Supplementary Information for

Giant piezoresistivity in a van der Waals material induced by intralayer atomic motions

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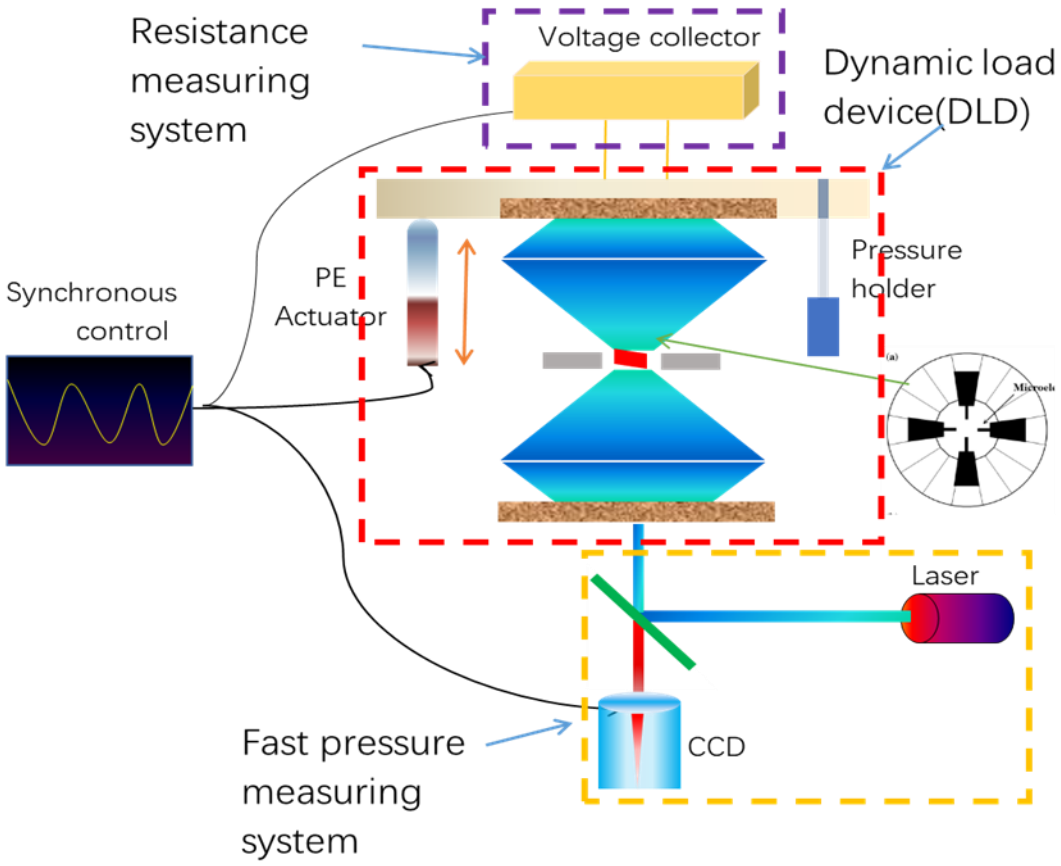
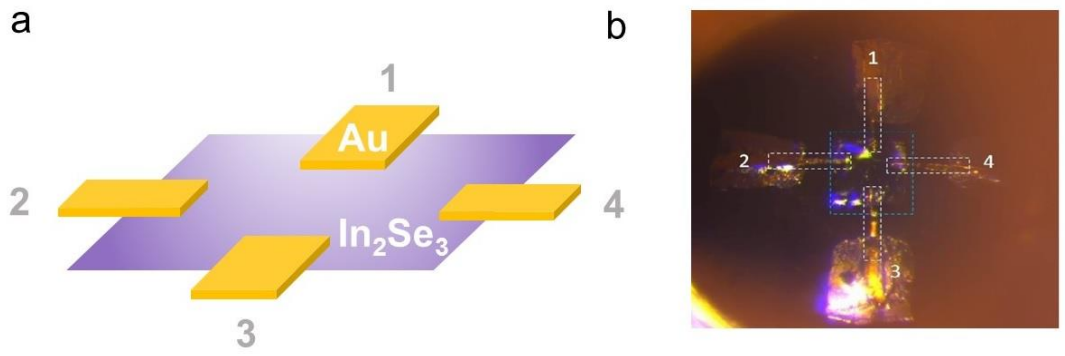
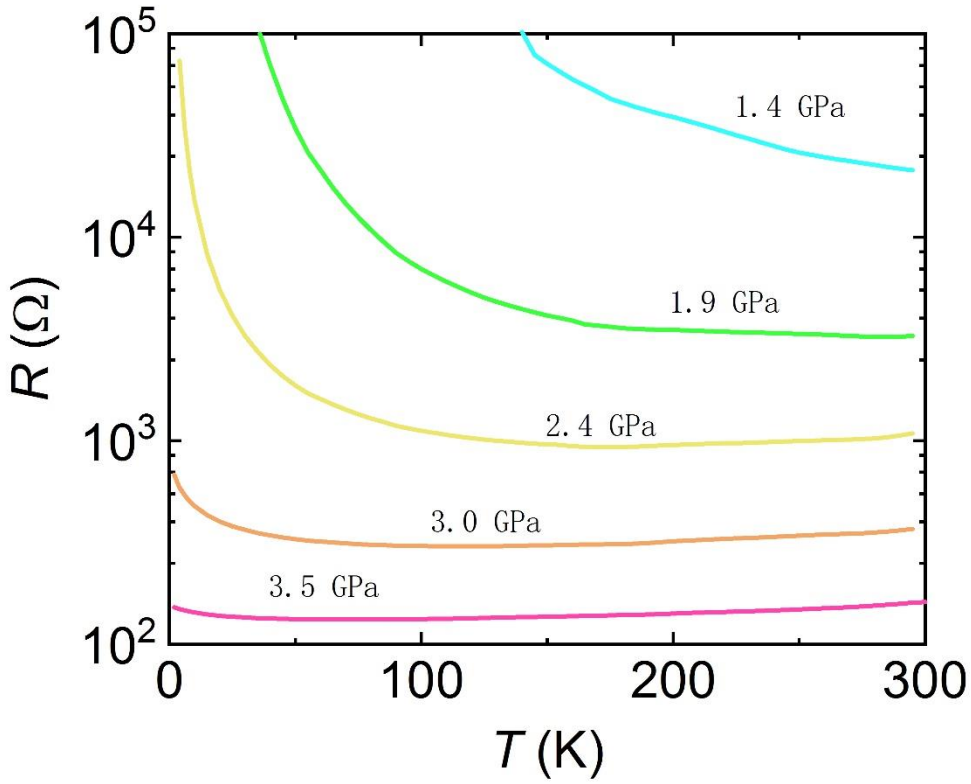
Supplementary Figures



