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Pressure-induced electronic topological transitions in the charge-density-wave material In_4Se_3

Yuhang Zhang [a, b], Liyan Song [a], Xuecheng Shao [a], Yan Li [a], Pinwen Zhu [a, *], Huailiang Xu [b, **], Junyou Yang [c, ***]

[a] State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China
[b] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China
[c] State Key Laboratory of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

High-pressure *in situ* angle dispersive X-ray diffraction (ADXRD) measurements were performed on the charge-density-wave (CDW) material In_4Se_3 up to 48.8 GPa. Pressure-induced structural changes were observed at 7.0 and 34.2 GPa, respectively. Using the CALYPSO methodology, the first high-pressure phase was solved as an exotic $Pca2_1$ structure. The compressional behaviors of the initial *Pnnm* and the $Pca2_1$ phases were all determined. Combined with first-principle calculations, we find that, unexpectedly, the *Pnnm* phase probably experiences twice electronic topological transitions (ETTs), from the initial possible CDW state to a semimetallic state at about 2.3 GPa and then back to a possible CDW state at around 3.5 GPa, which was uncovered for the first time in CDW systems. In the both possible CDW states, pressure provokes a decrease of band-gap. The observation of a bulk metallic state was ascribed to structural transition to the $Pca2_1$ phase. Besides, based on electronic band structure calculations, the thermoelectric property of the *Pnnm* phase under compression was discussed. Our results show that pressure play a dramatic role in tuning In_4Se_3's structure and transport properties.

1. Introduction

For decades, more and more attention is being focused on the CDW materials induced by quasi-one-dimensional lattice distortion (Peierls distortion) [1–3]. Because the occurrences of CDW order is well established in essentially all underdoped cuprates high-temperature superconductors (HTSCs) [4–18]. In addition, since CDW materials have been used as model systems for the understanding of the interplay among electrons, phonons and spins in strongly coupled electron–lattice systems [19].

It is known that the orthorhombic lattice structure (space group *Pnnm*) of In_4Se_3 is a CDW material under ambient conditions [20–22]. It contains quasi-two-dimensional layers stacked with weak interaction of van der Waals type along *a* direction, as seen in Fig. 1. Within the layer, $(In1\text{-}In2\text{-}In3)^{5+}$ multivalent clusters are connected with Se atoms by ionic-covalent bond, forming In-Se-In zigzag chains along the *c* axis [21,23]. In_4Se_3 has been thought to be suitable for fabrication of infrared optical fiber and nanowires [24–26], and applications of photovoltaic advices [27–29]. Furthermore, recently, excellent thermoelectric figure of merit *ZT* value of 1.48 at 705 K was achieved in single crystalline In_4Se_{3-x}, due to its extremely low thermal conductivity [20].

Pressure was recognized to be the cleanest method for tuning crystalline structures and the physical properties of these CDW compounds. For examples, pressure significantly raises the superconducting transition temperature T_c in almost established CDW compounds [30–42]. However, the precise nature of the CDW and its relationship with superconductivity is unclear [1,43]. Moreover, in particular, pressure-induced ETT, a modification of the topology of the Fermi surface, can result in significant enhancements of thermoelectric properties in strongly correlated systems [44–52]. Besides, Schwarz et al. reported that In_4Se_3 undergoes a structural transition at 8.8 GPa, while the structure of the high-pressure phase is still unknown [53]. Therefore, it is important to explore the structure and transport properties of In_4Se_3 by applying pressure, in order to find a better candidate for thermoelectric devices and

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: zhupw@jlu.edu.cn (P. Zhu), huailiang_xu@jlu.edu.cn (H. Xu), jyyang@mail.hust.edu.cn (J. Yang).

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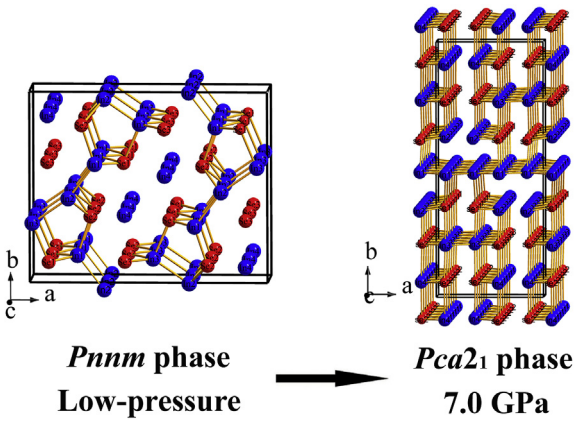

Fig. 1. Schematic representation of the *Pnnm* and $Pca2_1$ phases.

offer a platform for the exploration of novel superconductors.

Here, we report on the possible pressure-induced ETTs and structural transitions in In_4Se_3, for the first time, by *in-situ* high-pressure ADXRD measurements, using a diamond anvil cell (DAC), in conjunction with first-principles calculations.

2. Experimental details

In our experiments, purity In_4Se_3 powder was provided by Yang et al. [54]. Pressure was generated by a symmetric DAC with 300 μm diamond culet size. The powder was loaded in a 120 μm diameter hole drilled in the T-301 stainless steel gasket and chips of ruby were added as pressure calibrator [55]. A methanol-ethanol-water (16:3:1) mixture was employed as the pressure transmitting medium. *In situ* high-pressure ADXRD experiments were performed at the beamline X17C of the National Synchrotron Light Source (NSLS) using a monochromatic wavelength of 0.4095 Å. The average acquisition time was 300 s. The integration to conventional 2θ-intensity data was carried out with the FIT2D software [56]. Rietveld refinements were performed using the GSAS-EXPGUI package [57,58].

