Crystal structure of BaFe$_2$Se$_3$ as a function of temperature and pressure: phase transition phenomena and high-order expansion of Landau potential

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Abstract

BaFe$_2$Se$_3$ (*Pnma*, CsAg$_2$I$_3$-type structure), recently assumed to show superconductivity at $\sim 11$ K, exhibits a pressure-dependent structural transition to the CsCu$_2$Cl$_3$-type structure (*Cmcm* space group) around 60 kbar, as evidenced from pressure-dependent synchrotron powder diffraction data. Temperature-dependent synchrotron powder diffraction data indicate an evolution of the room-temperature BaFe$_2$Se$_3$ structure towards a high-symmetry CsCu$_2$Cl$_3$ form upon heating. Around 425 K BaFe$_2$Se$_3$ undergoes a reversible, first-order isostructural transition, which is supported by the differential scanning calorimetry data. The temperature-dependent structural changes occur in two stages, as determined by the alignment of the FeSe$_4$ tetrahedra and corresponding adjustments of the positions of Ba atoms. On further heating, a second-order phase transformation into the *Cmcm* structure is observed at 660 K. A rather unusual combination of isostructural and second-order phase transformations is parameterized within phenomenological theory assuming high-order expansion of the Landau potential. A generic phase diagram mapping observed structures is proposed on the basis of the parameterization.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Detailed structural properties of novel superconducting materials are a key component for understanding of the phenomenon. Polymorphism and phase transformations are of special interest as they bracket structural modifications where superconductivity may or may not exist. Enumeration of possible structural forms may be done with the help of *ab initio* calculations for many cases where stable structures correspond to various minima of the potential energy. Such an approach is, however, not an option for structures stabilized by a disorder or strongly anharmonic interactions. Such structures may exist at high temperatures and correspond to minima of the free energy that are difficult to deduce from an *ab initio* structure calculated for 0 K.
Phenomenological theory of phase transitions based solely on a symmetry basis helps to map those structures and relationships between them, but it has to be augmented by an experiment in order to constrain necessary polynomial expressions for the free energy and to orient phase diagrams in a space of physical parameters. Here we use a combination of diffraction experiments with phenomenological theory of phase transitions to uncover the unusual phase diagram of BaFe$_2$Se$_3$. For the title compound possible superconductivity at 11 K has been reported [1] thus manifesting a discovery of a potentially new class of superconducting materials and calling for extended search of the possible polymorphs.

The crystal structure of BaFe$_2$Se$_3$ was originally described in 1972 [2]. It adopts the CsAg$_2$I$_3$-type structure, Pnma space group and is closely related to the BaFe$_2$S$_3$ (Cmcm space group; CsCu$_2$Cl$_3$ type [2]) structure. The structures of BaFe$_2$S$_3$ and BaFe$_2$Se$_3$ were considered as derivatives from the SnNi$_3$ structure [3] in term of distortions of close-packed hexagonal layers [4]. In this approach, the main structural building units are Ba$_6$S$_2$ and Ba$_6$Se$_2$ trigonal prisms. In BaFe$_2$S$_3$ and BaFe$_2$Se$_3$ the Ba cations are coordinated by eight chalcogen atoms, six of which form trigonal prisms. The other two atoms cap two rectangular faces of the trigonal prisms, with the corresponding Ba-(S/Se) distances equal in BaFe$_2$S$_3$ and unequal in distorted BaFe$_2$Se$_3$. As a result of such a deformation, the BaFe$_2$Se$_3$ structure loses C-centering and adopts the Pnma symmetry.

