The compound BaFe$_2$Se$_3$ (Prmo) has been synthesized in the form of single crystals with the average composition Ba$_{0.992}$Fe$_{1.998}$Se$_3$. The Mössbauer spectroscopy used for investigation of the valence states of Fe in this compound at temperature ranging from 4.2 K till room temperature revealed the occurrence of mixed-valence state for iron. The spectrum is characterized by sharply defined electric quadrupole doublet above magnetic ordering at about 250 K. For the magnetically ordered state one sees four iron sites at least and each of them is described by separate axially symmetric electric field gradient tensor with the principal component making some angle with the hyperfine magnetic field. They form two groups occurring in equal abundances. It is likely that each group belongs to separate spin ladder with various tilts of the FeSe$_4$ tetrahedral units along the ladder. Two impurity phases are found, i.e., superconducting FeSe and some other unidentified iron-bearing phase being magnetically disordered above 80 K. Powder form of BaFe$_2$Se$_3$ is unstable in contact with the air and decomposes slowly to this unidentified phase exhibiting almost the same quadrupole doublet as BaFe$_2$Se$_3$ above magnetic transition temperature.

© 2015 Elsevier Ltd. All rights reserved.
magnetically ordered state [7]. No superconductivity was detected till practically the ground state of the system [8]. Single crystals were successfully synthesized, albeit all samples contain some spurious amounts of the FeSe superconductor [9]. Magnetic measurements on single crystals have been performed versus temperature as well confirming data obtained by other methods [10]. Band structure calculations for the Pnma form and within the LDA/LMTO approximation are reported, too [11]. These calculations show that antiferromagnetic coupling between ferromagnetic Fe₄ blocks leads to the lowest energy-state of the system. Early Mössbauer work was performed for BaFe₂S₃ (Cmcm) by using 14.41 keV resonant transition in ⁵⁷Fe. Mixed-valence was found for iron. The spectrum was composed of a quadrupole-split doublet [12]. Further work [13] revealed single magnetically split site for the BaFe₂S₃ compound and complex multiple site magnetically split spectra for the BaFe₂Se₃ (Pnma) compound. A magnetic ordering temperature was found to be at about 100 K for both compounds. This finding led to some speculations about spin fluctuation in BaFe₂Se₃ due to the discrepancy in the magnetic ordering temperatures found by the Mössbauer spectroscopy and neutron scattering [5]. Related compound BaFe₂Se₂O has been investigated by Mössbauer spectroscopy as well [3]. The electric field gradient (EFG) tensor acting on the iron nucleus was found in the magnetically ordered state (close to the ground state) with extremely large anisotropy parameter, and with the hyperfine field making some undetermined (and maybe variable) angle with the principal component of the EFG. The situation has some similarity to the situation in otherwise metallic systems like FeAs [14] and FeSb [15], where interplay between covalent and itinerant electrons including significant orbital contributions is important. Recent work [16] suggests that BaFe₂Se₃ compound exhibits properties of the orbital-selective Mott phase.

Therefore, the compound BaFe₂Se₃ deserves reinvestigation by the Mössbauer spectroscopy versus temperature especially in the magnetically ordered region.

2. Experimental

BaFe₂Se₃ single crystals were prepared by the Bridgman method. To this end the high purity (at least 4 N) powders of iron and selenium were combined in a molar ratio 2:3 and pressed into pellets of 5 mm-diameter. The prepared pellets were then sealed in a double-wall quartz ampoule together with a stoichiometric amount of metallic barium. The ampoule was heated to 1150 °C over 3 h and left at this temperature over 24 h to achieve suitable homogenization of the melt. Then the melt has been slowly (6 °C/h) cooled down to 750 °C followed by further annealing at this temperature for 20 h. Afterwards the material was cooled down to room temperature at the rate 200 °C/h. The method applied allowed for preparation of relatively brittle black crystallites, which cleave easily into plates.

Crystal structure of BaFe₂Se₃ sample was determined by means of the powder X-ray diffraction method. Measurements were performed at room temperature with D8 Advance Bruker AXS diffractometer using Cu Kα radiation (1.5406 Å). Measurements were done on crystal powdered in an inert atmosphere and loaded into the low background airtight sample holder to protect the material from oxidation. Reflections shown in the X-ray pattern (Fig. 1) were indexed within the orthorhombic crystal system (space group Pnma).

