Iron vacancy superstructure and possible room temperature antiferromagnetic order in superconducting Cs$_x$Fe$_{2-x}$Se$_2$

V. Yu. Ponomorozh and D. V. Sheptyakov  
*Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

E. V. Ponomorozh, A. Krzton-Maziopa, and K. Conder  
*Laboratory for Developments and Methods, PSI, CH-5232 Villigen PSI, Switzerland*

D. Chernyshov and V. Svitlyk  
*Swiss-Norwegian Beam Lines at ESRF, BP220, 38043 Grenoble, France*

Z. Shermadini  
*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*  
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Neutron and x-ray powder and single crystal synchrotron diffraction of Cs$_x$Fe$_{2-x}$Se$_2$ show the presence of superstructure reflections with propagation vector $k=\frac{4}{3}, \frac{1}{3}, 1$ with respect to the average crystal structure $I4/mmm$ ($a=4, c=15\text{Å}$). The propagation vector star corresponds to the 5 times bigger unit cell given by transformation $A=2a+b$, $B=-a+2b$, $C=c$. A solution for the atomic structure is found in the space groups $P42/n$ and $I4/m$ with an ordered pattern of iron vacancies corresponding to the iron deficiency $x=0.29$ and Cs stoichiometry $y=0.83$. The superstructure satellites are more pronounced in the neutron diffraction patterns suggesting that they can have some magnetic contribution. We have sorted out possible symmetry adapted magnetic configurations and found that the presence of AFM ordering with the ordered magnetic moment of Fe with $\zeta \approx 2\mu_B$ does not contradict to the experimental data. However, the solutions space is highly degenerate and we cannot choose a specific solution. Instead we propose possible magnetic configurations with the Fe magnetic moments in $(ab)$-plane or along $c$-axis. The superstructure is destroyed above $T_s \approx 500\text{K}$ by a first-order-like transition.

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I. INTRODUCTION

The recent discovery of the Fe-based 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. Other common properties are the layered structure and the low carrier density. Among the iron-based superconductors FeSe has the simplest structure with layers in which Fe cations are tetrahedrally coordinated by S atoms. Recently superconductivity at about 30K was found in $X_yFe_{2-x}Se_2$ for $X=K, Cs, Rb^{[3]}$. Muon-spin rotation/relaxation ($\mu$SR) experiments evidence that the superconducting state observed in $Cs_yFe_{2-x}Se_2$ below 28.5(2) K is microscopically coexisting with a magnetic phase with a transition temperature at $T_m = 478.5(3)$ K. The magnetic phase appears characterized by rather large static iron moments as the $\mu$SR signal is wiped out below $T_m$. Very recently the AFM order was reported in superconducting $K_{0.8}Fe_{1.6}Se_2$ with $T_N = 560$ K with the iron magnetic moment 3.31 $\mu_B$.

The average crystal structure of $X_yFe_{2-x}Se_2$ is the same as in the layered (122-type) iron pnictides with the space group $I4/mmm$. Different types of iron vacancy ordering in $Tl_yFe_{2-x}Se_2$ were observed long time ago$^{[5]}$, including the one with 5 times bigger unit cell. Due to renewed interest to the superconducting chalco- genides many new experimental studies on the vacancy ordering in $X_yFe_{2-x}Se_2$ ($X=K,Tl$) have appeared very recently$^{[11,12,13]}$.

In the present paper we report on the observation of superstructure in superconducting ($T_c = 28.5$ K) $Cs_yFe_{2-x}Se_2$ below $T_s \approx 500$ K and analyze the diffraction data assuming iron vacancy ordering and possible antiferromagnetic ordering of Fe at room temperature. The single crystals used in the present study are the same as in the Refs.$^{[13]}$

II. SAMPLES. EXPERIMENTAL

Single crystals of cesium intercalated iron selenides of nominal compositions $Cs_{0.8}(FeSe_{0.98})_2$ were grown from the melt using the Bridgman method as described in Ref.$^{[3]}$. Powder x-ray diffraction was performed using a D8 Advance Bruker AXS diffractometer with CuK$_\alpha$ radiation. For these measurements a fraction of the crystal was cleaved, powdered, and loaded into the low background airtight specimen holder in a He-glove box to protect the powder from oxidation. Differential scanning calorimetry (DSC) experiments were performed with a Netzsch DSC.
III. RESULTS AND DISCUSSION

![Graph]

**FIG. 1:** Fragment of the neutron diffraction pattern of Cs$_2$Fe$_{2-x}$Se$_2$. Contribution of the superstructure peaks refined in the powder profile matching mode for k = [0, 1, 1] with respect to the average crystal structure (I4/mmm with a = 3.96 Å, c = 15.29 Å) and the structure parameters fixed by the values from Table 1 is shown by red solid curve.

