornite are not clear at present. Some previous Mössbauer studies show a singlet line at room and lower temperatures [8, 9] with isomer shift $IS = 0.41$–0.47 mm/s [9, 10]. At the same time, other data show a Mössbauer doublet with $IS = 0.39$ mm/s and quadrupole splitting $QS \approx 0.22$–0.26 [11, 12]. It appears that there is no published data concerning NQR properties of bornite.

The motivation of the present study is an examination of room-temperature (RT) properties of bornite Cu_5FeS_4 copper ore by conventional and backscattering ^{57}Fe-Mössbauer techniques, discussion of their merits for in-situ real-time mineralogy analysis in the mining industry and preliminary considerations of ^{63,65}NQR method as a complementary technique.

2 Materials and experimental methods

Several natural bornite Cu_5FeS_4 samples have been investigated, with three of them used in the present study (designated samples No. 2, No. 3 and No. 8). Samples No. 2 and No. 3 originated from the Djhezgazgan deposit of copper ore, stratiform type, in Kazakhstan. Sample No.8 was collected at the Volkovskoe deposit of copper-iron-vanadium ore, magmatic type, in Ural, Russia. X-ray diffraction investigations (XRD) using Shimadzu X-Ray Diffractometer have confirmed the presence of bornite phases for all samples. It has been found also that sample No. 3 contains chalcocite Cu_2S as the dominating phase (approx. 65 % of chalcocite and 35 % of bornite), which, however, does not exhibit a ^{57}Fe-Mössbauer spectrum. Subsequent ^{57}Fe-Mössbauer studies have shown the presence of hematite α-Fe_2O_3 inclusion (under 5 %) in sample No.2. This hematite inclusion was not found by XRD due to its small amount and, most probably, ultra-dispersed state. Before the experimental studies, all three samples were crushed in an agate mortar to a particle size under 100 μm.

The room-temperature ^{57}Fe-Mössbauer experiments have been conducted in the absorption geometry using Wissel and IAI-RAS Mössbauer spectrometers equipped with a standard source of radioactive cobalt isotope (^{57}Co) in a rhodium matrix. Simultaneously, the room temperature measurements have been carried out using backscattering portative Mössbauer spectrometers MIMOS-II [3]. The Mössbauer spectra have been recorded in the constant acceleration mode. The calibration has been made using α-Fe as a reference absorber.

3 Results

The Mössbauer spectra for sample No. 8 obtained in backscattering in absorption geometry are shown in Fig. 1. The Mössbauer spectra for the other two samples are identical and are not shown here. The Mössbauer parameters for three samples studied are shown in Table 1 together with some previous literature data [11, 12].

4 Discussion

As can be seen from the results obtained, the Mössbauer spectrum for bornite at RT represents a doublet (Table 1, Fig. 1). These results are in agreement with the experimental data from [11, 12]. The discrepancies concerning the single lines (singlet) at RT [8, 9] are connected, most probably, with the velocity resolution or the quality of the samples (for example, the presence of impurity phases). Application of backscattering portative Mössbauer spectrometers MIMOS-II provides the same parameters as conventional Mössbauer spectroscopy in absorption geometry.

It should be noted that the interpretation of low temperature Mössbauer spectra for bornite is not obvious and is still debated. The discrepancies in earlier Mössbauer data (above and below the Neel temperature of 64–68 K) led researchers to different explanations of the nature of the magnetic properties of bornite: vacancy clustering [8, 11], mixed-valence state of iron (Fe^{2+}-Fe^{3+}) [9] and superparamagnetic relaxation [12]. However, the solution of this problem requires reexamination of low-temperature magnetic properties and Mössbauer parameters [13] together with other methods, and is out of the scope of the research reported here. We can prove here that the Mössbauer spectra for bornite Cu_5FeS_4 minerals at RT point to the distortions of FeS_4 units in the structure which leads to a quadrupole splitting (Table 1), unlike chalcopyrite $CuFeS_2$ which has no quadrupole splitting [14] . This is as expected from the complicated distorted-like structure of bornite Cu_5FeS_4 with 16 non-equivalent metal sites and vacancies, in contrast to chalcopyrite $CuFeS_2$, having one position for iron only.

