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Pressure evolution of the potential barriers of phase transition of MoS₂, MoSe₂ and MoTe₂

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Two-dimensional crystals with weak layer interactions, such as twisted graphene, have been a focus of research recently. As a representative example, transitional metal dichalcogenides show a lot of fascinating properties due to stacking orders and spin-orbit coupling. We analyzed the dynamic energy barrier of possible phase transitions in MoX₂ (X = S, Se and Te) with first-principles methods. In the structural transition from 2H_c to 2H_a, the energy barrier is found to be increased following an increase of pressure which is different from the phase transition in usual semiconductors. Among MoS₂, MoSe₂ and MoTe₂, the energy barrier of MoS₂ is the lowest and the stability of both 2H_c and 2H_a is reversed under pressure for MoS₂. It is found that the absence of a phase transition in MoSe₂ and MoTe₂ is due to the competition between van der Waals interaction of layers and the coulomb interaction of Mo and X in nearest-neighbor layer of Mo in both phases.

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Introduction

Transition metal dichalcogenides, MoX₂ (X = S, Se and Te), as a representative class of 2D layered materials which are readily available and well suited for experimental study, have attracted broad attention due to their rich physical properties and the potential applications in electronic and optoelectronic devices.^{1–5} The strong spin-orbit coupling in these materials offers opportunities to study spin-valley coupled 2D physics, such as spin- and valley-Hall effects.^{6–10} The weak screening has resulted in tightly bound excitons and strong luminescence from excitons due to the low dimensional limitation.^{11–15} Due to strong photoluminescence, and controllable valley and spin polarization, there is a focus on tuning band gaps and addressing the issue of photoluminescence.^{16–21} These materials consist of X–Mo–X sheets with these sheets being held together *via* van der Waals (vdW) interaction.²² Due to the weak interlayer interaction, one of the main uses of MoX₂, such as MoS₂, is in dry lubrication. This makes the mechanism of relative slipping between layers interesting.

Unlike graphene with monatomic sp² hybridization, the MoS₂ sheets with diatomic layer are coupled to each other by the d-orbital electronic states from Mo. The stacking of layers in different ways leads to the rich polymorphs of MoX₂, such as 2H_a and 2H_c. Under the appropriate conditions, it is possible that there are phase transitions between different structures.^{23,24}

Pressure is an effective parameter to analyze changes in structures and electronic properties, amenable to both experimental and theoretical study.^{25–29} In prior research, MoS₂ has been found to exhibit a phase transition from 2H_c to 2H_a. Under a pressure to 38.8 GPa, Aksoy *et al.* performed an X-ray diffraction study of MoS₂, identifying a possible transition at about 25 GPa.³⁰ Later, a 2H_a phase with space group *P63/mmc* was predicted near 26 GPa.^{31,32} The pressure dependence of electronic properties, elastic constants, and structural properties of bulk and few-layer MoS₂ has been investigated theoretically, with the recent experimental analysis of few-layer MoS₂ under pressure.^{33–38} Interestingly, it is reported recently that there is no phase transition from 2H_c to 2H_a for MoSe₂.³⁹ It is possible that the 2H_c phase is more stable for MoSe₂ under high pressure. The different behavior of MoX₂ under high pressure is an interesting topic. To the best of our knowledge, there is absence of reports about the dynamic processes of phase transitions and structure changes under high pressure for MoX₂.

In this work, we explore the dynamic processes of the structure changes of MoX₂ under high pressure using first-principles methods. It is found that 2H_c phase becomes more stable than 2H_a phase for MoSe₂ and MoTe₂ under pressure, while there is a phase transition for MoS₂. By analyzing the potential surface, there is a ground state for 2H_c phase and a local minimum for 2H_a phase at zero pressure. It is found that the energy barrier from 2H_c to 2H_a is increased for all three cases (MoS₂, MoSe₂ and MoTe₂), following an increase of pressure. It is considered that the different changes of lattice parameters which are related to the coupling of layers may take an important role in the different behaviors of the three cases.