The average crystal structure can be refined in the standard structure model. The iron site occupancy is refined to smaller than unity for both x-ray and neutron diffraction data indicating the presence of the vacancies on the iron sites. The structure parameters refined in this model are presented in Table 1 for both laboratory x-ray and NPD data. The neutron diffraction pattern has a set of extra diffraction peaks that can be indexed with the propagation k-vector k = [0, 1, 1], as shown in Fig. 1. However, the x-ray powder diffraction pattern contains only one clearly visible satellite (0, 0, 0) at q = 1 Å$^{-1}$, that allows one to suggest that the satellites seen by neutron might have magnetic contribution. The propagation vector $\mathbf{k} = \{0, 1, 1\}$ corresponds to the new unit cell given by the transformation $\mathbf{A}=2\mathbf{a}+\mathbf{b}$, $\mathbf{B}=-\mathbf{a}+2\mathbf{b}$, $\mathbf{C}=\mathbf{c}$ (the illustration of the lattice cell transformation is shown in Fig. 2). A good refinement of NPD pattern explaining the satellite peaks can be done with the supercell indicated above in the space groups $\text{P}4_2/n$ and $\text{I}4/m$. Using the fixed new atomic positions generated from the average crystal structure ($\text{I}4/\text{mmm}$) by applying the above basis transformation and releasing only the site occupancies and z-Se, similar as for the average structure, one immediately gets a reasonably good description of the superstructure peaks. Table 1 shows the atomic positions and details of the refinements. The Fe site splits in two sites in $\text{I}4/m$ (no. 87) and in three sites in $\text{P}4_2/n$ (no. 86, note to work in the second setting with origin at $-1$ post-matrix translation $\{1, 1, 1\}$ should be applied). Both groups give similar quality of the refinements of the single crystal data as we explain below, so we present the results only for $\text{I}4/m$ space group, which is more symmetric with respect to the iron sites. The atomic positions for $\text{I}4/m$ space group generated by the above transformation from average space group $\text{I}4/\text{mmm}$ are listed in Table 1. All "sym-
shown in Fig. 2. The lattice unit cell transformation to a new bigger tetragonal supercell shown by capital letters. The supercell shown by solid red lines corresponds to the propagation vector star generated by \( \mathbf{k}_1 = \left[ \frac{2}{5}, \frac{1}{5}, 1 \right] \). The dashed cell shows the twin domain that corresponds to the star generated by \( \mathbf{k}_2 = \left[ \frac{1}{5}, \frac{3}{5}, 1 \right] \). The k-vector stars are shown in Fig. 3. Iron vacancy ordering pattern in ab-plane is shown by blue circles. The brown and green circles show fully occupied Fe and Se positions projected to the ab-plane.

![FIG. 2: The lattice unit cell transformation to a new bigger tetragonal supercell shown by capital letters.](image)

The refined stoichiometry is \( \text{Cs}_9\text{Fe}_2\text{Se}_5 \). The Fe1 site occupancy was fixed to 1. Anisotropic atomic displacement parameters \( U_{ij} \) are in Å multiplied by \( 10^3 \). \( U_{eq} \) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor. Totally 40 parameters were refined using 6286 reflections 539 of which are independent. Final R factors are \( R_1 = 0.0860, \) \( wR_2 = 0.1955 \) \( [I > 2\sigma(I)] \) and \( R_1 = 0.0940, \) \( wR_2 = 0.2105 \) (all data).

| \( x \) | \( y \) | \( z \) | \( U_{xx} \) | \( \text{occ} \) |
|---|---|---|---|---|
| Cs1 | 0.0000 | 0.0000 | 0.0000 | 78(2) | 0.911(14) |
| Cs2 | 0.4041(2) | 0.8057(2) | 0.0000 | 75(2) | 0.81(1) |
| Se1 | 0.3924(2) | 0.7987(2) | 0.6551(2) | 55(2) | 1 |
| Se2 | 0.5000 | 0.5000 | 0.1488(2) | 54(2) | 1 |
| Fe1 | 0.3014(1) | 0.5938(1) | 0.25165(6) | 59(2) | 1 |
| Fe2 | 0.5000 | 0.0000 | 0.0000 | 56(2) | 0.27(2) |