Since the discovery, the physical properties of BaFe$_2$Se$_3$ have not been explored. Recently we have reported the synthesis, structural and magnetic properties of newly grown single crystals of the title compound [1]. They were found to exhibit a diamagnetic response around 11 K. Below $T_N$ = 240 K, long-range spin-block checkerboard antiferromagnetic (AFM) order is developed. The long-range AFM order disappears quite abruptly above 240 K, as shown in our previous work ([1], figure 5). However, the short-range AFM correlations persist up to room temperature. At 240 K the magnetic domain sizes show a jump-like decrease—the sizes estimated from the AFM Bragg peak broadening amounted to >650 Å below $T_N$ and about 20 Å at room temperature [1]. Although the binary FeSe phase was observed as an impurity (<0.8 mass %), bulk FeSe shows superconductivity at ~8.5 K [5–8], which is below the observed diamagnetic response. Following independent work indicated 255 K as the onset temperature for the antiferromagnetic ordering with a diamagnetic signal around 10 K. The sample was reported to contain the FeSe impurity as well [9]. Other studies on BaFe$_2$Se$_3$ indicated 256 K as a Néel temperature and reported an absence of superconductive response down to 1.8 K [10]. Interestingly, the iron-deficient semiconducting BaFe$_{1.7}$Se$_3$ phase did not exhibit long-range magnetic order in the 1.8–400 K temperature range [11]. Instead a spin-glass-like behavior was observed at about 50 K. Controversy in the literature data could originate from the fact that the physical properties of BaFe$_2$Se$_3$ strongly depend on the exact composition of the studied samples.

Here we further characterize BaFe$_2$Se$_3$ with the help of single crystal and powder diffraction of synchrotron radiation as a function of temperature and pressure. At variance with a previously proposed description in terms of BaSe$_{6/2}$ trigonal prisms, we parameterize the observed structural evolution as correlated rotations of relatively rigid double chains of shared FeSe$_4$ tetrahedra accompanied by a displacement of Ba cations. Such a description directly follows from our structural data and is further supported by a symmetry-based analysis in terms of deformation modes. We show that the transition between the two phases of the Cmcm and Pnma symmetries is induced by applying ~6 GPa pressure at room temperature. Interestingly, under constant ambient pressure a similar transition is observed on heating at 660 K. Therefore, the same Cmca phase can be stabilized in the expanded and contracted unit cells, i.e. with the longer and shorter bond lengths compared to the initial Pnma modification. We also found a first-order isostructural phase transition occurring around 425 K. The rather unusual combination of phase transformations calls for high-order terms in the Landau expansion of free energy; we propose a corresponding phenomenological model and validate it with experimental observations.

2. Experimental details

The single crystals of the BaFe$_2$Se$_3$ sample studied in this work are the same as in [1]. The crystals were grown from a melt of high-purity elements (at least 99.99%, Alfa) using the Bridgman method. Detailed description of the synthetic procedure can be found in our original work [1]. The studied crystal is fully stoichiometric with the exact composition equal to the nominal, i.e. BaFe$_2$Se$_3$. The composition was established by the Micro-XRF analysis and single crystal synchrotron radiation diffraction studies [1] and confirmed by powder neutron [1] and synchrotron (this work) radiation diffraction analysis.

2.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were performed with a Netzsch DSC 204F1 system. Measurements were performed on heating and cooling with a rate of 10 K min$^{-1}$ using a 20 mg sample encapsulated in a standard Al crucible. An argon stream was used during the experiment as a protecting gas. The experimental DSC curve is presented in figure 1.

2.2. Temperature- and pressure-dependent x-ray diffraction

High-temperature single-crystal data were collected with the MAR345 image plate detector (IP) at the Swiss–Norwegian Beam Lines, BM01A station at the ESRF (Grenoble, France) at 480 K using the wavelength of 0.69736 Å. For the collection at 480 K the detector was moved to a distance of 250 mm from the sample in order to obtain relatively high resolution low-angle reciprocal space maps. The resulting crystallographic resolution for the 480 K setup is 1.17 Å. A Cryostream 700 + N$_2$ blower was used to control
the temperature. Data were processed using the CrysAlis software [12]. The reciprocal layers of 480 K together with the original data collected at 150 K [1] (figure 2) indicate close similarity in spite of the fact that they were collected above and below the transition observed with DSC. The difference in the signal-to-noise ratios observed on the experimental data sets (figure 2) originates from the type of detector used. The presented 150 K data were collected with a CCD detector. Contrary to IP-based systems, CCD detectors offer fast readout time but feature intrinsic electronic noise, therefore they accumulate an additional detector-related background during the data collection. IP detectors make it possible to collect data with high signal-to-noise ratio, thus making it possible to observe weaker features of reciprocal space in greater detail; the mosaicity in the BaFe$_2$Se$_3$ sample is much better observed in the 480 K data set for the same reason.

