

Stability and electronic structure of magnesium hydride and magnesium deuteride under high pressure

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Abstract. Metal polyhydrides have attracted considerable attention because some of them become a metal under high pressure, and some undergo a phase transition into a superconductor. Some superconducting metal polyhydrides have recently been discovered with a high value of critical temperature (T_c) under pressure. In this research, we calculated the structures of MgH_2 , MgH_3 and MgD_3 under pressure between 0-300 GPa in order to determine the formation enthalpy and electronic property of their structures under high pressure by using density functional theory (DFT) based on the Quantum Espresso code. We found that the band structures reveal the metallic character of the compounds under high pressure. The energy band structures of MgH_x and MgD_x are exactly the same. However, their phonon dispersions are different due to the so-called isotope effect. We determined the composition stability by using the convex hull of Mg, H and the compounds. We found that MgH_3 becomes thermodynamically more stable than MgH_2 at around 150 GPa. The results of phonons confirm that they are dynamically stable. This finding is served as a basis for future superconducting calculations.

1. Introduction

Metal polyhydrides have received much of attention in condensed matter research because some of them become a superconductor with a high critical temperature (T_c) under higher pressure [1]. The Mg/Ca substituted hexahydride at 200 GPa, exhibiting superconductivity with $T_c = 288$ K [2]. In this research, we are interested in magnesium hydrides (MgH_x). MgH_2 is widely used for the application of the hydrogen storage in electric vehicles with high gravimetric and volumetric capacities of H_2 (7.7 wt% and 109 gH₂) [3,4]. Under high pressure, the hydrogen content can be increased and the compound composition can be evolved to MgH_x , where $x > 2$. We reported the relative structural stability of MgH_2 and MgH_3 in the pressure range of 0-300 GPa. We also substituted the hydrogen atoms with deuterium (D) to determine the dynamical stability under high pressure. This finding will provide a basis for future superconducting critical temperature calculations.

2. Computational methods

In this work, all the calculations were performed by using the density functional theory (DFT) [5, 6] and the self-consistent field method, as implemented in the Quantum-ESPRESSO code [7]. We used the Perdew-Burke-Ernzerhof (PBE) functional for the generalized gradient approximation (GGA) [8,9] and the projector-augmented wave (PAW) method [10] for the pseudopotentials. The kinetic energy cut off of the wave functions in the plane wave basis set was chosen at 80 Ry, and the k-point grid was chosen to be $12 \times 12 \times 12$ meshes for geometry optimization.

3. Results and discussion

The lattice parameters of MgH_2 and MgH_3 are presented in table 1. The structures of MgH_2 and MgH_3 are exhibited in figure 1. All structures were optimized under pressure between 0–300 GPa. The convex hulls in figure 2 showed that the Fm-3m structure of MgH_3 is thermodynamically stable between 100–300 GPa and 0–200 GPa for MgH_2 . Furthermore, MgH_3 becomes relatively more energetically favourable than MgH_2 at 150 GPa onwards. We also substituted the D atoms instead of the H atoms. Nevertheless, the enthalpies per atom of MgH_3 and MgD_3 are the same because the pseudopotentials are the same, only the masses of H and D are different.

Table 1. Lattice parameters of MgH_2 , MgH_3 at the atmospheric pressure (0 GPa).

	Space group	a (Å)	b (Å)	c (Å)	Density (g/cm ³)	Volume (Å ³)
MgH_2	Fm-3m	3.367	3.367	3.367	1.62	26.999
MgH_3	Fm-3m	3.327	3.327	3.327	1.74	26.042
MgD_3	Fm-3m	3.327	3.327	3.327	1.74	26.042

