



High pressure polyhydrides of molybdenum: A first-principles study



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ABSTRACT

We present results from first-principles calculations on molybdenum polyhydrides under pressure. In addition to the experimental ϵ -phase of MoH, we find several novel structures of MoH₂ and MoH₃ at pressures below 100 GPa. A hexagonal structure of MoH₂ becomes stable with respect to decomposition into MoH and H₂ above 9 GPa, and transforms into an orthorhombic structure at 24 GPa, which remains stable up to 100 GPa. MoH₃ is unstable relative to decomposition into MoH and H₂ over the whole pressure range studied. Electronic structure calculations reveal that molybdenum polyhydrides are metallic under pressure.

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1. Introduction

Transition metal hydrides are interesting owing to their potentially important physical properties such as hydrogen storage capability and hydrogen-mediated superconductivity [1–9]. The hydrogen:metal (H:M) ratio of transition metal hydrides is usually around 1, and rarely reaches 2 or more; however, some recent discoveries of di- and trihydrides of several *d* metals have considerably expanded this class of material [10–14]. For example, Li *et al.* found that rhodium metal absorbed H to form NaCl-type RhH at 4 GPa and fluorite-type RhH₂ at 8 GPa [11]. [Reply 1] Iridium trihydride has been successfully predicted in a theoretical work first [13,14] and then was successfully synthesized *in situ* at high pressures by synchrotron X-ray diffraction [12]. Pépin *et al.* synthesized two new iron hydrides, tetragonal FeH_{~2} at 67 GPa and simple cubic FeH_{~3} at 86 GPa [15]. These discoveries suggest that hydrides can show significantly increased H contents at high pressure.

Molybdenum, an important refractory metal with high melting point and toughness [16], crystallizes in a body centered cubic (*bcc*) structure under ambient conditions. Phase transformations in the Mo–H system have been studied by several groups [17,18] at high hydrogen pressures of up to 5 GPa and at temperatures up to 1200 K. The known phases are α , ϵ and γ , which have *bcc*, hexagonal close packed (*hcp*), and face centered cubic (*fcc*) metal lattices, respectively. The γ -phase is only stable at high temperatures, whereas the α - and ϵ -phase are stable at room temperature. The α -phase transforms to

the ϵ -phase at a hydrogen pressure of ~ 2.2 GPa. The H content of the α -phase is small; however, the H:M ratio increases significantly to ~ 1 in the ϵ - and γ -phases at high pressures.

The interest of the Mo–H system is not confined to the formation of crystals under high pressures but also extends to the chemical reactions to produce molecules. Wang and Andrews [19] demonstrated that laser-ablated Mo atoms reacted with H₂ to form molecules during condensation in excess argon, neon, and hydrogen. They identified four molybdenum hydrides molecules: MoH, MoH₂, MoH₄ and MoH₆, by isotopic substitution (H₂, D₂, HD, and H₂+D₂) and by comparison with vibrational frequencies obtained from first-principles calculations.

Inspired by these studies, we investigated H-rich MoH_{*n*} (*n*=1, 2 and 3) compounds under high pressures. We used CALYPSO method for crystal structure predictions. In addition to the experimental ϵ -phase of MoH, two structures of MoH₂ were predicted at high pressures, but MoH₃ was predicted to remain unstable over the pressure range considered. We report here details of the predicted structures and electronic properties, and compare them with previous experimental results.

2. Computational methods

The searches for low-energy crystalline structures of MoH_{*n*} with *n*=1, 2 and 3 were performed using our *calypso* methodology as implemented in the CALYPSO code [20–26]. [Reply 8] This method requires only chemical compositions for a given compound to predict stable or metastable structures at given external conditions (e.g., pressure) and has been benchmarked by various crystalline systems,

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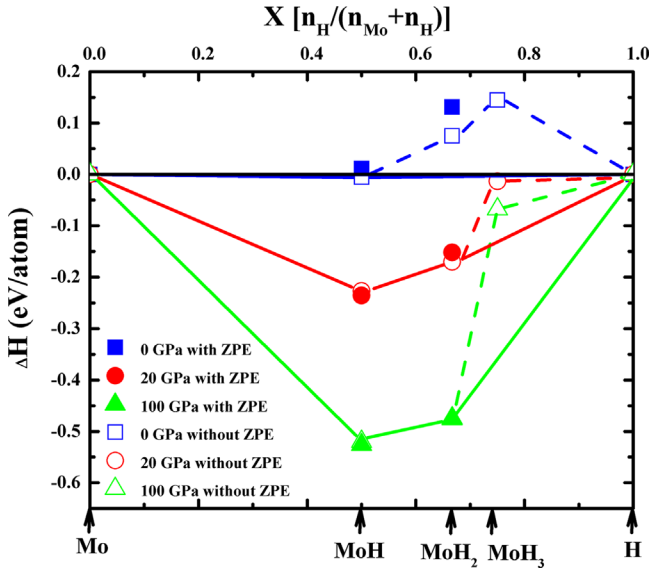


Fig. 1. Ground-state and static enthalpy of formation per atom of different MoH_n compositions with respect to their constituent elements with (solid) and without (hollow) the inclusion of zero point vibrational enthalpy (ZPE). For clarity, the hydrogen molar content for the ground state at $P=0$, 20 and 100 GPa is also shown ($x=0$ and 1 correspond to pure molybdenum and pure hydrogen, respectively).

