Structural evolution and phase transition mechanism of MoSe$_2$ under high pressure

Yifeng Xiao$^1$, Shi He$^1$, Mo Li$^2$, Weiguo Sun$^3$, Zhichao Wu$^{4*}$, Wei Dai$^{5*}$ & Cheng Lu$^{6*}$

MoSe$_2$ is a layered transition-metal dichalcogenide (TMD) with outstanding electronic and optical properties, which is widely used in field-effect transistor (FET). Here the structural evolution and phase transition of MoSe$_2$ under high pressure are systematically studied by CALYPSO structural search method and first-principles calculations. The structural evolutions of MoSe$_2$ show that the ground state structure under ambient pressure is the experimentally observed $P6_3/mmc$ phase, which transfers to $R3m$ phase at 1.9 GPa. The trigonal $R3m$ phase of MoSe$_2$ is stable up to 72.1 GPa, then it transforms into a new $P6_3/mmc$ phase with different atomic coordinates of Se atoms. This phase is extremely robust under ultrahigh pressure and finally changes to another trigonal $R-3m$ phase under 491.1 GPa. The elastic constants and phonon dispersion curves indicate that the ambient pressure phase and three new high-pressure phases are all stable. The electronic band structure and projected density of states analyses reveal a pressure induced semiconducting to metallic transition under 72.1 GPa. These results offer a detailed structural evolution and phase diagram of MoSe$_2$ under high pressure, which may also provide insights for exploration other TMDs under ultrahigh pressure.

Most transition-metal dichalcogenides (TMDs) are layered compounds, which contain insulators, semiconductors and metals, in which, some of them are superconductors. The molecular formulas of TMDs are MX$_2$, where M is the transition metals, such as W, Mo, Nb, Ta, Ti and others, X is the chalcogen, such as S, Se, Te and so on$^{1-6}$. Up to now, the ground state structures of TMDs under ambient conditions are extensively studied. According to the number of stacked layers, the possible structures of TMDs can be classified into 1T phase with trigonal antiprismatic, 2H phase with trigonal prismatic, 3R phase with trigonal prismatic, etc, which have many stacking patterns in common. Generally, the weak van der Waals force connect layers of TMDs and allow the atom/molecules to enter the interlayers and change their electronic properties$^{7,8}$. On the other hand, pressure can also cause the change of interlayer spacing and the interlayer slip, and lead to the varied structure and electronic properties of different TMDs$^{9,10}$.

MoSe$_2$ is a typical TMD with hexagonal phase stable structure at ambient conditions$^{11,12}$. It is an indirect bandgap semiconductor, with bandgap of about 1 eV. However, there is a very few structural evolutions of MoSe$_2$ under high pressure. In contrast, the structural phase transitions of MoS$_2$ under high pressure are extensively studied. Saha$^{11}$ et al. has carried out the first-principles calculations of MoS$_2$ under high pressure and confirmed the stable high-pressure phases in the pressure range of 100 GPa to 200 GPa, which are $P4/mmm$ and $I4/mmm$ structures. Kohulák et al.$^{12}$ has reported that MoS$_2$ transformed from semiconductor to metallic at 40 GPa. However, the interesting subject needs further attentions is that in the similar compound, whether MoSe$_2$ exists the similar pressure induced semiconductor to metal transition.

In the present paper, we focus on the structural transition and electronic properties of MoSe$_2$ under high pressure by using the structure search method and first-principles calculations. Our results show that MoSe$_2$ transfers from $P6_3/mmc$ structure to $R3m$ phase at 1.9 GPa, which is stable up to 72.1 GPa. Interestingly, as the pressure increase, MoSe$_2$ again transfers from $R3m$ phase to $P6_3/mmc$, however, it is metallic, which is different from the semiconducting $P6_3/mmc$ phase under ambient pressure. These results are different from the previous experiments showed that MoSe$_2$ is mostly stable as 2Hc phase below 100 GPa$^{11,12}$. This contradiction leads us...
to further explore the new phases and structural transition sequence of MoSe₂ under high pressure, especially at ultrahigh pressure.

