Pressure induced metallization with absence of structural transition in layered molybdenum diselenide

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Layered transition-metal dichalcogenides have emerged as exciting material systems with atomically thin geometries and unique electronic properties. Pressure is a powerful tool for continuously tuning their crystal and electronic structures away from the pristine states. Here, we systematically investigated the pressurized behavior of MoSe2 up to ~60 GPa using multiple experimental techniques and ab-initio calculations. MoSe2 evolves from an anisotropic two-dimensional layered network to a three-dimensional structure without a structural transition, which is a complete contrast to MoS2. The role of the chalcogenide anions in stabilizing different layered patterns is underscored by our layer sliding calculations. MoSe2 possesses highly tunable transport properties under pressure, determined by the gradual narrowing of its band-gap followed by metallization. The continuous tuning of its electronic structure and band-gap in the range of visible light to infrared suggest possible energy-variable optoelectronics applications in pressurized transition-metal dichalcogenides.
Transition-metal dichalcogenides (TMDs) 2H-MX₂ (M = Mo, W, and etc, X = S, Se, and Te) have recently attracted intense scientific and engineering interest because of their ease of fabrication and unique electronic structure. TMDs have strong chemical bonding within each X-M-X trilayer and weak van der Waals (vdW) interaction between neighbor trilayers in their crystal structures. This quasi two-dimensional (2D) nature grants TMDs facile three-dimensional (3D) to 2D crossover through methods like exfoliation. Band structure engineering on TMDs allows ones to explore exotic condensed matter phenomena and develop many potential applications. For example, the modification of their band structures from indirect-band-gap to direct-band-gap provides insights into opto-electronics and valley electronics. So far, the electronic structure engineering of TMDs has mainly been achieved through the following experimental methods: (i) applying electrical field to control the spin splitting and freedom of electrons; (ii) utilizing quantum confinement with samples thinning down into monolayers of MX₂; and (iii) employing stress or strain by bending or stretching the thin films or employing substrates with different lattice constants, as suggested by calculations.

Compared with the three methods mentioned above, high pressure is a powerful way to induce dramatic changes in their crystal structures and electronic structures. This qualifies high pressure as a desirable approach to explore the tunability of TMDs. In particular, the ability to continuously tune the crystal and electronic structures away from the pristine states is crucial to a wide array of applications, e.g., electromechanical devices, energy-variable opto-electronics, and energy-variable photovoltaics. Various pressure-induced electronic evolutions such as semiconductor to metal transitions have been observed in different materials. However, many of these electronic transitions were accompanied by first-order structural transitions. A pressure-induced first-order structural transition, by definition, involves a discontinuous change in the volume (of the unit cell). And the corresponding discontinuity in its electronic structure could limit the energy tunability for potential opto-electronic or photovoltaic applications. To overcome this challenge, we need to discover TMDs with continuous structural and electronic response.

Previous high pressure studies on MoS₂ clearly demonstrated that a first-order structural transition (2Hc-MoS₂ to 2Ha-MoS₂) occurred close to metallization. This transition may relate to the vdW interactions in between neighbor S-Mo-S trilayers. To prevent the 2Hc to 2Ha transition, the substitution of chalcogenide anions in MoS₂ is a potential route. Because Se₂⁻ has broader electron orbitals than S₂⁻’s that lead to stronger interlayer interactions, MoSe₂ may have totally different high pressure behavior. Experimentally, the structural and electronic behavior of compressed MoSe₂ remains to be fully explored. Interestingly, recent calculations have predicted that MoSe₂ metallizes between 28 to 40 GPa while preserving the 2Hc structure.

In our work, high pressure up to ~60 GPa was generated by a diamond anvil cell (DAC). X-ray diffraction (XRD) data and Raman spectra data indicate that MoSe₂ preserves the 2Hc structure without any structural transition. Ab-initio calculations for modeling the layer sliding process are presented to understand the contrasting behavior between MoSe₂ and MoTe₂, and further predict the structural stability of MoTe₂. Infrared (IR) spectra data and temperature-dependent electrical resistivity data demonstrate the highly tunable transport properties of MoSe₂. Electronically, both experiments and calculations show that pressure strongly modulates its band structure from semiconductor to metallic.