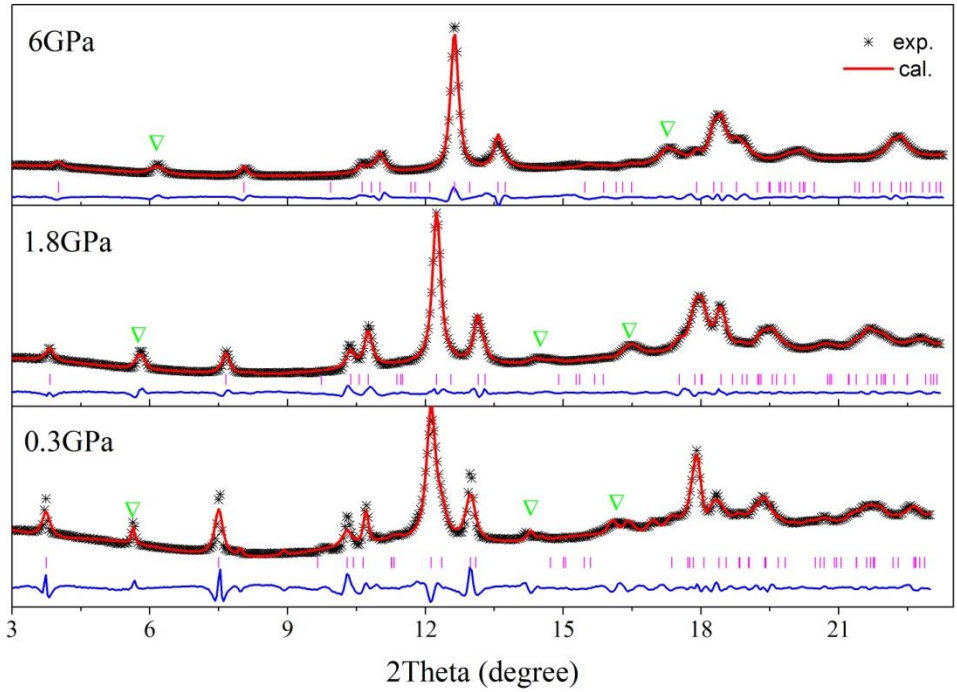
Supplementary Figure 1 | Dynamic electrical measurement system. A schematic diagram of the system for measuring the dynamic resistance response of β'-In_2Se_3 to pressure. The system includes three parts: (1) the dynamic loading device (DLD) with a symmetric diamond anvil cell (DAC) (red dashed box) in which the sample is loaded with four-wire resistance measuring method; (2) fast pressure measuring system (orange dashed box) and (3) resistance measuring system (purple dashed box). The three parts are synchronously controlled by an arbitrary-wave function generator.



