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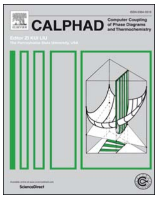

Density functional study of the thermodynamic properties and phase diagram of the magnesium hydride

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ABSTRACT

This paper focuses primarily on the P-T phase diagram determination by considering six polymorphs of magnesium hydride (α - rutile TiO_2, *P4₂/mnm*, β - cubic modified CaF_2, *Pa* $\bar{3}$, γ - orthorhombic PbO_2, *Pbcn*, $^{\delta'}$ - orthorhombic, *Pbca* and cubic - *Fm* $\bar{3}$ *m*). The Gibbs free energy and other thermodynamic properties were evaluated by DFT-based thermodynamic calculations, within the frame of the quasi-harmonic approximation, for the pressure range 0–10 GPa and temperatures between 0 and 1200 K. Furthermore, the structural, energetic, and electronic properties of the investigated structures are conversed.

1. Introduction

The metal hydrides are promising candidate materials for the hydrogen storage as the cleanest solution for electric vehicles and energy storages. In particular, the magnesium hydride is an attractive system for the hydrogen storage, as it is one of the systems with a high hydrogen weight content (7.6 wt%). However, magnesium has poor kinetics and thermodynamic properties, requiring high ab- and desorption temperatures. In order to improve the reaction speed at lower temperatures, the magnesium hydride is mixed with other metals. It is important to know the dependence of the magnesium-based hydrate stability and phase transitions on pressure and temperature, in order to find the proper paths for the formation and decomposition of magnesium hydrides phases.

Several polymorphs of magnesium hydride were identified as thermodynamically stable forms of MgH_2 for different pressure and temperature domains by experimental and theoretical investigations. The importance of knowledge of the various MgH_2 phase stability has led to an increase in research regarding the pressure-temperature phase diagram for the magnesium hydride. Under ambient conditions the magnesium hydride crystallizes as α-MgH_2 phase, with a rutile-type structure (space group $P4_2/mnm$) [1,2]. Bastide et al. found that under high pressure and temperature conditions the α-MgH_2 structure is transformed into β-MgH_2 (with a modified fluorite-type CaF_2 structure, space group *Pa* $\bar{3}$) and γ-MgH_2 (with an orthorhombic structure of α-PbO_2-type, space group *Pbcn*); by decreasing the pressure the β-MgH_2 is transformed into γ-MgH_2 [3]. Bortz et al. detected at high pressure the γ-MgH_2 phase by the X-ray and neutron diffraction measurements [4]. Vajeeston et al. [5,6] identified a phase transition from α-MgH_2 to γ-MgH_2 at 0.39 GPa by Density Functional Theory (DFT) calculations. Moriwaki et al. detected by the X-ray diffraction (XRD) measurements at room temperature the transition α → γ, but at much higher pressure of 9 GPa [7]. Moses et al. built the P-T phase diagram by DFT thermodynamic calculations and investigated the isotopic effects on the α, β and γ phases of the magnesium hydrides and identified the decomposition conditions [8]. Several other magnesium hydride phases are identified at high pressure by theoretical and experimental studies: $Pbc2_1$ [6,7], *Pbca* [6,7], *Pnnm* [5,9], *Fm* $\bar{3}$ *m* [5,10]. The successive phase transitions α($P4_2/mnm$) → γ(*Pbcn*) → β(*Pa* $\bar{3}$) → δ($Pbc2_1$) → ε(*Pnma*) were predicted by several DFT studies [5,6,10]. Cui et al. established a similar sequence of transitions by DFT-based enthalpy calculations, but found that δ is unstable [11]. A metastable phase of MgH_2 ($I4_1/amd$), which meets all the mechanical stability criteria for a tetragonal crystal, has been suggested by DFT calculations [12]. A new pressure-induced transition from the α-MgH_2 phase to an orthorhombic $CaCl_2$-type (*Pnnm*) phase has been predicted by ab initio phonon calculations [9]. Durandurdu identified by ab initio Molecular Dynamics simulations the transition of α-MgH_2 to $CaCl_2$-type phase around 5 GPa, which is stable up to 10 GPa. For values above 10 GPa a new phase with distorted-CaF_2 (*Pbcm*) structure is identified [13]. Lonie et al. predicted by DFT-based thermodynamics calculations several stable magnesium polyhydrides (MgH_n, $n > 2$) for $T = 0$ K and much higher pressures [14]. The cubic structure of fluorite-type, with the space-group *Fm* $\bar{3}$ *m* was theoretically considered as a possible structure of the magnesium