**Results**

**XRD and Raman spectroscopy.** The experimental set-up of the DAC is shown in Fig. 1a. Under compression, all XRD peaks for MoSe₂ continuously shift to larger 20 (smaller d-spacing) and no new peak is observed (Supplementary Fig. 1 and Supplementary Note 1). Decompression of the sample shows the shifts of all peaks are reversible. All patterns are consistent with the 2Hc structure and representative Rietveld refinements are shown in Supplementary Fig. 2 and Supplementary Table 1. The absence of a first-order structural transition is further supported by equation of state (EOS) data in Fig. 1b and normalized cell parameters versus pressure data in Fig. 1c, as neither of them exhibits any discontinuity. To fit the pressure-volume relation, a third-order Birch-Murnaghan (BM) EOS is employed. With unit-cell volume V₀ fixed at the experimental value of 120.8 Å³, the fitting yields a bulk modulus B₀ = 62(1) GPa and a derivative of bulk modulus B’ = 5.6(1). The relatively large value of B’ suggests a strong change of volume compressibility under pressure.

At ambient conditions, the structure of 2Hc-MoSe₂ features the X-M-X triple layers linked via vdW forces (Fig. 2a,b). During the initial compression, cell parameter c reduces by 10 and ~15% respectively. The gradual closure of the vdW gap is suggested by tracking the ratio of Se-Mo layer distance to Se-Se layer distance, where it drops fast at low pressure but decreases much slower at high pressure (Supplementary Fig. 3). In addition, we measured the Raman spectra under pressure (Supplementary Fig. 4 and Supplementary Note 2). See Fig. 1d, the vibrational modes A₁g and E₂g and the spacing between them shift successively under pressure. These observations indicate that the crystal structure of MoSe₂ continuously evolves from a quasi 2D structure to an isotropic 3D one without a structural transition.

**Structural calculations.** Our XRD and Raman results appear to be surprising—At ambient conditions, MoS₂ and MoSe₂ are iso-structural in crystal structures and possess highly similar electronic structures, and it is therefore natural to assume that the 2Hc to 2Ha transition would also occur in MoSe₂. Nonetheless, 2Ha structure does not fit the XRD patterns of MoSe₂ in the entire pressure region studied in this work. Though bearing highly similar Mo-Se chemical environments and the same space group (P6₃/mmc), 2Ha structure and 2Hc structure have distinct structural topologies. In 2Hc structure Mo occupies a 2b Wyckoff position while in 2Ha structure it occupies a 2c Wyckoff position. Also, the two adjacent units of X-Mo-X triple layers have contrasting stacking patterns in 2Hc and 2Ha (shown in Fig. 2a-d). To seek theoretical support of the structural stability of 2Hc-MoSe₂, we performed two sets of ab-initio calculations. We first confirmed that 2Hc-MoSe₂ is more stable than 2Ha-MoSe₂ based on the experimental unit cell at the highest pressure ~60 GPa. This is consistent with recent calculations showing the enthalpy difference between 2Ha and 2Hc of MoSe₂ keeps increasing from ambient pressure up to at least 130 GPa. We then calculated the cell parameters at different volumes based on 2Hc-MoSe₂ and the results agree well with our experimental data (Supplementary Fig. 5 and Supplementary Note 3). Note that the small discrepancy at low pressure comes from the limitations of ab-initio calculations in describing the vdW interaction.