For the temperature-dependent powder diffraction a small amount of the BaFe$_2$Se$_3$ single crystals was finely ground and placed into a glass capillary. Initially data were collected with the MAR345 detector in a transmission mode using the same wavelength of 0.69736 Å. The temperature was changed in a ramp mode with parallel collection of powder patterns from 80 to 500 K on heating and from 500 down to 360 K on cooling to check for a possible hysteresis using the Cryostream 700 + N$_2$ blower. Higher temperatures of up to 960 K were reached with an inhouse-developed heat blower. The high-temperature data were collected in a ramp mode using a Dectris Pilatus2M detector. Experimental data around 660 K are shown in figure 3.

For the pressure-dependent powder diffraction, the BaFe$_2$Se$_3$ single crystals were finely ground and loaded into the high-pressure diamond anvil cells (DAC). An ethanol–methanol mixture in a 1:4 ratio was used as a pressure-transmitting medium. For the powder diffraction data collection pressure was changed from ambient to 160 kbar with a typical step of 14 kbar. The sample was fixed by the stainless steel gasket with a hole of 0.3 mm in diameter. The effective pressure was calculated from the shift of the fluorescence signal from the ruby crystals also loaded into the cell. The experimental data set is presented in figure 4.

Both temperature- and pressure-dependent powder diffraction data were integrated and processed with the FIT2D software [13]; standard deviations were calculated with a
home-made software. Structural parameters were refined with the FullProf software [14].

3. Results

We start with the high-pressure experiment in DAC which indicates a structural phase transition at ∼60 kbar (figure 4). The data agree with the expected Pnma → Cmcm symmetry change, as can be noticed in particular from the 112, 401 and 013 reflections that fully disappear between 51.5 and 70.5 kbar (figure 5); those reflections are allowed in Pnma but forbidden in Bbmm space group (non-standard setting) if we preserve the Pnma unit-cell setting, or in Cmcm space group (standard setting) with axes relating to Pnma with a help of the [010 001 100] matrix (non-standard setting Pbnm). We denote the BaFe$_2$Se$_3$ structure present at room temperature and ambient pressure as α-BaFe$_2$Se$_3$ and the high-symmetry polymorph, isostructural to BaFe$_2$S$_3$, as γ-BaFe$_2$Se$_3$. The small number of data points and the limited quality of the high-pressure powder data do not allow us to make firm conclusions on the order of the transition; however, close to linear dependence of the intensity of discriminating reflections on pressure is indicative of a second-order phase transition (figure 5).

Extrapolation of the linear fit (figure 5, solid red line) suggests 54 kbar as a transition pressure. Volume versus pressure dependences for α- and γ-BaFe$_2$Se$_3$ phases fitted with the Murnaghan equation of state (1). The dashed bar indicates the expected position for the phase boundary. The inset shows c/a parameters ratio in the Pnma setting.

Structural data for the Cmcm polymorph as they follow from the Rietveld fit (figure 7, Cmcm space group, a = 8.780(1), b = 10.885(3), c = 5.2981(6) Å, Rp = 3.66, Rwp = 4.93, RB = 5.78; impurity peaks marked by * correspond to the binary FeSe phase, <0.8 mass %; relatively noisy difference profile results from the high induced strains at high pressures) of the 70 kbar data set are shown in table 2. The (212) and (400) peaks, which are almost overlapped at 0 kbar, diverge starting from 40 kbar as a result of anisotropic changes in the cell parameters with pressure (figure 6 inset, c/a parameters ratio in the Pnma setting is shown as an example). For the refinement of the high-pressure data a pseudo-Voigt profile together with preferred orientations in the [001], [311] and [312] directions was employed.

