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High-pressure studies on $T_c$ and crystal structure of iron chalcogenide superconductors

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Abstract

The superconducting transition temperature, $T_c$, in iron-based solids can be enhanced by applied pressure: $T_c$ increases from 8 to 37 K for the 11-type FeSe when the pressure is raised from 0 to 4 GPa. High-pressure studies can elucidate the mechanism of superconductivity in such novel materials. In this paper, we present a high-pressure study of Fe$(\text{Se}_{1-x}\text{Te}_x)$ and Fe$(\text{Se}_{1-x}\text{S}_x)$. In the case of Fe$(\text{Se}_{1-x}\text{Te}_x)$, the maximum $T_c$ under high pressure did not exceed the $T_c$ of FeSe, which can be attributed to the structural transition to the monoclinic phase. For Fe$(\text{Se}_{1-x}\text{S}_x)$ ($0 < x < 0.3$), $T_c$ exhibited a significant increase with pressure; however, the maximum $T_c$ under high pressure did not exceed the $T_c$ of FeSe. This may be due to the disorder induced by substituting S for Se, which is similar to the pressure effect on $T_c$ for the 1111-type superconductor Ca$(\text{Fe}_{1-x}\text{Co}_x)$AsF. The $T_c$ of Fe$(\text{Se}_{1-x}\text{S}_x)$ showed a complex behavior below 1 GPa, first decreasing and then increasing with increasing pressure. From high-pressure x-ray diffraction measurements, the $T_c$ ($P$) curve was correlated with the local structural parameter.

Keywords: superconductivity, crystal structure, pressure effect, Fe$(\text{Se}_{1-x}\text{Te}_x)$, Fe$(\text{Se}_{1-x}\text{S}_x)$

1. Introduction

The discovery of the iron-based superconductor LaFeAsO$_{1-x}$F$_x$ with a $T_c$ of 26 K had a significant impact on condensed matter physics, triggering rapid efforts in finding new superconductors [1]. Shortly after the discovery of LaFeAsO$_{1-x}$F$_x$, application of pressure raised its $T_c$ up to 43 K [2]. This result indicates that high-pressure experiments are an important route for exploring iron-based superconductors. In particular, the $T_c$ of FeSe exhibits a large enhancement, from 8 K at atmospheric pressure to 37 K at 4 GPa [3–5].

The crystal structure of the 1111-type superconductor LaFeAsO$_{1-x}$F$_x$ is tetragonal (space group $P4/mnm$) and consists of a stack of alternating LaO$_{1-x}$F$_x$ and FeAs layers. Partial replacement of O with F introduces charge carriers into the FeAs layers. Similar to the 1111-type superconductors, the 11-type FeSe has edge-sharing FeSe$_4$ layers with the...
crystal structure composed of a stack of Fe$_2$Se$_2$ layers along the c-axis. $T_c$ increased with the substitution of Se by S or Te [6–8]. For the Fe(Se$_{1-x}$Te$_x$) system, the maximum $T_c$ is 14 K at $x = 0.5$. Compared to the 1111-type superconductors, the 11-type superconductors have a more simple crystal structure with no carrier reservoir layer, such as a LaO layer. While the charge transfer between different layers plays an essential role in the superconductivity of the 1111-type superconductors, structural changes are effective for the electronic state of the 11-type superconductors since there are no carrier reservoir layers.

For iron-based superconductors, the strong correlation between the crystal structure and superconductivity has been discussed [9,10]. In 1111-type LaFeAsO$_{1−x}$F$_x$, $T_c$ increases with decreasing ionic radius of the rare earth element, reaching a $T_c$ of 56 K for Nd and Sm [11]. This tendency is consistent with the enhancement of $T_c$ under high pressure. Lee et al. [9,10] performed extensive structural studies of 1111-type compounds and showed that $T_c$ is well correlated with the shape of the FeAs$_4$ tetrahedron. For the optimally doped 1111, 122, and 11-type superconductors, $T_c$ changes toward the maximum $T_c$ when the FeAs$_4$ tetrahedron approaches a regular shape, where the Fe–As–Fe bond angle is 109.47°. The anion height, defined as the distance between the tetragonal Fe lattice layer and the anion atom, was also correlated with superconductivity [11,12]. However, the 1111-type superconductors have almost the same Fe–As bond length owing to their common covalent nature. Since the anion height is determined by the bond length and bond angle, the relation between the anion height and superconductivity is equivalent to the relation between the bond angle and superconductivity.

