Intrinsic crystal phase separation in the antiferromagnetic superconductor Rb$_y$Fe$_{2-x}$Se$_2$: a diffraction study

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Abstract

The crystal and magnetic structures of the superconducting iron-based chalcogenides Rb$_y$Fe$_{2-x}$Se$_2$ have been studied by means of single-crystal synchrotron x-ray and high-resolution neutron powder diffraction in the temperature range 2–570 K. The ground state of the crystal is an intrinsically phase-separated state with two distinct-by-symmetry phases. The main phase has the iron vacancy ordered $\sqrt{5} \times \sqrt{5}$ superstructure (I4/m space group) with AFM ordered Fe spins. The minority phase does not have $\sqrt{5} \times \sqrt{5}$-type of ordering and has a smaller in-plane lattice constant $a$ and larger tetragonal $c$-axis and can be well described by assuming the parent average vacancy disordered structure (I4/mmm space group) with the refined stoichiometry Rb$_{0.60(5)}$(Fe$_{1.10(5)}$Se)$_2$. The minority phase amounts to 8–10% mass fraction. The unit cell volume of the minority phase is 3.2% smaller than the one of the main phase at $T = 2$ K and has quite different temperature dependence. The minority phase merges with the main vacancy ordered phase on heating above the phase separation temperature $T_P = 475$ K. The spatial dimensions of the phase domains strongly increase above $T_P$ from 1000 to $>2500$ Å due to the integration of the regions of the main phase that were separated by the second phase at low temperatures. Additional annealing of the crystals at a temperature $T = 488$ K, close to $T_P$, for a long time drastically reduces the amount of the minority phase.

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

1. Introduction

The discovery of the Fe-based pnictide superconductors has triggered a remarkable renewed interest for possible new routes leading to high-temperature superconductivity. As observed in the cuprates, the iron-based superconductors exhibit interplay between magnetism and superconductivity, suggesting the possible occurrence of unconventional superconducting states. Among the iron-based superconductors FeSe has the simplest structure, with layers in which Fe cations are tetrahedrally coordinated by Se [1]. Recently superconductivity at about 30 K was found in chalcogenides X$_y$Fe$_{2-x}$Se$_2$ for X = K, Cs, Rb [2–4]. An average crystal structure of X$_y$Fe$_{2-x}$Se$_2$ is the same as in the layered (122-type) iron pnictides with the space group I4/mmm [5]. The principal difference of the new chalcogenides X$_y$Fe$_{2-x}$Se$_2$ (X = K, Tl, Rh, Cs) is the presence of a superstructure due to the iron vacancy ordering and strong antiferromagnetism (AFM) with large iron magnetic moments [6–21]. There is a general agreement on the presence of the $\sqrt{5} \times \sqrt{5}$ vacancy ordered structure and a second minority phase

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possessing different structure with additional reflections with propagation vector \( \frac{1}{2} \), which is often referred to as a \( \sqrt{2} \times \sqrt{2} \) structure. An important question whether the antiferromagnetically and vacancy ordered state (AFMV) microscopically coexists with the superconductivity (SC) remains open. In the transmission electron microscopy experiment [11, 22], the superstructure \( \sqrt{5} \times \sqrt{5} \) was observed together with the \( \sqrt{2} \times \sqrt{2} \) structure in certain areas in non-SC crystals of \( \text{K}_x \text{Fe}_{2-x} \text{Se}_2 \) (\( x = 0.4-0.5 \)), whereas the SC crystals (\( x = 0.3-0.4 \)) showed a phase-separated state along the \( c \)-axis with \( \sqrt{5} \times \sqrt{2} \) superstructure and disordered 122-structure. In the focusing synchrotron diffraction experiments [14, 15] the presence of phase-separated competing phases is reported in SC \( \text{K}_x \text{Fe}_{2-x} \text{Se}_2 \): a majority \( \sqrt{5} \times \sqrt{5} \) phase and a minority phase (30\%) having an in-plane compressed lattice volume and \( \sqrt{2} \times \sqrt{2} \) weak superstructure. The minority phase disappears on heating above 520 K. The compressed phase with \( \sqrt{2} \times \sqrt{2} \)-superstructure has been also observed in the single-crystal neutron diffraction experiments [16]. This phase was tentatively described in \textit{Pnma} space group with an Fe vacancy model [16]. Scanning tunneling microscopy studies of the local structural and electronic properties [17] also show charge density modulation with a well-defined order of Fe vacancies, and a superconducting \( \text{K(FeSe)}_2 \) phase containing no Fe vacancies [20].