The refined structure has been compared to the low-symmetry phase with the help of ISODISTORT software [15]. Such an analysis makes it possible to describe a low-symmetry structure as a distorted version
of the parent high-symmetry analogue. The distortions are split into a finite set of contributions (symmetrical modes) induced by irreducible representations of the parent structure space group. The full comparison of two structures in terms of symmetrical modes together with their definitions are presented in the supplementary material (available at stacks.iop.org/JPhysCM/25/315403/mmedia), tables 1 and 2. The modes responsible for the transition comprise rotations of the Fe(Se/S)₄ tetrahedra together with displacements of Ba cations. In γ-BaFe₂Se₃ (figure 8, on the left, projection along the c axis is shown) the FeSe₄ tetrahedra are aligned in the horizontal plane. The α-BaFe₂Se₃ ambient-pressure structure (figure 8, on the right, projection along the b axis is shown) is obtained through a tilting of the tetrahedra along the γ-BaFe₂Se₃ c axis (BaFe₂Se₃ b axis); the tetrahedra located in the unit cell are rotated counterclockwise while the tetrahedra on the cell edges are rotated clockwise (figure 8).

The rotations of the FeSe₄ tetrahedra during the transition induce changes in the environment of Ba atoms as well. These changes mirror the differences in the coordination of the Ba atoms in BaFe₂S₃ and BaFe₂Se₃, described in section 1 of the paper. The Ba cations are coordinated by eight Se atoms, six of which form trigonal prisms. The other two atoms which cap two rectangular faces of the trigonal prisms have the corresponding Ba–Se distances equal in γ-BaFe₂Se₃ and unequal in distorted α-BaFe₂Se₃.

The structural changes between the ambient- and high-pressure modifications of BaFe₂Se₃ are strictly related by a group–subgroup scheme which is presented in the Bärmighausen [16–19] formalism in figure 9. The klassengleiche symmetry reduction of index 2 (k2) from Cmcm to Pbnm (non-standard setting of Pnma) leads to the emergence of superstructure reflections for the ambient-pressure phase. The latter is isotypic with RbCu₂I₃ [20, 21].

![Figure 8. Transformation from the γ-BaFe₂Se₃ (left) to α-BaFe₂Se₃ (right) structure through a rotation of the FeSe₄ tetrahedra.](image-url)
The symmetry reduction leads to a reduction of the site symmetry for the Ba, Se1, and Fe sites and a splitting of the 8g Se2 site into two fourfold 4c sites. The resulting selenium sites Se2 and Se1 have distinctly different \( x \) and \( y \) parameters as compared to the high-symmetry phase. This allows the rotation of the tetrahedral units. The iron atoms at the centers of the tetrahedra remain almost at the ideal positions.

This kind of phase transition seems to be very sensitive to changes in the atom size. Applying pressure on the selenide one obtains the structure of the sulfide. Such displacive phase transitions can also be expected for the alkali metal halocuprates ACu\( _2 \)X3 (A = Rb, Cs; X = Br, I). Most of these halides adopt the \( \text{Cmcm} \) structure at room temperature [21] and might show the \( \text{Pnma} \) phase upon cooling.

The characteristic peak in the experimental DSC data (figure 1) indicates a first-order phase transition at 426 K on heating and at 415 K on cooling. The observed temperature hysteresis of 11 K also agrees with a first-order character of the transition. Since the 150 K and room-temperature structures have been reported before [1], we start from the single-crystal diffraction experiment at 480 K in order to determine the features of the BaFe2Se3 structure above the transition. Visual inspection of the raw single-crystal diffraction data does not reveal any apparent differences between the 150 and 480 K datasets (figure 2, \( h1l \) layers are shown as an example). The quasi-1D structure along the \( b^* \) direction results in a mosaicity in the \( a^*c^* \) planes, which is more clearly observed at 480 K as a result of an improved signal-to-noise ratio of the IP detector compared to the CCD detector and a high-resolution experimental setup, as was mentioned in section 2.

Transformation from the low-temperature \( \text{Pnma} \) structure (figure 2) to a more symmetrical \( \gamma \)-phase (\( \text{Cmcm} \)) on heating could be expected, similar to the pressure-induced transformation. However, the experimental 480 K pattern indicates a persistence of the primitive unit cell. For instance, presence of the 112 reflections (figure 2), which would violate possible \( C \)-centering (or \( B \)-centering for the original \( \text{Pnma} \) unit-cell setting), indicates that the 480 K structure is not transformed into the BaFe2S3 \( \text{Cmcm} \) structure. Therefore, the first-order phase transition detected by DSC is not related to the expected polymorphism and detailed structural analysis is required to uncover its nature.