For 11-type Fe(Se$_{1−x}$Te$_x$), the bond length changes with increasing Te concentration. Since the Fe–Te and Fe–Se bond lengths are about 2.57 and 2.39 Å, respectively [10], there are two kinds of tetrahedrons, resulting in structural disorder [13]. This disorder may be very effective for superconductivity owing to the large difference between the anion height for Se and Te (0.24 Å) deduced from the structural analysis of single-crystal Fe(Se$_{0.44}$Te$_{0.56}$) [14]. However, the $T_c$ of Fe(Se$_{1−x}$Te$_x$) increases as the tetrahedron approaches a regular tetrahedron, except for FeSe, where the orthorhombic structure seems to suppress superconductivity. The $T_c$ ($P$) curve of FeSe does not agree with the relation between the bond angle and $T_c$. Mizuguchi et al. [11] plotted $T_c$ as a function of the anion height for several iron-based superconductors, wherein $T_c$ peaked at an anion height of approximately 1.35 Å. The pressure dependence of $T_c$ for FeSe agrees with this tendency. The structural similarity of the iron-based family is reflected in the electronic structure. The experimental results correlating the local crystal structure and superconductivity were supported by theoretical calculations [15].

For FeSe, $T_c$ was reduced by compression beyond the optimum pressure because of the structural phase transition to a hexagonal structure, which is not superconducting [5]. Since this pressure-induced phase transition is suppressed by the substitution of Te for Se, a greater enhancement in $T_c$ is expected for Te-doped FeSe under high pressure. For Fe(Se$_{0.5}$Te$_{0.5}$), which has the maximum $T_c$ in the Fe(Se$_{1−x}$Te$_x$) system, $T_c$ was enhanced up to 27 K at around 2 GPa [16]. One of the reasons why the maximum $T_c$ of Fe(Se$_{0.5}$Te$_{0.5}$) did not exceed the $T_c$ of FeSe is that a structural transition to the monoclinic phase occurs at high pressures [17]. On the other hand, no superconductivity was detected for FeTe; rather, it exhibited magnetic and structural transitions at ~70 K [18,19]. These phase transitions are suppressed, and superconductivity appears upon the substitution of Te by Se. This behavior is similar to those of FeAs-based superconductors when FeTe is regarded as a parent compound of the Fe(Se$_{1−x}$Te$_x$) system [6,7,20–22]. In this paper, we report a systematic investigation of the pressure effect on superconductivity in Fe(Se$_{1−x}$Te$_x$) for $x > 0.5$. High-pressure effects for Fe(Se$_{1−x}$Te$_x$) $(x < 0.5)$ have already been studied extensively.

Disorder is induced in FeSe when the Se atom is substituted by Te or S. The disorder is smaller in Fe(Se$_{1−x}$S$_x$) than Fe(Se$_{1−x}$Te$_x$), because the ionic radius of S (1.84 Å) is closer to that of Se (1.98 Å) than that of Te (2.21 Å). In the Fe(Se$_{1−x}$S$_x$) system, the low-temperature orthorhombic phase is suppressed rapidly with S substitution [23]. Although a similar suppression of the orthorhombic phase is observed in the Fe(Se$_{1−x}$Te$_x$) system, there is a miscibility gap in the low-concentration range of Te (0.05 < $x$ < 0.35) [6–8]. However, for Fe(Se$_{1−x}$S$_x$), a solid solution can be formed for $x < 0.3$. Then the Fe(Se$_{1−x}$S$_x$) system is suitable for the investigation of the low-concentration range. Although Fe(Se$_{1−x}$Te$_x$) could not exceed the maximum $T_c$ of FeSe under high pressure, it is interesting to examine whether the $T_c$ of Fe(Se$_{1−x}$S$_x$) $(0 < x < 0.3)$ exceeds the value for FeSe. Electrical resistivity measurements showed a complex behavior below 1 GPa: $T_c$ first decreased and then increased with pressure. In this paper, we report electrical resistivity and x-ray diffraction measurements under high pressure for Fe(Se$_{1−x}$S$_x$) $(0 < x < 0.3)$. In addition, the correlation between $T_c$ and the local crystal structure is presented.

