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Abstract

We report on a comparative study of the crystal structure and the magnetic properties of FeSe$_{1-x}$ ($x=0.0-0.15$) superconducting samples by neutron powder-diffraction and magnetization measurements. The samples were synthesized by two different methods: a “low-temperature” one using powders as a starting material at $T\simeq 700$ °C and a “high-temperature” method using solid pieces of Fe and Se at $T\simeq 1075$ °C. The effect of a starting (nominal) stoichiometry on the phase purity of the obtained samples, the superconducting transition temperature $T_c$, as well as the chemical stability of FeSe$_{1-x}$ at ambient conditions were investigated. It was found that in the Fe-Se system, a stable phase exhibiting superconductivity at $T_c \simeq 8$ K exists in a narrow range of selenium concentration (FeSe$_{0.974\pm 0.005}$).
Synthesis, crystal structure and chemical stability of the superconductor \( \text{FeSe}_{1-x} \)

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We report on a comparative study of the crystal structure and the magnetic properties of \( \text{FeSe}_{1-x} \) \((x = 0.0 - 0.15)\) superconducting samples by neutron powder diffraction and magnetization measurements. The samples were synthesized by two different methods: a "low-temperature" one using powders as a starting material at \( T \approx 700^\circ \text{C} \) and a "high-temperature" method using solid pieces of Fe and Se at \( T \approx 1075^\circ \text{C} \). The effect of a starting (nominal) stoichiometry on the phase purity of the obtained samples, the superconducting transition temperature \( T_c \), as well as the chemical stability of \( \text{FeSe}_{1-x} \) at ambient conditions were investigated. It was found that in the Fe-Se system a stable phase exhibiting superconductivity at \( T_c \approx 8 \text{K} \) exists in a narrow range of selenium concentration (FeSe0.974±0.005).

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I. INTRODUCTION

The discovery of Fe-based superconductors has attracted considerable attention to the pnictides. Superconductivity is detected now in various pnictide families as \( \text{e.g.} \) the single-layer \( \text{ReO}_1\text{–}_2\text{Fe}_2\text{FeAs} \) (\( \text{Re} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Ho} \) and \( \text{Y} \)). The double-layer \( \text{MF}_2\text{As}_2 \) (\( \text{M} = \text{Ba}, \text{Sr}, \text{and Ca} \)), the oxygen free single-layer \( \text{LiFeAs} \) and \( \text{FeAs} \) etc. The common structural feature of all these materials is the Fe-As layers co-ordinated by As. Recently, superconductivity with a transition temperature of \( T_c \approx 8 \text{K} \) was discovered in \( \beta\text{-FeSe}_{1-x} \) with \( \text{PhO-structure} \). This compound also has a Fe square lattice with Fe atoms tetrahedrally co-ordinated by Se similar to the structure of FeAs layers in the single- and the double-layer pnictides. In this respect \( \text{FeSe}_{1-x} \), consisting of the "superconducting" Fe-Se layers only, can be considered as a prototype of the known families of Fe-based superconductors and, consequently, is a good model system to study mechanisms leading to the occurrence of superconductivity in this new class of materials.

As is stated in the literature, there are two different routes to synthesize superconducting \( \text{FeSe}_{1-x} \). The first one uses Se and Fe powders as the starting material and is performed in sealed silica tubes at 400-700°C. Hereafter we call it the "low-temperature" synthesis (LTS). This method, however, was shown to result in samples with relatively high amount of impurities. According to Ref. 16, \( \text{FeSe}_{1-x} \) with \( x = 0.18 \) was found to consist of a superconducting phase and a small amount of elemental selenium, iron oxide and iron silicide (reaction product with silica ampoule). For a higher average selenium content \((x = 0.12)\), some amount of hexagonal (NiAs-type) FeSe phase was detected in addition to impurity phases listed above. The superconducting transition temperature was found to be at \( \approx 8 \text{K} \), being independent of the initial Se content. The second procedure proposed in the recent work of McQueen et al. 17 starts from Fe pieces and Se shot. The Fe and Se pieces sealed in silica ampoule were first held at 750°C (3-5 days), then heated up to 1075°C (3 days) followed by a fast decrease down to 420°C and quenched. The synthesis was completed by additional annealing of the sample (sealed in a new ampoule) at 300-500°C followed by quenching. Superconductivity was found to exist only in a very narrow range of stoichiometry. For FeSe0.99 (Fe1.01Se) magnetization measurements showed \( T_c \approx 85 \text{K} \) whereas \( T_c \) for FeSe0.98 (Fe1.02Se) decreased down to \( \approx 5 \text{K} \) and went to zero (at least down to 0.6K) for FeSe0.97 (Fe1.03Se). Hereafter we call this procedure the "high-temperature" synthesis (HTS). In comparison with LTS, the samples prepared by HTS do not contain iron oxide impurities 17.