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Computational methods

The present calculations are performed within density functional theory using accurate frozen-core full-potential projector augmented-wave (PAW) pseudopotentials, as implemented in the VASP code.^{40,41} We did calculations with the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) and with added vdW corrections.⁴² The plane-wave basis sets and k -space integrals are chosen to ensure that the total energy is converged at 1 meV per atom level. A kinetic energy cutoff of 500 eV for the plane wave expansion is found to be sufficient. The Brillouin zones are sampled with dense Γ -centered $16 \times 16 \times 4$ grids. The effect of dispersion interaction is included by the empirical correction scheme of Grimme (DFT + D/PBE).⁴³ This approach has been successful in describing layered structures.

The calculated lattice constants a and c of bulk MoS_2 are 3.192 Å and 12.465 Å. For MoSe_2 and MoTe_2 , the lattice parameters a and c are 3.319 Å and 13.113 Å, 3.526 Å and 14.162 Å, respectively. These are all similar to the experimental values for MoS_2 , MoSe_2 and MoTe_2 . The small overestimate of the lattice constants with the PBE functional is not significant for our analysis about the effects of pressure on the structural transition. The method for applying pressure in the present calculations was to add external stress to stress tensor in VASP code,⁴¹ and the structures of bulk MoX_2 with different phases were then optimized under the specified hydrostatic pressure. The added external stress is isotropic and compressive to simulate the real conditions in experiments. We analyzed the energy barriers for transformations between the different phases for pressures up to 28 GPa. It may be noticed that there is Pulay stress in the calculations due to the incompleteness of the plane wave basis set. With the proper plane wave basis set, the small Pulay stress can be ignored in the large range of pressure (0–28 GPa) in this work.

Results and discussion

Phase transition of MoX_2 under pressure

As a result of the different ways of stacking of layers, there are two well-known phases, $2H_c$ and $2H_a$, with hexagonal symmetry.

The $2H_c$ phase is of $P63/mmc$ space group and $2H_a$ has the same space group. The difference of both phases is due to the relative plane slipping between the nearest-neighbor layers. In the hexagonal plane of the unit cell, there are three special sites which can be occupied by Mo, namely sites a (0, 0), b ($1/3$, $2/3$) and c ($2/3$, $1/3$). In the kind of $2H$ structures, there are two layers of Mo in one unit cell and each layer has hexagonal symmetry with space group $P\bar{6}m2$. Therefore, there are just two stacking ways for Mo double layers which are topologically different, such as aa and ab stacking which result in the $2H_a$ and $2H_c$ phase (in Fig. 1a), respectively. At zero pressure, it is found that $2H_c$ phase is more stable than $2H_a$ phase for all three cases: MoS_2 , MoSe_2 and MoTe_2 .

We calculated the energies of $2H_c$ and $2H_a$ phases for three cases under different pressures. In the calculation, the added vdW interaction, which is found to be important for the interlayer interactions even at high pressure, is considered. In Fig. 1b, we show the change of enthalpy following an increase of pressure. It should be noticed that the contributions of zero-point energy and entropy are ignored, since both phases are very similar from the local chemical bonding point of view. The enthalpy difference between $2H_c$ and $2H_a$ changes substantially with pressure and the trend is obviously different for the three cases (Fig. 1b). Up to 28 GPa, the relative enthalpy of MoTe_2 increases with pressure and that of MoSe_2 does not change obviously. For MoS_2 , there is a phase transition at about 13 GPa. These results are consistent with the recent report about the experimental observation of $2H_a$ phase of MoS_2 under high pressure and the absence of a phase transition for MoSe_2 under high pressure.^{27,28,39}

Energy surface, pathway and energy barrier

In the unit cell of $2H_c$ phase, the second layer of MoX_2 is stacked with a rotation of 60° along the z axis relative to the first layer which is one of two basic types of stacking ways. Another one is where there is no rotation between nearest-neighbor MoX_2 layers which forms the basis of $3R$ -type MoX_2 . Usually, the rotation between nearest-neighbor layers with vdW interactions is more difficult than the relative plane slipping between layers due to the higher energy barrier which the rotation needs