In order to understand the contrasting structural behavior between MoS₂ and MoSe₂, we further carried out layer sliding simulations for MoS₂, MoSe₂, and MoTe₂ at ~20 GPa. The side...
and top views of 2Hc-type and 2Ha-type structures are shown in Fig. 2a–d. The transition from 2Hc to 2Ha can be realized by systematically shifting half of the atoms (one unit of X-Mo-X triple layers) in a unit cell. As illustrated in Fig. 2a, we defined one sliding path by the red arrows for this transition. For MoS2, the unit-cell volume is fixed at the experimental value at 20 GPa. After initial relaxation of the atomic positions within the 2Hc-type structure, the S-Mo-S layer distances are fixed during the layer sliding. The same procedures were performed on MoSe2 under 23 GPa (our experimental data) and MoTe2 under 20 GPa (based on previous theoretical data). The total energies of 2Hc structures are set to be zero as references, marked by a broken line. For MoS2, the unit cell volume was fixed at experimental data under 20 GPa. After electronic relaxation of the atomic positions, the S-Mo-S layer distance of structure was set to be a constant during the layer sliding. The same procedures were performed on MoSe2 under 23 GPa (our experimental data) and MoTe2 under 20 GPa (theoretical data).

Figure 1 | Experimental set up and structural and vibrational responses under pressure. (a) Schematic of the high pressure DAC set up. (b) Pressure-volume data from XRD measurement and the curve represents a third-order BM-EOS fitting. (c) Normalized cell parameters a/a0 and c/c0 versus pressure. The error bars given by EXPGUI-GSAS are smaller than the size of the markers. (d) Evolution of vibrational modes A1g and E2g and their difference (E2g – A1g) under pressure, measured by Raman spectroscopy.

Figure 2 | Structural details of 2Hc – and 2Ha – MoX2 and layer sliding calculations. (a) The side view (projected on ab plane) of 2Hc structure in MoS2, MoSe2, and MoTe2. X represents S, Se and Te. The red arrows represent one sliding path for the 2Hc to 2Ha transition, where one unit of X-Mo-X triple layers (marked by a blue box) shifts systematically in ab plane. (b) The top view (projected on ab plane) of 2Hc structure. (c) The top view of 2Hc structure. (e) The total energy of MoS2, MoSe2, and MoTe2 as a function of relative sliding from 2Hc to 2Ha. The total energies of 2Hc structures are set to be zero as references, marked by a broken line. For MoS2, the unit cell volume was fixed at experimental data under 20 GPa. After electronic relaxation of the atomic positions, the S-Mo-S layer distance of structure was set to be a constant during the layer sliding. The same procedures were performed on MoSe2 under 23 GPa (our experimental data) and MoTe2 under 20 GPa (theoretical data).
barrier in order to undergo the 2Hc to 2Ha transition. The maximum energy barrier is $\sim 0.3$ eV for MoSe2 and $\sim 0.5$ eV for MoTe2, which are significantly higher than $\sim 0.15$ eV for MoS2. More importantly, 2Hc-MoSe2 and 2Hc-MoTe2 bear higher energies than the initial 2Hc structures, which would make this transition unfavorable. However, in the case of MoSe2, the 2Ha structure becomes energetically favorable. Note that the X-Mo-X layer distance is fixed in this set of calculations. Realistically in compressed MoS2, the S-Mo-S distance and unit cell volume drop significantly higher than during the 2Hc to 2Ha transition32–35, which allows the total change in enthalpy to be continuous at zero temperature.

**IR spectroscopy.** The lattice response of MoSe2 at high pressure will inevitably change its electronic structure, and thus its optical properties which strongly depend on the electronic structure. Our data shows that MoSe2 undergoes a large electronic evolution where band-gap narrowing is followed by metallization of MoSe2. Fig. 3 shows the measured synchrotron IR spectra and its analysis (details are shown in Supplementary Note 4). Below 16.3 GPa, the transmittance spectra (Fig. 3a) look similar, where a transmission window extends from 0.06 to 1.0 eV. At pressure above 20.2 GPa, the 0.3–1.0 eV region develops into a tilted curve and keeps collapsing into lower energy region, indicating the band-gap’s narrowing. At above 40.7 GPa to the highest pressure, nearly zero transmission is observed in between 0.15 to 1.0 eV, suggesting the metallization of MoSe2. Another way to interpret the IR data is from the viewpoint of the optical density (OD) $A_\lambda$, (see Supplementary Fig. 6 for the plot of OD versus energy). OD or $A_\lambda$ is defined as $-\log(T)$ (T as the transmittance). It can be easily seen from the energy-pressure-OD map in Fig. 3b that a clear changeover of low OD (in semiconducting state) to high OD (in metallic state) occurs between 20 to 35 GPa.