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hydride [5,10], but it has not been experimentally identified. The DFT-based studies predict it as a relevant structure for the magnesium hydride alloyed with transition metals $Mg_xTM_{1-x}H_2$, $x \leq 0.75$ (TM as Sc, Ti, V, Cr and Zr) [15,16] and for multifilm MgH_2/TMH_2 systems [17].

Although the stability of the magnesium hydride polymorphs has been the subject of many experimental and computing investigations, the complete P-T phase diagram of the magnesium hydride has not yet been determined. For some other crystalline systems of interest for the hydrogen storage there are complete P-T phase diagrams [18]. Zeng et al. collected the experimental data and calculated the P-T phase diagram for α-MgH2 decomposition at low pressures (up to 0.03 GPa) and high temperatures (up to 900 K) [19]. As far as we know, the only P-T phase diagram for high pressures (up to 8 GPa) and temperatures (up to 1000 K) in the literature is the one determined by Moser et al. [8] by DFT thermodynamic calculations for the polymorphs α, β and γ of the magnesium hydride, for the three hydrogen isotopes. In the present study we report the results of the comprehensive thermodynamic calculations and the P-T phase diagram of six magnesium hydride structures: α-MgH_2, β-MgH_2, cubic-MgH_2, γ-MgH_2, δ'-MgH_2 and ε-MgH_2 [20].

Because of the high computational efforts and complexity of the DFT-based thermodynamic calculations [21] we have limited the present study to the MgH_2 crystalline phases by the harmonic approximation and do not consider their decomposition. The MgH_2 decomposition takes place at high temperatures and it is necessary to consider the anharmonic contributions to the Gibbs free energy. Moreover, the identification of the most stabile configuration of the six polymorphs for each degree of hydrogen vacancy is computationally demanding and involves a huge number of magnesium hydride configurations corresponding to various degrees of hydrogen vacancy concentrations, from the genuine MgH_2 (no hydrogen vacancy) to the case of separated hydrogen gas and metallic magnesium (complete decomposed hydride). Such an extensive study is currently underway in our group.

2. Computational methods

The results from the calculations presented in this study were obtained within DFT, using the plane-wave pseudopotential method as implemented in the Quantum Espresso code [22]. The Projector Augmented-Wave potentials generated with pslibrary.0.3.1 [23] were employed for the magnesium and hydrogen atoms to model the ion-electron interactions with the generalized gradient approximation (GGA) [24] for the exchange-correlation functional in the formalism of Perdew, Burke and Ernzerhof (PBE) [25]. The DFT benchmarks show that the PBE functional gives the best geometry and good binding energies for magnesium hydride systems, with the lowest computational effort for large systems [26]. The energy cutoff of the plane-wave basis was chosen as 55 Ry. The Brillouin zone (BZ) is discretized by Monkhorst-Pack scheme [27] with a spacing of 0.04 $Å^{-1}$ between the k-points, as a good compromise between the calculation accuracy and the computational effort. This separation corresponds to a grid $6 \times 6 \times 6$ for the bulk unit cell of the α-MgH_2. The chosen plane-wave cutoff and the number of k-points ensure a better total energy convergence than 2.4×10^{-5} Ry/cell. The tolerance threshold of the self-consistent field calculation was less than 1×10^{-9} Ry/atom. The full and partial geometry equilibration continues until the forces converge to less than 5×10^{-5} Ry/Å and all the stress components are less than 0.005 GPa.