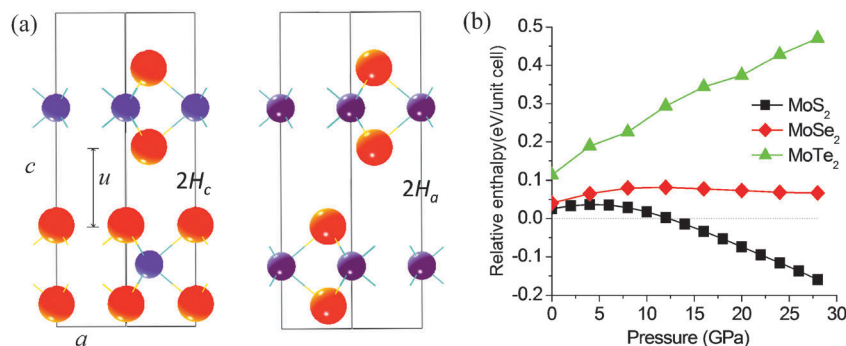


Fig. 1 Structures of both phases $2H_c$ and $2H_a$ of hexagonal AB-stacking MoX_2 ($X = \text{S, Se and Te}$) (a) and relative enthalpies of $2H_c$ and $2H_a$ as a function of pressure for MoS_2 , MoSe_2 and MoTe_2 (b). Note that the enthalpy of $2H_a$ MoX_2 is defined to be zero for each pressure.



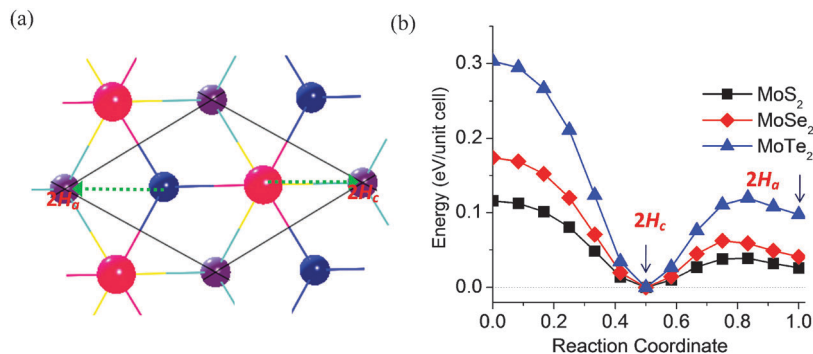


Fig. 2 Schematic representation of the relative plane sliding between two MoX₂ (X = S, Se and Te) layers for a unit cell of hexagonal MoX₂ with 2-layer structure by AB stacking (a), and the variation of total energy per unit cell along the path indicated by the arrow in (a) under zero pressure (b). Note that the structure becomes 2H_a phase if the Mo atom of the second layer indicated in (a) moves to the site labeled "2H_a", and becomes 2H_c phase if the X atom of the second layer indicated in (a) moves to the site labeled "2H_c".

to go through. Under pressure, the layers with weak interaction slip more easily relative to each other.

For single-layer MoX₂ with 2H-type structure, there is rotational symmetry of C₃ along the z-axis. Therefore, in the case of the way of layer stacking to which 2H_c and 2H_a phases belong, there are two kinds of pathways with high symmetry, as shown in Fig. 2a. For each kind of pathway, there are three pathways which is equivalent with C₃ symmetry. We simulated the energy surfaces along the two kinds of pathways for MoS₂, MoSe₂ and MoTe₂ in Fig. 2b. It can be found that there are two local energy minima in the surface including the ground state and meta-stable state. Actually, the two states are corresponding to 2H_c and 2H_a phases, respectively. Around the two local minima, there is an energy barrier on both sides which is about 0.3 eV per unit cell relative to the ground state 2H_c. The energies of 2H_a phase are about 26, 41 and 97 meV per unit cell higher than those of 2H_c for MoS₂, MoSe₂ and MoTe₂, respectively. The barrier from 2H_c to 2H_a is 38.8, 62.2 and 119.8 meV per unit cell for the three cases, respectively. Therefore, if there is a phase transition between 2H_c and 2H_a, it is easier for MoS₂ than for MoSe₂ and MoTe₂.