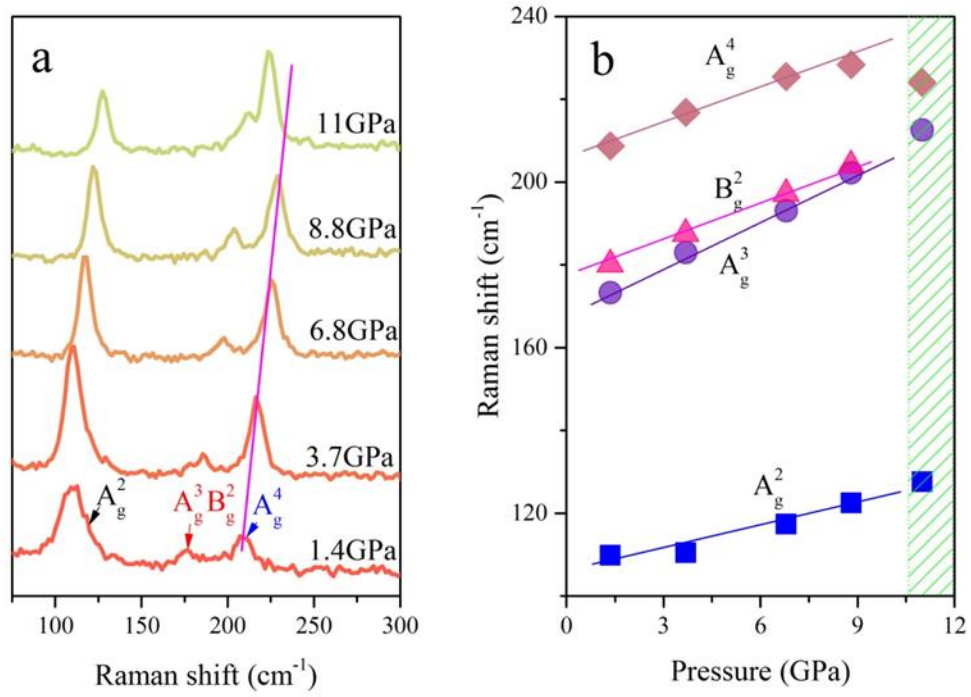
Supplementary Figure 2 | Hall measurements. (a) The electrode configuration of four probes used for Hall coefficient (R_H) measurements. (b) The image of a typical sample measured in a DAC. The white rectangles numbered with 1,2,3,4 indicate the gold electrodes, and the blue square denotes the β'-In_2Se_3 sample.