Structural refinement of the single-crystal data shows that the \( \text{Pnma} \) structure does evolve towards the \( \text{Cmcm} \) symmetry (figure 10), albeit the undistorted \( \text{Cmcm} \) structure is evidently not reached at 480 K. Comparison of bond lengths and bond angles for the 150 and 480 K experiments using the same \( \text{Pnma} \) description indicates that the originally proposed key structural elements—BaSe\( _{6/2} \) prisms—show strong deformation with temperature. At variance, FeSe double chains behave as nearly rigid blocks. Thus both the shape and size of the Ba coordination polyhedra change from 150 to 480 K with an increase of the Ba–Se distances averaged over 3 NN by \( \sim 0.064 \) Å while the Fe–Se distances averaged over 4 NN show only a 0.01 Å change. Albeit crystal’s quality precludes data collection suitable for proper analysis of charge density and related bonding, our observations agree with stronger directional bonding within double chains, and weaker, presumably ionic, bonding between chains and the barium atoms. Structural evolutions in the related RbCu\( _4 \) and CsCu\( _4 \) compounds have been similarly described in terms of rotations of the Cu\( _4 \) tetrahedra [21].

Similar conclusions are drawn from the analysis of symmetry-allowed deformations done with the ISODISTORT software [15]. The analysis is based on the comparison for two structures determined at 150 and 480 K and parameterization of the observed differences in terms of distortion modes induced by irreducible representations of the space group symmetry (supplementary material (available at stacks.iop.org/JPhysCM/25/315403/mmedia), table 3; displacive mode definitions are presented in table 4), here we note that the core structural difference between two data sets is the rotation of the FeSe4 tetrahedra within the \( ac \) plane. The Ba atoms adjust their positions following their eight-fold coordination by the Se atoms; the shifts take place mainly along the crystallographic \( c \) direction with a minor component along...
the a direction. The Fe atoms serve as rotation centers for the FeSe$_4$ tetrahedra and, consequently, undergo only slight displacements. All atomic movements take place solely in the ac plane (figure 10). Note that all the distortions do not change the symmetry, i.e. the space group Pnma remains the same, in agreement with the experiment. The results of structural refinement and crystal data for the BaFe$_2$Se$_3$ single crystal collected at 480 K are presented in tables 3 and 4.

Therefore the transition observed with DSC around 425 K (figure 1) is isostructural in the sense that two phases are of the same space group symmetry and corresponding atoms occupy the same Wyckoff positions and thus must be of a displacive type.

The above proposed description of BaFe$_2$Se$_3$ using the FeSe$_4$ tetrahedra shows a clear structural relation with the previously discovered iron chalcogenide superconductors. The orthorhombic BaFe$_2$Se$_3$ phase is composed of the infinite double chains of FeSe$_4$ tetrahedra propagating along the b (Pnma setting) crystallographic direction with the Ba cations filling the capped trigonal prisms (figure 11, left). The tetragonal series of the Fe$_{1-x}$Se and A$_{1-x}$Fe$_2$$_{2-y}$T$_2$ (A—alkali metals, T—chalcogen atoms) [22, 23] phases are composed of layers of the Fe(Se/T)$_4$ tetrahedra with the alkali metals being intercalated between the planes (figure 11, right). Despite crystallizing in different symmetries they share a common structural feature—Fe(Se/T)$_4$ units as basic structural blocks. Those units form double chains for BaFe$_2$Se$_3$ (1D) and planes for Fe$_{1-x}$Se and A$_{1-x}$Fe$_2$$_{2-y}$T$_2$ (2D) thus opening a question on other possible topologies compatible with superconductivity.

Probing structural behavior at the transition and throughout the whole temperature range by means of single-crystal analysis is time- and resource-consuming. Therefore synchrotron x-ray powder diffraction using a 2D image plate data recording was employed to probe the structure in fine steps throughout a wide temperature range.