Theoretical methods
We have conducted a systematical structure search for MoSe₂ under high pressure based on Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) approach and first-principles calculations. The advantages of these techniques are to predict the stable and metastable structures at the given chemical compositions within certain condition. The total energies and electronic properties are calculated within the density functional theory (DFT) framework, as it has implemented by Vienna ab initio simulation package (VASP) code. The projector augmented wave (PAW) method has employed in the DFT calculations to describe electron–ion interactions in MoSe₂. The 4d⁹, 5s¹ and 4s², 4p⁴ are treated as the valence electrons for Mo and Se atoms, respectively. We set the cutoff energy of 600 eV for the wave-function to expand plane waves and select dense Monkhorst–Pack k meshes to ensure all enthalpy calculations are converged in 1 meV/atom. The phonopy code has used to calculate the phonon dispersion curves using 2×2×1 supercells for P6₃/mmc, R3m, and R-3m phases of MoSe₂. Based on the ground state structures of MoSe₂ under different pressure, the energy band structure, density of states, and elastic properties are also calculated and discussed in detail.

Results and discussion
We have predicated about 1000 potential structures for MoSe₂ at each selected pressure. The top 100 candidate structures of MoSe₂ under 0 GPa, 50 GPa, 100 GPa, 200 GPa, and 500 GPa are reoptimized by high accuracy calculations. We have successfully identified the experiment observed P6₃/mmc (2H) phase under ambient pressure, which verifies that the CALYPSO method is perfectly suitable for MoSe₂ and the searched results are reliable. It can be seen from Fig. 1a that the enthalpies of R3m and P6₃/mmc phases are almost the same when the pressure increase from 0 to 100 GPa. Interestingly, some potential low energy phases at low-pressure range are all layered structures. Thus, we have considered the van der Waals (VDW) interactions in the DFT calculations under low-pressure between 0 to 10 GPa. From Fig. 1b, we can clearly find that the energy of P6₃/mmc phase is lower than that of R3m phase at 0 GPa to 1.9 GPa, and the energy of R3m phase is lower than that of P6₃/mmc phase with pressure ranged of 1.9 GPa to 72.1 GPa. In fact, the transform pressure of MoSe₂ from R3m phase to P6₃/mmc phase is about 2.5 GPa by without considering the VDW interactions, which maybe due to that the Mo and Se atoms are relatively heavy and the influences of VDW interactions on the energy calculations of MoSe₂ are negligible. When the pressure is higher than 72.1 GPa, a new P6₃/mmc phase is uncovered, which is different from the initial P6₃/mmc phase. The main differences are the crystal lattice parameters and atomic coordinates of Se atoms. It is extremely robust under ultrahigh pressure and final changes to the trigonal R-3m phase under 491.1 GPa. The structural phase transition of MoSe₂ under ultrahigh pressure is shown in Fig. 1c. The corresponding crystal structures of MoSe₂ under high pressure up to 500 GPa are shown in Fig. 2. To further prove the structural stability of MoSe₂, we have calculated the formation energies of possible phases and considered the potential energy decomposition to bulk Se and Mo crystals and relevant Mo–Se compounds. The calculations once again indicate that MoSe₂ is stable. The detailed results are shown in Fig. S1 in the Supplementary Information.

From Fig. 2, we can find that the unit cell of P6₃/mmc is stacked repeatedly with a period of two MoSe₆ layers, while cells of R3m and R-3m are stacked repeatedly with a period of three MoSe₆ layers. The optimized lattice parameters and atomic coordinates of the four phases are listed in Table 1.

We now test the chemical, dynamical, and mechanical stabilities of MoSe₂. The cohesive energy of MoSe₂ can be calculated by the formula following:

\[ E_{coh} = \frac{xE_{Mo} + yE_{Se} - E_{Mo,Se}}{x + y}, \]  

(1)
where $E_{Mo}$, $E_{Se}$, and $E_{MoSe_2}$ are the energies of Mo atom, Se atom, and a unit cell of MoSe$_2$, respectively. The cohesive energies of the four candidate of MoSe$_2$ (0 GPa P6$_3$/mmc, 20 GPa R3m, 80 GPa P6$_3$/mmc and 500 GPa R-3m) are $-13.49$, $-13.29$, $-1.83$, and $-5.29$ eV per atom, respectively. These results indicate that the bulk MoSe$_2$ is strongly bonded with good chemical stability. Subsequently, we have calculated the phonon dispersion curves of four structures of MoSe$_2$ within different pressures. The results are displayed in Fig. 3. There is no presence of imaginary frequency in the Brillouin zone, which indicates that these four phases of MoSe$_2$ are dynamically stable.

Meanwhile, we have calculated the elastic constants of the four phases of MoSe$_2$ under different pressures, which are P6$_3$/mmc phase at 0 GPa, R3m phase at 20 GPa, P6$_3$/mmc phase at 80 GPa, and R-3m phase at 500 GPa. The elastic constants are listed in Table 2. The stability criteria of hexagonal and trigonal crystal structure are $C_{11} > |C_{12}|$, $(C_{11} + C_{12}) > 2C_{13}^2$, $(C_{11} - C_{12})C_{44} > 2C_{14}^2$ for trigonal crystal and $C_{11} > 0$, $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11} + C_{12}) > 2C_{13}^2$ for hexagonal crystal. According to the above criteria, we note that the calculated elastic constants match well with the stability criteria in corresponding space group symmetries. Thus, we can conclude that these four phases of MoSe$_2$ are mechanically stable.