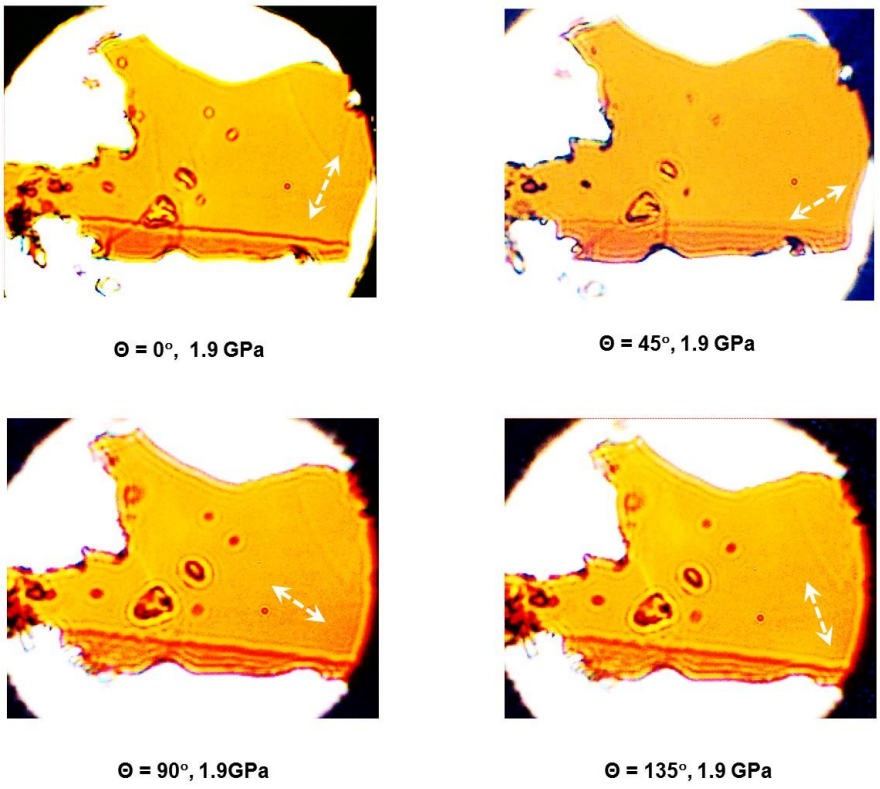
Supplementary Figure 3 | Temperature dependent resistance for extended pressure. The curves were obtained in a DAC in order to extend measurement to higher pressure.



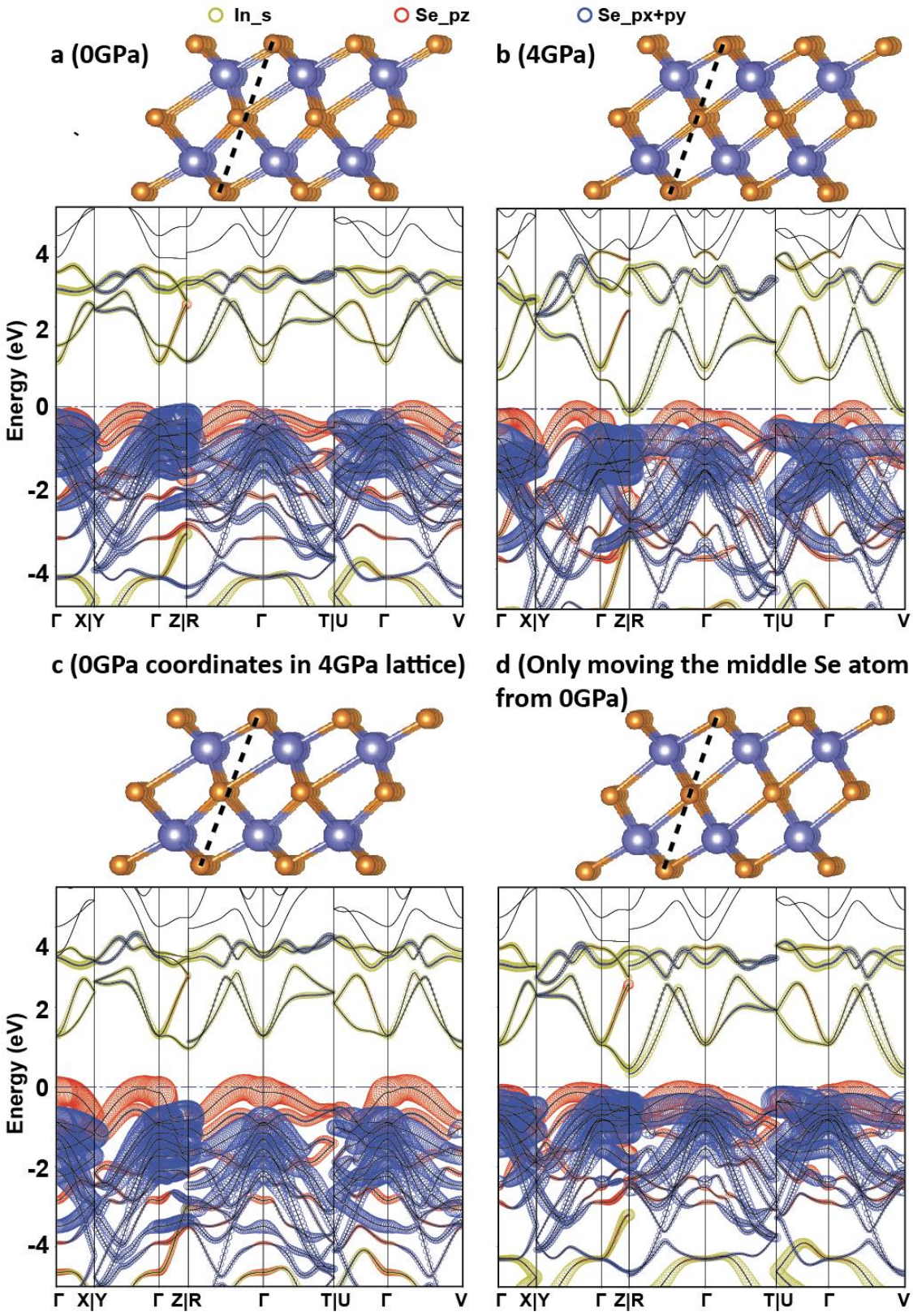
Supplementary Figure 4 | Le Bail fitting of the XRD spectra. The Lebail profile fitting patterns in β'-In2Se3 with monoclinic structure under 0.3GPa, 1.8GPa, and 6GPa. The black aterisks are the experimental data points, the red lines represent the fitting patterns, the magenta stick marks are the calculated Bragg reflections and the residuals are shown by the blue lines. The open green triangle indicates the peaks which belong to the impurity.