In our previous work [23] we have also reported on the observation of the second minority in-plane compressed phase (MCP) phase with \( \frac{1}{2}, \frac{1}{2}, L \) Bragg rods in \( \text{Cs}_x \text{Fe}_{2-x} \text{Se}_2 \). In this paper we present explicit evidence of intrinsic phase separation and the temperature evolution of the crystal structures of both phases in full detail from \( T = 1.5 \) to 570 K in superconducting crystals of \( \text{Rb}_x \text{Fe}_{2-x} \text{Se}_2 \).

2. Samples: experimental details

Single crystals of rubidium intercalated iron selenides of nominal compositions \( \text{Rb}_{0.85} \text{(FeSe}_{0.98} \text{)}_2 \) and \( \text{Rb}_{0.45} \text{(Fe}_{0.9} \text{Se})_2 \), denoted as K43 and K72 were grown from the melt using the Bridgman method as described in [3]. 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 20 mg samples encapsulated in standard Al crucibles. An argon stream was used during the whole experiment as protecting gas. Neutron powder diffraction (NPD) experiments were carried out at the SINQ spallation source of Paul Scherrer Institute (Switzerland) using the high-resolution diffractometer for thermal neutrons HRPT [24]. The samples used in the NPD experiments at low (below room temperature using a cryostat) and high (with a furnace) temperatures were K72 and K43, respectively. The samples for the NPD were prepared by pulverization of relatively large (100–200 mg) pieces of the single crystals in an inert atmosphere. The superconducting state has been identified by ac-susceptibility measurements with small pieces of the crystals using a conventional PPMS magnetometer. The onset of the diamagnetic response amounted to \( T_c = 27 \) and 24 K for K72 and K43 samples, correspondingly. We note that for the diffusion measurements significantly bigger amounts of crystals were used in comparison with the macroscopic measurements. The low-temperature macroscopic magnetic properties were studied in detail in [25] by means of superconducting quantum interference device (SQUID) and torque magnetometry with the crystal identical to the crystal K72 of the present paper. Both crystals had the same \( T_c \) and chemical composition determined by micro-XRF technique [26]. Additionally, we have prepared two more samples from the original K72 and K43 crystals. The fresh pieces of both crystals K72 and K43 were annealed in closed ampules for 100 h and 50 h, respectively, at temperature \( T = 488 \text{ K} \), which is in the vicinity of the phase separation temperature \( T_P \). The annealed versions of samples were studied by NPD only at room temperature (section 3.7).

The refinements of crystal and magnetic structures from neutron powder diffraction data were carried out with the FULLPROF [27] program, with the use of its internal tables for scattering lengths and magnetic form factors. Single-crystal diffraction data were collected at the SNBL beamline BM1A at the ESRF synchrotron in Grenoble (France) with a MAR345 image-plate area detector using \( \lambda = 0.6977(1) \text{ Å} \). Intensities were indexed and integrated with CrysAlis [28], empirical absorption correction was made with SADABS [29], structure refinement with SHELXL97 [30].