To deeply understand of the effect of pressure on the electronic properties, the evolution of electronic band structure and density of states of the four phases of MoSe$_2$ are shown in Fig. 4. At 0 GPa, the ground state structure is P6$_3$/mmc phase. It can be seen from Fig. 4a, the P6$_3$/mmc phase is a direct bandgap semiconductor with bandgap of 1.22 eV. With pressure increasing, the bandgap is slowly decreasing. At 1.9 GPa, the structure P6$_3$/mmc transforms to R3m phase, which is an indirect bandgap semiconductor. The bandgap is 0.154 eV under 20 GPa (see Fig. 4b). From 20 to 500 GPa, MoSe$_2$ becomes to a metal as shown in Fig. 4c.d.

The detailed total and partial density of states are calculated (see Supplementary Information, Fig. S3). The states above $-5.5$ eV in P6$_3$/mmc phase at 0 GPa, $-7.5$ eV in R3m phase at 20 GPa, and $-10$ eV in P6$_3$/mmc at 80 GPa are mostly originated from Mo-$d$ and Se-$p$ orbitals. The Mo-$d$ and Se-$p$ orbitals show strong $p-d$ hybridization and indicate obviously covalent bonding characteristics of Mo–Se chemical bond. In P6$_3$/mmc phase, the orbitals have more overlapping at 80 GPa than 20 GPa, which proves that covalent properties of Mo–Se bond is strengthened by increasing the pressure. In Fig. S3d, we can see a noticeable peak at $-12$ eV in the density of states of R-3m phase at 500 GPa, which are mainly contributed by the $p$ orbitals of Mo atoms. Furthermore,
Table 2. The calculated elastic constants of MoSe₂.

| Pressure (GPa) | Structure   | C₁₁ (GPa) | C₁₂ (GPa) | C₁₃ (GPa) | C₁₄ (GPa) |
|---------------|-------------|-----------|-----------|-----------|-----------|
| 0             | P₆₃/mmc     | 173       | 57        | 118       | 58        |
| 20            | R₃m         | 267       | 70        | 194       | 100       |
| 80            | P₆₃/mmc     | 501       | 145       | 678       | 180       |
| 500           | R-3m        | 1659      | 826       | 2171      | 417       |

Figure 3. The phonon dispersion curves of MoSe₂. (a) P₆₃/mmc under 0 GPa, (b) R₃m under 20 GPa, (c) P₆₃/mmc under 80 GPa, and (d) R-3m under 500 GPa, respectively.

Figure 4. Band structure and projected density of states of MoSe₂. (a) P₆₃/mmc phase at 0 GPa, (b) R₃m phase at 20 GPa, (c) P₆₃/mmc phase at 80 GPa, and (d) R-3m phase at 500 GPa, respectively.
except for Mo-\(d\) and Se-\(p\) orbitals, the contributions from Mo-\(p\) orbitals are visibly increased compared with low pressure conditions. This may due to the firmer structural phase diagram of and the central symmetric transformation occurs again on the top two shown in the red square of Fig. 5. In the third step, the structure evolution of different from the previous two steps. The structural transformation happens at the middle layers of the GPa, 1

\[ R_3 \]

\[ 0 \text{ GPa to 500 GPa.} \]

\[ (a) \]

\[ \text{with the same atomic number of Mo and Se stoms by using the supercell of 1} \]

\[ 3 \times \]

\[ \text{supercell for P6}_3/mmc \]

\[ \text{phase at 20 GPa, (c) 1} \times \]

\[ 1 \times \]

\[ 3 \text{ supercell for P6}_3/mmc \]

\[ \text{at 80 GPa, and (d) 1} \times \]

\[ 1 \times \]

\[ 2 \text{ supercell for R-3m phase at 500 GPa, respectively.} \]

\[ \text{Figure 5.} \]

\[ \text{The schematic diagram of four phases of MoSe}_2 \]

\[ \text{under different pressures in the pressure range of} \]

\[ 0 \text{ GPa to 500 GPa. (a) 1} \times \]

\[ 1 \times \]

\[ 3 \text{ supercell for P6}_3/mmc \]

\[ \text{phase at 0 GPa, (b) 1} \times \]