Surprisingly, the \( \text{FeSe}_{1-x} \) samples synthesized by LTS and HTS techniques were found to be rather different. Indeed, in LTS samples superconductivity was found in a rather extended range of Se content (at least up to \( x = 0.18 \)) while for the HTS superconductivity was detected only in a very narrow region corresponding to \( 0.01 \leq x \leq 0.025 \). In addition, McQueen et al. 17 reported, that below 300°C the tetragonal \( \text{FeSe}_{1-x} \) converts into a hexagonal (NiAs-type) phase which is not superconducting. Therefore, quenching from temperatures above 300°C was used for synthesizing HTS samples. On the other hand, no special care for fast cooling of LTS samples needs to be taken. In order to resolve these controversies we performed comparative studies of the superconducting \( \text{FeSe}_{1-x} \) samples synthesized by both methods (LTS and HTS) described above. We have improved a method of synthesis using powder starting materials and investigated the effect of stoichiometry on the phase purity of the obtained samples and its superconducting transition temperature. Based on the neutron powder diffraction data we have revised Fe-Se concentration phase diagram proposed by Okamoto 18.
II. EXPERIMENTAL DETAILS

AC and DC magnetization (\(M_{AC}/M_{DC}\)) measurements were performed using Quantum Design PPMS and MPMS magnetometers at temperatures ranging from 2 to 300 K. The AC field amplitude and the frequency were 0.1 mT and 1000 Hz, respectively. The DC magnetization experiments were performed after zero-field cooling and field cooling the samples at \(\mu_0 H = 0.1\) mT. The superconducting transition temperature \(T_c\) was determined as an intersection of the linearly extrapolated \(M_{AC}(T)/M_{DC}(T)\) with the \(M = \text{const}\) line (see Fig. 1).

Neutron powder diffraction (NPD) experiments were carried out at the SINQ spallation source at the Paul Scherrer Institute (PSI, Switzerland) using the high-resolution diffractometer for thermal neutrons HRPT (the neutron wavelengths \(\lambda = 1.494\) Å and 1.155 Å). The refinements of the crystal structure parameters were done using FULLPROF program \(^{21}\) with the use of its internal tables for neutron scattering lengths.

![FIG. 1: (Color online) Temperature dependencies of the DC magnetization (\(M_{DC}\), zero-field cooling, 0.1 mT) of LT085 sample. The superconducting transition temperature \(T_c\) and the superconducting (\(M_{SC}\)) and the magnetic (\(M_{mag}\)) responses of the sample are determined as shown in the figure. The inset shows dependencies of \(M_{mag}/M_{SC}\) and Fe impurity concentration as a function of the nominal Se content.](image)

III. RESULTS AND DISCUSSION

A. Sample synthesis

Two types of samples using the LTS and the HTS procedure were prepared. Samples of a nominal composition \(\text{FeSe}_{0.85}, \text{FeSe}_{0.87}, \text{FeSe}_{0.92}, \text{FeSe}_{0.96}, \text{FeSe}_{0.98}, \) and \(\text{FeSe}\) (LT085, LT087, LT092, LT096, LT098 and LT100) were prepared by a solid state reaction similar to that described in Refs. \(^{10,17}\). The cold pressed mixtures of Fe and Se powders were sealed in quartz ampoules and then heated up to 700°C followed by annealing at 400°C. Powders of Fe and Se of a minimum purity of 99.99% were used as starting materials.