3. Results and discussion

3.1. Phase separation and symmetry of the phases

Figure 1 shows a slice of the reciprocal space near the \( [lkl] \) plane. The superstructure reflections belonging to two twin domains can be easily identified. Each twin domain is described by a four-armed star as discussed in [7]. The propagation vector star spanned by the propagation vector \( k_1 = [\frac{2}{3}, \frac{1}{3}, 1] \) corresponds to the new five times bigger unit cell given by the basis transformation \( A = 2a + b \), \( B = -a + 2b \), \( C = c \), where the lower case letters stand for the basis of the parent average \( I4/mmm \) structure with \( a \sim 4 \), \( c \sim 15 \text{ Å} \). The capital letters denote the basis of the vacancy ordered AFMV phase with \( I4/m \) structure [7]. There is some confusion in the literature regarding the \( k \)-vector value. We note that in the centered lattices the propagation vector can contain integer components because the centered basis is larger than primitive. In the present case of an \( I \)-centered lattice adding an integer 1 to only one of its components does not transform the propagation vector to an equivalent one, e.g. \( [\frac{2}{3}, \frac{1}{3}, 0] \) is not equivalent to \( k_1 \). One can choose an equivalent to \( k_1 \) propagation vector \( k'_1 = [-3, 1, 5, 0] \). In the primitive basis both \( k_1 \) and \( k'_1 \) correspond to the same unique propagation vector \( k_{1p} = [2/5, -2/5, 4/5] \), which is
One can clearly see a splitting of the rods along $c$-direction in the 3D long range superstructure. There are superstructural Bragg main phase but a distinctly different crystal phase without one to conclude that the MCP is not simply a block of the average structure model.

However the fact that the MCP has different symmetry allows a careful inspection of the satellite peaks does not reveal any splitting. As an example, figure 2 shows a surface plot of the main Bragg peak $(220)_A$ and the satellite $(1.4, 0.2, 0)_A (3, -1, 0)$, which are also indicated in figure 1. This splitting can be attributed to the presence of the minority in-plane compressed phase (MCP). The symmetry of the MCP was reported to be not higher than monoclinic due to the 4-fold splitting of $(00L)$ peaks with large $L$ in $(a^*b^*)$-plane.

In contrast to the main AFMV phase the MCP phase does not possess similar additional superstructure reflections. A careful inspection of the satellite peaks does not reveal any splitting. As an example, figure 2 shows a surface plot of the main Bragg peak $(220)_A$ and the satellite $(1.4, 0.2, 0)_A (3, -1, 0)$, which are also indicated in figure 1. We use the underscore $A$ to denote the indexing in the average structure model $I4/mmm$, whereas the $hkl$-indices without subscript refer to the 5 times bigger $I4/m$ unit cell. One can clearly see a splitting of the $(200)_A$ peak, but the shape of the satellite peak is symmetric. The crystals of $X_xFe_{2-x}Se_2$ are quite fragile and often contain blocks. However the fact that the MCP has different symmetry allows one to conclude that the MCP is not simply a block of the main phase but a distinctly different crystal phase without 3D long range superstructure. There are superstructural Bragg rods along $c^*$ (the $(\frac{1}{2}, \frac{1}{2}, 0)$ section of the rod with integration $\pm 0.1c^*$ is shown in figure 2) with in-plane propagation vector $(\frac{1}{2}, \frac{1}{2})$ that are commensurate with the minority compressed phase as shown in [23]. These Bragg rods must originate from a 2D superstructure in the tetragonal $(ab)$ plane in the MCP phase. The contribution of the Bragg rods to the powder diffraction patterns is too small to be taken into account.

Figure 3 shows the experimental NPD pattern and the Rietveld refined profile. There are two main phases in the refinement: the main AFMV phase with $I4/m$ crystal structure and $\tau_2$ ($I4/m'$) AFM order [8] and the second MCP phase. There is a small fraction of elemental Fe impurity ($<0.3\%$ mass fraction), which can actually be neglected in the refinements. Both the peak positions and intensities of the MCP phase are well described by the average $I4/mmm$ structure and $\tau_2$ ($I4/m'$) AFM order [8]. Figure 3 shows the experimental NPD pattern and the Rietveld refined profile. There are two main phases in the refinement: the main AFMV phase with $I4/m$ crystal structure and $\tau_2$ ($I4/m'$) AFM order [8] and the second MCP phase. There is a small fraction of elemental Fe impurity ($<0.3\%$ mass fraction), which can actually be neglected in the refinements. Both the peak positions and intensities of the MCP phase are well described by the average $I4/mmm$ structure and $\tau_2$ ($I4/m'$) AFM order [8].