2. Previous high-pressure studies of 11-type materials

2.1. FeSe

FeSe shows a strong pressure effect on $T_c$ [3–5]: $T_c$ increases up to 37 K at 4 GPa, after a step-like rise around 1–2 GPa [23]. This effect was clarified by nuclear magnetic resonance (NMR) measurements [23,24]. The temperature dependence of the inverse relaxation times $1/T_1 T$ in NMR measurements under high pressure linked superconductivity with the antiferromagnetic spin fluctuation mode. Both the antiferromagnetic spin fluctuation and $T_c$ were enhanced gradually with increasing pressure up to 1.4 GPa. However, above 1.4 GPa, $T_c$ increased rapidly, which was attributed to the suppression of spin fluctuations [23].

It is important to understand the pressure dependence of $T_c$. High-pressure x-ray measurements were carried out for FeSe using synchrotron radiation [4,5]. The Fe–Se–Fe bond
angle $\alpha$ decreased from 104.53° to 103.2° with application of pressure of up to 9.0 GPa. While $T_c$ increases significantly with pressure, the FeSe$_{5-\text{Se}_{0.5}}$ tetrahedron deviates from the regular tetrahedron. This result is inconsistent with the 1111-type structure, in which $T_c$ changes toward the maximum $T_c$ when the FeAs$_4$ tetrahedron approaches a regular shape [9]. On the other hand, the anion height of FeSe decreases with increasing pressure; in particular, it drops around 1 GPa. With further compression, the anion height decreases to a minimum value of 1.42 Å around 4–6 GPa. The drop around 1–2 GPa corresponds to the rapid increase in $T_c$. Thus, $T_c$ correlates well with the anion height for FeSe. Above 6 GPa, the anion height exhibits a slow increase that might be correlated with the decrease in $T_c$. Moreover, $T_c$ is reduced at higher pressures where the structural phase transition to the hexagonal phase occurs. Note that in absence of phase transitions, $T_c$ is expected to increase with pressure.

2.2. $F_e(Se_{1-x}Te_x)$

The $T_c$ of 8 K for FeSe increases with the substitution of Se by Te [6–8]. It shows a maximum value of $T_c = 14$ K for Fe(Se$_{0.5}$Te$_{0.5}$) at atmospheric pressure. While carrier doping was not attained by atomic substitution of Se with Te, suppression of the low-temperature orthorhombic phase seems to enhance $T_c$. For Fe$_{1.03}$Se$_{0.57}$Te$_{0.43}$, a bell-shaped pressure dependence of $T_c$ was reported, with the maximum $T_c$ of 23 K at 3.1 GPa. This maximum $T_c$ does not exceed the $T_c$ of FeSe [17]. From high-pressure x-ray measurements for Fe$_{1.03}$Se$_{0.57}$Te$_{0.43}$ using synchrotron radiation, a structural phase transition from the orthorhombic to monoclinic phase was observed around 2–3 GPa at low temperatures. $T_c$ was reduced at higher pressures. A bell-shaped pressure dependence of $T_c$ was also reported for FeSe$_{0.5}$Te$_{0.5}$ having a $T_c$ of 14 K at atmospheric pressure [16]. The high-pressure x-ray diffraction data indicated that the anion height also correlates with $T_c$, as observed for FeSe. High-pressure NMR data linked superconductivity with the antiferromagnetic spin fluctuation mode, as shown for FeSe [23].