Sample \(\text{FeSe}_{0.94}\) (HT094) was synthesized similar to the route of McQueen et al. \(^{17}\) - by solid state reaction using pieces of Fe and Se of a minimum purity of 99.99%. The sample was heated in the sealed quartz ampoule up to 1075°C followed by annealing at 400°C. In contrast to McQueen et al. \(^{17}\) no quenching from high temperatures was made. The sample was cooled down to the room temperature at a rate of 200°C/h.

Note that for the samples synthesized by both LTS and HTS techniques all the grindings/pelletizings were performed under helium atmosphere. The samples studied in the present work are listed in the Table II.

B. Se content and impurity phases

The chemical composition of the main (superconducting) phase and the concentration of the impurity phases were determined by means of neutron powder diffraction. First we present the results obtained for the \(\text{FeSe}_{1-x}\) samples with nominal Se contents 0.85 ≤ \(1 - x\) ≤ 0.98 (LT085–LT098 and HT094). Room temperature NPD experiments show that all these samples contain the same tetragonal phase \(\text{FeSe}_{1-x}\) (space group \(P4/mm\)) as a main phase. The refined selenium occupancy (selenium...
stoichiometry) is about 0.974(2) and is independent of the starting composition and the route of the synthesis (LTS, HTS). A typical example of Rietveld refinement of NPD data is shown in Fig. 2 for the LT098 sample. Impurity phases are hexagonal FeSe (space group $P6_{3}mmc$) in a quantity of $\sim 1\%$ (molar %) and Fe (space group $I\bar{m}3m$). The amount of the metallic Fe was found to decrease monotonically with increasing Se content from $\geq 12.5\%$ for FeSe$_{0.85}$ to $\geq 0.5\%$ for FeSe$_{0.98}$. Note, that for all the samples studied the presence of any oxides was not detected. The "cleanest" sample is LT098 which contains, in total, less than 2% of the secondary phases and has a nominal composition FeSe$_{0.98}$, the same as is refined for the main tetragonal phase FeSe$_{0.975(3)}$. The amount of impurity phases found in the samples, the refined stoichiometry of the main tetragonal phase and its unit cell parameters are listed in Table I.

The results of the structural analysis were further confirmed by magnetic susceptibility measurements. As follows from Table I, all FeS$_{1-x}$ samples ($0 < x \leq 0.15$) have almost the same transition temperatures ($T_{c} \sim 8.2 - 8.4$ K) and, consequently, very similar doping (concentration of charge carriers). In addition, the paramagnetic offset ($M_{mag}$), seen at $T > T_{c}$ was found to decrease with increasing Se content just following the dependence of Fe impurity phase as the function of the nominal Se content $1 - x$ (see the inset in Fig. 1). Note that in Ref. 22 the observation of the paramagnetic offset at $T > T_{c}$ as well as the static magnetic contribution seen in zero-field muon-spin rotation experiments were attributed to the presence of Fe impurities.

By increasing the Fe:Se ratio up to 1:1 the situation was drastically changed. The Rietveld refinement of NPD data on FeSe (LT100) sample reveals that the main tetragonal phase content is substantially decreased down to $\sim 83.03\%$. The content and the composition of the impurity phases were also changed: only 0.46% of Fe and, instead of a hexagonal NiAs-type phase, $\sim 16.51\%$ of the trigonal Fe$_{7}S_{8}$ (space group $P3_{1}21$) was detected. Magnetization experiments also show the substantial decrease in the superconducting fraction which was found to be of about 10% at $T = 3$ K.