The primitive cells of all the investigated compounds in the present study are presented in Fig. 1.

The Murnaghan Equation of States (EOS) [28–30] relates by a simple polynomial equation the volume V and its equilibrium value V_0, the bulk modulus B and its derivative B':

$$E(V) = E_0 + \frac{B_0 V}{B'}\left[\frac{(V_0/V)^{B'}}{B'-1} + 1\right] - \frac{V_0 B_0}{B'-1} \tag{1}$$

For each of the investigated systems, the equilibrium volume V_0 is determined by full (the lattice parameters and the fractional coordinates of atoms) geometry equilibration of the unit cells. The system energy $E(V)$ is calculated for at least nine volumes around the equilibrium value V_0, with an incremental step of $10\%V_0$. For each volume, the crystal shape and the atomic fractional coordinates are optimized. The parameters E_0, B and B' are determined by fitting the EOS, given in Eq. (1).

At very low temperatures, the system energy is only dependent on the system volume and the pressure can be estimated by [31]

$$P(V) = -\frac{dE}{dV} = \frac{B_0}{B'}\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right] \tag{2}$$

In order to build the *P-T* phase diagram we have to estimate the Gibbs free energy, taking into account the temperature effects. Therefore, we have to consider the phonon contribution to the Helmholtz free energy. The phonon spectrum is calculated for each of the volume values by the Density-Functional Perturbation Theory method [32], using the module *thermo_pw* [33] of the package Quantum Espresso. The quasi-harmonic model was applied for the calculations of the thermodynamic properties.

Neglecting any possible rotational contribution, the Helmholtz free energy of an ordered crystalline phase versus the volume V and temperature T is:

$$F(V, T) = E_0(V) + \frac{1}{2}\sum_{\vec{q},\nu} \hbar\omega(\vec{q}, \nu, V) + k_B T \sum_{\vec{q},\nu} \log(1 - e^{-\frac{\hbar\omega(\vec{q},\nu,V)}{k_B T}}) \tag{3}$$

where $\vec{q}$ is a wavevector in the Brillouin zone (BZ), ν is the phonon branch index and $\omega(\vec{q}, \nu, V)$ is the phonon frequency of the ν-th branch at wavevector $\vec{q}$ for the volume V. The Gibbs energy can be evaluated from the Helmholtz energy $F(P, T)$ by adding the product pressure-volume

$$G(P, T) = F(P, T) + PV \tag{4}$$

The complete phase diagram for the six magnesium hydrides investigated was built by the PhaseGO toolkit [34], which computes the Gibbs free energy by using the data (volume, energy and the phonon density of states) provided by the *thermo_pw* calculations with Quantum Espresso.

3. Structural relaxation

We first studied the effect of the relaxation starting from the experimentally or theoretically determined structures. The total energy of the system computed by the DFT method depends on the atomic positions; hence we can minimize the energy function with respect to the positions. The total energy of MgH_2, as a function of lattice parameter, was calculated and the Hellmann–Feynman forces were minimized by using the Variable Cell-Shape Relaxation ("vc-relax") method, preserving the symmetry of the crystal [36]. The available data in the literature and the present calculated crystal parameters, atom equilibrium positions, bulk modulus B and its derivative B' for all systems investigated are given in Table 1. The good agreement of our results with other available data validates our calculation approach (see Table 1).

4. Equation of state and pressure transitions

The dependence of the energy on the unit cell volume obtained by Murnaghan EOS fitting for the different magnesium hydride structures are presented in Fig. 2. The minimum of the curves gives the equilibrium volume V_0 and the equilibrium energy E_0. The parameters E_0 and V_0 obtained by fitting the EOS and those corresponding to the equilibrium structures are in very good agreement, which indicates the validity of the EOS for the investigated systems.