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# Pressure-induced isostructural phase transition and charge transfer in superconducting FeSe

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#### ABSTRACT

We present extensive investigations of the crystallographic phase diagram and electronic properties of the Fe-based superconductor FeSe under extreme conditions (high pressure (HP) and low temperature (LT)) by synchrotron X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). An isostructural phase transition (Tetragonal (T)  $\rightarrow$  high-pressure Tetragonal (T')) is discovered in FeSe at ~2.8 GPa based on the axial ratio c/a with finer pressure step as observed in Fe-As-based superconductor such as EuFe<sub>2</sub>As<sub>2</sub>. We also find a pressure-induced T'  $\rightarrow$  MnP-type phase transition at 7.6 GPa in FeSe, which is consistent with the documented pressure-induced high-spin  $\rightarrow$  low-spin transition (~6–7 GPa). These results reveal the pressure-induced structural phase transition sequence in FeSe at room temperature to be T  $\rightarrow$  T'  $\rightarrow$  T'+MnP-type at pressures of 0–10.6 GPa, enriching the crystallographic phase diagram. The HPLT XRD data also indicate that a sluggish structural phase transition (*Cmma*  $\rightarrow$  *Pmma*) begins at 7.5 GPa, and these two phases coexist up to 26.5 GPa. The HP X-ray absorption near-edge spectroscopy (XANES) measurement shows that  $E_o$  of Se experiences a pressure-induced shift to high energy, evidencing strongly charge transfer between Fe and Se under high pressure. Our results shed lights on the correlation between crystallographic/electronic structure and superconductivity in this material.

1. Introduction

Iron selenide (Fe<sub>1+x</sub>Se, hereafter denoted as "FeSe") is the simplest Fe-based layered superconductor with superconducting transition temperature ( $T_c$ ) of 8 K [1]. It has a tetragonal anti-PbO-type structure (P4/nmm) at room temperature (RT) and planar FeSe slabs that resemble the FeAs slab layers in the Fe-based superconductors such as La( $O_{1-x}F_x$ )FeAs and EuFe<sub>2</sub>As<sub>2</sub>. The relative chemical simplicity of FeSe makes it a perfect candidate for understanding the interplay of structure, magnetism and superconductivity in the Fe-based superconducting family. It is known that

\* Corresponding author. E-mail address: wanglin@hpstar.ac.cn (L. Wang). Fe-As-based superconductors undergo concomitant structural and magnetic phase transitions as the temperature decreases. However, reported experimental results demonstrated that the temperature-induced structural phase transition in FeSe does not result in the occurrence of a static magnetic structure (long-range magnetic ordering) [1]. It has been suggested that the superconducting phase of FeSe only exists in samples prepared with artificial Se deficiency and is very sensitive to stoichiometry and external conditions [2]. FeSe, compared with the Fe-As-based superconductor, is less toxic and much easier to handle. More importantly, FeSe superconductor shows weak anisotropy and is convenient to fabricate into devices. Although the  $T_c$  of bulk FeSe ( $T_c = 8$  K) is low, it increases drastically under pressure ( $T_c = 37$  K; Ref. [3]), by carrier doping ( $T_c = 40-48$  K; Refs [4,5]), or in the mono layer limit ( $T_c = 65-109$  K, Ref. [6]). Therefore, FeSe has attracted sustained attentions from







experimental and theoretical researchers since the discovery of its superconductivity.

Since the reported  $T_c = 8$  K of FeSe is modest, it is important to establish the relationship between superconducting transition temperature and pressure. The  $T_c$  can be enhanced substantially by the application of pressure, and the superconducting onset temperature can reaches ~37 K at 7–9 GPa [7]. However, at higher pressures, a decrease is observed with the  $T_c \sim 6$  K when the pressure approaches 20 GPa [3,8]. Later on, M. Bendele et al. observed that the overall increase of the  $T_c$  is nonmonotonic with a local maximum at ~0.8 GPa, followed by a local minimum at around 1.2 GPa [9]. Subsequent experiments with finer pressure steps revealed, however, a local minimum at 1.5 GPa [10]. Recently, an enhancement of  $T_c$  in a three-plateau process was observed in FeSe, that is,  $T_c \sim 10(2)$  K for 0–2 GPa,  $T_c \sim 20(5)$  K for 3–5 GPa, and  $T_c \sim 35$ (5) K for 6–8 GPa [11]. To elucidate the driving mechanism behind the large enhancement of  $T_c$  in FeSe under high pressure, it is important to compare the superconducting phase diagram with the observed structural changes using high-pressure and lowtemperature (HPLT) X-ray diffraction (XRD) techniques.

Like the Fe-As-based superconductor, besides applied physical pressure, spin fluctuations and magnetic ordering are also important parameters for tailoring the  $T_c$  of FeSe. The unusual superconducting properties of FeSe are presumably related to its magnetism, in which its magnetic ground state is intensely debated [12]. The FeSe electronic nematicity occurs below ~90 K [13,14] at ambient pressure, while a magnetic ordered state is absent. Unlike the Fe-As-based superconductor, magnetic ordering of FeSe emerges when applying pressure above 1 GPa [15]. K. Kothapalli et al. observed that nematicity and magnetism in FeSe under applied pressure are indeed strongly coupled using synchrotronbased high-energy XRD and time-domain Mossbauer spectroscopy [16,17]. The ordering temperature  $T_N$  increases with pressure (up to 1.4 GPa) [18], which shows a dome-shaped pressure behavior (up to ~8 GPa) [19]. High-pressure nuclear magnetic resonance (NMR) studies on FeSe showed a close correlation between the spin-lattice parameter and  $T_c$ , and strong spin fluctuations near the superconducting state [20,21]. Recent synchrotron X-ray emission spectroscopy and *ab initio* calculations performed by R. S. Kumar et al. showed a pressure-induced smooth high-spin to low-spin transition in FeSe superconductor [22,23]. Based on ab initio calculations, they suggested that the spin moment change can be attributed to pressure-induced electron delocalization or spin crossover of Fe. Here, the X-ray absorption spectroscopy (XAS) measurements provide experimental evidence of a pressureinduced charge transfer between Fe and Se.

