Pressure evolution of the potential barriers of phase transition of MoS$_2$, MoSe$_2$ and MoTe$_2$

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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 MoX$_2$ (X = S, Se and Te) with first-principles methods. In the structural transition from 2H$_a$ to 2H$_c$, the energy barrier is found to be increased following an increase of pressure which is different from the phase transition in usual semiconductors. Among MoS$_2$, MoSe$_2$ and MoTe$_2$, the energy barrier of MoS$_2$ is the lowest and the stability of both 2H$_c$ and 2H$_a$ is reversed under pressure for MoS$_2$. It is found that the absence of a phase transition in MoSe$_2$ and MoTe$_2$ 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.

Pressure is an effective parameter to analyze changes in structures and electronic properties, amenable to both experimental and theoretical study. In prior research, MoS$_2$ 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 MoS$_2$, identifying a possible transition at about 25 GPa. Later, a 2H$_a$ phase with space group P6$_3$/mmc was predicted near 26 GPa. The pressure dependence of electronic properties, elastic constants, and structural properties of bulk and few-layer MoS$_2$ has been investigated theoretically, with the recent experimental analysis of few-layer MoS$_2$ under pressure. Interestingly, it is reported recently that there is no phase transition from 2H$_c$ to 2H$_a$ for MoSe$_2$. It is possible that the 2H$_a$ phase is more stable for MoSe$_2$ under high pressure. The different behavior of MoX$_2$ 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 MoX$_2$.

In this work, we explore the dynamic processes of the structure changes of MoX$_2$ under high pressure using first-principles methods. It is found that 2H$_a$ phase becomes more stable than 2H$_c$ phase for MoSe$_2$ and MoTe$_2$ under pressure, while there is a phase transition for MoS$_2$. By analyzing the potential surface, there is a ground state for 2H$_a$ phase and a local minimum for 2H$_c$ phase at zero pressure. It is found that the energy barrier from 2H$_a$ to 2H$_c$ is increased for all three cases (MoS$_2$, MoSe$_2$ and MoTe$_2$), 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.\textsuperscript{10,41} We did calculations with the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) and with added vdW corrections.\textsuperscript{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 × 16 × 4 grids. The effect of dispersion interaction is included by the empirical correction scheme of Grimme (DFT + D/PBE).\textsuperscript{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,\textsuperscript{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 P6$_3$/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 P6$_3/m$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$_c$ and 2H$_a$ 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$_c$ phase of MoS$_2$ under high pressure and the absence of a phase transition for MoSe$_2$ under high pressure.\textsuperscript{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 = 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.
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 2Hc and 2Ha 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 metastable state. Actually, the two states are corresponding to 2Hc and 2Ha 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 2Hc. The energies of 2Ha phase are about 26, 41 and 97 meV per unit cell higher than those of 2Hc for MoS2, MoSe2 and MoTe2, respectively. The barrier from 2Hc to 2Ha 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 2Hc and 2Ha, it is easier for MoS2 than for MoSe2 and MoTe2.

Phase transition between 2Hc and 2Ha 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 2Hc to 2Ha 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.

In Fig. 3a, we plot the change of enthalpy along the pathway from 2Hc to 2Ha for MoS2 under different pressures. It is obvious that 2Ha becomes more stable than 2Hc with an increase of pressure. In Fig. 3b, the energy barrier from 2Hc to 2Ha 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. At 13 GPa, the energy barrier for the phase transition from 2Hc to 2Ha 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. 2Ha phase does not become more stable than 2Hc. In addition, the energy barrier from 2Hc to 2Ha is increased following an increase of pressure, as shown in Fig. 4b and 5b. Interestingly, among the
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 MoS$_2$ due to a slip between layers and not in MoSe$_2$ and MoTe$_2$. Intuitively, it would be more difficult in MoS$_2$, 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 MoSe$_2$ and MoTe$_2$. The coulomb interaction between S ions from different layers is repulsive. Even under a pressure of 28 GPa, the distance between S ions from nearest-neighbor MoS$_2$ layers is 2.83 Å in 2H$_a$ phase (2.67 Å in 2H$_c$ 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 MoSe$_2$ and MoTe$_2$, the phenomenon is similar to that in MoS$_2$. In MoSe$_2$, 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 MoTe$_2$, 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 $a$ which indicates the distance between layers has a similar trend to that of parameter $c$. It is noticed that the parameters $c$ and $a$ 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 $a$ 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$_c$ is more stable than 2H$_a$ with an increase of pressure and there will be a possible phase transition for...
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 2H₄ structure is stronger than that in 2H₆ structure, due to the shorter distance between Mo and X in two layers for 2H₄ 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 2H₄ MoS₂ is the strongest and the 2H₆ phase of MoS₂ becomes more stable than 2H₄ 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 2H₄ to 2H₆ 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 2H₄ to 2H₆.

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