2.3. FeTe

FeTe exhibited a phase transition from the tetragonal to monoclinic phase at 70 K and atmospheric pressure [18, 19]. While the non-superconducting monoclinic phase was suppressed by pressure and successive structural and magnetic transitions were observed under high pressure, pressure-induced superconductivity was not observed up to 19 GPa [25]. However, the crystal structure for this material has not been determined precisely under high pressure.

3. Experimental details

Polycrystalline $Fe_{1+y}(Se_{1-x}Te_x)$ and $Fe(Se_{1-x}S_x)$ samples were synthesized by a sintering method [8]. The samples were confirmed to have a tetragonal PbO structure. Electrical resistivity measurements under high pressure were performed using a standard four-probe method. Pressures up to 3.0 and 8 GPa were generated using a piston-cylinder (CuBe/NiCrAl) type cell and a cubic anvil press [26], respectively. A liquid pressure-transmitting medium (Daphne 7474) was used to maintain hydrostatic conditions [27]. A diamond anvil cell (DAC) was used for electrical resistivity measurements under pressures up to 19 GPa using NaCl as the pressure-transmitting medium. Powder x-ray diffraction measurements were carried out using the DAC with Daphne 7474 as the pressure-transmitting medium. A Rigaku D/MAX 2000 diffractometer ($\lambda_{Mo} = 0.7103$ Å) was used for the investigation of crystal structure at room temperature. A synchrotron x-ray beam ($\lambda = 0.6175$ Å) was used down to 60 K at the Photon Factory, KEK. The diffraction pattern was analyzed by RIETAN-FP Rietveld programs to obtain the precise crystal structure. Fine ruby powder scattered in the sample chamber was used to determine the applied pressure using the standard ruby fluorescence method.

4. Results and discussion

Figure 1(a) shows the pressure dependence of $T_c$ for $x = 0.5$, 0.75, 0.8, and 0.9 for $Fe_{1+y}(Se_{1-x}Te_x)$. Although $T_c$ shows the maximum value of 14 K at atmospheric pressure for $x = 0.5$, the maximum $T_c$ under high pressure is 37 K for FeSe. The $T_c$ of Fe (Se$_{0.5}$Te$_{0.5}$) increased with pressure, showing a bell shape as mentioned earlier [16]. For $x = 0.75$ and 0.8, $T_c$ increased with pressure, and had maximum values of 15 K and 14 K, respectively. However, the initial rate of increase in $T_c$ tended to become smaller with increasing Te concentration $x$, as shown in figure 1(b). For $x = 0.90$, the initial slope is negative. Figure 2 shows the maximum $T_c$ under high pressure and the onset $T_c$ at atmospheric pressure in Fe(Se$_{1-x}Te_x$) as a function of $x$. The maximum $T_c$ under high pressure decreased with increasing Te concentration. Although the structural transition from tetragonal to hexagonal phase is suppressed with increasing Te concentration, the maximum $T_c$ under high pressure does not exceed the maximum $T_c$ of FeSe. It is possible that the low-temperature monoclinic phase reported for $x = 0.5$ is stabilized under high pressure.
which results in a $T_c$ decrease. This decrease could also be affected by the disorder of the anion height. If the FeSe$_4$ and FeTe$_4$ tetrahedra affect the superconductivity positively and negatively, respectively, then the maximum $T_c$ under pressure would decreases with increasing Te concentration. Future structural studies at low temperatures are necessary to explain these pressure effects.

Figure 3 shows the pressure dependence of $T_c$ for $Fe(Se_{1-x}S_x)$ ($x = 0.1, 0.2$, and $0.3$). The $T_c$ ($P$) curve of FeSe was reported by Okabe et al [12]. A $T_c$ ($P$) minimum is observed for $x = 0.2$ and $0.3$ around $0.8$ GPa. Although $T_c$ shows a large enhancement above this pressure, similar to iron-pnictide superconductors, the maximum $T_c$ does not exceed that for FeSe.