For an indirect-band-gap semiconductor, the absorption coefficient is proportional to the square of the energy difference of the photon energy and band-gap$^{43}$. Using this empirical model for semiconductors, we obtained the indirect-band-gap $E_g$ via linear extrapolations of $(h\nu A_\lambda)^{1/2}$ where $h\nu$ is the photon energy. A representative extrapolation is shown in Supplementary Fig. 7. The fitted $E_g$ value at 20.2 GPa is 0.4 eV. From 20.2 to 35.1 GPa, $E_g$ keeps decreasing (see Fig. 3c). From 40.7 GPa to the highest pressure, $E_g$ is nominally zero. We notice that the trend of band-gap decrease at below 41 GPa could not be well described by a linear fitting. The non-linearity is also shown in previous calculations on band-gap’s dependence on applied strain$^{23}$. The lack of data points and inaccuracies in optical measurement prevent us from determining the best function for the band-gap – pressure relation. However, as a simple approach to guide eyes, we fit the data with a parabolic curve, which yields $E_g = -0.08(2)P + 0.0010(3)P^2$, indirect-band-gap ($E_g$) in unit of eV and pressure ($P$) in unit of GPa. The extrapolated band-gap at ambient pressure is 1.6(3) eV, which is in good agreement with previous reports$^{18,44,45}$.

**Electrical resistivity.** We also measured the temperature-dependent resistivity up to 42 GPa (Supplementary Note 5 and Supplementary Fig. 8). At low pressures (Fig. 4a), the temperature ($T$) – resistivity ($\rho$) curves at below 23.4 GPa exhibit negative $d\rho/dT$ throughout all temperatures, indicating the presence of a semiconducting state. From 27.0 to 37.0 GPa, the high-temperature region shows positive $d\rho/dT$ whereas the low-temperature region has negative $d\rho/dT$ (see Fig. 4b). At above 41.0 GPa, positive $d\rho/dT$ is observed in all temperatures, implying the metallization of MoSe2. A comparison of our room temperature resistivity data on MoSe2 (Fig. 4c) with previous data on MoS2 shows that there are dissimilar trends in between them$^{34,35}$. For MoS2, the room temperature resistivity dropped strongly at below 15 GPa and then reached a plateau at higher pressure$^{34,35}$, which was related to a first-order structural transition. In sharp contrast, for MoSe2, the decrease of its room temperature resistivity is nearly exponential, fit by log ($\rho$) = 1.9(1)–0.134(5) $P$, resistivity ($\rho$) in unit of $\Omega$ cm$^{-1}$.

**Figure 3 | IR transmittance spectra and analysis.** (a) Representative IR transmittance spectra at high pressures, numbers show pressures in unit of GPa. The 0.23–0.28 eV region is obscured by diamond phonon absorptions from the DAC. (b) Pressure – energy – optical density (OD) contour, OD is defined as $-\log(T)$ while $T$ is the transmittance. (c) Evolution of band gap under pressure. Circles are extrapolated indirect band gaps and the curve shows a parabolic fit of the band gap versus pressure. The band gap closure is observed at $\sim 40$ GPa.
and pressure (P) in unit of GPa. Pressure allows the room temperature electrical resistivity of MoSe₂ to decrease more than six orders of magnitude from ambient to 41.6 GPa.