Studies of the crystal structure of the main phase as a function of temperature were performed on the sample LT085 in the temperature range 20-300 K on both cooling and heating. Figure 3 shows the lattice constants $a$, $b$, and the unit cell volume as a function of temperature. At temperature $T=100$K there is a transition from the tetragonal to orthorhombic structure on cooling similar as observed in Ref. 18. The low temperature structure is well refined in the space group $Cmma$. The building block of the crystal structure is SeTe$_{4}$ square pyramid with Se-atom in the apex. In the high temperature phase the pyramid is regular, whereas in the orthorhombic phase the neighboring Fe-Se-Fe bond angles become different as shown in Fig. 4. The Fe-Se bond length amounts to 2.386(2) Å at low temperature and it is not changed at the transition. Neither temperature hysteresis nor the unit cell volume jump were observed indicating that the transition is of the second order type. The transition temperature in our sample FeSe$_{0.963(5)}$ (100 K) is different from the one reported for FeSe$_{0.91}$ (70 K)18 that might be related to the different Se stoichiometry. However, as described above our synthesis techniques always produce the main tetragonal phase with approximately the same concentration with the average value of about $x=0.974$.

![Figure 3](image-url)  
FIG. 3: $a$, $b$ unit cell parameters and unit cell volume $V$ as a function of temperature. In the tetragonal phase the lattice constant is multiplied by $\sqrt{2}$.

![Figure 4](image-url)  
FIG. 4: Fe-Se-Fe bond angles as a function of temperature in FeSe$_{0.963(5)}$. The refinements of the diffraction data were made assuming low symmetry phase (space group $Cmma$). The high temperature crystal structure is tetragonal and both Fe-Se-Fe angles would be the same by symmetry in $P4/nmm$ group.
TABLE I: Summary of the neutron powder diffraction (NPD) and magnetization results for FeSe$_{1-x}$ samples prepared by LTS and HTS methods.

<table>
<thead>
<tr>
<th>sample</th>
<th>nominal composition</th>
<th>$T_c$ (K)</th>
<th>phase content (molar %)</th>
<th>unit cell parameters ($\text{Å}$) of the tetragonal phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT085a FeSe$_{0.85}$</td>
<td>- FeSe$_{0.994(11)}$ (P$_4$/nmm) 71.75±1.75% Fe ($Im3m$) 26.23±0.85% FeSe ($P6_3/mmc$) 2.02±0.38%</td>
<td>a=3.77413(14) c=5.52141(31)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT085 FeSe$_{0.85}$</td>
<td>8.28 FeSe$_{0.963(5)}$ (P$_4$/nmm) 86.38±0.98% Fe ($Im3m$) 12.46±0.33% FeSe ($P6_3/mmc$) 1.16±0.18%</td>
<td>a=3.77280(4) c=5.52496(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT087 FeSe$_{0.87}$</td>
<td>8.34 FeSe$_{0.978(4)}$ (P$_4$/nmm) 91.53±0.91% Fe ($Im3m$) 7.70±0.23% FeSe ($P6_3/mmc$) 0.77±0.14%</td>
<td>a=3.77280(4) c=5.52303(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT092 FeSe$_{0.92}$</td>
<td>8.44 FeSe$_{0.976(4)}$ (P$_4$/nmm) 94.50±0.89% Fe ($Im3m$) 4.50±0.21% FeSe ($P6_3/mmc$) 1.00±0.13%</td>
<td>a=3.77335(4) c=5.52368(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT094 FeSe$_{0.94}$</td>
<td>8.21 FeSe$_{0.977(3)}$ (P$_4$/nmm) 92.91±0.70% Fe ($Im3m$) 6.36±0.16% FeSe ($P6_3/mmc$) 0.73±0.09%</td>
<td>a=3.77294(4) c=5.52421(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT096 FeSe$_{0.96}$</td>
<td>8.43 FeSe$_{0.978(4)}$ (P$_4$/nmm) 96.02±1.07% Fe ($Im3m$) 1.94±0.23% FeSe ($P6_3/mmc$) 2.04±0.19%</td>
<td>a=3.77338(5) c=5.52415(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT098 FeSe$_{0.98}$</td>
<td>8.21 FeSe$_{0.973(3)}$ (P$_4$/nmm) 98.31±0.59% Fe ($Im3m$) 0.57±0.05% FeSe ($P6_3/mmc$) 1.12±0.08%</td>
<td>a=3.77381(2) c=5.52390(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT100 FeSe$_1$</td>
<td>~ 8.0 FeSe$_{0.968(3)}$ (P$_4$/nmm) 83.03±0.61% Fe ($Im3m$) 0.46±0.05% Fe$_7$Se$_8$ (P$3_1$21) 16.51±0.28%</td>
<td>a=3.77353(4) c=5.52382(7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C. Phase diagram