The X-ray fluorescence method applying micro-beam was used to determine composition maps of the sample. The average composition amounts to Ba₀.⁹⁹₂Fe₁.⁹⁹₈Se₃. The absorber for Mössbauer spectroscopy was made in the powder form mixing 33 mg of the material with graphite and pressing into pellet having 14 mm diameter. In order to avoid oxidation the pellet was covered by the triple fluoropolymer layer. The absorber was made in above form and packed into silica ampoule (used for transportation) within the glove box filled with argon. Mössbauer spectra were obtained in the transmission geometry with the help of the Renon MsAa-4 spectrometer. A commercial ⁵⁷Co(Rh) source kept at ambient conditions was used. Sample temperature was set and controlled by...
using ICE helium cryostat. Spectra were fitted within transmission integral approximation by means of the Mosgraf-2009 suite[18]. Mössbauer spectra were recorded in two subsequent series. Spectra of the series 1 were collected in the order: at room temperature and 4.2 K. Spectra of the following series 2 were obtained in the temperature range 80–270 K with the increasing temperature. A time period between two series was two months and the epoxy resin layer was slightly damaged due to the thermal shock experienced during series 1. Additional spectrum was obtained at 80 K one month after series 1.

3. Results and discussion

Mössbauer spectra of series 1 are shown in Fig. 2. Sub-spectra are shown as well (this statement applies to subsequent Fig. 3, too). They are numbered in the same order as respective contributions to the total cross-section in Table 1. One has to bear in mind that the sum of sub-spectra areas is slightly greater than respective total spectral area due to the saturation effect. However this effect is small for spectra in question as even at 4.2 K the effective dimensionless absorber thickness was about 0.23, and slightly less at higher temperatures, i.e., about 0.19 at room temperature. The room temperature spectrum consists of two quadrupole doublets. A doublet showing minor

![Graph of Transmission % vs Temperature]

**Fig. 3.** $^{57}$Fe Mössbauer spectrum obtained between series (top) and spectra belonging to series 2. Sub-spectra are numbered in the same order as respective contributions in Table 1.

| $T$ (K) | $C$ (%) | $S$ (mm/s) | $\Delta$ (mm/s) | $B$ (T) | $\theta$ (°) | $\Gamma$ (mm/s) |
|---------|---------|------------|-----------------|--------|-------------|----------------|
| Series 1 |         |            |                 |        |             |                |
| RT      | 94      | 0.504      | 0.958           | –      | –           | 0.18           |
| 6       | 0.59    | 0.24       | –               | –      | 0.3         |
| 4.2     | 29      | 0.64       | 1.14            | 27.0   | 51          | 0.28           |
| 16      | 0.68    | 1.14       | 27.9            | 64     |
| 29      | 0.62    | 0.60       | 24.7            | 35     |
| 19      | 0.62    | 0.84       | 23.0            | 27     |
| 4       | 0.46    | 0.24       | 5.2             | –      | 0.1         |
| 3       | 0.55    | 0.27       | –               | –      | 0.1         |
| One month after series 1 | | | | | | |
| 80      | 26      | 0.64       | 1.26            | 25.9   | 53          | 0.28           |
| 25      | 0.62    | 0.66       | 23.7            | 35     |
| 18      | 0.62    | 0.84       | 21.9            | 24     |
| 7       | 0.79    | 2.76       | 23.6            | 68     |
| 22      | 0.47    | 0.18       | 4.3             | –      | 0.7         |
| 2       | 0.58    | 0.36       | –               | –      | 0.1         |
| Series 2 – two months after series 1 | | | | | | |
| 80      | 24      | 0.65       | 1.26            | 25.9   | 54          | 0.27           |
| 21      | 0.62    | 0.60       | 23.7            | 34     |
| 16      | 0.61    | 0.78       | 22.0            | 23     |
| 7       | 0.90    | 2.70       | 24.2            | 73     |
| 32      | 0.49    | 0.06       | 3.9             | –      | 0.62        |
| 180     | 19      | 0.61       | 1.20            | 21.3   | 55          | 0.26           |
| 16      | 0.61    | 0.72       | 19.4            | 39     |
| 12      | 0.56    | 0.66       | 18.0            | 19     |
| 4       | 0.90    | 2.76       | 18.8            | 79     |
| 49      | 0.47    | 0.89       | –               | –      | 0.48        |
| 240     | 23      | 0.63       | 0.90            | 14.3   | 55          | 0.53           |
| 8       | 0.53    | 0.48       | 12.2            | 25     | 0.20        |
| 69      | 0.50    | 0.91       | –               | –      | 0.40        |
| 270     | 96      | 0.509      | 0.951           | –      | –           | 0.25           |
| 4       | 0.68    | 0.14       | –               | –      | 0.1         |