**Electronic structure.** To better understand the electronic evolution of MoSe₂ that determines its highly tunable optical and electrical transport properties, we performed *ab-initio* calculations on the electronic structure of MoSe₂ at four representative pressures. The results undoubtedly demonstrate the pressure-induced band-gap narrowing and metallization. At ambient pressure, seen from Fig. 5a, the band structure is consistent with previous results. It has a direct-band-gap $E_{K,K}$ (~1.8 eV) at K and an indirect-band-gap (~1.3 eV) that locates in between $\Gamma$ and $\Gamma$-$K$ conduction band (CB) valley. The bottom of CB between $\Gamma$ and $K$ mainly originates from the Mo $d_{xy}$ and $d_{x^2-y^2}$ orbitals, and the top of valence bands (VBs) at $\Gamma$ comes from the Mo $d_{z^2}$ orbital. Meanwhile, the $d_{xz}$ and $d_{yz}$ dominated CBs are further from the Fermi-level ($E_F$). Higher pressure results in a strong decrease of its indirect-band-gap and induces large movements of the orbitals towards the $E_F$. At 23 GPa, shown in Fig. 5b, the indirect-band-gap becomes as small as 0.5 eV. Albert decreasing, the direct-band-gaps remain at large values, e.g., $E_{K,K}$ is ~1.4 eV. Remarkably, pressure allows the $d_{xz}$ and $d_{yz}$ orbitals to gain more overlap with Se $p$ orbitals and thus largely widen their band dispersions. In comparison, the $d_{xy}$ and $d_{x^2-y^2}$ orbitals are less impacted due to smaller overlap with Se $p$ orbitals. As a consequence (see Supplementary Note 6), one $d_{xz}$ and $d_{yz}$ dominated CB quickly goes down at K point and forms two CB valley minimum together with the previous $d_{xy}$ and $d_{x^2-y^2}$ dominated CB.

Metallic band structures are obtained by further increasing the pressure. For example, seen from Fig. 5c at 41 GPa, there lies density of states across the $E_F$. The $d_{xy}$ and $d_{x^2-y^2}$ dominated CB valley minimum crosses below the $E_F$, while the other CB valley minimum is still slightly above the $E_F$ (see Supplementary Fig. 9). At 58 GPa, shown by Fig. 5d, both CB valley minima cross below the $E_F$. It is worth mentioning that even at as high as 58 GPa, the 'indirect' feature of the band structure is still well maintained: although the CBs and VBs overlap in energy range, no direct cross is seen. To be specific, the energy separation at $K$ is as large as ~0.6 eV. Meanwhile, the relative shifts of CBs and VBs generate a number of hole pockets (e.g., at $\Gamma$ and A) and electron pockets (e.g., at K). These pockets may largely affect the low-temperature electrical and optical transport properties of MoSe₂.

**Discussions**

Our experiments and calculations clearly demonstrate the absence of structural transition in MoSe₂. One empirical understanding of the contrasting behavior in MoS₂ and MoSe₂ involves the different localizations of $p$ orbitals among chalcogenide anions $S^{2-}$, $Se^{2-}$, and $Te^{2-}$. The $3p$ orbitals of $S^{2-}$ dominate the electronic structure in MoS₂ while the $4p$ and $5p$ orbitals are primary for MoSe₂ and MoTe₂ correspondingly. $4p$ and $5p$ orbitals are much more delocalized than $3p$ orbitals, which would give rise to strong interaction within the vdW gaps of MoSe₂ and MoTe₂ to prevent this sliding process, vice versa for MoS₂. We can safely conclude that it is easier for 2H c-MoS₂ to experience a structural transition through sliding in between neighbor S-Mo-S layers, but this does not apply to MoSe₂ or MoTe₂. Beside from the effects of chalcogenides anions, the effects of transition metal cation should also be considered in determining the stabilities of layered structures. For example, recent calculations proposed that the interlayer Mo-Mo $d$-electron propagation should be considered in determining the stability of layered structures. More importantly, size effect of different transition metal cations is also expected to change the interlayer interactions. Previous studies on WS₂ and WSe₂ showed that they experience continuous lattice contractions.
under pressure. W^{2+} has broader electron orbitals and may introduce stronger interlayer interactions than Mo^{2+}, which results in the absence of layer sliding in WS_{2}. In a more general perspective, stronger interlayer interactions help stabilize the structures of TMDs and are more likely to yield continuous lattice response under extreme environments such as pressure.