Despite several years of intensive research, the crystallographic information of FeSe under extreme conditions (high pressure and/ or low temperature) is still inconsistent reported by different research groups. At room temperature (RT), there are three different phase transition sequences reported. (1) It was found that tetragonal FeSe undergoes a structural phase transition (P4/nmm  $\rightarrow PG_3/mmc$ ) starting at ~ 7 GPa at RT and shows wide pressure range of coexistence [3,24]. (2) However, a structural transformation  $P4/nmm \rightarrow Pbnm$  was observed above 12 GPa by G. Garbarino et al. [25]. (3) Later on, a tetragonal  $\rightarrow$  monoclinic phase transition was observed in FeSe under high pressure at about 3 GPa using X-ray scattering and Raman spectrum [26]. On the LT side, there are two viewpoints. (1) The pressure evolution of the LT (16 K) crystal structure and bonding of FeSe was studied by S. Margadonna et al. using synchrotron XRD up to 14 GPa, revealing a small bulk modulus and transformed into hexagonal phase above 9 GPa [8]. (2) In addition, a pressure-induced transition to *Pbnm* phase above 1.2 GPa at 8 K was reported in R. S. Kumar et al.'s experimental results [27]. On the structural phase transition (P4/mmm  $\rightarrow$ 

*Cmma*) side, it is found that a suppression of the transition temperature with increasing pressure up to about 2 GPa [11,28].

Due to the inconsistency of structure variation investigations under high pressure previously reported in FeSe, here we experimentally and theoretically confirmed the structural evolution and electronic structures of FeSe using HP-XRD, HP-XAS techniques together with first principles calculations. We investigate the interesting possibility of whether FeSe could undergo a pressureinduced isostructural phase transition (tetragonal  $(T) \rightarrow$  collapsed tetragonal (cT)), as observed in Fe-As-based superconductor such as CaFe<sub>2</sub>As<sub>2</sub> and EuFe<sub>2</sub>As<sub>2</sub> [29,30]. We present a pressure-induced T  $\rightarrow$  T' (high-pressure tetragonal phase) transition in high quality FeSe<sub>0.82</sub> using a finer pressure step, which enriches the crystallographic phase diagram of FeSe. To gain insight into the correlation between structural changes and superconducting properties, we also investigated the structural evolution behaviors of FeSe<sub>0.82</sub> using a combined HPLT synchrotron XRD technique. Our main crystallographic results are summarized in the phase diagram of Fig. 1 (a)-(e). In addition, the relationship between the  $T_c$  and crystal structure of FeSe<sub>0.82</sub> is discussed, as well as a comparison with the Fe-As-based superconductor.

## 2. Experimental (single crystal growth, XRD and XAS) and density functional theory (DFT) details

FeSe crystals were grown using a vapor self-transport approach [31]. Powder XRD analysis was used to determine the phase purity of the crystals. More details on the crystal growth and characterization (magnetic and transport properties measurement) can be found in Ref. [31]. The single crystal samples were ground in a mortar to obtain a fine powder sample used in the following high pressure synchrotron XRD and absorption experiments. We performed two independent high-pressure XRD experiments at room and low temperatures (10 K), respectively. The high-pressure synchrotron XRD experiment was carried out using a symmetric diamond anvil cell. Two independent high-pressure XRD experiments were carried out up to 10.6 and 26.5 GPa at room and low



**Fig. 1.** Schematic polymorphism of FeSe under extreme conditions (high pressure, and low temperature), CN is short for coordination number of Fe. For convenient comparision, the lattice parameters of T and T' phases were shown.

temperature, respectively. The two-dimensional image plate patterns were converted to one-dimensional data using the Fit2D software package [32]. The experimental pressures were determined by the pressure-induced fluorescence shift of ruby [33]. The XRD patterns were analyzed with Rietveld refinement using the GSAS program package [34] with a user interface EXPGUI [35]. High-pressure X-ray absorption spectroscopy (XAS) experiments at Se K-edge were performed at beamline of 20-BM-B of Advanced Photon Source in the transmission mode. The raw extended X-ray absorption fine structure (EXAFS) data were pre-processed to obtain  $\chi(k)$  by conventional methods using the software ATHENA [36].

First-principles calculations were performed in the framework of density functional theory (DFT) with the Vienna *ab initio* simulation package [37]. The generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) parametrization was implemented to describe the exchange correlation functions [38]. Hydrostatic pressure was applied by adding Pulay stress to the diagonal elements of the stress tensor. At each pressure, the unit cell is fully optimized for atomic position, cell shape and cell volume.

#### 3. Experimental results

## 3.1. The pressure-induced isostructural phase transition (T $\rightarrow$ T) in FeSe\_{0.82} under RT

Our sample phase quality was characterized using XRD techniques [39], and no impurity phases were detected in the sample investigated here. Fig. 2 presents the angle-dispersive XRD patterns of FeSe<sub>0.82</sub> under various pressures at RT. The sample was pressurized in finer steps of ~ 0.5 GPa. At first glance, the figure clearly shows that the Bragg peaks shift toward higher angles owing to lattice contraction without any modification to the overall peak profiles, and no new diffraction peaks were observed in the XRD patterns up to a pressure of 6.4 GPa. Under low pressure ( $\leq$ 2.8 GPa) the Bragg diffraction peak (110) is on the right of (002), which is corresponding to the variation of lattice parameters of a and c for *P4/nmm* phase. The Bragg diffraction peaks of (110) and (002) exhibit a movement to the higher diffraction angle as the pressure increases. However, we found that Bragg diffraction peak (002) shifted faster compared to (110), as shown in the inset of Fig. 3 (b). This evidences that *c*-axis is more easily compressible than that of *a*-axis in *P*4/*nmm* phase.

