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Alloying Effect Study on Thermodynamic Stability of MgH$_2$ by First-principles Calculation

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First-principles calculations based on density functional theory were performed to study the effect of alloying on the thermodynamic stability of MgH$_2$ hydride (rutile and fluorite structures) with transitional metals (TM=Sc, Ti, Y) and group IIA elements (M=Ca, Sr, Ba). The results indicate that fluorite structure of these hydrides are more stable than its relative rutile structure at low alloying content (less 20%), structural destabilization of MgH$_2$ appears in the alloying cases of Ti, Sr and Ba respectively. The structure-transition point from rutile structure to fluorite structure is at around 20% for MgH$_2$-TM, and about 40% for MgH$_2$-M. The formation enthalpy of fluorite Mg$_{0.5}$Ba$_{0.5}$H$_2$ is about 0.3 eV and higher than that of fluorite MgH$_2$, indicating that its hydrogen-desorption temperature at atmospheric pressure will be much lower than that of pure MgH$_2$. Good consistency between experimental and calculated data suggests that above-adopted method is useful to predict structural transition and properties of MgH$_2$ based hydrides for hydrogen storage.

Key words: MgH$_2$, First-principles study, Alloying, Destabilization, Structural transition

I. INTRODUCTION

As one of the most promising hydrogen storage materials, magnesium hydride (MgH$_2$) has attracted huge interest in hydrogen storage field due to its abundant resource, low cost and high hydrogen-storage capacity of 7.6 wt%. However, its application in hydrogen-storage is limited because of its poor hydrogen absorption and desorption performance. In practice it often takes several hours for (de)hydrogenation at a relatively higher temperature about 623 K [1−3].

To improve the hydrogenation kinetics of Mg hydride, a large number of experimental and theoretical investigations have been performed extensively in the last decades. These studies have shown that doping the third foreign elements into MgH$_2$ is an efficient way to decrease dehydrogenation temperature and expedite kinetics of MgH$_2$ [4−6]. Kelkar and co-authors have found that the Mg−H bond in Al-doped MgH$_2$ is more susceptible to dissociation and thus the thermodynamic stability of MgH$_2$ is decreased [7, 8]. The TMs (Ti, Mn, and Ni) doping influence on (110) surface of MgH$_2$ has been investigated by Dai et al. [9, 10]. They have found that Ti atoms prefer to occupy both substitutional [9] and interstitial sites [10], while Mn and Ni tend to occupy the interstitial sites near the surface of MgH$_2$. An investigation performed by Er et al. [11] has shown that for TM (TM = Sc, Ti, V, and Cr) concentration approaching x=0.2 in Mg$_x$TM$_{1−x}$H$_2$, the fluorite structure with cubic H environment becomes more stable than the rutile one. Mamula et al. have investigated electronic structure and charge distribution topology of MgH$_2$ doped with 3d transition metals using the full potential (linearized) augmented plane waves method with addition of local orbitals (FP-LAPW+LO and APW+LO), and found that along the 3d series TMs accomplish different kinds of bonding with the nearest and next-nearest neighbor hydrogen atoms that in general weaken related Mg−H bonds and destabilize the surrounding MgH$_2$ matrix [12].

A major improvement in discharge kinetics resulting from alloying Mg with Sc has been reported by Notten et al [13]. Up to 80% of Mg contents, the reversible capacity exceeded 5 wt% and the corresponding desorption properties were still excellent. The Mg-Sc system has been extensively studied by using several diffraction techniques, and it was found that the ternary hydride retains the fluorite-type structure of pure ScH$_2$ [14]. This structure contains large empty octahedral interstitials, which facilitate rapid hydrogen diffusion.

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This has recently been confirmed by Conradi *et al.* [15]. NMR measurements have shown that the hopping rates of hydrogen between different hydrogen sites in ScH_2 and $Mg_{0.65}Sc_{0.35}H_2$ are about seven and eight orders of magnitude more rapid than that in MgH_2, respectively. Recently, based on the theoretical considerations presented by Vajeeston *et al.* [16] and their experimental finding [17], Pauw and co-authors [18] have further concluded that for MgH_2 the transformation from a rutile-type structure to a fluorite-type structure could be accelerated by alloying with transition metals.

In this work, based on two crystallographic modifications of MgH_2 (rutile-type and fluorite-type), a theoretical investigation based on density functional theory (DFT) of MgH_2-transitional metals (TM=Sc, Ti, Y) and MgH_2-group IIA elements (M=Ca, Sr, Ba) was carried out. The destabilizing mechanism of MgH_2 alloying with TM/M for hydrogen storage performance was also discussed via analyzing the change in the calculated enthalpy of formation, lattice parameters, and electron density of states (DOS).

II. COMPUTATIONAL DETAILS

All DFT calculations were performed using the Vienna *ab initio* Simulation Package [19]. The interactions between core and valence electrons were described with the projector augmented wave method [20]. Perdew-Burke-Ernzerhof implemented generalized gradient approximation [21] was used to treat the exchange and correlation energies. The plane-wave energy cutoff was set to 400 eV and the k-point mesh in the Brillouin zone was about $0.03 \times 2\pi$ Å^{-1} in all calculations. During structure optimization the lattice parameters, volume and atom positions were allowed to relax fully within symmetry restrictions. The convergence criterion for total energy was set to 10^{-5} eV during the self-consistent calculations.