In this section stoichiometry of the main phase and the phase composition of the studied samples are discussed based on the existing Fe-Se binary phase diagrams elaborated by Okamoto et al. and McQueen et al. Figure 5 shows a combined phase diagram based on the previously published data. Lines correspond to the part of the binary phase diagram reported in Ref. 19. The stripe, centered at around 49.5 atomic percent of Se, corresponds to a range of existence of tetragonal above 300°C and hexagonal FeSe$_{1-x}$ (NiAs-type) below 300°C as proposed in Ref. 17. The circles correspond to the samples with different nominal Se content studied in this work. The refined Se-occupancy was found to be 0.980(3), implying that the systematic error is smaller than 0.005.

From the data presented in Fig. 5 the following important statements emerge: (i) the stability field of the superconducting tetragonal FeSe phase as proposed in Ref. 17 does not overlap with that reported in Ref. 19. According to Ref. 17 the tetragonal phase exist only at high temperatures but it is transformed to the hexagonal one below 300°C; (ii) all the samples studied in our work contain the superconducting tetragonal phase as the main phase with almost the same average stoichiometry (FeSe$_{0.974(2)}$) and display the same $T_c \approx 8$K. This is in disagreement with the results of Ref. 17 because the compounds with the stoichiometries shown by points in the inset of Fig. 5 would have to display lower ($\sim$5 K) or even vanishing $T_c$; (iii) the present work demonstrates that there large amount of the impurity phases. Therefore the refined Se-occupancy may have some systematic error for these samples. Most NPD measurements were performed with the wavelength $\lambda = 1.494$ Å because it provides the optimal conditions for refining the structure parameters of the main pase (large $q$-range) and determination of the impurity phases (good resolution). Further check for the possible systematic error in the Se-occupancy due to its correlation with the atomic displacement parameters measurements of the most pure sample with yet shorter wavelength $\lambda = 1.155$ Å were performed. The refined Se-occupancy was found to be 0.980(3), implying that the systematic error is smaller than 0.005.
FIG. 5: (Color online) The Fe-Se phase diagram after Okamoto Ref. 19 (lines) and McQueen et al. Ref. 17 (vertical colored stripe). The black circles correspond to the nominal composition of the samples studied in the present work. In the inset the refined selenium stoichiometry (1-x) of the main superconducting tetragonal FeSe phase. It looks that the composition of this phase is stoichiometry of the superconducting tetragonal FeSe and the refined selenium stoichiometry (1-x) of the main phase. According to our NPD studies FeSe0.98 (LT098) sample contains, in total, less than 2% of impurity phases. Consequently, our data do not prove an existence of tetragonal - hexagonal phase transition on cooling at ∼ 300°C as proposed in Ref. 17. Our data suggest very narrow range, or even strictly defined stoichiometry of the superconducting tetragonal FeSe1−x phase. It looks that the composition of this phase is located between the fields proposed in both Refs. 17, 19. An additional confirmation of the correct locus of the tetragonal phase on the phase diagram comes from investigation of a phase composition of the LT100 sample (nominally FeSe1.08). According to the phase diagram this sample should be in the two phase region (βFeSe–αFe7Se8) at room temperature. Using a lever rule ~18% Fe7Se8 would be expected being in a good agreement with 16.5% as found from NPD data (see Table I).