According to the binary phase diagram of Fe-Se [40], the  $P6_3$ / mmc phase is a high-temperature nonsuperconducting phase, while P4/nmm phase is a low-temperature superconducting phase. Usually, certain percentage of P63/mmc phase was included when synthesizing P4/nmm phase due to the close free energy of these two phases. Therefore, the existence of  $P6_3/mmc$  phase severely affects the investigation on superconductivity of P4/nmm phase. Fig. 3 (a) exhibits a typical Rietveld refinement of the present P4/ *nmm* phase of FeSe<sub>0.82</sub>. The vertical bars represent the calculated position of the diffraction peaks. The good fitting results confirmed the high purity of our sample, which support firm basis on intrinsic study of FeSe performed here. The peak width of (001) as function of pressure was shown in Fig. 3 (b), from which we found that the peak width did not show the nonmonotonic variation with pressure. The (001) peak width decreases as the pressure increasing to~2.8 GPa and then increases with the pressure further increasing.

No splitting or occurrence of new diffraction peaks are observed below 6.4 GPa. Therefore, the indexing, lattice constant refining and peak fitting processes are based on the space group P4/nmm below 6.4 GPa [1]. The pressure dependences of relative lattice parameters  $a/a_0$  and  $c/c_0$  for P4/nmm phases of FeSe<sub>0.82</sub> are reported in inset of



**Fig. 2.** Angle dispersive XRD pattern of FeSe<sub>0.82</sub> under various pressures at RT. The Miller indices for *P*4/*nmm* phase were shown at the bottom of the figure. A pressure-induced T  $\rightarrow$  T' transition was observed from the present fine pressure steps measurements. The T' phase coexisted with the *Pnma* phase above 7.6 GPa.

Fig. 3 (c). The lattice parameters homogeneously decrease as the pressure increases for the P4/nmm phase of FeSe<sub>0.82</sub>. However, the slope of the lattice parameters versus pressure is different. It was found that *c*-axis is more compressible than that of *a*-axis. To gain further information about this phenomenon, the axial ratio c/aversus pressure was plotted in Fig. 3 (c). It is interesting to note that c/a shows remarkable inflection point at ~2.8 GPa. In other words, c/aa exhibits a marked decrease as the pressure increasing to ~2.8 GPa and then shows feeble variation as the pressure further increasing. Because no new diffraction peaks were observed from the XRD pattern in present investigated pressure range, we propose this is a pressure-induced isostructural phase transition  $(T \rightarrow T')$  without crystallographic symmetry change as observed in other Fe-As superconductors such as Nd(O<sub>0.88</sub>F<sub>0.12</sub>)FeAs [41] and EuFe<sub>2</sub>As<sub>2</sub> [30] under high pressure. Notably, the enhancement of  $T_c$  is correlated to the distortion of FeAs<sub>4</sub> tetrahedron during pressure-induced  $T \rightarrow cT$ transition in Fe-As-based superconductors. The transition pressure of iso-structure phase transition is close to the 122-type Fe-based superconductor CaFe<sub>2</sub>As<sub>2</sub> [29]. Furthermore, the distance of Se-Se intralayers in T' phase of FeSe at 3.4 GPa is 2.405 Å, which approaches the threshold value (2.4 Å) of Se-Se bonding formation as shown in Fig. 1 (a) and (b).



**Fig. 3.** (a) Typical Rietveld refinement of FeSe<sub>0.82</sub> under RT at 0.2 GPa. The vertical bars represent the calculated positions of the diffraction peaks. The difference between the observed (ball) and the fitted patterns (line) is shown at the bottom of the diffraction peaks. (b) The diffraction peak (001) width as a function of pressure. The inset shows the pressure dependence of the Bragg diffraction peaks (002) and (110). (c) The axial

The single diffraction lines of (110) and (102) broaden above 7.6 GPa and few new peaks appear at high pressures as shown by the downward arrows in Fig. 2. Furthermore the intensity of the new appeared diffraction peaks increase as the pressure increasing. It is concluded that a structural transition occurred above 7.6 GPa. As a candidate of the crystal structure for the high-pressure phase of FeSe<sub>0.82</sub> above 7.6 GPa, a hexagonal NiAs-type structure was nominated by S. Medvedev et al. [3], since NiAs-type structure is an accompanying nonsuperconducting phase when synthesizing FeSe. The NiAs-type ( $P6_3/mmc$ , Z = 2) and MnP-type (Pnma, Z = 4) structures are two most common AB-type structures in binary compounds. MnP-type is one of the common structures distorted from NiAs-type. Therefore, MnP-type structure is also a considered high-pressure phase model suggested by G. Garbarino and R. S. Kumar et al. [25,27]. The inconsistent high-pressure phase information on FeSe proposed by different research groups was probably due to the close crystallographic relationship between these two models. It can be seen from Fig. 4 (a) that most of our observed strong XRD pattern was indexed to T' phase, and the rest of the diffraction peaks match well with MnP-type phase than that of NiAs-type phase. Therefore, we propose a pressure-induced structural phase transition  $T \rightarrow T' \rightarrow T' + Pnma$  in FeSe<sub>0.82</sub> as the pressure increasing to 10.6 GPa under RT based on our XRD data analysis, which is different from the experimental results in Refs. [3,24]. The FeSe sample was very sensitive to stoichiometry [2] and external conditions. This may elucidate the discrepancy on structural transition sequence reported by different research groups.

NiAs-type and MnP-type are two promising candidates for assigning the high-pressure phase of FeSe at RT in Refs. [3,24,25,27], in which these experimental XRD data are markedly indexed with the P6<sub>3</sub>/mmc and Pnma, respectively. From a crystallographic view point, *Pnma* is one of the subgroups of P6<sub>3</sub>/ mmc. To solve this confusion, the simulated XRD patterns for both MnP-type and NiAs-type FeSe at ~38 GPa are shown in Fig. 4 (b). It can be seen from Fig. 4 (b) that the MnP-type shows more diffraction peals compared to NiAs-type. However, it is interesting to note that the overall profile for the strong diffraction peaks (diffraction/background  $\geq$  10%) in MnP-type shows high resemblance with that of NiAs-type. For the MnP-type candidate, the intensity of weak diffraction peaks in XRD pattern under ~30 GPa will become comparable with the background due to the high stress, sample thinning, and weakened phase quality under high pressure. Moreover, the different chemical composition for FeSe may also play an important role in tailoring its structural evolution behavior under extreme conditions.