Series of experimental temperature-dependent powder patterns indicate that the observed 112, 401, 013 reflections that would violate C-centering of the possible high-temperature BaFe$_2$S$_3$ Cmcm structure (Bbmm space group in the Pnma unit-cell setting) do not disappear up to the
Figure 12. Dependence of the $a$ unit-cell parameter (left) and Se$_3$ $z$ coordinate (right) from temperature.

Figure 13. Temperature dependence of the unit-cell volume. The dashed bar indicates the phase boundary.

Figure 14. Temperature dependence of the intensity of the 112 peak.

temperature of 500 K, in agreement with the single-crystal data. Careful inspection reveals a nearly linear decrease of their intensities with heating (intensities of 112 reflections are shown on figure 14, black data points).

Powder diffraction data were refined with the FullProf [14] software in the $Pnma$ model in the full temperature range from 80 to 500 K. Anomalies are present in the behavior of all structural parameters, with the most prominent for the $a$ cell parameter (figure 12, left) and the $z$ coordinates of the Se atoms (figure 11, right, the Se$_3$ $z$ coordinate is shown). Changes in the unit-cell volume with temperature are presented in figure 13.

As seen from the temperature-dependent behavior of the $a$ unit-cell parameter (figure 12, left), structural changes commence at the temperature of 340 K. Around 425 K the $a$ unit-cell parameter undergoes rapid decrease and the Se$_3$ coordinates experience sudden jumps (figure 12, right, the Se$_3$ $z$ coordinate is shown). The structural changes at 425 K are abrupt enough to exhibit first-order response on the DSC curve (figure 1). The only anomaly at the temperature-dependent behavior of the unit-cell volume, if any, may be seen around 365 K. Hysteresis in the structural parameters further supports the first-order nature of the transition.

The temperature evolution of the BaFe$_2$Se$_3$ structure can therefore be tentatively divided into two regions: from 80 to about 340 K, and from 340 to 500 K. In both temperature regions the transition is manifested as a rotation of the FeSe$_4$ tetrahedra with corresponding adjustments of the Ba positions, as concluded from the simulations using the ISODISTORT tool [15]. While in the first temperature region both rotations of the FeSe$_4$ units and movements of Ba atoms are nearly equally involved in the transition, the structural changes in the 340–500 K region are dominated by a displacement of the Ba atoms. We denote the low-temperature (below 340 K) BaFe$_2$Se$_3$ phase as $\alpha$ and the high-temperature (from 340 to at least 500 K) one as $\beta$. The two phases have the same space group symmetry but feature a small difference in coordination and chemical bonding, a consequence of change in the lattice parameters.

Upon further increase of the temperature the $Pnma$-$Cmcm$ transition is observed around 660 K (figure 3) not shown by Hong and Steinfink [2]. Dependence of the intensity of the 112 reflection with temperature is shown in figure 14.
Black data points correspond to the data obtained with the cryostream blower, red data points correspond to the data obtained with the heat blower. Refined structural parameters of the BaFe2Fe3 Cmcm modification at 660 K are presented in Table 5.

The linear coefficients of thermal expansion defined as $\alpha = \frac{1}{V_0} \frac{V - V_0}{T - T_0}$, with $V_0(V)$ and $T_0(T)$ being the initial (final) unit-cell volume and the sample temperature, are $5.08 \times 10^{-5}$ (T interval 100–300 K) for $\alpha$-BaFeSe$_3$, $3.39 \times 10^{-5}$ K$^{-1}$ (T interval 400–500 K) for $\beta$-BaFeSe$_3$, and $5.58 \times 10^{-5}$ K$^{-1}$ (T interval 660–960 K) for $\gamma$-BaFeSe$_3$.