ranging from elements to binary and ternary compounds [27–31]. Structural optimizations, enthalpies, electronic structures and phonons were calculated using first-principles method as implemented in Vienna ab initio simulation program (VASP) [32] and projector-augmented plane-wave (PAW) potentials [33] with an energy cutoff of 700 eV, [Reply 2.2] in order to ensure that the enthalpy calculations are converged to better than 1 meV/atom. The Mo and H potentials have $4d^55s^1$ and $1s^1$ as valence states, respectively, employing the PBE functional. large. [Reply 2.4] DFTD3 was used to estimate dispersion corrections when calculating the enthalpy of pure H. Uniform Monkhorst-Pack (MP) [34] meshes for Brillouin zone sampling with resolutions of $2\pi \times 0.06 \text{ \AA}^{-10}$ and $2\pi \times 0.03 \text{ \AA}^{-1}$ were employed in the structure predictions and subsequent calculations respectively. This ensures that enthalpy calculations are better converged than 1 meV/formula unit. The phonon frequencies were calculated by the supercell approach [35] as implemented in the PHONOPY code [36]. Converged results were obtained with a $3 \times 3 \times 3$ supercell for $P6_3/mmc$ -MoH and a $2 \times 2 \times 2$ supercell for $Pnma$ - MoH_2 at 100 GPa.

3. Results and discussion

First, we discuss the ground states of MoH_n ($n=1, 2$ and 3) obtained at 0 to 100 GPa. The convex hull in Fig. 1 illustrates the stability of these compounds via plots of the enthalpies of formation

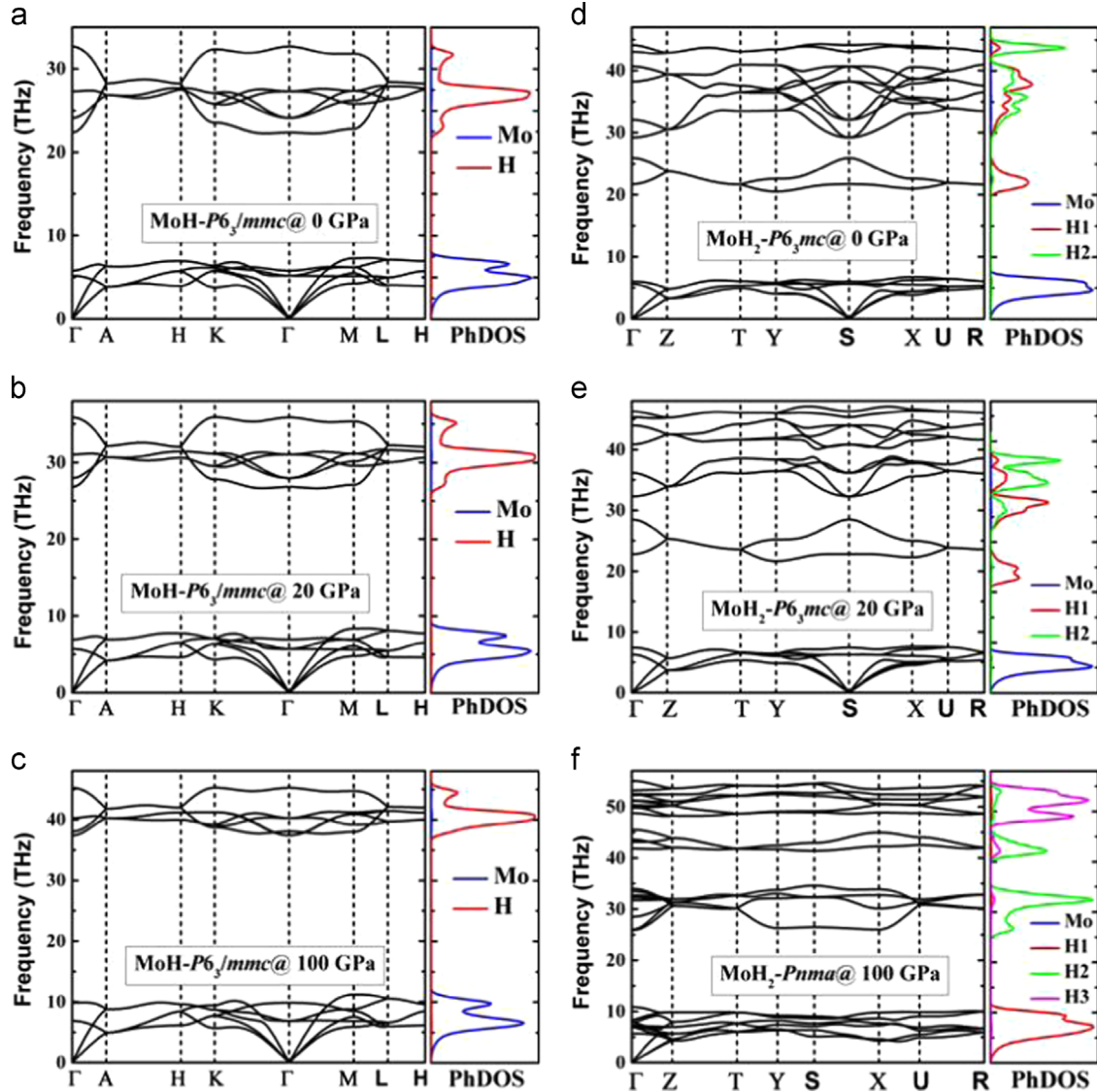


Fig. 2. Phonon dispersions and projected phonon density of states (PhDOS) for MoH and MoH_2 at 0, 20 and 100 GPa.

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