Phase transition between 2H_c and 2H_a is different from the usual structural transition in which there are breaking and re-bonding of chemical bonds. For the layered MoX₂, it is just the relative slipping in response to the possible phase transition under weak perturbation, such as when the pressure is not very high. To simulate the phase transition of MoX₂ under pressure, an expanded nudged elastic band method is adopted by building the potential reaction path with a series of intermediate images and relaxing the structures of the intermediate images. The internal coordinate of Mo atom of the first layer in the unit cell is fixed. A series of points along the pathway from 2H_a to 2H_c is set for the atomic coordinates of the second layer. For some point of the pathway, the internal coordinate of Mo atom of the second layer is fixed. Then the parameters of the whole cell including the lattice parameters need to be relaxed under the fixed pressure while the internal coordinates of other atoms are also relaxed in the unit cell. From these processes, we can obtain the enthalpies of a series of structures along the pathway at the fixed pressure.

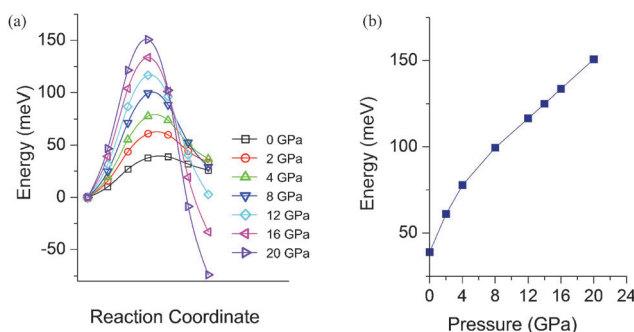


Fig. 3 Variation of enthalpy from the layered structure 2H_c MoS₂ to 2H_a MoS₂ following the pathway of plane sliding indicated in Fig. 2a for different pressures (a) and energy barrier as a function of the pressure calculated by PBE/GGA with dispersion interactions (b). Note that the total energy is given relative to the total energy of 2H_c MoS₂ at zero pressure and the barrier energy is calculated with a unit cell of double-layer MoS₂.

In Fig. 3a, we plot the change of enthalpy along the pathway from 2H_c to 2H_a for MoS₂ under different pressures. It is obvious that 2H_a becomes more stable than 2H_c with an increase of pressure. In Fig. 3b, the energy barrier from 2H_c to 2H_a following a change of pressure is plotted. The barrier has a trend of increasing with an increase of pressure. It is different from the usual structural transition in which the barrier decreases following an increase of pressure, such as the phase transition of BN from low-density phase to low-energy phase.²⁶ At 13 GPa, the energy barrier for the phase transition from 2H_c to 2H_a is about 120 meV per unit cell. Fortunately, the barrier is not so high, from this theoretical analysis. This may be the reason that the phase transition is observed in MoS₂. For deducing the increase of barriers under pressure, one may perform experiments about phase transitions of MoS₂ with pressure under different temperatures.