4. Discussion

The diffraction experiments presented here revealed that, depending on temperature and pressure conditions, BaFe$_2$Se$_3$ can be found in $\alpha$ (Pnma), $\beta$ (high-temperature Pnma) or $\gamma$ (Cmcm) forms. The first two polymorphs are isosctructural in the sense that they are characterized by the same space group and Wyckoff positions, but differ in terms of structural evolution and in particular with thermal expansion coefficients. The last polymorph found above 60 kbar at room temperature and above 660 K at ambient pressure is a structure with a more symmetric arrangement of the FeSe double chains and Ba cations. It seems from the diffraction and DSC data that the pressure- and temperature-induced transitions $\alpha$ $\rightarrow$ $\gamma$ and $\beta$ $\rightarrow$ $\gamma$ are, within the limit of our experimental resolution, of second order, while the $\alpha$ $\rightarrow$ $\beta$ transition is of first order. Considering the $\gamma$ phase as parent, one finds that the order parameter (OP) responsible for the distortions present in $\alpha$- and $\beta$-structures relates to $Y^+_{2\gamma}$ irreducible representation (Irrep) which belongs to the $Y$-point of the orthorhombic Brillouin zone [24]. Microscopically the OP is expressed as rotation of the FeSe double chains together with a shift of the Ba ions normal to the rotation axis. The $\alpha$ and $\beta$ forms being both of the same symmetry differ by the value of rotational and shifting components.

Such a combination of second-order phase transition with strongly first-order isosctructural transformation is unique and, to our knowledge, has not been encountered in an experiment before. There are, however, theoretical indications that such an unusual structural evolution can be parameterized in the frame of the phenomenological theory of phase transitions assuming a high degree of nonlinearity for free energy as a function of OP [26].

As just mentioned, the structural antiferrodistortive phase transition Cmcm ($Z_p = 2$)–Pnma ($Z_p = 4$) is induced by the single-component OP $Y^+_{2\gamma}$. The OP image group, isomorphous to the $C_1$ point group, contains an ‘inversion operation’ changing the sign of OP (A2g group in notations of [22]). The relevant Landau potential is a one-component order-parameter expansion containing, therefore, only even powers of the order parameter $\eta$:

$$\Phi(\eta) = a_1 \eta^2 + a_2 \eta^4 + a_3 \eta^6 + a_4 \eta^8 + \ldots + a_m \eta^{2m}. \quad (2)$$

The phase diagrams and physical anomalies corresponding to the potentials with maximal OP degrees $m = 4$ and $m = 5$ have been earlier studied in detail by Gufan and Larin [25, 26], see also a review of the results in [27].

The equation of state for the $8^\circ$ model (2) and corresponding stability conditions are

$$\frac{d\Phi}{d\eta} = 2\eta \cdot (a_1 + 2a_2 \eta^2 + 3a_3 \eta^4 + 4a_4 \eta^6) = 0; \quad (3)$$

$$\frac{d^2\Phi}{d\eta^2} = (2\eta)^{-1} \cdot \frac{d\Phi}{d\eta} + 8\eta^2 \cdot (a_2 + 3a_3 \eta^2 + 6a_4 \eta^4) \geq 0. \quad (4)$$

It should be emphasized that the $8^\circ$ expansion (2) is the lowest degree which allows describing two isosctructural low-symmetry phases. At $a_3 \geq 0$, $a_4 > 0$, equation (3) has only two real solutions: $\eta = 0$ (I) describes a parent high-symmetry phase, and $\eta^2 \neq 0$ (II) corresponds to a distorted low-symmetry structure. However, at $a_3 < 0$ and $a_4 > 0$ (the latter should be positive in any $8^\circ$ model as the highest degree term, in order to ensure its global stability) two ‘low-symmetry’ real solutions do exist: I1 and II2 differ by the magnitude of the order parameter $\eta \neq 0$.

Stability limits for the parent phase I and two distinct but isosctructural phases I1 and II2 one finds from equation (4); phase transition lines are defined by the energy equality conditions: $\Phi_1 = \Phi_{II1,2}$, $\Phi_{II1} = \Phi_{II2}$. Figure 15 shows the phase diagram in the ($a_1$–$a_2$) plane, corresponding to the model (2), and the order parameter $\eta$ as a function of the phenomenological variable $a_1$ for the representative thermodynamic paths.