Fig. 4 (c) exhibits the measured pressure dependence of volume for FeSe<sub>0.82</sub> up to 10.6 GPa at RT. The fitted (2nd Birch-Murnaghan equation of state (EOS) [42]) bulk modulus ( $B_0$ ) for T and T' phase is equal to 28.4(2) and 36.4(4) GPa, with the ambient unit cell volume ( $V_0$ ) of 78.36(1) and 77.27(2) Å<sup>3</sup>, respectively. The T and T' phases coexist in certain pressure regime as shown in green rectangular field. Notably, the bulk modulus of 28.4 GPa–36.4 GPa for T and T' phases is significantly smaller than that of the "1111"-type NdFeAsO<sub>0.88</sub>F<sub>0.12</sub> (102 GPa) [41], "122"-type EuFe<sub>2</sub>As<sub>2</sub> (58.1 GPa) [30], and "111"-type Na<sub>1-x</sub>FeAs (52.3 GPa) [43]. Since FeSe lacks carrier layers compared to Fe-As-superconductors, the structure of FeSe is significantly more compressible under modest externally applied pressures.

ratio (*c*/*a*) as a function of pressure under RT. For facilitating a better observation of noticeable variation of *c*/*a*, two dashed lines were plotted in different pressure regimes. The inset shows the pressure dependence of the relative lattice parameters ( $a/a_0$  and  $c/c_0$ ) of FeSe<sub>0.82</sub>.



**Fig. 4.** (a) Angles dispersive XRD pattern of FeSe<sub>0.82</sub> under 10.6 GPa from the present work. The two dashed rectangles mark the new appeared diffraction peaks grown from the parent phase. The calculated (cal.) XRD patterns with space group *P4/nmm*, *Pnma*, and *P6<sub>3</sub>/mmc* with lattice parameters corresponding to ~ 10 GPa. (b) For illustrating the similarity and difference between *Pnma* and *P6<sub>3</sub>/mmc* phases of FeSe, the simulated XRD patterns for these two phases under 38 GPa at RT was shown. (c) The pressure

#### 3.2. The structural evolution of FeSe<sub>0.82</sub> under HPLT

The rise in the  $T_c$  to 37 K around 6–8 GPa demonstrates a strong correlation between superconductivity and crystal structure. Therefore, we investigated the structural changes in FeSe<sub>0.82</sub> using synchrotron XRD at LT down to 10 K near  $T_c$ . For LT measurements, the DAC was cooled down to 10 K in a continuous helium flow type cryostat. Fig. 5 shows the XRD patterns obtained under HPLT. With decreasing temperature FeSe undergoes a tetragonal (*P4/nmm*) to orthorhombic (*Cmma*) phase transition below 90 K [13]. Similarly, we observed an orthorhombic pattern at 10 K under ambient pressure. At HPLT conditions, R. S. Kumar et al. found that a sluggish structural phase transition (*Cmma*  $\rightarrow$  *Pnma*) begins as early as 1.6 GPa [27]. The *Pnma* phase becomes the major phase with a large volume collapse of 19% above 9 GPa and the *Cmma*  $\rightarrow$  *Pnma* transition completely accomplishes above 26 GPa according to their high-resolution synchrotron powder XRD data analysis.

The present general structural transformation sequence in FeSe agrees well with the experimental data [27]. However, we discovered two novel differences in the transformation information in our experimental data compared to Ref. [27]. (1) The present critical pressure (24.6 GPa) for forming major phase (*Pnma*) under HPLT conditions is higher than that of Ref. [27] (9 GPa). (2) The *Cmma* and *Pnma* phases with roughly equal percentage still coexist at ~ 26.5 GPa as shown in Fig. 5. We interpreted this as a subtle



**Fig. 5.** Selected angle dispersive XRD patterns of FeSe<sub>0.82</sub> under various pressures at 10 K (the pressure value is listed at the left of figure with unit in GPa). The blue and red dotted lines are the guides for observing the occurrence of structural phase transition (*Cmma*  $\rightarrow$  *Pnma*). The diffraction peak marked with a green dashed line is due to the stainless steel gasket (noted as "g" in the figure) and sample (high pressure MnP-type phase). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dependence of volume for FeSe<sub>0.82</sub> at RT, the lattice volume and bulk modulus for T and T' phases are derived from the EOS fitting. The green rectangular regime marked the coexistence of T and T' phases. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

chemical composition difference between the present (FeSe<sub>0.82</sub>) and Ref. [27] (FeSe<sub>0.98</sub>) since the structural evolution behavior of FeSe is sensitive to chemical composition and external conditions as mentioned above [2]. The diffraction peak (~10.5°), marked with a green dashed line was due to the stainless steel gasket and sample (MnP-type phase). It is noted that this diffraction peak intensity was enhanced as the pressure increases ( $\geq$ 5.7 GPa). Our further XRD data analysis demonstrated that the diffraction peaks (211) and (112) for high-pressure phase (*Pnma*-type) overlap with the gasket around this Bragg diffraction angle (~10.5°).

There are large discrepancies between the different studies of FeSe at high pressure due to the different pressure conditions and sample preparations. The most important difference regards the superconducting behavior in different crystallographic phases. In one study, the  $T_c$  was found to increase continuously up to 22 GPa [25]. However, in another study, the  $T_c$  decreased to 22 K at 10.5 GPa, and showed no sign of superconductivity at higher pressure (>12 GPa) was observed [24]. Fig. 5 shows that the lowpressure (Cmma) and high-pressure (Pnma) phases coexist between 7.5 and 26.5 GPa. The change of  $T_c$  is nonmonotonic and shows a dome shaped maximum at around 6-8 GPa [11,19]. The absence of superconductivity below  $T_c$  is due to the occurrence of a larger fraction of the *Pnma* phase at higher pressure. The present HPLT XRD result is apparently hinged on the electronic transport measurement. Therefore, the superconductivity observed in FeSe at high pressure (>12 GPa) is not intrinsic. Based on the present highpressure XRD data under RT and LT, we suggest that the remnant small fraction of the low-pressure Cmma phase in the sample gives rise to this discrepancy.