In Fig. 4a and 5a, the changes of enthalpies along the pathway are plotted for MoSe₂ and MoTe₂. 2H_a phase does not become more stable than 2H_c. In addition, the energy barrier from 2H_c to 2H_a is increased following an increase of pressure, as shown in Fig. 4b and 5b. Interestingly, among the



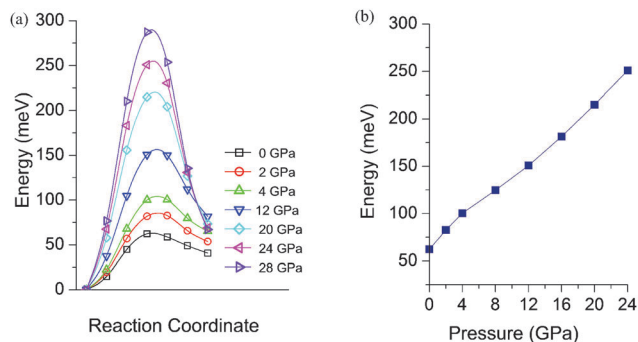


Fig. 4 Variation of enthalpy from the layered structure $2H_c$ MoSe₂ to $2H_a$ MoSe₂ following the pathway of plane sliding indicated in Fig. 2a for different pressures (a) and energy barrier as a function of the pressure calculated by PBE/GGA with dispersion interactions (b). Note that the total energy is given relative to the total energy of $2H_c$ MoSe₂ at zero pressure and the barrier energy is calculated with a unit cell of double-layer MoSe₂.

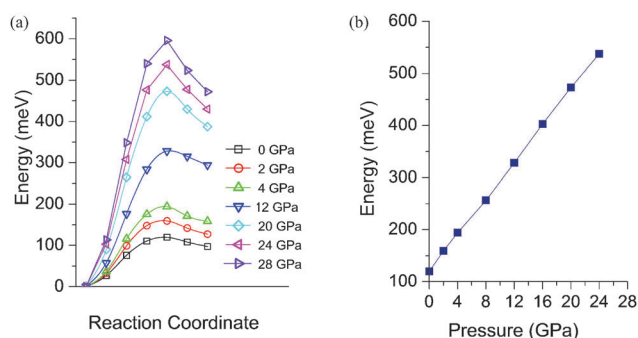


Fig. 5 Variation of enthalpy from the layered structure $2H_c$ MoTe₂ to $2H_a$ MoTe₂ following the pathway of plane sliding indicated in Fig. 2a for different pressures (a) and energy barrier as a function of the pressure calculated by PBE/GGA with dispersion interactions (b). Note that the total energy is given relative to the total energy of $2H_c$ MoTe₂ at zero pressure and the barrier energy is calculated with a unit cell of double-layer MoTe₂.

change of energy barrier of the three cases under pressure, the increase of MoTe₂ is the fastest one and that of MoS₂ is the slowest one. This may be due to the largest p orbitals of Te among the three cases. In the processes from $2H_c$ to $2H_a$, the X atom of the second layer needs to go through the middle of two nearest-neighbor X atoms of the first layer which corresponds

to the configuration of the energy barrier. Therefore, with increasing pressure, the shorter distance between layers leads to the increase of the barrier. The larger p orbitals of X atoms also results in the increase of the barrier.

From the above results, the phase transition happens only in MoS₂ due to a slip between layers and not in MoSe₂ and MoTe₂. Intuitively, it would be more difficult in MoS₂, where S is very reactive and the lattice constant is small. The main reason is the p orbitals of X are hybridized with the d orbitals of Mo and the charge transfer from Mo to S makes the S ion more negative than Se and Te in MoSe₂ and MoTe₂. The coulomb interaction between S ions from different layers is repulsive. Even under a pressure of 28 PGa, the distance between S ions from nearest-neighbor MoS₂ layers is 2.83 Å in $2H_c$ phase (2.67 Å in $2H_a$ phase) and is larger than the bond length of S–S bond (2.05 Å). The repulsive interaction between S ions from different layers makes the slip between layers easy. In MoSe₂ and MoTe₂, the phenomenon is similar to that in MoS₂. In MoSe₂, the distance between Se ions from nearest-neighbor layers under 28 GPa is 2.96 Å in $2H_c$ (2.86 Å in $2H_a$) and is larger than the bond length of Se–Se bond (2.29 Å). In MoTe₂, the distance between Te ions from nearest-neighbor layers under 28 GPa is 3.15 Å in $2H_c$ (3.10 Å in $2H_a$) and is larger than the bond length of Se–Se bond (2.64 Å).

