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# Raman and X-ray diffraction studies of superconducting FeSe under pressure

Tzu-Wen Huang [a,*], Chih-Ming Lin [b], Hwo-Shuenn Sheu [d], Tsu-Lien Hung [a,c], Kuo-Wei Yeh [a], Po-Chun Hsu [a], Yi-Lin Huang [a], Fong-Chi Hsu [a], Maw-Kuen Wu [a]

[a] *Institute of Physics, Academia Sinica, Taipei 11529, Taiwan*
[b] *Department of Applied Science, National Hsinchu University of Education, Hsinchu 30014, Taiwan*
[c] *Department of Physics, National Tsing-Hua University, Hsinchu 30013, Taiwan*
[d] *National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

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ABSTRACT

A phase transition was observed in the tetragonal FeSe superconductor under high pressure at around 2.55 GPa using X-ray scattering and Raman spectrum. From X-ray powder diffraction (XRD) experiments, the slope of the unit cell volume versus pressure curve change slightly at around 2.55–4 GPa, and the Bragg peaks of FeSe tetragonal phase disappear when the pressure reaches 11.4 GPa. We also found the superconducting transition temperature $T_c$ increases and reaches a maximum value of ~37 K at ~3–4 GPa. The compressibility value ($dV/dP$) shows an abrupt change from 2.39 (Å$^3$/GPa) to 0.94 (Å$^3$/GPa) from pressure values of 0–2.55 GPa to 2.55–11.4 GPa. A similar phase transition was also observed in the Raman spectra under pressure.

## 1. Introduction

FeSe with the PbO structure is a key member of the family of new high-$T_c$ iron pnictide and chalcogenide superconductors, as it possesses the basic layered structure of edge-sharing distorted $FeSe_4$ tetrahedron, which is believed to be the most ingredient of the iron-based superconductors. The application of hydrostatic pressure rapidly increases $T_c$ and reaches a broad maximum of 37 K at 4–7 GPa before decreasing to 6 K upon further compression to 14 GPa [1–4]. A phase transition from tetragonal FeSe to a lower-symmetry of monoclinic lattice was identified at about 4 GPa, and monoclinic FeSe further changed into a hexagonal phase while the pressure reached 12–14 GPa. These result points out that the structural distortion at the iron plane and superconductivity is closely related. In this study, we performed the XRD and Raman scattering experiments to probe the pressure-induced phase transition in FeSe in order to gain more insight into the details of the correlation between structural distortion and superconductivity.

## 2. Experiments

Angle dispersive XRD (ADXRD) measurements were performed using beamline BL01C2 [5] at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, with a wavelength of 0.619926 Å (20 KeV). Beyond the pre-focusing mirror, a double crystal monochromator, which used the Si(1 1 1) plane to yield the monochromatic beam, is followed by a refocusing toroidal mirror. The $FeSe_{0.88}$ crystals were pulverized and then mixed with the internal gold standard [6,7]. The mixture was then put in the gasket hole in the Mao-Bell-type diamond anvil cell with approximate 600 μm diameter anvil faces. Methanol/ethanol mixture was used as pressure-transmitting medium. Powder diffraction patterns were recorded using a fixed Mar345 imaging plate (IP) detector at a distance of 260 mm from the sample. The incident beam was collimated at 150 μm in diameter. For Mar345, the radius of the diffracted rings on the IP plate was measured in pixels, and each pixel corresponds to either 100 or 150 μm in linear dimension. The raw 2D data were converted to 1D profile by using ESRF Fit2D software [8].

## 3. Discussion

Fig. 1a shows the X-ray powder diffraction spectra from ambient pressure to 12.81 GPa. The data show that a phase transition from FeSe tetragonal phase to monoclinic was observed at a transition pressure ($P_s$) 4 GPa, and the sample symmetry becomes hexagonal when pressure is larger than 10 GPa. Detailed Rietveld refinements of the diffraction data give insight to the pressure effect on the crystal structure of $FeSe_{0.88}$. The lattice constants a and c were found slightly modified by pressure, as shown in the insert of Fig. 1b. The reduction in lattice constant a is only about 6% while lattice constant c decreases almost 10% at 12 GPa pressure. Fig. 1b plots the volume of $FeSe_{0.88}$ in various pressures. It is interesting to note that a change in slope appears at $P_s$. This is another evidence

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* Corresponding author. Tel.: +886 2 2789 8958; fax: +886 2 2783 4187.
*E-mail address:* twhuang@phys.sinica.edu.tw (T.-W. Huang).

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of the symmetry change in $FeSe_{0.88}$ as one expects the compressibility of the sample below and above $P_s$ is different.