\( \mathbf{k}_1 = \left[ \frac{2}{5}, \frac{1}{5}, 1 \right] \) and \( \mathbf{k}_2 = \left[ \frac{1}{5}, \frac{3}{5}, 1 \right] \) by solid and dashed lines, respectively. These two \( \mathbf{k} \)-vectors correspond to two twin domains as shown in the figure can be easily identified. The angle between \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) is \( \tau \). The basis functions \( \psi \) for the spin of an iron atom in general \((16i)\)-position for \( \tau \) (two in \((ab)\)-plane) and for \( \tau \) (one along c-axis) are given for illustration of possible magnetic structures.

| \( \tau, \psi \) | \( h_1 \) | \( h_{14} \) | \( h_{15} \) | \( h_{25} \) | \( h_{38} \) | \( h_{28} \) | \( h_{39} \) |
|---|---|---|---|---|---|---|---|
| \( \tau_2 \) | 1 | 1 | 1 | -1 | -1 | -1 | -1 |
| \( \tau_3 \) | 1 | i | -i | 1 | i | -i | -i |
| \( \tau_5 \) | 1 | -1 | 1 | -1 | 1 | i | -i |
| \( \tau_7 \) | 1 | i | -i | 1 | i | -1 | i |
| \( \psi_{14}, ab \) | 1.0 | 0.0 | -i | 1.0 | -i | -1.0 | 0.0 |
| \( \psi_{14}, ab \) | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | -1.0 | -1.0 |
| \( \psi_{7, e} \) | 1 | -i | -i | -1 | 1 | i | -i |

![FIG. 3: A slice of the reciprocal space showing \([hk0]\) plane. The indexing is given in the average cell \((I4/mmm)\). The satellite reflections are indicated by red arrows for \( k \)-vectors corresponding to \( \tau \)-vectors.](image)

Since both vacancy superstructure and possible magnetic structure with \( k = 0 \) contribute to the same neutron Bragg peaks one needs the reliable crystal structure data to disentangle possible magnetic contribution. For this purpose several data sets were collected in the single crystal x-ray synchrotron experiment at room temperature and at 536K above \( T_m \) and \( T_s \). In addition, a limited slice of reciprocal space around \((-\frac{2}{5}, -\frac{4}{5}, 0)\) satellite was collected at heating to identify the transition. Figure 3 shows a slice of the reciprocal space near \([hk0]\) plane. The superstructure reflections belonging to two domains as shown in the figure can be easily identified. The angle be-

| \( h_1 \) | \( h_{14} \) | \( h_{15} \) | \( h_{25} \) | \( h_{38} \) | \( h_{28} \) | \( h_{39} \) |
|---|---|---|---|---|---|---|
| 1 | 4 | 4 | -1 | -1 | -1 | -1 |
| 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| \( m_{12} \) | -1 | -1 | -1 | -1 | -1 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 |

| \( \psi_{7, e} \) | 1 | -i | -i | -1 | 1 | i | -i |

TABLE III: Irreps \( \tau_i, i = 1.8 \) of the space group \( I4/m \) (no. 87) for \( k \)-vector \( k = 0 \). Numeration of the irreps is in accordance with Kovalev book \((k = k_{14}, \text{table } T121)\). \( \tau_4 = \tau_3 \tau_2, \tau_6 = \tau_3 \tau_2, \tau_8 = \tau_7 \tau_2 \). The basis functions \( \psi \) for the spin of an iron atom in general \((16i)\)-position for \( \tau_4 \) (two in \((ab)\)-plane) and for \( \tau_7 \) (one along c-axis) are given for illustration of possible magnetic structures.
FIG. 4: Fragment of the experimental NPD pattern and the refined profiles for three magnetic models given by symmetry adapted basis functions in \( I4/m \) space group. The full profile is shown by dashed blue line, the solid red lines show magnetic contributions to the profile. The curves for \( \tau_7 \) and \( \tau_2 \) are shifted along \( y \)-axis for better visibility. See text for details.

between the domains amounted to 53.2° in accordance with the drawing of Fig. 2. Note that the extra peaks are centered around forbidden nodes, because they are satellites of the Bragg peaks from the adjacent \( [hk1] \) and \( [hk-1] \) planes. The refined structure parameters together with the reliability factors are given in the Table III. Due to the strong absorption correction effects the atomic displacement parameters ADP can have an overall systematic shift. The refinement of the single crystal data in \( P4_2/n \) space group gives slightly worse, but still acceptable reliability factors that we list here for completeness \( R_1 = 0.0860, \) \( wR_2 = 0.2131 \) \( [ I > 2\sigma(I) ] \) and \( R_1 = 0.1283, wR_2 = 0.2885 \) (all data). One can notice additional diffraction spots at \( (\frac{7}{2}, \frac{7}{2}, 0) \) in Fig. 3. These spots are actually a projection of satellite rods at \( (\frac{7}{2}, \frac{7}{2}, l) \). The in-plane propagation vector is equal to \( [1 \frac{1}{2} \frac{1}{2}] \) in both average cell and supercell. We do not have any model to account for this additional superstructure, but it must correspond to a 2D-ordering within the \((ab)\)-plane, e.g. an ordering of vacancies in Cs layers without correlations between the layers along \( c \)-axis.

