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Prediction of stable ground-state and pressure-induced phase transition of molybdenum monosulfide

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ABSTRACT

Several new stable phases of MoS at ambient and high pressures were uncovered by using the global minimization of energy surfaces merging ab initio total energy calculations, and a phase transition order of *Imm*2 → *Pnma* → *Pm-3m* was revealed. The transition pressures are 5.5 GPa and 45.3 GPa, respectively, retrieved from the calculated formation enthalpy. The mechanical and dynamical stabilities of these phases were determined by the elastic constants and phonon dispersions. Moreover, the calculated band structures show that the *Imm*2 and *Pnma* phases are indirect band gap semiconductors, whereas the *Pm-3m* phase shows metallic character. The electron localization function calculations of these three stable phases were also been analyzed.

1. Introduction

The molybdenum disulfide (MoS_2) [1–7], due to its fascinating various physical and chemical properties, has attracted immense attention recently in the low-power transistor, hydrogen storage and lithium ion batteries. Though the bulk MoS_2 is an indirect band gap semiconductor, it acquires a direct band gap of 1.8 eV when thinned to the monolayer limit [4]. With the high-symmetry valleys and the unique two-dimensional structure of a monolayer MoS_2, MoS_2 finds a wide application in many novel electronic and optoelectronic devices. Furthermore, by embedding impurity species to fill the S vacancies in the monolayer MoS_2, one can make the basal plane of monolayer MoS_2 to be catalytically active. Ma et al. [6] studied a CO catalytic oxidation on a Fe-embedded monolayer MoS_2 (Fe-MoS_2), showing that its S vacancy can strongly constrain the trapped Fe atoms with a high diffusion barrier (~2.0 eV), and the charge transfer and orbital hybridization between adsorbates and Fe atoms results in a highly active catalytic dynamics. MoS_2 is also a promising candidate for the anode material in lithium ion batteries. Shi et al. [7] reported that by using a high-throughput solvent thermal method, they synthesized a 1D multiwall carbon nanotubes (MWNTs) nanocomposites which are coated by nanosheet MoS_x ($2 \le x \le 3$) under 200 °C. Their method can remarkably improve the specific capacity up to 1000 mAh/g at the current density of 50 mA/g. There are also many theoretical and experimental studies on other molybdenum sulfides, such as Mo_2S_3 [8,9], Mo_6S_8 [10,11] and Mo_5S_n (n = 5–15) [12], etc. With a solid-gas reaction between porous Al_2O_3, which is impregnated with MoO_3 and H_2S gas, Che et al. [8] synthesized a Mo_2S_3 of sulfide nanostructures, and demonstrated that addition of H_2 gas leads to the formation of MoS_2 nanotubes. Murugan et al. [12] systematically investigated the Mo_5S_n (n = 5–15) clusters, showing that the stability cab be influenced by the Mo-S bonds, and Mo_5S_n with n = 6, 8 or 11 are the most stable phases.

Comparing with other molybdenum sulfides, the structure of Molybdenum monosulfide (MoS) at ambient and high pressures were rarely studied. Recently, by using evolutionary search algorithm, Kohulák et al. predicted the structure of MoS at 120 GPa is CsCl structure [13]. later, Pan et al. [14] compared five MoS structures and found that the most stable MoS structure at ambient pressure is hexagonal. The detailed pressure-induced phase transition of MoS is not clear, hitherto. In this paper, to find the stable structures of MoS at ambient and high pressures, we systematically explored the most stable phases of MoS at pressures up to 100 GPa by using crystal structure searching technique. For the new MoS phases, we studied the crystal structures, stabilities, and the bonding characters in detail.

2. Computational methods

In order to find the most stable phase of MoS, the crystal structure prediction based on global minimization of energy surfaces merging ab initio total energy calculations as implemented in CALYPSO code [15]

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was used. The variable cell structure predictions at pressures of 0, 10, 20, 40, 60 and 100 GPa with one to eight formula units (f.u.) were performed. For each pressure, we searched 30 generations, and for each generation, 30 structures were generated by particle swarm optimization (PSO). Structural relaxations and electronic calculations were performed using the Vienna ab initio simulation package (VASP) [16] in the framework of density functional theory with the generalized-gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [17]. The projector-augmented wave method [18] was used to describe the electron-ion interaction. We used a cutoff energy of 350 eV for the expansion of the wave function into the plane wave basis set. Monkhorst-Pack *k*-point meshes with a grid of $2\pi \times 0.02$ Å^{-1} for Brillouin zone sampling were chosen to ensure that the total energies converged to be better than 1 meV/atom. The band structures calculations of semiconductor phases were performed by HSE06 hybrid functional [19]. The phonon frequencies were calculated by a supercell approach as implemented in PHONOPY code [20], with the forces calculated from VASP. The independent elastic constants were calculated by the stress-strain method, and the bulk modulus, Young's modulus, shear modulus, and Poisson's ratio were derived from the Voigt-Reuss-Hill approximation [21].