Fig. 2 shows the pressure dependence of the Raman active *B*1*g* and *Eg* modes of $FeSe_{0.88}$. The results show that the peak positions of both *B*1*g* and *Eg* mode behaves slightly differently under pressure. We observed that in $FeSe_{0.88}$ compounds the *B*1*g* phonon frequency at first increases as pressure increases, then decreases rapidly at about 3 GPa, and eventually becomes almost constant above 4 GPa. On the other hand, the Fe *Eg* mode was found to decrease as pressure increases over the whole pressure range but with a lower decreasing rate above 4 GPa. These results provide a clear support to the structural phase transition derived from the X-ray results. The results also suggest that *B*1*g* mode plays an important role in superconductivity, as its variation with pressure is consistent with the change in $T_c$ with pressure. It is also noted that the pressure effect on *Eg* mode, which describes the Fe motion in the ab plane, behaves similarly to that of the unit cell volume. A possible effect of this *Eg* mode is to play key role in the structural distortion observed at low temperature. It has been established that the low temperature structural distortion is closely related to the occurrence of superconductivity [9,10]. In this low temperature structural distortion the unit cell is elongated along the [1 1 0] direction in the tetragonal phase and transformed it to the monoclinic phase. The local environment of Se points out a one-dimensional like pyramids chain along the 110 vector. It is believed that this monoclinic phase with an anisotropy chain provides the driving force to induce superconductivity.

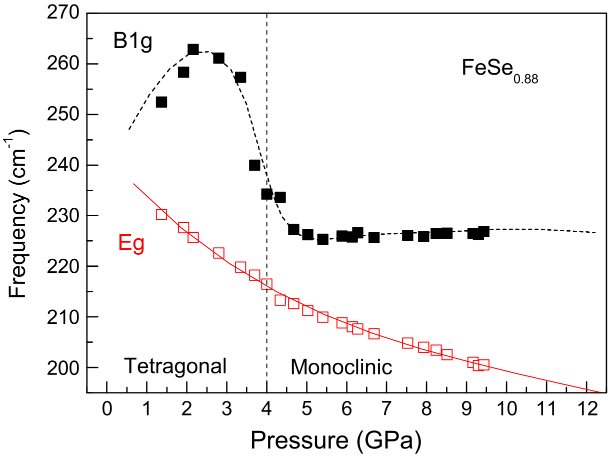

**Fig. 2.** The Raman shift for *B*1*g* (black close square) and *Eg* (red open square) mode in $FeSe_{0.88}$ system as pressure increasing from normal to 18 GPa. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

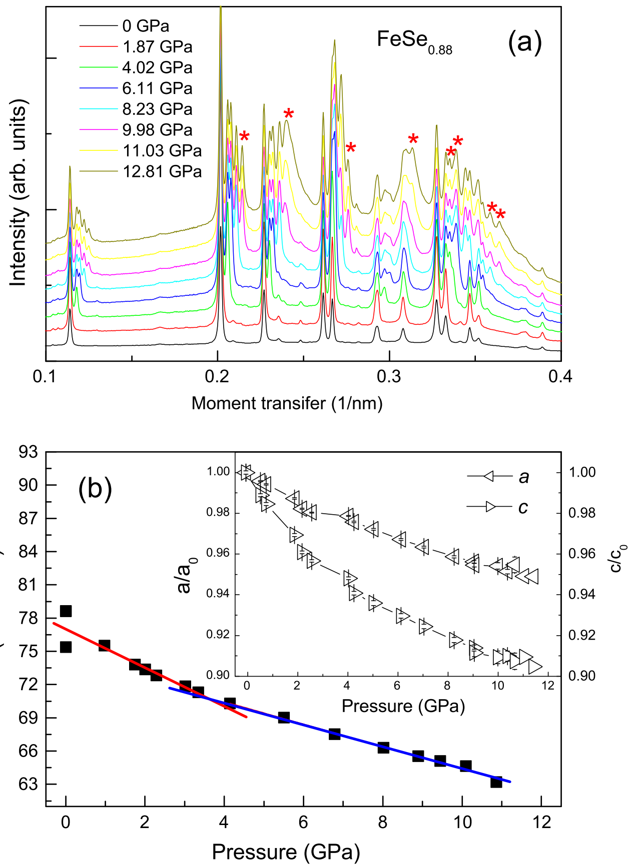

**Fig. 1.** (a) The XRD spectrum as the pressure dependence from 0 GPa to 12.81 GPa (from bottom to top). The hexagonal phase was marked as star symbol. (b) The volume and lattice constants (insert) as function as pressure.

In summary, we observe a phase transition at about 3 GPa pressure from tetragonal symmetry to monoclinic symmetry in FeSe superconductor from the X-ray scattering and Raman experiments. We also observed a close correlation of the change in *B*1*g* mode with the change in $T_c$ under pressure. These results further confirm the importance of low temperature structural distortion to the occurrence of superconductivity. However, more detailed electronic properties studies at ambient and high pressures are needed to better understand whether the Fermi surface nesting [11] or the spin fluctuation [12] plays the key role to the formation of superconductivity.

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