Supplementary Figure 5 | Raman spectra at high pressures. a The Raman spectra of β'-In_2Se_3 at different pressures, and **b** the pressure dependence of experimental Raman-active mode frequencies of four vibration modes A_g^2, A_g^3, B_g^2, A_g^4. The solid lines are guidance for eyes.

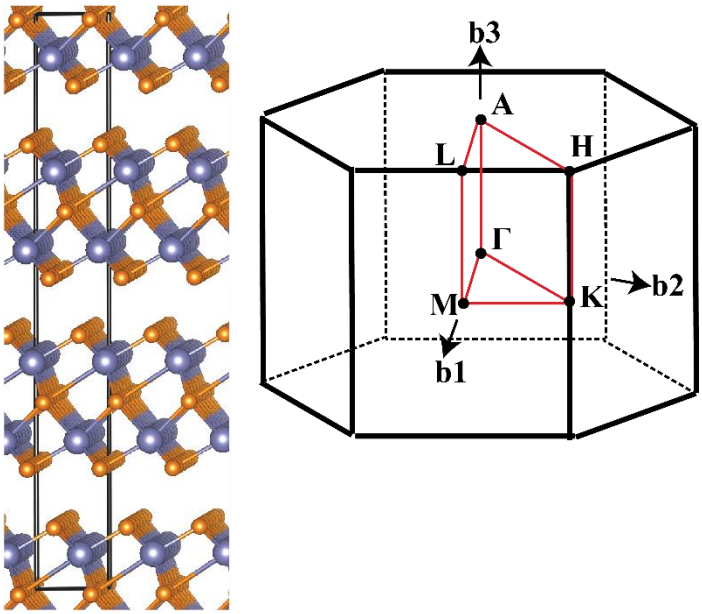


Supplementary Figure 6 | Linear polarized optical imaging. The sequential optical microscopy images of β'-In_2Se_3 pressurized at 1.9 GPa are obtained by using the linear polarized light along different directions. The white double arrow denotes the initial polarization direction. No domain contrast is observed in the images.