#### 3.3. XANES study of charge transfer in FeSe<sub>0.82</sub> under high pressure

Rationalizing the relationship between the superconductivity, the normal-state nematic order and the pressure-induced antiferromagnetic order is indispensable for achieving a better understanding of the high- $T_c$  in FeSe. We now turn to study the effect of pressure on charge transfer of Se in FeSe<sub>0.82</sub> to obtain electronic information using XANES techniques. The previous work has shown that XANES technique can be carried out in a diamond anvil cell allowing detailed studies of charge transfer in rare earth metal elements and compounds such as EuNi<sub>2</sub>P<sub>2</sub> [44]. Fig. 6 (a) shows the Se *K*-edge XANES spectra of FeSe<sub>0.82</sub> obtained under selected pressure. As shown in Fig. 6 (a), the XANES edge shifted to high



**Fig. 6.** (a) XANES spectra at ambient temperature for Se at selected pressures up to 18.3 GPa. The dashed lines are guide for eyes. For clearly observing the energy shift under high pressure, the XANES spectra around  $E_0$  are enlarged in the right panel (b).

energy as the pressure increasing. For facilitating a better comparison of the XANES data at different pressures, in Fig. 6 (b) we present the XANES close to  $E_0$ . The Se *K*-edge of FeSe<sub>0.82</sub> collected at various pressures exhibit notable variation, indicating the electronic structure of FeSe<sub>0.82</sub> is tailed by applied pressure. Recent synchrotron X-ray emission spectroscopy and *ab initio* calculations performed by R. S. Kumar et al. show a pressure-induced smooth high-spin to low-spin transition in FeSe ~ 6–7 GPa [22,23].

It is interesting to note that high-spin  $\rightarrow$  low-spin transition did not result in obvious chemical valence change. Based on *ab initio* calculation, they suggested that the spin moment change could be attributed to pressure-induced electron delocalization or spin



**Fig. 7.** Schematic crystal structures for *P*4/*nmm* and *Pnma* phases of FeSe, in which the SeFe<sub>4</sub> pyramid and FeSe<sub>4</sub> tetrahedron were stacked layered along *c*-axia (a). The *Pnma*-type phase could be considered as a 3D network comprising FeSe<sub>6</sub> octahedra with edge- and face-share connections (b). (c)  $k^2$ -weighted XAFS spectra,  $k^3 \cdot \chi(k)$ , for FeSe<sub>0.82</sub> under selected pressures (0 GPa, 4.9 GPa, and 18.3 GPa corresponding to the T, T', and O'' phases, respectively) at RT.

crossover of Fe. The electronic structure, such as spin state and chemical valence, is dominated by Fe 3d electrons and that have a strong hybridization with interacting Se orbitals. Fe is reported to have a divalent configuration with varying degree of co-valency in FeSe as established by previous Mössbauer experiments [12,13]. The present XAS study is consistent with the reported results [45]. The XANES results reported here show that the chemical valence of Fe in FeSe is not integral +2 but a nonintegral, which contrasts with the documented results.

#### 4. Discussion

The structure of T and T' phase for FeSe is shown in Fig. 7 (a), in which SeFe<sub>4</sub> pyramid and the FeSe<sub>4</sub> tetrahedron are shown. The coordination number (CN) for Se in T and T' phases is the same (CN = 4). The amplitude in *k* space should be similar with each other as shown in Fig. 7 (b). The amplitude shows an appreciable change as the pressure increased to 18.3 GPa. From Fig. 1 we obtained the CN of Se in both MnP-type and NiAs-type was 6. Therefore, our experimental EXAFS results are markedly consistent with our XRD results.

Despite several years of intensive research, the physical mechanism responsible for such a high  $T_c$  is still elusive. One of the most important reasons is that the crystallographic phase diagram and transformation sequence is very sensitive to sample chemical composition and external conditions (temperature, pressure, etc.). The detailed reported and present studies of structural transformation on FeSe are tabulated as a function of applied pressure and temperature (see Table 1). The present high-quality sample and fine pressure step measurement enabled us to obtain novel structural evolution behavior of FeSe under extreme conditions, which is indispensable in exploring superconducting behavior of FeSe.

Now we turn to the volume variation in pressure-induced spin and structural transition in FeSe. It is known that the electronic collapse (such as  $4f \rightarrow 5d$ ) as well as spin state transition (high-spin  $\rightarrow$  low-spin) usually gives rise to the appreciable lattice volume discontinuous shrinkage such as in the rare-earth monochalcogenides (SmS, EuTe) [46], and manganese chalcogenides (MnS and MnSe) [47] under high pressure. However, the reported high-spin  $\rightarrow$  low-spin transition in FeSe [22,23] did not results in the large discontinuous lattice volume shrinkage in this work as well as other research group's results. This anomalous behavior of FeSe is probably correlated with its distinct crystal structure. The ionic radius of Fe in the high-spin state with CN = 4 in P4/nmm phase is 0.63 Å. With the pressure increasing the ionic radius of Fe for low-spin state with CN = 6 in Pnma phase becomes 0.61 Å. Therefore, the decrease of ionic radius for Fe between high-spin and low-spin states is just 0.02 Å. This would be one of the reasons in explaining the pressure-induced high-spin  $\rightarrow$  low-spin transition in FeSe without noticeable lattice volume collapse.