Structural changes under high pressure

Following an increase of pressure, the lattice constants and volumes of both $2H_a$ and $2H_c$ are decreased for the three cases, as is known. The decrease of lattice parameter c for both phases is faster than that of parameter a . This can be attributed to the weak interaction between layers. Under pressure, the parameter u which indicates the distance between layers has a similar trend to that of parameter c . It is noticed that the parameters c and u of $2H_a$ are larger than those of $2H_c$ for the three cases at zero pressure. This may be the reason that the $2H_c$ phase is more stable than $2H_a$ for the three cases.

With an increase of pressure, the parameters c and u of $2H_a$ become smaller than those of $2H_c$, as shown in Fig. 6. From rough evaluation, the vdW interaction between layers will increase following the decrease of layer distance. This means it is possible that $2H_a$ is more stable than $2H_c$ with an increase of pressure and there will be a possible phase transition for

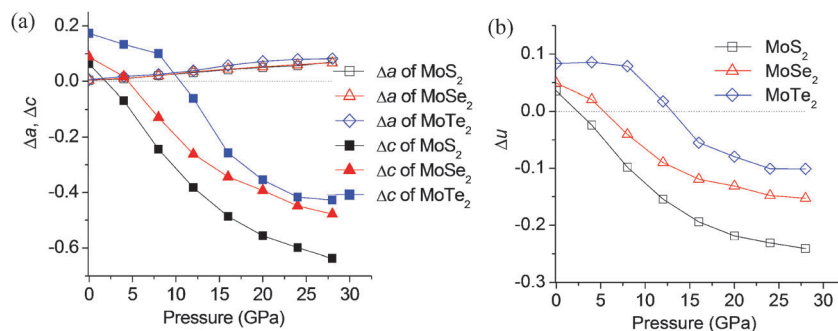


Fig. 6 Difference between lattice constants (a and c) of $2H_a$ and of $2H_c$ ($\Delta a = a(2H_a) - a(2H_c)$, $\Delta c = c(2H_a) - c(2H_c)$) as a function of pressure (a) and difference between lattice parameter u (defined in Fig. 1a) of $2H_a$ and of $2H_c$ ($\Delta u = u(2H_a) - u(2H_c)$) as a function of pressure for MoX₂ (X = S, Se and Te).



MoS₂, MoSe₂ and MoTe₂. However, the phase transition only happens for MoS₂. This may be attributed to another effect in that the coulomb interaction between Mo of one layer and X of nearest-neighbor layer in 2H_c structure is stronger than that in 2H_a structure, due to the shorter distance between Mo and X in two layers for 2H_c phase under pressure. Therefore, both effects (vdW and coulomb interactions) compete with each other, following an increase of pressure. In the three cases, the changes of parameters Δc and Δu of MoS₂ under pressure are the largest ones. This may mean that the vdW interaction of 2H_a MoS₂ is the strongest and the 2H_a phase of MoS₂ becomes more stable than 2H_c under pressure.

Conclusions

With the first-principles method, we studied the dynamic processes of phase transitions of MoX₂ (X = S, Se and Te). The calculation results show that MoS₂ has a phase transition and the phase transition in MoSe₂ and MoTe₂ is absent under pressure and are consistent with the recent experimental observation in MoS₂ and MoSe₂. For the structural transition from 2H_c to 2H_a in MoX₂, the dynamic energy barrier is increased following an increase of pressure. This is attributed to the decrease of layer distance. Among MoS₂, MoSe₂ and MoTe₂, the energy barrier of MoS₂ is the lowest due to the small p orbitals of S compared to those of Se and Te. The absence of phase transition in MoSe₂ and MoTe₂ is attributed to the competition between vdW and coulomb interactions. The transition from semiconductor to metallic conductor in MoX₂ under pressure is due to the strong coupling of layers and is not related to the structural phase transition from 2H_c to 2H_a.

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