Previous studies have reported many electronic transitions such as insulator to metal or semiconductor to metal transitions in the group of binary chalcogenides, see for example, Bi_{2}X_{3}, Sb_{2}X_{3}, and Ag_{2}X. For structures starting with vdW gaps at ambient conditions, the closure of their vdW gaps is generally accompanied or followed by first-order structural transitions where large structural re-constructions or atomic movements take place. However, in the case of MoSe_{2}, the metatllization process does not involve any sudden change in the crystal structure, which allows its electronic structure to be continuously tuned. Through multiple experimental techniques combined with ab-initio calculations, we demonstrate that the band-gap of MoSe_{2} is robustly conserved with the appearance of two conduction band minima. This highlights pressure's dramatic role in tuning the electronic properties of TMDs. Our layer sliding calculations highlight the role of the chalcogenide anions in stabilizing either structural change under pressure. Our layer sliding calculations show that the band-gap of MoSe_{2} in ambient pressure is a strong function of pressure.

In conclusion, we comprehensively studied the high pressure behavior of MoSe_{2} up to \sim 60 GPa through a series of structural, vibrational, optical, and electrical measurements combined with ab-initio calculations. 2H_{c}-MoSe_{2} evolves from an anisotropic 2D layered structure to an isotropic 3D one without any sudden structural change under pressure. Our layer sliding calculations highlight the role of the chalcogenide anions in stabilizing either 2H_{c} or 2H_{a} layered structures. Electronically, MoSe_{2} undergoes a semiconductor to metal transition, and correspondingly exhibits highly tunable optical and electrical properties. Upon compression, the ‘indirect’ feature of its electronic structure is robustly conserved with the appearance of two conduction band minima. The large and continuous tuning of its electronic structure may have potential applications in energy-variable (visible to IR) optoelectronics and photovoltaics.

Methods

Sample growth. High quality stoichiometric MoSe_{2} single crystals were grown by direct vapor transport technique. Elemental Mo and Se (99.9% purity, purchased from Koch Light Ltd.) of the stoichiometric ratio were sealed in a quartz ampoule at pressure better than 10^{-7} Torr. The ampoule was placed in a two-zone horizontal furnace where the temperatures were slowly raised from room temperature to 1.060 and 1.080 °C for growth zone and source zone respectively. This temperature gradient was then maintained for \sim 188 h to produce single crystal platelets of MoSe_{2}. The shiny and gray crystals have a typical thickness of \sim 4 \mu m and area of \sim 3 mm \times 3 mm. The purity and homogeneity are checked by electron microprobe analysis.

High pressure experiments. Single crystals of MoSe_{2} were used for the high pressure IR, Raman, and resistivity measurements. Powders of MoSe_{2} were grounded from single crystals for the high pressure XRD measurements. Ruby spheres were used for determining pressure for all experiments. Neon was used as the pressure transmitting medium for the XRD and Raman experiments. Angle dispersive XRD experiments were performed at beamline 16-BMD of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The Rietveld fitting was performed using GSAS-EXPGUI package. The Raman spectra were collected.
using a Renishaw inVia micro Raman system with a 514 nm laser excitation line. High-pressure IR measurements were conducted at beamline U2A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). A MoSe₂ single crystal was sandwiched between the pressure transmitting medium (KBr) and one side of the cuvet. Infrared measurements were performed on a Bruker Vertex 80v FT-IR spectrometer coupled to a Hyperion-2000 microscope with a MCT mid-band detector. Fringes in raw IR data were removed by filtering high frequency terms after Fourier transformation. For temperature-dependent four-probe resistivity measurement, cubic BN was used as the insulating layer, and four electrodes were cut from Pt foils. The temperature-dependent sheet resistance of the sample was measured with Van der Paul geometry by cooling down to 10 K in a liquid helium cryostat. Pressures were measured at room temperature. More details are described in the supplementary information.

**Ab-initio calculations.** The Vienna ab-initio Simulation Package (VASP) was employed to optimize crystal structures and calculate electronic structures with the framework of local density approximation density functional theory. The projector augmented wave (PAW) pseudo-potential was used and the kinetic energy cutoff was fixed to 450 eV for all the calculations. For structural calculations in comparison with experiments, the unit cell volume is fixed while the cell parameters and atomic positions are fully relaxed. For band structure calculations, the lattice constants were fixed to be experimental values, and then the atomic positions are fully relaxed. HSE06 hybrid function was employed to improve the band structure calculations.

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Additional information
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