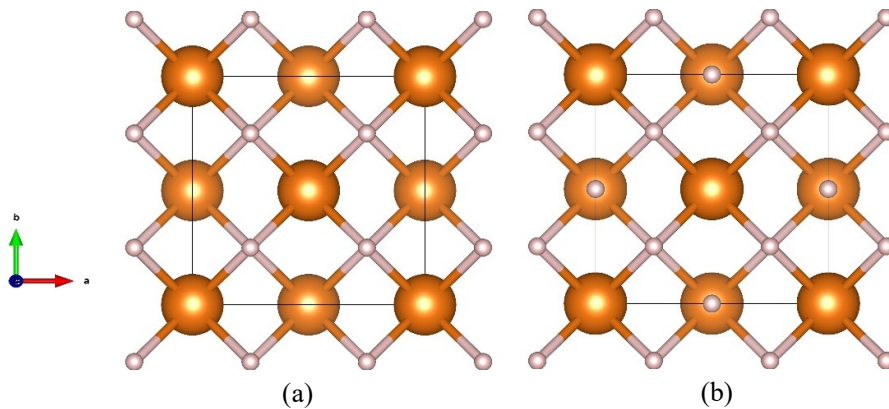


Figure 1. The crystal structures of fcc MgH_2 (a) and fcc MgH_3 (b) (draw by VESTA [11]). The structure of MgD_3 is the same as of MgH_3 .

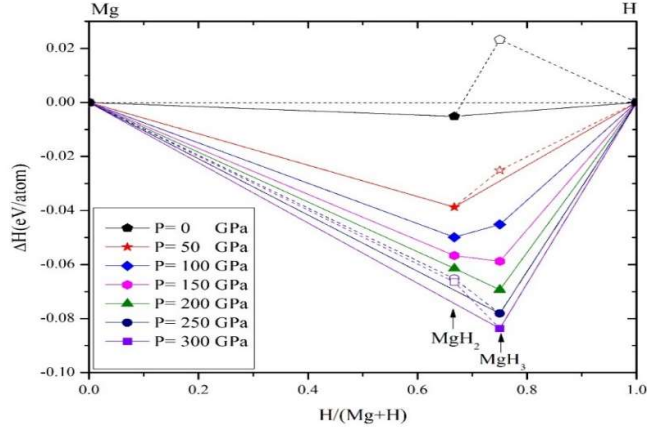


Figure 2. The enthalpy per atom of MgH_2 and MgH_3 are presented in the form of the convex hull. (solid markers refer to a stable structure, whereas transparent markers refer to a meta-stable structure.)

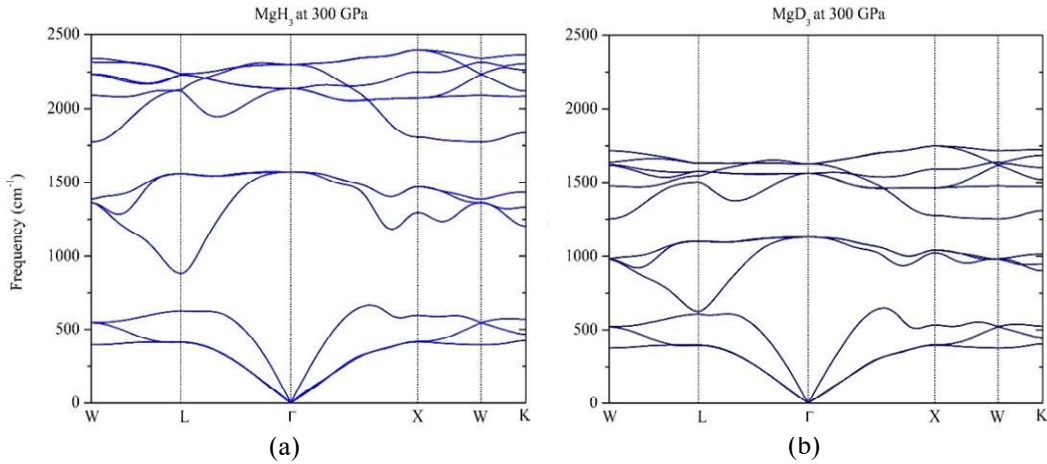


Figure 3. The phonon dispersions of MgH_3 (a) and MgD_3 (b) at pressure 300 GPa.