D. The chemical stability of FeSe

In order to study the chemical stability of FeSe-samples the LT085 sample was powderized and stored in air for 14 hours (LT085a) and than measured by means of NPD. In Fig. 6 the Rietveld refinement of a neutron diffraction pattern of LT085a sample (solid line) together with as-prepared LT085 sample (dotted curve) taken at room temperature are presented. The sample underwent drastic changes after exposing in air. Volume fraction of the main tetragonal phase was decreased from 93% down to 84%, whereas quantity of Fe increases from 6% up to 13%, at the same time the increase of the of the hexagonal phase content was not so pronounced. The diffraction peaks of the main phase of LT085a sample show severe broadening, and at the same time the atomic displacement parameters (Debye-Waller factor) increase by 1.5 times, thus implying the presence of both large scale defects (like dislocations or the presence of new-phase particles) and point defects (e.g. vacancies). Additionally, it was found that the stoichiometry of the main phase becomes almost 1:1 (Fe:Se). The integral counting rates (scale factors) further reveal, that about 20–30% of the main phase was lost (most probably it became amorphous).

FIG. 6: (Color online) Neutron powder diffraction pattern of LT085 and LT085a samples at T=290 K measured at HRPT with the wavelength λ = 1.886 Å. The red dotted curve corresponds to the as prepared sample (LT085). The solid black curve was obtained after exposing the sample for 14 hours in the air (LT085a). See text for details.

In order to figure out the reason of FeSe1−x degradation, additional experiments were performed. The FeSe0.98 (LT098) sample was divided in 3 parts. Each of them was further powderized and exposed in pure helium, oxygen and air atmosphere. Figure 7 shows $M_{DC}(T)$ curves obtained for the different parts of the sample. It is obvious that both, air and oxygen, lead to a dramatic degradation of the superconducting properties. Indeed, the superconducting volume fraction decreases by more than a factor of 5, while the $T_c$ onset shifts to the lower temperature. At the same time the superconducting transition becomes very broad – the magnetization decreases continuously from $T_c$ down to 2 K. We sup-
pose, therefore, that by exposing FeSe sample in the air or in the oxygen atmosphere it decomposes by oxidizing (most probably forming SeO$_2$).

![Graph](image)

**FIG. 7:** (Color online) Temperature dependencies of the DC magnetization ($M_{DC}$, zero-field cooling, 0.1 mT) of LT098 sample. The experimental data correspond to the sample: (●) as prepared; (○) powderized/exposed in the air; (■) powderized/exposed in pure oxygen.

### IV. CONCLUSIONS

A comparative study of the crystal structure and the magnetic properties of the superconductor FeSe$_{1-x}$ synthesized at lower temperatures from powders and at higher temperatures from pieces of metal - was performed. The effect of a starting (nominal) stoichiometry on a phase purity of the obtained samples and their superconducting transition temperatures $T_c$ was studied. On the base of our neutron powder diffraction data we have revised the Fe-Se concentration phase diagram proposed by Okamoto$^{10}$. In particular, we have found that in the Fe-Se system a stable phase exhibiting superconductivity at $T_c \approx 8K$ exists in the narrow range of selenium concentration (FeSe$_{0.97\pm0.005}$).

As revealed by NPD study, at $T \approx 100$ K FeSe$_{1-x}$ undergoes a second order structural phase transition from a tetragonal phase (space group $P4/nmm$) to an orthorhombic (space group $Cmma$) on cooling. Fe-Se-Fe bond angles in the FeSe$_4$ pyramids become different in low temperature phase, whereas the Fe-Se bond lengths are not changed at the transition.

The chemical stability of FeSe samples exposed in air and pure oxygen atmosphere was studied. It was found, that after exposing in air the structure gets many defects, as revealed by NPD diffraction peaks broadening and the large increase in the atomic displacement parameters. The amount of both impurity phases increases about two times reaching 26% for metallic iron and 2% for hexagonal FeSe. This leads to a dramatic degradation of the superconducting properties, which was proved by magnetization measurements.

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14. M.J. Pitcher, D.R. Parker, P. Adamson, S.J.C. Herkelrath,