$k2 = [\mu, -\mu, \nu]$ in Kovalev notation [31] or C-point $[\nu - \mu, \nu + \mu, 0]$ of primitive tetragonal BZ in CDML [32].

The single-crystal diffraction shows (figure 1) that the parent average structure Bragg peaks are split similar to as reported in [23]. The splitting is especially well seen at higher $hk$ indices, due to both better resolution and a larger distance between the peaks, e.g. the peak (420) in figure 1. This splitting can be attributed to the presence of the second MCP phase. The symmetry of the MCP was reported to be not higher than monoclinic due to the 4-fold splitting of $(00L)$ peaks with large $L$ in $(a^*b^*)$-plane [23].
structure with smaller $a$ and larger $c$ lattice constants. In the powder diffraction pattern the MCP contribution mainly overlaps with the peaks of the main phase, but there are some peaks that are very well separated due to the high resolution of NPD data. For instance the (200)$_A$ ([240]) peak, which is also shown in figure 1, shows a clear splitting and the peak (200)$_A$ from MCP is shifted to higher 2$\theta$ because of the smaller $a$-constant as shown in the inset of figure 3.

The peaks of the main phase that overlap with the second phase peaks are those peaks of the $I4/m$ structure that originate from the parent average phase. Disregarding the second phase in the analysis leads to an effective increase of the weight of the parent reflections and, as a result, underestimation of the superstructure reflections. In the single-crystal diffraction experiment it is especially difficult to extract the true integrated intensity of the main phase for the Bragg reflections with small $hk$-indices due to low resolution.

The true symmetry of the MCP phase might be lower than tetragonal [23], but this deviation seems to be too small to be accounted in the powder ND experiment for the minority phase with about 10% contribution to the diffraction intensities. Anyway, we do not even have a model for the basis transformation that would account for the additional splitting of (00$L$) peaks of the MCP phase in the $(ab)$-plane observed in the single-crystal diffraction experiment [23].

3.2. DSC and temperature dependences of Bragg peaks

The inspection of differential scanning calorimetry (DCS) signal reveals three peaks (figure 4). The peak at the highest temperature $T_S$ is associated with the structure transition to the vacancy disordered phase on heating. DSC is especially sensitive to the first-order phase transitions due to the release of latent enthalpy. The second-order phase transitions, such as AFM ordering, can also be seen in DSC curves as smaller peaks due to the abrupt changes in heat capacity and the transition temperature. The middle peak at $T_P$ is associated with the AFM transition and the peak at lowest temperature $T_I$ is related to the phase separation transition, as we show below.

Figure 5 shows the temperature dependence of the integrated intensities of the three selected neutron diffraction peaks indicated in figure 3. In the used magnetic model ($\tau_2$ or $I4/m$ with the spins along the $c$-axis) the peak (110) has purely crystal structure contribution. Note, that allowing spin components in $(ab)$ in the same $\tau_2$ symmetry would result in the appearance of the magnetic contribution in all superstructure peaks in general. The doublet (101)/(002) has both magnetic and structure contribution. One can see that the (110) peak becomes abruptly zero above $T_S = 555$ K and the doublet peak intensity flattens above the Néel temperature $T_N =$ 525 K. The peak (321) seems to have only a magnetic contribution and vanishes above $T_N$. The transition temperatures seen by NPD might be different from the ones seen by DSC due to the temperature gradient between the thermocouple, which are mounted on the outer side of the vanadium container and the sample. Alternatively the difference might be due to different doping level, as noted in [33], where higher values of $T_N$ and $T_C$ were observed. Not exactly the same piece of sample was used for DSC and NPD.

3.3. Structure model

The structure of the main phase is the vacancy ordered $I4/m$, whereas the structure of the second MCP is vacancy disordered $I4/mmm$ with the structure parameters listed in table 1. The fraction of the second phase amounted to 10% and 8% for the samples K72 and K43, respectively. Since the minority phase fraction is small we used a constrained structure model. The atomic displacement parameters (ADP) were chosen to be the same in both phases for the same types of elements. In the refinement of the data collected above room temperature the occupancies of the Rb and Fe of the MCP were fixed. The occupancy of the Rb2 site (2a)

![Figure 4](image-url)  
Figure 4. Differential scanning calorimetry (DSC) signal as a function of temperature. Three peaks are observed: the largest at $T_P = 535$ K corresponds to the structure phase transition due to the vacancy ordering, $T_S$ and $T_P$ are related to AFM ordering and phase separation, respectively.