The pressure-induced lattice volume collapse was an interesting and important phenomenon in physics, chemistry, and materials science. The first example (cerium, Ce), which is also the prototypical one, is reported to exhibit pressure-induced isostructural phase transition, the well-known  $\gamma \rightarrow \alpha$  phase transition at 0.7 GPa and RT with a volume collapse of ~16% [48]. This sharp volume shrink might be related to an itinerant-localized transition of the f electrons [49]. However, the pressure-induced  $P4/nmm \rightarrow Pnma$ phase transition accompanied by large volume shrinkage (see Fig. 8 (a)) in FeSe is not due to the high-spin  $\rightarrow$  low-spin transition in Fe, because the transition pressure of high-spin  $\rightarrow$  low-spin (~6 GPa) is prior to that of  $P4/nmm \rightarrow Pnma$  (~12 GPa). PbCrO<sub>3</sub> has a cubic perovskite structure with an anomalously large volume. Its lattice parameter (4.00 Å) is much larger than that of cubic SrCrO<sub>3</sub> (3.82 Å) even though the atomic radius of Sr (1.44 Å) is close to that of Pb (1.49 Å)[50]. A pressure-induced cubic  $\rightarrow$  cubic isostructural phase transition was found in PbCrO<sub>3</sub>, and accompanied by a 9.8% volume collapse [51,52], which is interpreted as the anomalously large volume at ambient conditions combined with first order localized to itinerant electronic transition. The crystallographic structure for ambient P4/nmm phase of FeSe might be considered as a quasitwo-dimensional (Q2D) layered structure with FeSe<sub>4</sub> tetrahedral parallel along *c*-axis as shown in Fig. 7 (a). However, the MnP-type FeSe could be considered as a three dimensional (3D) network comprising FeSe<sub>6</sub> octahedra with edge- and face-sharing connection. Furthermore, the pressure-induced P4/nmm-type  $\rightarrow$  Pnmatype phase transition in FeSe is involved in CN change (P4/nmm, CN = 4, *Pnma*, CN = 6, see Fig. 1). From the view of atomic sphere stacking model, the octahedron shows higher occupation ratio than that of tetrahedron. We propose that the Q2D versus 3D crystal structure and CN change (CN = 4 versus CN = 6) in P4/nmm-type  $\rightarrow$ Pnma-type simultaneously give rise to the volume shrinkage in FeSe. Fig. 8 (b) shows that the pressure-induced Cnma-type  $\rightarrow$ Pnma-type transition is also accompanied by large volume shrinkage, and the mechanism is similar with P4/nmm-type  $\rightarrow$ Pnma-type. The unit cell volume for Cmma phase obtained from this work exhibits larger volume than that in Refs. [8,27] at the same pressure. This contradiction may be due to the different stoichiometry of the samples and temperature conditions (HP-XRD experiments were performed under 16 K in Ref. [8], 8 K in Ref. [27] and 10 K in this work).

To further understand the structural and electronic phase transition, the Fermi surface (FS) was simulated by first principles calculations as shown in Fig. 9. Firstly, the FS for T and T' phases

#### Table 1

Collected data of reported and present work (PW) on the pressure-induced structural phase transition of FeSe under extreme conditions (high pressure and/or low temperature). Several techniques (such as XRD, neutron diffraction, Raman spectroscopy, etc.) have been used to characterize structural phase transition. Here, we just list the results obtained from AD-XRD in this table. The T, T', O', O'', M, and H denote the tetragonal (*P4/nmm*), high-pressure tetragonal (*P4/nmm*), orthorhombic (*Cmma*), orthorrhombic (*Pnma*, MnP-type), monoclinic, and hexagonal (*P6<sub>3</sub>/mmc*, NiAs-type) phases of FeSe, respectively. The pressure transmitting medium (silicone oil (SO), daphne oil (DO), Methanol/ethanol mixture (ME), neon, and helium) is one of the most important parameters in tuning the structural evolution behavior in FeSe.

Chemical composition	Pressure medium	Maximum Pressure	Temperature	Transition sequence (GPa)	Ref.
Fe <sub>1:01</sub> Se	SO	38 GPa	300 K	$T \rightarrow H (7 \text{ GPa})$	[3]
				T+H (7—38 GPa)	
FeSe <sub>0.88</sub>	ME	12.8 GPa	300 K	$T \rightarrow M (4 \text{ GPa})$	[26]
				$M \rightarrow H (12-14 \text{ GPa})$	
FeSe <sub>0.977</sub>	helium	12.4 GPa	300 K	$T \rightarrow H (8.5-12 \text{ GPa})$	[24]
FeSe <sub>0.82</sub>	helium	26.5 GPa	300 K	$T \rightarrow O'' (\geq 12.5 \text{ GPa})$	[25]
Fe <sub>1.03</sub> Se	DO	14 GPa	16 K	$O' \rightarrow H (12.1 \text{ GPa})$	[8]
FeSe <sub>0.98</sub>	neon	33 GPa	300 K	$T \rightarrow O'' (13 \text{ GPa})$	[27]
	helium	31 GPa	8 K	$O' \rightarrow O'' (\geq 9 \text{ GPa})$	
FeSe <sub>0.82</sub>	SO	10.6 GPa	300 K	$T \rightarrow T' \rightarrow T'+O'' (0-10.6 \text{ GPa})$	PW
		26.5 GPa	10 K	$O' \rightarrow O'' (\geq 24.6 \text{ GPa})$	



**Fig. 8.** Pressure dependence of the FeSe unit cell volume at RT (a) and LT (b) from the literature and present work. Both of the structural phase transitions (*P4*/*nmm*  $\rightarrow$  *Pnma* (RT) and *Cmma*  $\rightarrow$  *Pnma* (LT)) show discontinuous variation at critical pressure.



**Fig. 9.** Simulated Fermi surface of tetragonal phase (*P*4/*nmm*, T and T') FeSe at 0 (a) and 3 GPa (b), orthorhombic phase (*Pnma*, O'') at 13 GPa (c), and orthorhombic phase (*Cmma*, O') at 0 GPa (d), 6 GPa (e) and 12 GPa (f), respectively.

under 0 and 3 GPa was shown in Fig. 9 (a) and (b), respectively. The profile of FS for T phase at 0 GPa shows the characteristic of discrete cylinder. As the pressure increases to 3 GPa (T' phase) the profile of FS is distorted into dumbbell-shaped cylinder. For the *Pnma* phase, the FS shows remarkable variation compared with T and T' phases. Furthermore, the LT phase (*Cmma*) under selected pressure (0 GPa, 6 GPa, and 12 GPa) was also investigated (Fig. 9 (d), (e) and (f)). The profile change under high pressure was consistent to the structural phase transition *Cmma*  $\rightarrow$  *Pnma*.