Another portative instrumentation for the express bulk mineralogical analysis of copper ore is nuclear quadrupole resonance (NQR) technique [4–7] which can be applied on ^{63,65}Cu isotopes. This spectroscopy tool is suitable for observation of NQR effect for the case of non-magnetic copper sulfides, such as covellite CuS [15], and "zero-field" nuclear magnetic resonance (ZF-NMR) effect for the magnetically ordered copper sulfides, for example, chalcopyrite $CuFeS_2$ [6]. Actually, in chalcopyrite $CuFeS_2$ due to antiferromagnetic ordering of Fe spins below $T_N = 823$ K the copper nuclei feel the internal magnetic field created by the electronic magnetic moments of iron and thus exhibit not a pure NQR, but an NMR spectrum at this field. As applied to bornite Cu_5FeS_4, we anticipate the presence of copper NQR spectrum at RT because of lower Neel temperature of $T_N \approx 64$–68 K [9, 13]. At the
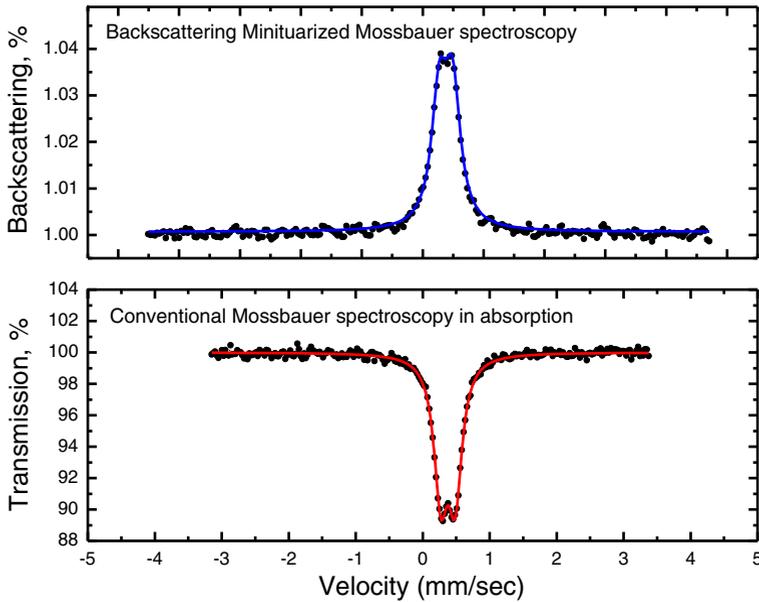
Fig. 1 The Mössbauer spectra of natural bornite Cu_5FeS_4 (sample No. 8) obtained using the backscattering miniaturized (MIMOS) (*top*) and conventional (*bottom*) Mössbauer spectroscopy instruments

Table 1 The Mössbauer parameters for several samples of bornite Cu_5FeS_4 at RT

Sample	QS, mm/s	IS, mm/s	S, %	Source
No. 2, Natural	0.216	0.38	100	This study, in absorption
	0.218(9)	0.383(8)	100	This study, MIMOS-II
No. 3, Natural	0.206	0.38	100	This study, in absorption
	0.216(3)	0.37(2)	100	This study, MIMOS-II
No. 8, Natural	0.213	0.38	100	This study, in absorption
	0.218(8)	0.382(7)	100	This study, MIMOS-II
Synthetic	0.224	0.389	100	[11]
Natural	0.218	0.376	100	[11]
Synthetic	0.23(1)	0.39(1)	–	[12]

Parameters are defined as follows: *QS* = splitting for doublet, *IS* = isomer shift with respect to α-Fe, *S* = area for doublet

same time, 16 non-equivalent metal sites in the bornite structure could lead to the numerous overlapping of NQR signals from ^{63,65}Cu isotopes below about 3 MHz which, more probably, cannot be separated and used effectively for identification of bornite in copper ore. Our attempt to find ^{63,65}Cu NQR signals of bornite at RT was unsuccessful, possibly due to a low signal-to-noise ratio. However, further search for NQR signals from bornite is important and this will be reported in the future.

5 Conclusions

Both conventional and backscattering portative Mössbauer spectroscopic studies prove that bornite Cu_5FeS_4 exhibits a doublet spectrum at RT with quadrupole splitting $QS \approx 0.20$–0.23 mm/s and isomer shift $IS \approx 0.37$–0.39 mm/s with respect to iron. The availability portative Mössbauer spectrometers MIMOS are sufficient to detect and identify the bornite ore in case of in-field employment of MIMOS. In contrast, the opportunity to use portative NQR spectrometers as phase-diagnostic tool for bornite ore is not clear. Application of Mössbauer spectroscopy at low temperatures together with other methods is important to elucidate the magnetic properties of bornite.

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