Figure 4. X-ray diffraction patterns of $Fe(Se_{0.8}S_{0.2})$ measured at room temperature and at different pressures. The structural phase transition from tetragonal ($P4/nmm$) to hexagonal ($P6_3/mmc$) phase is progressing with pressure and completes above $9$ GPa. Peaks due to the hexagonal phase are designated by an asterisk (*)

is observed for $x = 0.2$ and $0.3$ with a minimum at around $0.8$ GPa. Above this pressure, large enhancement of $T_c$ was observed, similar to FeSe where $T_c$ increased after showing anomalous behavior, as mentioned in the previous section. For $Fe(Se_{1-x}S_x)$, such a minimum in $T_c$ might be related to the anomalous pressure dependence around $1–2$ GPa in FeSe. The maximum $T_c$ values for $x = 0.1$ and $0.2$ ($34.8$ and $36.3$ K, respectively) do not exceed the maximum $T_c$ value of FeSe. High-pressure electrical resistivity measurements for $x = 0.2$ were performed up to $16$ GPa using a DAC. Although the pressure dependence of $T_c$ is the same as the data obtained using the cubic anvil press below $8$ GPa, no trace of superconductivity was observed in the $R(T)$ curve beyond $10$ GPa, which is a rather low pressure compared to the case of FeSe. This is likely due to the structural transition to the hexagonal phase, as observed in FeSe.

X-ray diffraction measurements under high pressure were carried out for $Fe(Se_{0.8}S_{0.2})$ up to $8$ GPa and down to $60$ K. The structural phase transition from tetragonal ($P4/nmm$) to hexagonal ($P6_3/mmc$) phase was completed above $9$ GPa at room temperature, as shown in figure 4. This transition is correlated with the suppression of superconductivity, as observed in the resistivity measurements. The pressure dependences of the normalized lattice constants and volume for $Fe(Se_{0.8}S_{0.2})$ are shown in figure 5. The linear compressibility along the $a$- and $c$-axis is $0.007$ and $0.027$ GPa$^{-1}$. 
Figure 5. (a) Pressure dependences of the normalized lattice constants $a/a_0$ and $c/c_0$ of Fe(Se$_{0.8}$S$_{0.2}$). The compression is highly anisotropic, with the $c$-axis being four times as compressible as the $a$-axis. (b) Pressure dependence of the normalized volume $V/V_0$. The compressibility is estimated as $0.039 \text{ GPa}^{-1}$, which is slightly larger than the values of FeSe ($0.035 \text{ GPa}^{-1}$) and FeTe ($0.032 \text{ GPa}^{-1}$).

Figure 6. Rietveld refinement profile of Fe(Se$_{0.8}$S$_{0.2}$) for the x-ray diffraction pattern measured at 4.2 GPa and 60 K using synchrotron radiation at the Photon Factory of KEK. Refinements are given for both the tetragonal and hexagonal structures.

Figure 7. (a) Pressure dependence of the crystal coordinate $z$ of (Se$_{0.8}$S$_{0.2}$) at 10, 100 and 200 K. An anomalous change is seen around 1 GPa. The $z$ value of FeSe was reported by Margadonna et al [4]. (b) Pressure dependence of the anion height showing a similar anomaly.

Crystal parameters were obtained from the Rietveld refinement analysis using RIETAN-FP programs. The $c$-axis is thus four times as compressible as the $a$-axis. The compression is highly anisotropic. From the fitting of the compression curve using the third-order Birch–Murnaghan equation of state, compressibility is estimated as $0.039 \text{ GPa}^{-1}$, which is slightly larger than the values for FeSe ($0.035 \text{ GPa}^{-1}$) and FeTe ($0.032 \text{ GPa}^{-1}$).