#### 5. Conclusion

In summary, we have mapped out the pressure and temperature phase diagram of FeSe and captured a pressure-induced  $T \rightarrow T'$  transition in FeSe. The mechanism of the pressure-induced  $T \rightarrow T'$  transition in FeSe is probably due to the charge transfer and electronic phase transition (such as the topology change of Fermi surface) rather than spin transition. The present experimental XRD data under high pressure at RT reveal that FeSe crystalizes into T'+MnP-type phase at ~10 GPa, which shows disparity with the reported pure NiAs-type as well as the MnP-type. Moreover, X-ray *K*-absorption edge measurement of selenium has been studied under high pressure. It showed that the edge shifts towards high energy side, demonstrating a charge transfer between Fe and Se under high pressure. Furthermore, the change in local crystal structure is another important factor for explaining the enhancement of  $T_c$  by applying pressure.

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#### References

- [1] F.C. Hsu, J.Y. Luo, K.W. Yeh, T.K. Chen, T.W. Huang, P.M. Wu, Y.C. Lee, Y.L. Huang, Y.Y. Chu, D.C. Yan, M.K. Wu, Proc. Natl. Acad. Sci. U.S.A. 105 (2008) 14262.
- [2] F. Sun, Z.N. Guo, H.H. Zhang, W.X. Yuan, J. Alloys Compd. 700 (2017) 43.
- [3] S. Medvedev, T.M. McQueen, I.A. Troyan, T. Palasyuk, M.I. Eremets, R.J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, C. Felser, Nat. Mater. 8 (2009) 630.
- [4] M. Burrard-Lucas, D.G. Free, S.J. Sedlmaier, J.D. Wright, S.J. Cassidy, Y. Hara, A.J. Corkett, T. Lancaster, P.J. Baker, S.J. Blundell, Simon J. Clarke, Nat. Mater. 12 (2013) 15.
- [5] Y. Miyata, K. Nakayama, K. Sugawara, T. Sato, T. Takahashi, Nat. Mater. 14 (2015) 775.
- [6] J.F. Ge, Z.L. Liu, C.H. Liu, C.L. Gao, D. Qian, Q.K. Xue, Y. Liu, J.F. Jia, Nat. Mater. 14 (2015) 285.
- [7] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, Y. Takano, Appl. Phys. Lett. 93 (2008), 152505.
- [8] S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, K. Prassides, Phys. Rev. B 80 (2009), 064506.
- [9] M. Bendele, A. Ichsanow, Yu. Pashkevich, L. Keller, Th. Strässle, A. Gusev, E. Pomjakushina, K. Conder, R. Khasanov, H. Keller, Phys. Rev. B 85 (2012), 064517.
- [10] S. Masaki, H. Kotegawa, Y. Hara, H. Tou, K. Murata, Y. Mizuguchi, Y. Takano,

J. Phys. Soc. Jpn. 78 (2009), 063704.

- [11] K. Miyoshi, K. Morishita, E. Mutou, M. Kondo, O. Seida, K. Fujiwara, J. Takeuchi, S. Nishigori, J. Phys. Soc. Jpn. 83 (2014), 013702.
- [12] Q.S. Wang, Y. Shen, B.Y. Pan, X.W. Zhang, K. Ikeuchi, K. Iida, A.D. Christianson, H.C. Walker, D.T. Adroja, M. Abdel-Hafiez, X.J. Chen, D.A. Chareev, A.N. Vasiliev, J. Zhao, Nat. Commun. 7 (2016) 12182.
- [13] T.M. McQueen, A.J. Williams, P.W. Stephens, J. Tao, Y. Zhu, V. Ksenofontov, F. Casper, C. Felser, R.J. Cava, Phys. Rev. Lett. 103 (2009), 057002.
- [14] S.H. Baek, D.V. Efremov, J.M. Ok, J.S. Kim, Jeroen van den Brink, B. Büchner, Nat. Mater. 14 (2015) 210.
- [15] T. Terashima, N. Kikugawa, S. Kasahara, T. Watashige, T. Shibauchi, Y. Matsuda, T. Wolf, A.E. Böhmer, F. Hardy, C. Meingast, H.V. Löhneysen, S. Uji, Phys. Soc. Jpn. 84 (2015), 063701.
- [16] K. Kothapalli, A.E. Bohmer, W.T. Jayasekara, B.G. Ueland, P. Das, A. Sapkota, V. Taufour, Y. Xiao, E. Alp, S.L. Bud'ko, P.C. Canfield, A. Kreyssig, A.I. Goldman, Nat. Commun. 7 (2016) 12728.
- [17] A.E. Böhmer, K. Kothapalli, W.T. Jayasekara, J.M. Wilde, B. Li, A. Sapkota, B.G. Ueland, P. Das, Y.M. Xiao, W.L. Bi, J.Y. Zhao, E.E. Alp, S.L. Bud'ko, P.C. Canfield, A.I. Goldman, A. Kreyssig, arXiv: 1803.09449 (2018).
  [18] M. Bendele, A. Amato, K. Conder, M. Elender, H. Keller, H.-H. Klauss,
- [18] M. Bendele, A. Amato, K. Conder, M. Elender, H. Keller, H.-H. Klauss, H. Luetkens, E. Pomjakushina, A. Raselli, R. Khasanov, Phys. Rev. Lett. 104 (2010), 087003.
- [19] J.P. Sun, K. Matsuura, G.Z. Ye, Y. Mizukami, M. Shimozawa, K. Matsubayashi, M. Yamashita, T. Watashige, S. Kasahara, Y. Matsuda, J.-Q. Yan, B.C. Sales, Y. Uwatoko, J.-G. Cheng, T. Shibauchi, Nat. Commun. 7 (2016), 12146.
- [20] T. Imai, K. Ahilan, F.L. Ning, T.M. McQueen, R.J. Cava, Phys. Rev. Lett. 102 (2009), 177005.
- [21] J.P. Sun, G.Z. Ye, P. Shahi, J.-Q. Yan, K. Matsuura, H. Kontani, G.M. Zhang, Q. Zhou, B.C. Sales, T. Shibauchi, Y. Uwatoko, D.J. Singh, J.-G. Cheng, Phys. Rev. Lett. 118 (2017), 147004.
- [22] R.S. Kumar, Y. Zhang, Y.M. Xiao, J. Baker, A. Cornelius, S. Veeramalai, P. Chow, C.F. Chen, Y.S. Zhao, Appl. Phys. Lett. 99 (2011), 061913.
- [23] J.M. Chen, S.C. Haw, J.M. Lee, T.L. Chou, S.A. Chen, K.T. Lu, Y.C. Liang, Y.C. Lee, N. Hiraoka, H. Ishii, K.D. Tsuei, Eugene Huang, T.J. Yang, Phys. Rev. B 84 (2011) 125117.
- [24] D. Braithwaite, B. Salce, G. Lapertot, F. Bourdarot, C. Marin, D. Aoki, M. Hanfland, J. Phys. Condens. Matter 21 (2009), 232202.
  [25] G. Garbarino, A. Sow, P. Lejay, A. Sulpice, P. Toulemonde, M. Mezouar,
- [25] G. Garbarino, A. Sow, P. Lejay, A. Sulpice, P. Toulemonde, M. Mezouar, M. Núñez-Regueiro, Europhys. Lett. 86 (2009) 27001.
- [26] T.W. Huang, C.M. Lin, H.S. Sheu, T.L. Hung, K.W. Yeh, P.C. Hsu, Y.L. Huang, F.C. Hsu, M.K. Wu, Physica C 470 (2010) S502.
- [27] R.S. Kumar, Y. Zhang, S. Sinogeikin, Y.M. Xiao, S. Kumar, P. Chow, A.L. Cornelius, C.F. Chen, J. Phys. Chem. B 114 (2010) 12597.
- [28] P.S. Wang, S.S. Sun, Y. Cui, W.H. Song, T.R. Li, R. Yu, H.C. Lei, W.Q. Yu, Phys. Rev.