The second-order transition line between I and II1 ($\Phi_{II1} = 0$) starts at a triple point $N(a_1 = 0, a_2 = a^2_3/4a_4)$. The line of the first-order transitions I–II1 is

$$a_1^q = \frac{a_3}{a_4} \cdot a_2^q + \left[ -\frac{4}{27} \left(\frac{a_5^q}{a_4} \right)^3 \right]^{1/2}, \quad (5)$$

$$a_1^q = a_1 - \frac{a_3}{9a_4^2}, \quad a_2^q = a_2 - \frac{a_3^2}{3a_4}. \quad (5)$$

The isosctructural transition line I1–II2 is a straight line segment (NE) of

$$a_1 = \frac{a_3}{2a_4} a_2 - \frac{a_3^3}{9a_4^2}. \quad (6)$$

It is tangential to the first-order transition line I–II2 (5), and ends at the critical point $E[a_1 = -a_3^3/16a_4^2, a_2^q = 3a_3^5/8a_4]$. The OP jump at the isosctructural phase transition (on the line NE) corresponds to

$$\Delta(\eta^2) = \frac{1}{3a_4} \cdot [-a_3 + (a_1^2 - 3a_2a_3)^{1/2}]. \quad (7)$$

### Table 5. Structural data for the Cmcm polymorph of BaFe$_2$Se$_3$ at 660 K (Cmcm space group, $a = 9.2300(3)$, $b = 11.9088(4)$, $c = 5.5022(1) \, \AA$, $R_p = 7.62$, $R_{wp} = 8.07$, $R_b = 3.13$).

| Atom | site | $x$   | $y$   | $z$   | $B_{iso}$ |
|------|------|------|------|------|----------|
| Ba   | 4c   | 1/2  | 0.1818(2) | 1/4 | 2.41(4)  |
| Set  | 4c   | 1/2  | 0.2657(3) | 1/4 | 1.54(4)  |
| Set  | 8g   | 0.2067(2) | 0.3780(2) | 1/4 | 1.54(4)  |
| Fe   | 8e   | 0.3545(3) | 1/2  | 0 | 1.15(4)  |
In order to map the special (phase transition) points and lines experimentally measured in the \( P-T \) coordinate system onto the 2D space of the phenomenological parameters \( a_1-a_2 \), it is convenient to employ a linear transformation for
\[
\begin{align*}
  a_1(T, P) &= a_1(T-T_0) + \beta_1(P-P_0), \\
  a_2(T, P) &= a_2(T-T_0) + \beta_2(P-P_0).
\end{align*}
\] (8)

This establishes the \((P, T) \leftrightarrow (a_1, a_2)\) correspondence, using a minimal number of parameters: \( \alpha_i, \beta_i, T_0 \), and \( P_0 \). Both coordinate systems are shown in figure 16 along with the transformation points measured in our experiments.

One concludes that the singular points observed in our experiments fit well to the topology of the phase diagram which resulted from minimization of the phenomenological Landau potential (2).

As we have shown experimentally, microscopic realization of the order parameter appears as rotations of the FeSe tetrahedra combined with displacements of the Ba cations. There is no symmetry restriction for both deformations to respond similar on an external stimulus; they both correspond to the same Irrep as well as any mixture of them. However, it is intuitively clear that a rotation of infinite double chains and shifts of cations filling the space between the chains would have different effects in terms of the internal energy and also in terms of the crystal volume affected by such distortions. As we have shown above, in order to parameterize such a complex response one has to keep high-order terms in the series expansion of the free energy; thus appearance of both rotational and shifting components of the OP may require a highly nonlinear interaction potential. The nature of this nonlinearity in terms of local interactions has yet to be uncovered by ab initio calculations.

5. Conclusions

We report two new modifications of BaFe\(_2\)Se\(_3\) that can be found at different thermodynamic conditions. We characterized all of them with the help of single-crystal and powder diffraction techniques. A symmetry-based analysis of the relationship between different forms is augmented by detailed structural information on the pathways connecting the different phases. The phase transitions are described with the help of phenomenological theory and a generic phase diagram mapping. To the best of our knowledge, this is the first reliable observation of coupled structural and isostructural phase transitions induced by the same symmetry-breaking order parameter.

We show that at least thermal expansion and compressibility differ for different forms of BaFe\(_2\)Se\(_3\). In the case of a potential stabilization of the \( \beta \) and \( \gamma \) forms by doping, one may expect that other physical properties would also be affected by polymorphism; however, the range of existence of different phases as a function of chemical doping is still an open question.

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