\[ 1 \times \]

\[ 2 \text{ supercell for R3m phase at} \]

\[ 20 \text{ GPa, (c) 1} \times \]

\[ 1 \times \]

\[ 3 \text{ supercell for P6}_3/mmc \]

\[ \text{at 80 GPa, and (d) 1} \times \]

\[ 1 \times \]

\[ 2 \text{ supercell for R-3m phase at 500 GPa, respectively.} \]

\[ \text{We return again to search the potential structural phase transition mechanisms of MoSe}_2 \]

\[ \text{under high pressure. To clearly compare the four phases of MoSe}_2 \]

\[ \text{under different pressure, we have displayed the crystal structure with the same atomic number of Mo and Se stoms by using the supercell of 1} \times \]

\[ 1 \times \]

\[ 3 \text{ for P6}_3/mmc \]

\[ \text{phase at 0} \]

\[ \text{GPa, 1} \times \]

\[ 1 \times \]

\[ 2 \text{ for R3m phase at 20 GPa, 1} \times \]

\[ 1 \times \]

\[ 3 \text{ for P6}_3/mmc \]

\[ \text{phase at 80 GPa, and 1} \times \]

\[ 1 \times \]

\[ 2 \text{ for R-3m phase at 500 GPa, respectively. The schematic diagrams are shown in Fig. 5.} \]

\[ \text{From Fig. 5, we find that the structural phase transitions of MoSe}_2 \]

\[ \text{under high pressure are attributed to the chiral structure transitions of the top two MoSe}_2 \]

\[ \text{layers marked in red rectangles and the middle two MoSe}_6 \]

\[ \text{layers displayed in blue rectangles. The evolution of phase transitions is constituted by three steps. In the first step, three-unit cells of P6}_3/mmc \]

\[ \text{phase translate into two R3m unit cell at 1.9 GPa. The main changes occur at the top two MoSe}_2 \]

\[ \text{layers in P6}_3/mmc \]

\[ \text{and R3m phases, which is a chiral transform of the two MoSe}_2 \]

\[ \text{layers with mirror symmetry. In the second step, the two-unit cells of R3m phase return to three P6}_3/mmc \]

\[ \text{unit cells, and the central symmetric transformation occurs again on the top two MoSe}_2 \]

\[ \text{layers. However, the interlayer spacing of the top two MoSe}_2 \]

\[ \text{layers decreases from 4.28 to 2.67 Å as pressure increasing from 0 to 80 GPa, as shown in the red square of Fig. 5. In the third step, the structure evolution of MoSe}_2 \]

\[ \text{under ultrahigh pressure is different from the previous two steps. The structural transformation happens at the middle layers of the MoSe}_6 \]

\[ \text{as shown in the blue rectangles of Fig. 5. The three-unit cells of P6}_3/mmc \]

\[ \text{phase return to two R-3m unit cells, with a chiral structure transition of the middle two MoSe}_2 \]

\[ \text{layers. Furthermore, it is easy to find that the pressure induced semiconducting to metallic transition of MoSe}_2 \]

\[ \text{under high pressure, which is mainly attributed to the different stacking modes of the MoSe}_2 \]

\[ \text{layers in different phases of MoSe}_2 \]. These results offer important insights for exploration the evolutions of structures and electronic properties of other TMDs at extreme conditions.

**Conclusion**

In summary, we have performed comprehensively structure predictions of MoSe\(_2\) under high pressure up to 500 GPa by CALYPSO method and first-principles calculations. Three new high pressure phases of MoSe\(_2\) are uncovered, and the phase transition sequence follows the order of P6\(_3\)/mmc \( \rightarrow \) R3m \( \rightarrow \) P6\(_3\)/mmc \( \rightarrow \) R-3m. The energy band structure calculations indicate MoSe\(_2\) are evolution from direct bandgap semiconductor to indirect bandgap semiconductor, eventually, to a metal with pressure increase. These attractively electronic properties are due to the chiral structure changes of the top two MoSe\(_6\) layers in MoSe\(_2\). The present findings establish the structural phase diagram of MoSe\(_2\) under high pressure and describe the evolutions of structures and electronic properties of MoSe\(_2\), which offer important insights for exploration other TMDs at extreme conditions.
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**Author contributions**
Y.X.: wrote and edited the manuscript, made the figures. Y.X. and S.H.: carried the main responsibility for the data analysis. M.L., W.S., Z.W. and C.L.: carried out to review and supervision of the manuscript.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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**Correspondence** and requests for materials should be addressed to Z.W., W.D. or C.L.

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