![Figure 5](image-url)  
Figure 5. Temperature dependences of selected neutron diffraction peaks. The vertical lines at $T_P$, $T_N$ and $T_S$ indicate phase separation, Néel temperatures and crystal structure transitions, respectively.
is refined to the larger than one values for the lower statistics ND patterns that were collected during the temperature scans. The contribution of the Rb2 site to the structure factor is four times smaller due to small Rb2 site multiplicity. The refinements in the model assuming equal occupancies of both Rb sites (i.e. ideal disorder over the Rb sites) give only slightly worse reliability factors and similar structure parameters of both phases. The diffraction peak line shape parameters that are responsible for the size and microstrain broadening effects were constrained to be the same for both phases. This is a fair approximation, keeping in mind that the second phase amounts to less that 10% and disappears on heating. One can see from figure 3 that the peak shape of the MCP phase is well described under the above assumption. The magnetic model is the block spin antiferromagnetic structure $t_2$ ($I4/m$) with the spins on the Fe2 site aligned along the $c$-axis [8]. The presence of the magnetic moment on Fe1 is forbidden by $t_2$ symmetry. The contribution of the Fe1 site to the diffraction intensity as well as to the total Fe stoichiometry is much smaller than the contribution of the Fe2 sites due to the four times smaller number of Fe1 atoms. However, the refined site occupancy of Fe1 is not very small and amounts to about 16%. We have also observed substantial occupancy of the Fe1 (4d) site in our previous single-crystal diffraction experiment [7].

The secondary MCP phase has a smaller refined Rb stoichiometry than in the main phase and no vacancies on the Fe site with the formula Rb$_{0.60(5)}$(Fe$_{1.10(5)}$Se)$_2$ (table 1). The refined Fe site occupancy is slightly larger than 100%. This might be caused by the presence of a small amount of vacancies on Se sites. If one rescales the Rb stoichiometry assuming exactly two Fe per formula, one gets Rb$_{0.55(5)}$. The phase separation on two phases was reported in NMR study [34] with composition of the minority vacancy disordered phase Rb$_{0.5}(\text{FeSe})_2$ deduced from intensity measurements. The crystal [34] had similar superconducting transition temperature $T_c = 32$ K, and the strong difference in Rb stoichiometry looks rather surprising if one assumes that the minority phase is responsible for SC.

### 3.4. Temperature dependence of phase separation

To follow the temperature dependence of the phase fractions we calculate the phase fractions from the scale factors $S$. The overall phase scale factor $S$ is a coefficient in front of the calculated $|F(H)|^2$, where $F(H)$ are the unit cell structure factors. $S$ is proportional to $N/v_0$, where $N$ is the number of unit cells (or amount of the phase material), and $v_0$ is the unit cell volume [35]. Figure 6 shows the refined overall scale factors $S1$ and $S2$ multiplied by the respective unit cell volumes for both phases. This product is proportional to the amount of the phase in the neutron beam. For convenience, the $S(T)v_0(T)$ values were normalized to be in units of mass fraction for the temperature $T = 325$ K, assuming that the two phases total 100%. For other temperatures no normalization was done, so the sum of the phase fractions $F1$ and $F2$ (figure 6) might not preserve 100%. We did not perform the normalization intentionally to see where the minority phase transforms on heating. One can see from figure 6 that the minority phase fraction starts to decrease at 470 K and reaches less than 2% level above 490 K. At the same time the amount of the main phase is increased, implying that the minority phase transforms to the main vacancy ordered phase. On cooling back to room temperature the second MCP phase appears again, apparently due to the phase separation at $T_p = 475$ K. The first DSC peak at $T_p$ (figure 4) can be identified as the temperature of the phase separation (or phase merging). Figure 6 has two sets of experimental points. We had noticed that the refined scale parameters $B (\bar{A}^2)$ were constrained to be the same for the same atom types. $x^2$ and $R_{wp}$ are the global chi-square and weighted R-factor for the whole pattern. The magnetic moment M-Fe is in units of $\mu_B$ and calculated per Fe2 site (i.e. assuming o-Fe2 = 1).
The low-temperature scan with the sample K72 was first performed from 2 K up to room temperature and then the pattern (or crystal structure in general) above $T_p$. Though the crystal looks like a single phase above $T_p$ it still can have an inhomogeneous vacancy distribution, but this is difficult to detect since this inhomogeneity amounts to, at maximum, 10%. We would like also to note that the true symmetry of MCP is lower than tetragonal, as can be seen from single-crystal synchrotron diffraction [23]. In this respect the symmetry of low-temperature MCP is lower than the $I4/m$ symmetry of the high-temperature vacancy ordered phase. Originally, the crystal was grown from the melt at the temperatures much higher than $T_p$ and $T_S$ and had probably a single-phase $I4/mmm$ vacancy disordered structure. On cooling below $T_S$ the vacancies were ordered, resulting in $I4/m$ structure. If we assume that in the temperature region between $T_p$ and $T_S$ the crystal consists of two phases with ideally matched crystal metrics, but one without vacancy ordering and might be different from $I4/mmm$ structure, then we should also admit that the phase separation had initially happened on cooling already below $T_S$ after the crystal growth.