Using the structure data for \( I4/m \) from the single crystal x-ray experiment we made an attempt to evaluate the magnetic contribution in the NPD data. We assume that only fully occupied Fe1 site has a magnetic moment. All the structure parameters from Table III where fixed in the subsequent NPD refinements. Only overall ADP was introduced to account for the absorption effects in the x-ray experiment. The space group \( I4/m \) has eight one dimensional irreducible representations (irreps) for \( k = 0 \), and all eight irreps enter three times in the magnetic representation for the iron in general (16i) position. The irreps in Kovalev notation[19] are listed in Table III. There are four complex irreps with Herring coefficient 0 and four real irreps that correspond to the respective Shubnikov groups of \( I4/m \). We sorted out all the irreps and found that there are different magnetic configurations with the moment size about \( 2\mu_B \) per iron site that do not contradict to the NPD data. The magnetic R-factors amounted to 17.5-24.5% for different irreps. For the illustration of the magnetic contribution we show in Table III and in Fig. 4 two “orthogonal” magnetic models. For \( \tau_1 \) we choose the basis functions with the moments in the \((ab)\) plane, whereas for \( \tau_7 \) the moments are parallel to \( c \)-axis. Both models have practically the same magnetic Bragg R-factors 18.5 and 17.5%, respectively. We note that the

FIG. 5: Integrated intensity of \((0,-2,0)\) superstructure satellite, lattice constants obtained from the synchrotron measurements and differential scanning calorimetry (DSC) signal as a function of temperature. The superstructure satellite intensity was obtained from the single crystal measurement on heating. The lattice constants were refined from powder diffraction synchrotron data both on heating and cooling.

\[ I_{\text{arb. units}} \]
\[ c \ (\AA) \]
\[ a \ (\AA) \]
\[ T_s \]
\[ \text{DSC (arb. units)} \]
magnetic moment sizes on the Fe sites are not restricted to be the same by symmetry for complex irreps even if we consider the basis function only along one axis. For instance $\psi_\tau$ can be multiplied by an arbitrary phase factor $\exp(i2\psi)$ that would result in two different moment values. By choosing the phase $\varphi = \pi/4$ all the moments are constrained to be the same.

The model proposed in Ref. 6 corresponds to $\tau_2$ with the Shubnikov symbol $I4/m$'. Unfortunately, we do not observe an explicit magnetic contributions in (101) Bragg peak as observed in Ref. 6 in K-intercalated FeSe. This might be partially due to the fact that for the lattice constants of Cs$_2$Fe$_2$−$x$Se$_2$ the (101) and (002) appear at the same scattering angle. In addition, in our case of Cs$_2$Fe$_2$−$x$Se$_2$ the magnetic contribution is not so large. For comparison we show also the contribution of this model ($\tau_2, ||c|$) to the diffraction pattern (Fig. 4). One can see that the contributions of both $\tau_2$ and $\tau_7$ models are very similar (there are small differences hardly visible on the figure scale), but the magnetic configurations are different, namely for $\tau_2$ the constant moment configuration corresponding to the operators listed in the table are 1,-1,1,1,-1,-1, whereas for $\tau_7$ 1,1,1,1,-1,-1,-1. Probably the $\tau_7$ model would also fit the data of Ref. 6. We would like to stress that the possible solutions are highly degenerate by the values of the R-factors and we cannot choose a specific model on the basis of our experimental data.

Figure 5 shows the integrated intensity of the superstructure satellite and the lattice constants as a function of temperature obtained in the single crystal and powder synchrotron diffraction experiments. The intensity gradually disappears with transition temperature $T_s \simeq 500$ K, whereas the lattice constants exhibit a pronounced hysteresis indicating a first order phase transition. The unit cell volume is linear and does not have a visible peculiarity in the temperature region shown in Fig. 5. Interestingly, the c-lattice constant shows a decrease by 0.1% at the transition to the disordered phase. The crystal structure above $T_s$ is well refined in the $I4/mmm$ model (Table 1). The DSC signal has two peaks, one large at a higher temperature and the second small one at lower temperature, which had been associated with the onset of the magnetic order from $\mu$SR -experiment. The large DSC peak seems to be originated from the vacancy order-disorder transition at $T_s \simeq 500$ K.

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