3. Results and discussions

The crystal structures of the predicted phases are shown in Fig. 1, where the lattice parameters and atomic coordinates are listed in Table 1. The *Pmn*2$_1$-MoS has four atoms in a unit cell (see Fig. 1(a)), with the atomic coordinates: S 2a(0, 0.86099, 0.88208) and Mo 2a(0.5, 0.61602, 0.57119). Both S and Mo atoms are four coordinated. The *Amm*2-MoS has 12 atoms in a unit cell (see Fig. 1(b)), with the atomic coordinates: S1 4e(−0.5, −0.17132, −0.23353), S2 2a(0, 0, −0.77912), Mo1 4d(0, −0.18801, −0.57409), and Mo2 2b(−0.5, 0, −0.45488). The cell formula of *Pmmn*-MoS is Mo_2S_2, and its atomic coordinates are: S 8g(0, 0, 0.67065), and Mo 8g(0, 0.5, 0.09659). It is found that Mo_2S_2 is layered along *c*-direction, as shown in Fig. 1(c), and the S and Mo atoms are four-coordinated. Moreover, the ground state of MoS is predicted to be the orthorhombic *Imm*2 phase (No. 44) at 0 GPa. The *Imm*2-MoS has 12 atoms per unit cell, including two inequivalent S

Table 1
Calculated lattice parameters and atomic coordinates.

	Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	Atomic coordinates
*Pmn*2$_1$	0	3.013	4.528	4.686	S 2a(0, 0.86099, 0.88208) Mo 2a(0.5, 0.61602, 0.57119)
*Amm*2	0	3.148	12.083	5.323	S1 4e(−0.5, −0.17132, −0.23353) S2 2a(0, 0, −0.77912) Mo1 4d(0, −0.18801, −0.57409) Mo2 2b(−0.5, 0, −0.45488)
Pmmn	0	4.463	3.11	4.381	S 8g(0, 0, 0.67065) Mo 8g(0, 0.5, 0.09659)
*Imm*2	0	11.660	3.306	5.555	S1 4c(−0.20851, 0.5, −0.3335) S2 2a(0, 0, −0.93326) Mo1 4c(0.11511, 0, −0.56923) Mo2 2b(0, 0.5, −0.28775)
Pnma	0	6.189	3.152	6.012	S 4c(0.78841, 0.25, 0.43015) Mo 4c(0.51370, 0.75, 0.30101)
	10	6.104	3.094	5.934	
	40	5.906	2.966	5.798	
Pm-3m	0	3.009			S 1a(0, 0, 0) Mo 1b(0.5, 0.5, 0.5)
	50	2.851			
	100	2.758			

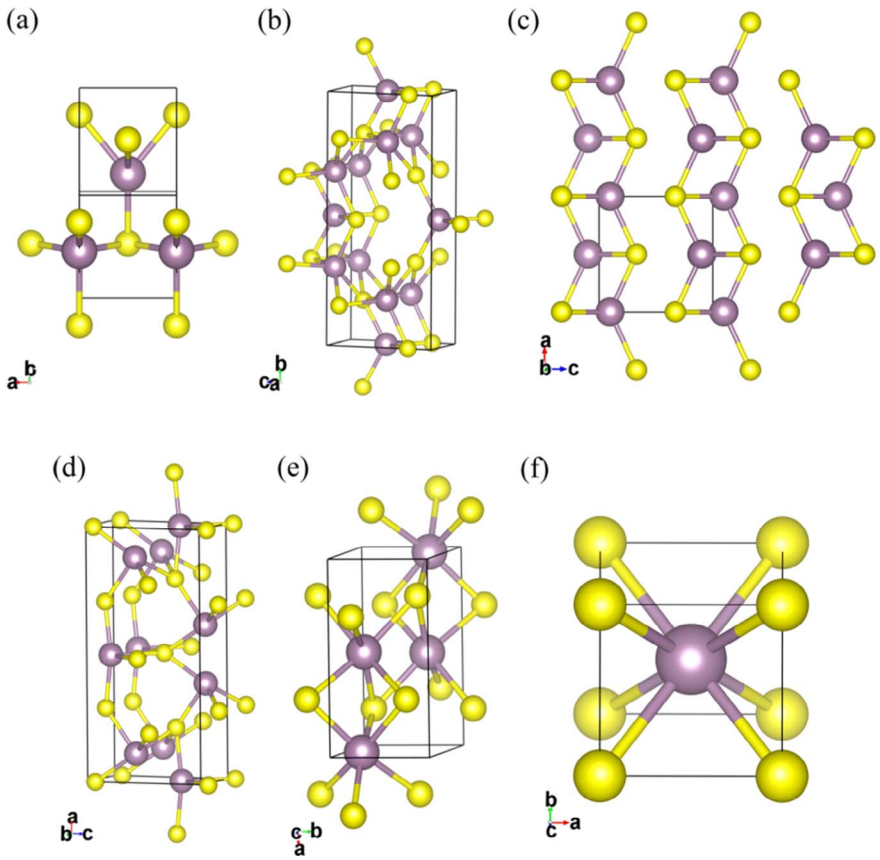

Fig. 1. Crystal structures of *Pmn*2$_1$ (a), *Amm*2 (b), 2 × 2 × 2 supercell of *Pmmn* (c), *Imm*2 (d), *Pnma* (e) and *Pm-3m* (f) phases. The yellow and purple spheres represent the S and Mo atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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