3.5. Temperature dependence of the structures

The temperature dependence of the lattice constants is shown in figure 7 for both phases. One can see an abrupt shrinking of the lattice constant $c$ and an expansion in $ab$-plane of the main phase at the structural order–disorder transition at $T_S$, similar to reported in [7, 10]. The second phase is compressed in the $ab$-plane and expanded along the $c$-axis. The main phase has a 3.3% larger unit cell volume at $T = 2$ K. The phases have quite different temperature dependences of the lattice constants and unit cell volumes, which are also shown in the figure 7. The volume of the second phase increases significantly faster with the temperature increase above $T \approx 150$ K. The lattice constants of the MCP phase at the temperatures above $T_p$ might be not accurate due to its very small fraction at these temperatures.

The Fe and Rb occupancies and magnetic moment on Fe at temperatures above room temperature are shown in figure 8. As we noted above, the occupancy of the Rb2 (2a) above unity is probably related to some correlation effects and lower statistics of the experimental data of the temperature scan. However we prefer to use this unconstrained model to see the trends of the changes for all occupancies. Above $T_S$ the occupancies of two sites of Fe are strongly correlated if refined in the $I4/m$ structure, and show large error bars. Nevertheless this type of fit very clearly shows a jump-like leveling of the Fe occupancies due to structure order–disorder transition at $T_S$. The magnetic moment gets nonzero values ($<1$ $\mu_B$) if refined above $T_N$, due to correlation with the crystal structure parameters. The refinements were made in two phase model below 500 K and in one phase model (only main $I4/m$ phase) above 500 K.

3.6. Irreversibility effects below room temperature

The low-temperature scan with the sample K72 was first performed from 2 K up to room temperature and then the...
second time after cooling to 2 K again up to 120 K. The closed symbols in figure 7 show the second scan datapoints.

The lattice constant \( c \) of the second MCP phase has oppositely decreased by 0.09(1)%, resulting in an overall change of the relative unit cell volumes by 0.10(2)%, which is clearly seen in figure 7. This type of behavior is difficult to rationalize in a single-phase system. We believe that the irreversibility reflects a metastable character of both phases in the phase-separated state. When the second phase appears from the main phase on cooling below \( T_P \) it has 2% smaller unit cell volume (figure 7). Since the second phase is created along the whole single-crystal volume without the destruction (pulverization) of the crystal it is possible that there are some unrelaxed strains/pressure along the phase boundaries and the resulting state is not a thermodynamically ground state. On further cooling, the forces acting on the phase boundaries are changed due to the change in the relative phase volumes \( V_1/V_2 \). As a result of such cycling the strains on the phase boundaries can be relaxed and the phases get closer to the equilibrium state with the larger unit volume of the main phase and the smaller MCP phase volume.