We performed structure prediction through a global minimization of free energy surfaces merging ab initio total-energy calculations via CALYPSO methodology [59]. For the first-principles calculations, the density functional theory with the Perdew-Burke-Ernzerhof exchange-correlation as implemented in the Vienna Ab initio Simulation Package (VASP) code [60] and the generalized gradient approximation (GGA) [61] is implemented on a projector augmented wave (PAW) basis [62,63]. The PAW method based upon the frozen core approximation with $5s^25p^1$ and $4s^24p^4$ electrons as valence for In and Se, respectively, was adopted. Integration in the Brillouin zone was performed using special *k* points generated with $4 \times 4 \times 4$ mesh parameter grids. Convergence tests give a kinetic energy cutoff as 300 eV, ensuring convergence of the total energy within 10^{-3} meV/atom. The lattice parameters were directly taken from the Rietveld refinement. The theoretical atomic positions are electronically relaxed based on the experimental atomic positions.

3. Results and discussion

The selected ADXRD patterns are shown in Fig. 2 and S1. It can be seen that the first and second pressure-induced structural transitions of In_4Se_3 started at about 7.0 and 34.2 GPa, respectively, where new peaks appeared. Decompression experiment shows that structural transition was irreversible, see Fig. 2. As can be seen in Fig. 3a and b, Rietveld refinements of ADXRD patterns clearly

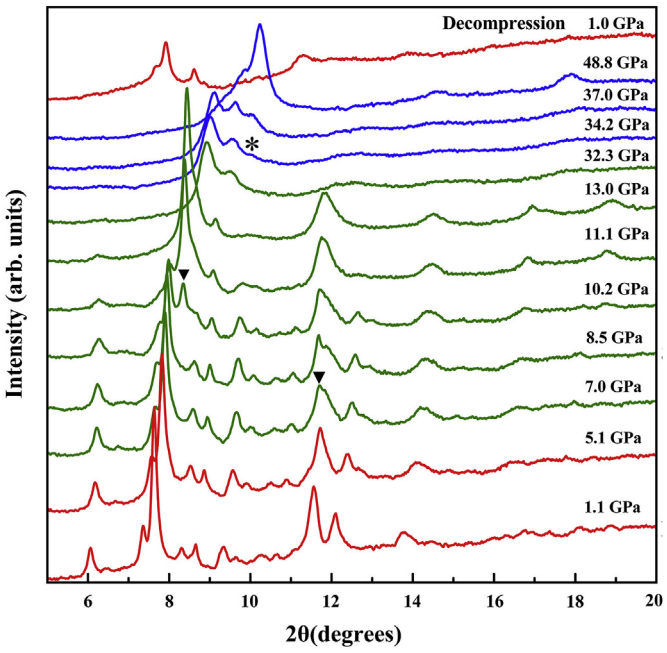

Fig. 2. Angle dispersive X-ray powder diffraction patterns of In_4Se_3 under high pressure at room temperature. Arrow and asterisk represent new diffraction peaks.

illustrate that the initial *Pnnm* phase is still stable at 5.1 GPa. The detailed refinement results, such as lattice parameters and atomic coordinates, are shown in the Supplementary Material. Fig. 2 clearly illustrates that the first structural transition is not completed up to 13.0 GPa. To solve the crystal structure of the first high-pressure phase, the structure prediction via CALYPSO methodology was performed [59] and the best fitting was achieved for an exotic orthorhombic structure (space group $Pca2_1$). Fig. 3c shows the Rietveld refinement for the $Pca2_1$ phase at 20.2 GPa, which has a good fitting with the ADXRD pattern. The relative experimental results of Rietveld refinement were located in the Supplementary Material.

During the compression process from 1.1 to 3.5 GPa, the (In1-In2-In3) clusters show nearly straight at 2.3 GPa, which leads to the quasi-two-dimensional layers all connected by the formation of In2-Se3 bonds at that pressure (see Fig. S2). The detailed bond lengths in *Pnnm* structure are located in Supplementary Material. The schematic representation of the $Pca2_1$ phase of In_4Se_3 is located in Fig. 1 and S3. It is indicated that the $Pca2_1$ structure is built up of stacking *a-c* plane layers of rhombus network of In1 atoms along *b* axis. Between two close In1 atoms layers, the warped *b-c* plane network layers consisting of In-Se ionic-covalent bonds are piled along *a* direction.

The evolution of the cell parameters in *Pnnm* phase is presented in Fig. 4. The contraction of the lattice parameters is anisotropic. It can be seen that *a* direction are more compressible than *b* and *c* directions, which is due to the weak intermolecular bond along *a* direction and strong covalent-ionic interactions within the warped *b-c* plane layers. For the overlapping diffraction peaks in the pressure region of mixed phases, it is difficult to identify the peak positions exactly. Therefore, we only display the lattice parameters of the $Pca2_1$ phase at above 13.0 GPa.

The volume per four formula units as a function of pressure is shown in Fig. S4. These *P-V* data are fitted to the usual Birch-Murnaghan (BM) equation of state (EOS) [64]. By fixing first-pressure derivative $B_0' = 4$, we obtained B_0 of 47.2(8) GPa and $V_0 = 775.16(4)$ Å^3 for the *Pnnm* phase. The lower B_0 is likely