Lett. 117 (2016), 237001.

- [29] A. Kreyssig, M.A. Green, Y. Lee, G.D. Samolyuk, P. Zajdel, J.W. Lynn, S.L. Bud'ko, M.S. Torikachvili, N. Ni, S. Nandi, J.B. Leão, S.J. Poulton, D.N. Argyriou, B.N. Harmon, R.J. McQueeney, P.C. Canfield, A.I. Goldman, Phys. Rev. B 78 (2008), 184517.
- [30] Z.H. Yu, L. Wang, L.H. Wang, H.Z. Liu, J.G. Zhao, C.Y. Li, S. Sinogeikin, W. Wu, J.L. Luo, N.L. Wang, K. Yang, Y.S. Zhao, H.K. Mao, Sci. Rep. 4 (2014) 7172.
- [31] U. Patel, J. Hua, S.H. Yu, S. Avci, Z.L. Xiao, H. Claus, J. Schlueter, V.V. Vlasko-Vlasov, U. Welp, W.K. Kwok, Appl. Phys. Lett. 94 (2009), 082508.
- [32] A. Hammersley, S. Svensson, M. Hanfland, A. Fitch, D. Hausermann, High Pres. Res. 14 (1996) 235.
- [33] H.K. Mao, J. Xu, P. Bell, J. Geophys. Res. 91 (1986) 4673.
- [34] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 1994.
- [35] B.H. Toby, J. Appl. Crystallogr. 34 (2001) 210.
- [36] B. Ravel, M. Newville, J. Synchrotron Radiat. 12 (2005) 537.
- [37] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
- [38] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [39] W. Kraus, G. Nolze, J. Appl. Crystallogr. 29 (1996) 301.
- [40] H. Okamoto, J. Phase Equil. 12 (1991) 383.
- [41] J.G. Zhao, L.H. Wang, D.W. Dong, Z.G. Liu, H.Z. Liu, G.F. Chen, D. Wu, J.L. Luo, N.L. Wang, Y. Yu, C.Q. Jin, Q.Z. Guo, J. Am. Chem. Soc. 130 (2008) 13828.
- [42] F. Birch, Phys. Rev. 71 (1947) 809.
- [43] Q.Q. Liu, X.H. Yu, X.C. Wang, Z. Deng, Y.X. Lv, J.L. Zhu, S.J. Zhang, H.Z. Liu, W.G. Yang, L. Wang, H.K. Mao, G.Y. Shen, Z.Y. Lu, Y. Ren, Z.Q. Chen, Z.J. Lin, Y.S. Zhao, C.Q. Jin, J. Am. Chem. Soc. 133 (2011) 7892.
- [44] C.Y. Li, Z.H. Yu, W.L. Bi, J.Y. Zhao, M.Y. Hu, J.G. Zhao, W. Wu, J.L. Luo, H. Yan, E.E. Alp, H.Z. Liu, Physica B 501 (2016) 101.
- [45] X.D. Qi, J.Y. Wang, J.H. Kuo, K.A. Yates, L.F. Cohen, J. Alloys Compd. 509 (2011) 6350.
- [46] A. Chatterjee, A.K. Singh, A. Jayaraman, Phys. Rev. B 6 (1972) 2285.
- [47] Y.G. Wang, L.G. Bai, T. Wen, L.X. Yang, H.Y. Gou, Y.M. Xiao, P. Chow, M. Pravica, W.G. Yang, Y.S. Zhao, Angew. Chem. Int. Ed. 55 (2016) 1.
- [48] A.W. Lawson, T.Y. Tang, Phys. Rev. 76 (1949) 301.
- [49] N. Lanata, Y.X. Yao, C.Z. Wang, K.M. Ho, Phys. Rev. Lett. 111 (2013), 196801.
- [50] M. Wu, L.R. Zheng, S.Q. Chu, Z.X. Qin, X.J. Chen, C.L. Lin, Z. Tang, T.D. Hu, J. Phys. Chem. C 118 (2014) 23274.
- [51] W.S. Xiao, D.Y. Tan, X.L. Xiong, J. Liu, J.A. Xu, Proc. Natl. Acad. Sci. U. S. A. 107 (2010) 14026.
- [52] J.G. Cheng, K.E. Kweon, S.A. Larregola, Y. Ding, Y. Shirako, L.G. Marshall, Z.Y. Li, X. Li, António M. dos Santos, M.R. Suchomel, K. Matsubayashi, Y. Uwatoko, G.S. Hwang, J.B. Goodenough, J.S. Zhou, Proc. Natl. Acad. Sci. U. S. A. 112 (2014) 1670.