From the results of figure 2, we calculated the phonon dispersions of MgH_3 and MgD_3 in order to confirm the dynamical stability between $P = 150\text{--}300$ GPa. The examples of the phonon dispersion at 300 GPa are shown in figure 3. The phonon frequencies involving H of MgH_3 are higher than those involving D of MgD_3 at the same k point. This is the so-called isotope effect [12], which can be observed from the replacement of the hydrogen atoms (H) with the deuterium atoms (D). In fact, the mass of deuterium is twice heavier than the mass of hydrogen. Therefore, the phonon frequencies involving the vibrations of the hydrogen atoms are $\sqrt{2}$ times higher than those of deuterium atoms as $\omega \propto \frac{1}{\sqrt{m}}$. By closer inspection, we found that the phonon frequencies below 750 cm^{-1} in the left panel of figure 3 belong to the vibrations of the Mg atoms. These frequencies are mostly intact in the right panel of figure 3. However, the phonon frequencies above 750 cm^{-1} in the left panel of figure 3 belong to the vibrations of the hydrogen atoms. The corresponding modes in the right panel have $\frac{1}{\sqrt{2}}$ times lower frequencies than in the left panel of figure 3. These are due to the vibrations of the heavier deuterium atoms. These phonon dispersion results will be used as a basis for future superconducting critical temperature calculations.

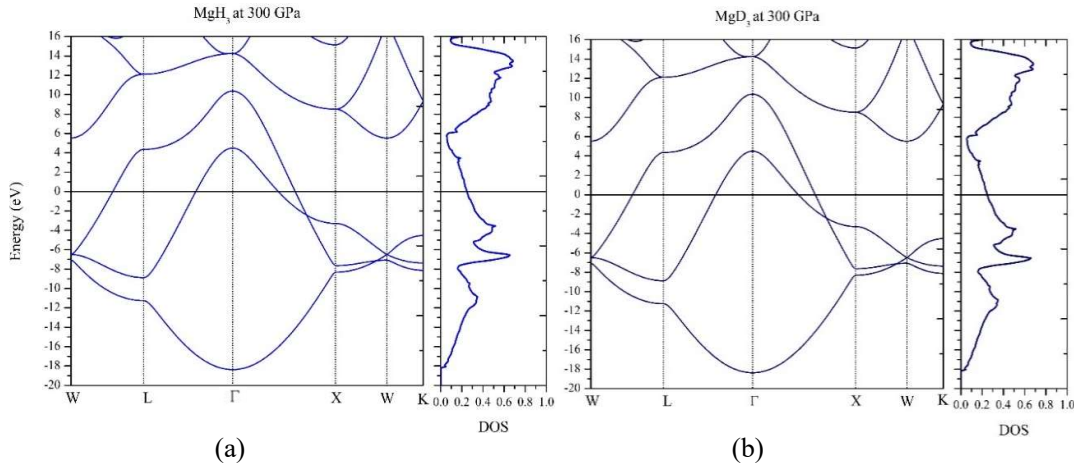


Figure 4. The electronic band structures of MgH₃ (a) and MgD₃ (b) at pressure 300 GPa.

In addition, we calculated the electronic band structure of MgH₃ and MgD₃ between $P = 150\text{--}300$ GPa. The example of the electronic band structure of MgH₃ and MgD₃ at 300 GPa is shown in figure 4. The associating electronic density of states (DOS) is also shown. The electronic structures and their DOS show that MgH₃ and MgD₃ are metallic under pressure. However, at this level of DFT calculations, there is no distinction between the electronic structures of MgH₃ and MgD₃. In the future work, the van der Waals interaction will be included in order to distinguish between H and D, as suggested in the case of solid hydrogen under high pressure [13]. For simplicity of discussion, the BCS theory showed that $T_c \propto \omega_D e^{-\frac{1}{N_F V}}$ [1], where ω_D is the Debye frequency of the material (in units of temperature, or to be precise the Debye temperature), N_F is the density of electron at the Fermi level, and V is the electron-phonon interaction. Our calculations of the phonon dispersion and electronic structure provide the knowledge of ω_D and N_F . However, V is quite computationally expensive and will be pursued in our future work.

4. Conclusion

In this work, we have calculated the convex hull of MgH₂ and MgH₃ under pressure from 0–300 GPa by using DFT. We found that MgH₃ is thermodynamically stable between 100–300 GPa, and becomes relatively more energetically favourable than MgH₂ at 150 GPa onwards. The phonon calculations confirmed that MgH₃ is dynamically stable under high pressure, and the phonon frequencies of MgD₃ is $\frac{1}{\sqrt{2}}$ times lower than those of MgH₃ due to the isotope effect. We also reported the electronic band structures for MgH₃ and MgD₃, which appear to be exactly the same.

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