Hypothetically, one could argue that the transition at \( T_P \) is not a phase separation transition, but a second crystal structure transition to a new structure which we simply could not identify. This new structure below \( T_P \) should have yet bigger superstructure unit cell to accommodate all the Bragg reflections observed in the experiment. However, the presence of the irreversibility favors the non-single phase state of the crystal.

3.7. Change of composition after annealing at \( T_P \)

To further check the two-phase model we have performed annealing of both samples at the temperature \( T = 488 \) K...
in the vicinity of the phase separation temperature \( T_P \), as described in section 2. After that, the room-temperature neutron powder diffraction patterns were collected. Figure 9 shows the diffraction pattern of the annealed K72 sample. One can see that the amount of the second MCP phase is drastically decreased in comparison with the original sample K72 (figure 3). At the same time the amount of the Fe impurity phase has increased, as can be clearly seen from the (110) peak intensity at \( 2\theta = 55.43^\circ \) (the intensity at this \( 2\theta \)-position has practically zero contribution from the main phase). In addition to the decrease in the amount of the MCP, its structure becomes further in-plane compressed (\( a = 5.83 \) Å) after annealing, as also clearly seen from the shift of the peak (200)\(_A\) in figure 9 in comparison with figure 3. The refined minority phases content has changed from 10.9\% MCP, 0.3\% Fe (mass fraction) for the original K72 to 5.8\% MCP, 1.4\% Fe for the annealed K72, and from 8\% MCP, \(<0.3\% \) Fe for the original K43 to 4.7\% MCP, 1.1\% Fe for the annealed K43. This observation provides additional evidence in favor of the metastable character of the minority phase. The appearance of elemental Fe is in accordance with the larger stoichiometry of the iron in the minority phase (Fe2.2) in comparison with the main AFMV phase (Fe1.6). In a recent paper [36], the evolution of the precipitate morphology during heat treatment in K\(_{x}Fe_{2−x}Se_{2}\) has been studied in detail by scanning electron microscopy (SEM) measurements.

### 4. Summary

The crystal and magnetic structures of the superconducting Rb\(_{x}Fe_{2−x}Se_{2}\) have been studied by means of single-crystal synchrotron x-ray and neutron powder diffraction (NPD) and differential calorimetry (DSC) in the temperature range from 2 to 570 K. The ground state of the crystal is an intrinsically phase-separated state with two distinct-by-symmetry phases. The main phase possesses the iron vacancy ordered \( \sqrt{5} \times \sqrt{5} \) superstructure (\( I4/m \) space group) with AFM ordered Fe spins. The minority phase does not have \( \sqrt{5} \times \sqrt{5} \)-type of ordering and has smaller in-plane lattice constant \( a \) and larger tetragonal \( c \)-axis. The NPD data can be very well described by assuming the parent average vacancy disordered structure (\( I4/mmm \) space group) of the minority phase with the refined stoichiometry Rb\(_{0.60(5)}\)Fe\(_{1.10(5)}\)Se\(_{2}\). The minority phase amounts to 8\%–10\% mass fraction. The unit cell volume of the minority phase is 3.2\% smaller than that of the main phase at \( T = 2 \) K and has a different temperature dependence. We note that the true crystal symmetry of the minority phase might be lower than tetragonal, but due to its small amount and powder averaging the average \( I4/mmm \) approximation works very well.

The minority phase fraction, calculated from structure refinements of the NPD data, decreases at phase separation temperature \( T_P = 475 \) K and reaches less than 2\% level above 490 K. At the same time the amount of the main phase is increased, providing direct evidence that the minority phase transforms to the main vacancy ordered phase. The spatial dimensions of the phase domains strongly increase above \( T_P \) due to the integration of the regions of the main phase that were separated by the second minority MCP phase at low temperatures. The phase transition of the pure main phase to the vacancy disordered structure occurs at higher temperatures \( T > 525 \) K.

The phase separation, the antiferromagnetic and the order–disorder transition temperatures observed in NPD experiment have the respective peaks in DSC calorimetry temperature scans.

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