The symbol $T$ stands for the absorber temperature (RT – denotes room temperature). The symbol $C$ denotes relative contribution of the particular component, while the symbol $S$ stands for a total shift versus room temperature $\alpha$-Fe. The symbol $A_Q$ stands for the quadrupole coupling constant including sign for magnetically split components, while the symbol $\Delta$ denotes quadrupole splitting of the components without hyperfine magnetic field. The symbol $B$ stands for the hyperfine magnetic field, while the symbol $\theta$ denotes angle between principal component of the electric field gradient and hyperfine magnetic field. The symbol $\Gamma$ stands for the absorber line width.

using ICE helium cryostat. Spectra were fitted within transmission integral approximation by means of the Mosgraf-2009 suite [18]. Mössbauer spectra were recorded in two subsequent series. Spectra of the series 1 were collected in the order: at room temperature and 4.2 K. Spectra of the following series 2 were obtained in the temperature range 80–270 K with the increasing temperature. A time period between two series was two months and the epoxy resin layer was slightly damaged due to the thermal shock experienced during series 1. Additional spectrum was obtained at 80 K one month after series 1.
contribution (6% of the total cross-section) is due to the spurious phases (see Table 1 for details). The major doublet exhibits rather narrow lines indicating unique iron site in the magnetically disordered BaFe$_2$Se$_3$ compound. A total spectral shift and quadrupole splitting confirm that iron stays in the mixed-valence state [12]. The spectrum obtained at 4.2 K could be fitted by six different iron sites. Two of them belong to the minor phases with the total contribution of about 7%. One of these phases (3%) is superconducting FeSe [2]. Hence, there are four different iron sites in magnetically ordered BaFe$_2$Se$_3$. Each of them could be fitted by the axially symmetric electric field gradient tensor (EFG) with the principal axis making some polar angle with the hyperfine magnetic field. They form two groups with approximately the same abundance. The group with the larger magnetic field has slightly larger shift (lower electron density on the nucleus) in comparison with the second group. The quadrupole coupling constant is larger within this group while the polar angle is larger as well and closer to the magic angle of the pole coupling constant is larger within this group while the polar angle between groups is about 30° might be an indication of the twist between FeSe$_4$ tetrahedral units along the ladder.

Spectrum obtained at 80 K one month since the series 1 and spectra of the series 2 are shown in Fig. 3. They are characterized by increasing amount of the unidentified phase amounting to 4% in the 4.2 K spectrum of series 1. A contribution due to this phase masks eventually contribution of the superconducting FeSe. This phase has very small hyperfine magnetic field of about 5.2 T at 4.2 K and it becomes magnetically disordered above 80 K. It is interesting to note that the hyperfine pattern of this phase is hard to distinguish from the pattern of BaFe$_2$Se$_3$ at room temperature. Despite decomposition of the sample one observes a contribution to the spectrum due to unperturbed BaFe$_2$Se$_3$ with a magnetic transition at about 250 K in accordance with the neutron scattering data [5].