The collected data and the Rietveld refinement profile for Fe(Se$_{0.8}$S$_{0.2}$) at 1.6 GPa and 60 K are shown in figure 6. The crystal coordinate $z$ of (Se$_{0.8}$S$_{0.2}$) is plotted in figure 7(a). This value increases rapidly up to 2 GPa and then linearly increases above 2 GPa. For FeSe, $z$ increases linearly as shown in the same figure. Since a large value of $z$ is favorable for the structural transition from tetragonal to hexagonal phase, the transition occurs at a lower pressure for Fe(Se$_{0.8}$S$_{0.2}$) than FeSe. On the other hand, the bond length for Fe–Se(S) decreases with a rate of $0.004 \text{ GPa}^{-1}$ as shown in figure 8(a), which is smaller than the linear compressibility of the lattice constants $a (0.007 \text{ GPa}^{-1})$ and $c (0.027 \text{ GPa}^{-1})$. Therefore, the Fe–Se(S)–Fe bond angle $\alpha$ shown in figure 8(b) decreases and the crystal coordinate $z$ increases due to compression along the $a$-axis. The interval between the Fe–Se(S) layers is largely compressed initially with application of pressure. Since the lattice constant $c$ decreases monotonously with pressure and $z$ increases steeply below 2 GPa, the anion height, which was calculated as $z \times c$, peaks around 1–2 GPa, as shown in figure 7(b). In the pressure range of 1–2 GPa, the $T_c (P)$ curve takes a minimum value. Note that the decrease of $T_c$ below 1.5 GPa corresponds to an increase in the anion height. Thus, the superconductivity of Fe(Se$_{0.8}$S$_{0.2}$) is strongly correlated with the local crystal structure [28]. However, the maximum $T_c$ of 27 K around...
5 GPa is smaller than the maximum \( T_c \) of FeSe. It is likely that the disorder of the anion height reduces the \( T_c \) for S-doped FeSe under high pressure, which is similar to the case of Ca(Fe\(_{1-x}\)Co\(_x\))AsF [29]. For Ca(Fe\(_{1-x}\)Co\(_x\))AsF, the parent compound exhibits pressure-induced superconductivity, and the maximum \( T_c \) obtained at high pressures decreases with increasing Co concentration. It is likely that the disorder of the superconducting layers induced by direct doping into FeAs layers prevents enhancement of superconductivity. Consequently, the highest \( T_c \) in Ca(Fe\(_{1-x}\)Co\(_x\))AsF under high pressure was obtained in the parent compound.

5. Conclusions

We have reported recent results of high-pressure experiments for 11-type iron-based superconductors. For Fe(Se\(_{1-x}\)Te\(_x\)), the pressure-induced enhancement of \( T_c \) decreases with increasing Te concentration \((x > 0.5)\). Although the \( T_c \) of Fe(Se\(_0.5\)Te\(_{0.5}\)) increased with pressure up to 26 K, FeSe \((x = 0)\) showed the highest \( T_c \) of 37 K in the Fe(Se\(_{1-x}\)Te\(_x\)) system. Since the non-superconducting FeTe exhibits structural and magnetic phase transitions at 70 K at atmospheric pressure, it is possible that a structural phase transition and/or disorder of the anion height prevents enhancement of \( T_c \) at \( x > 0.5 \).

Structural studies at low temperatures are necessary to explain these pressure effects.

For Fe(Se\(_{1-x}\)S\(_x\)), the maximum \( T_c \) under high pressure is 34.8 and 36.3 K for \( x = 0.1 \) and 0.2, respectively, which is close to the maximum value for FeSe. \( T_c \) shows a minimum around 0.8 GPa for \( x = 0.1 \) and 0.2, which might be related to spin fluctuations as indicated for FeSe.

X-ray diffraction measurements for \( x = 0.2 \) suggest that this pressure dependence of \( T_c \) is strongly correlated with the anion height, that is, superconductivity correlates with the local crystal structure. The maximum \( T_c \) of 27 K around 5 GPa is smaller than the maximum \( T_c \) of FeSe, probably due to the disorder induced by the atomic substitution of Se. A similar reduction of \( T_c \) due to disorder induced by atomic substitution has been observed in our recent results for 1111-type Ca(Fe\(_{1-x}\)Co\(_x\))AsF.

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