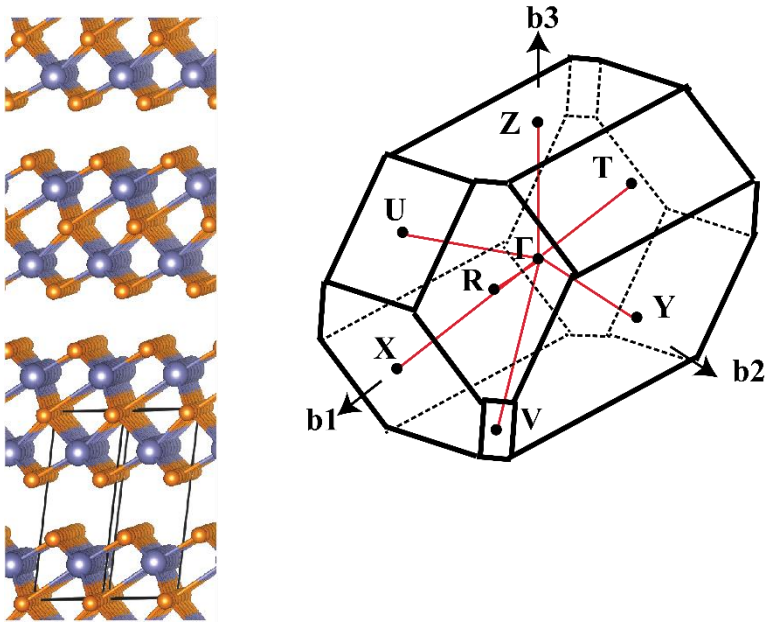


Supplementary Figure 7 | DFT calculations. a Relaxed structure at 0 GPa pressure. **b** Relaxed structure from 4 GPa pressure. **c** Hypothetical model where atomic

coordinates obtained at 0 GPa were set directly in the compressed lattice at 4GPa. **d** Hypothetical model based on 0 GPa model but with manually shifted Se atom to the 4GPa position. (Note that the structure is still β'-In_2Se_3, but the unit cell is defined using a monoclinic lattice. The unit cell and Brillouin zone can be found in Supplementary Figure 9.)



Supplementary Figure 8 The hexagonal unit cell of relaxed β'-In_2Se_3 (black lines on the left) and its Brillouin zone.



Supplementary Figure 9 The monoclinic unit cell of relaxed β'-In_2Se_3 (black lines on the left) and its Brillouin zone.

Supplementary Notes

Supplementary Note 1: Dynamic resistance measurement. The dynamic response of resistance under pressure was measured in a high-pressure dynamic measurement system, as shown in **Supplementary Figure 1**. In the experiments, the sample was compressed up to around 3 GPa at first. The data collecting process was starting in decompressing run repeating as decompressing → compressing → decompressing → compressing→ ⋯ and modulated by the periodic signals in a pressure range of 3 GPa to lower pressure.

Supplementary Note 2: Details of Hall measurement

The Hall coefficient (R_H) are measured using Van der Pauw Geometry as shown in **Supplementary Figure 2**. In order to exclude the contribution due to longitudinal misalignment voltage and thermoelectric effects, such as Nernst effect, the direction of applied field and current were reversed at each given temperature and field. The Hall voltage was then derived from the antisymmetric part of the transverse voltage.

Supplementary Note 3: Le Bail fitting and Birch-Murnaghan equation of state. The XRD data were analyzed by Le Bail refinement using the GSAS software. All the data at pressure up to 6.9 GPa can be well reproduced by the monoclinic structure with space group C2/m, as shown in **Supplementary Figure 3**. The volume V was fitted to the third-order Birch-Murnaghan equation of state(BM-EOS): $P = \frac{3}{2}K_0\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} -\right.$

$\left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right] \times \left\{1 + \frac{3}{4}(K_0' - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$, where K_0 and K' is the bulk modulus and first pressure derivative of the bulk modulus at zero pressure, respectively. V_0 is the volume at ambient pressure, and P is the pressure.

Supplementary Note 4: DFT calculations to check the dominating effect of middle Se atoms on band gap closure.

As the pressure goes from 0 GPa to 4 GPa, several things take place at the same time, which includes two primary structural changes: the contraction and the deformation of the lattice, and the motion of the middle Se atom. In the calculation, we can conveniently examine each individual effect by creating two hypothetical models shown in **Supplementary Figure 7c and 7d** without relaxation. **Supplementary Figure 7c** shows a model that uses the atomic coordinates obtained at 0 GPa into a 4 GPa lattice. This model only considers the effects of the lattice contraction and deformation. While **Supplementary Figure 7d** shows a model where only the central Se atom is shifted to the 4 GPa position while other atomic positions are kept the same as in a 0 GPa lattice. In this assumption we have only considered the effect of the shift of the central Se atom.

As seen from the band structure shown in **Supplementary Figure 7**, the contraction and deformation of the lattice brings the band gap to 0.97 eV (**Supplementary Figure 7c**), down from 1.2 eV in the 0 GPa scenario (**Supplementary Figure 7a**). In comparison, the shift of the middle Se atom exhibits a much more reduced band gap of

0.46 eV (**Supplementary Figure 7d**). These results clearly demonstrate that although both effects contribute to the bandgap reduction, the shift of the middle Se atom plays a dominating role.