4. Conclusions

In general, Mössbauer spectroscopy sees the same long-range magnetic ordering temperature as other methods including neutron scattering. A discrepancy in magnetic ordering temperatures seen before [13] is due to the instability of the powder form of this compound in the contact with the air at ambient temperature. A decomposition product might be related to the recently discovered phase of BaFe$_2$Se$_3$ formed at high-pressure [4]. The Mössbauer spectra of the decomposition product and the BaFe$_2$Se$_3$ phase are almost the same above the long-range magnetic ordering temperature of BaFe$_2$Se$_3$. It seems that magnetic ordering of BaFe$_2$Se$_3$ leads to some atomic position variation, as the EFG tensors observed at low temperature seem to look like due to the differentiation of the unique EFG seen above magnetic transition. Presence of two groups of iron sites seen in the magnetically ordered state is likely to reflect presence of two spin ladders within the structure. Different angles between principal axis of EFG and hyperfine field for various iron sites confirm various tilts of the FeSe$_4$ tetrahedral units along spin ladders.

Acknowledgments

This work was supported by the National Science Center of Poland, Grant no. DE/C-2011/03/B/ST3/00446. A.K.-M. acknowledges the financial support founded by the National Science Center of Poland, Grant no. DE/C-2013/09/B/ST3/03391.

References

[1] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, J. Am. Chem. Soc. 130 (2008) 3296.
[2] A. Blachowski, K. Ruebenbauer, J. Zukrowski, J. Przewoźnik, K. Wojciechowski, Z.M. Stadnik, J. Alloys Compd. 494 (2010) 1.
[3] M. Valdor, P. Adler, Y. Prots, U. Burkhardt, L.H. Tjeng, Eur. J. Inorg. Chem. 36 (2014) 6150. http://dx.doi.org/10.1002/ejic.201402805.
[4] V. Svitlyk, D. Chernyshov, E. Pomjakushina, A. Krzton-Maziopa, K. Conder, V. Pomjakushin, R. Pütter, V. Dimitrijev, J. Phys.: Condens. Matter 25 (2013) 315403.
[5] Y. Nambu, K. Ohgushi, S. Suzuki, F. Du, M. Andreev, Y. Uwatoko, K. Munakata, H. Fukazawa, S. Chi, Y. Ueda, T.J. Sato, Phys. Rev. B 85 (2012) 064413.
[6] S. Dong, J.-M. Liu, E. Dagotto, Phys. Rev. Lett. 113 (2014) 187204.
[7] C. Monney, A. Uldry, K.J. Zhou, A. Krzton-Maziopa, E. Pomjakushina, V.N. Strocov, B. Delley, T. Schmitt, Phys. Rev. B 88 (2013) 165103.
[8] J.M. Caron, J.R. Neilson, D.C. Miller, A. Llobet, T.M. McQueen, Phys. Rev. B 84 (2011) 180409(R).
[9] A. Krzton-Maziopa, E. Pomjakushina, V. Pomjakushin, D. Sheptyakov, D. Chernyshov, V. Svitlyk, K. Conder, J. Phys.: Condens. Matter 23 (2011) 402201.
[10] H. Lei, H. Ryu, A.I. Frenkel, C. Petrovic, Phys. Rev. B 84 (2011) 214511.
[11] M.V. Medvedev, I.A. Nekrasov, M.V. Sadovskii, JETP. Lett. 95 (2012) 33.
[12] W.M. Reiff, I.E. Grey, A. Fan, Z. Eliezer, H. Steinfeil, J. Solid State Chem. 13 (1975) 32.
[13] M. Reissner, W. Steiner, H. Boller, ICAME-2001 Proceedings (Oxford, U.K., 2001), in: M.F. Thomas, J.M. Williams, T.C. Gibb (Eds.), Hyperfine Interact. (C), 197, Springer Science Business Media, Dordrecht, 2002, p. 2002.
[14] A. Blachowski, K. Ruebenbauer, J. Zukrowski, Z. Bukowski, J. Alloys Compd. 582 (2014) 167.
[15] K. Komödra, A.K. Jasek, A. Blachowski, K. Ruebenbauer, A. Krzton-Maziopa, 2014, arXiv:1406.7767.
[16] M. Mourigal, S. Wu, M.B. Stone, J.R. Neilson, J.M. Caron, T.M. McQueen, C.L. Broholm, 2014, arXiv:1411.3337.
[17] J. Rodríguez-Carvajal, Physica B 192 (1993) 55.
[18] K. Ruebenbauer, L. Duraj, (www.elektron.up.krakow.pl/mosgraf-2009).