Two types of crystal structure of MgH_2 which are the rutile structure (tetragonal, P42/mnm) and fluorite structure (cubic, Fm-3m) are generally considered. In this work, the super cell models containing 8 metal atoms (seen in Fig.1) were established in order to consider the effect from different alloying contents on the formation enthalpy of the two structural modifications.

In general, the stability of any compound can be evaluated by its formation enthalpy. The formation enthalpy of MgH_2 based hydrides can be defined as:

$$\Delta H_f = E_{Mg_{1-x}M_xH_2} - [(1-x)E_{Mg} + xE_M] - E_{H_2} \quad (1)$$

where $E_{Mg_{1-x}M_xH_2}$, E_{Mg} and E_M are the calculated total energies of $Mg_{1-x}M_xH_2$, Mg, and M bulk materials, and E_{H_2} is the energy of isolated H_2 molecule.
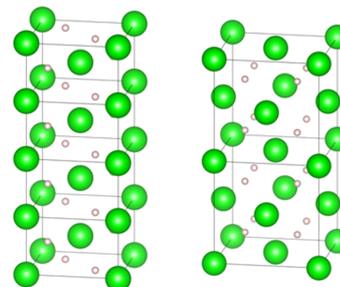
FIG. 1 $1 \times 1 \times 4$ cell of the rutile structure (left, tetragonal, P42/mnm) and $1 \times 1 \times 2$ cell of the fluorite structure (right, cubic, Fm-3m). The big spheres are Mg atoms, and the small spheres are H atoms.

III. RESULTS AND DISCUSSION

A. MgH₂-TM system hydrides

Calculated formation enthalpies of MgH_2-TM (TM=Sc, Ti, Y) hydrides are shown in Fig.2. The calculated formation enthalpy of rutile MgH_2 is -0.64 eV (or -61.8 kJ/mol), which has about 20% difference compared with the literature value (-77 kJ/mol) [22], but agrees well with the theoretical results (-0.66 eV) [13, 16−18]. Considering that the experiment was carried out under 673 K, so these calculated values at ground state are acceptable.

In the case of MgH_2 with rutile structure, the formation enthalpies decrease with the increase of alloying content of Sc and Y, indicating that rutile structure of MgH_2 is stabilized by alloying with Sc or Y. While an apparent increase of formation enthalpy is obtained when alloying with Ti in the range of 0−37.5%, $Mg_{0.625}Ti_{0.375}H_2$ has a higher formation enthalpy value of -0.45 eV, which is 0.19 eV higher than that of pure MgH_2, but the formation enthalpy will decrease when the alloying content of Ti is above 37.5%.

In the case of MgH_2 with fluorite structure, the structure of pure MgH_2 is less stable than the rutile structure of MgH_2. But the fluorite structure becomes more stable than the rutile structure when Sc, Ti or Y atoms doping content reaches 20%, which indicates that $Mg_{0.8}TM_{0.2}H_2$ energetically prefers to a cubic fluorite structure. This is consistent with the experimental findings suggested by X-ray diffraction [13, 14]. It also agrees well with the results of electrochemical experiments, which has reported that alloying with 20% of transitional metal can greatly improve the hydrogen desorption kinetic performance [23].

Figure 2 shows an important point, 20% of alloying content is a structure transition point from rutile structure to fluorite structure, the formation enthalpy of fluorite structure of MgH_2 becomes more negative than that with rutile structure when x is above 0.2. As to $Mg_{1-x}Ti_xH_2$ calculation, the rutile structure is destabilized by 0.17 eV when x=0.25. The most unsta-
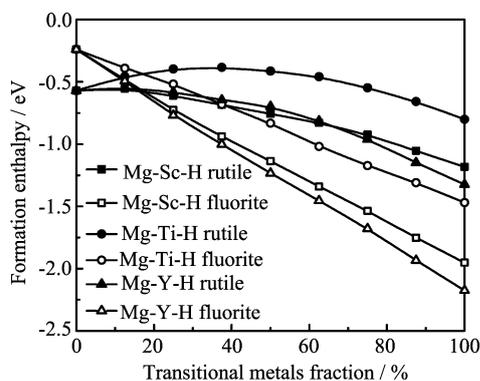
FIG. 2 Formation enthalpy of Mg-TM hydrides.

FIG. 3 Formation enthalpy of Mg-M hydrides.

ble status is around $x=0.375$, the formation enthalpy of $Mg_{0.5}Ti_{0.5}H_2$ is -0.39 eV, which is 0.24 eV more positive than that of pure MgH$_2$. However, the fluorite structure still becomes the most stable one at $x=0.2$, similar to Mg-Sc system. These results are in accordance with the results reported by Pauw *et al.* [18]. MgH$_2$-TM system hydrides have the structure-transition tendency from rutile structure to fluorite structure at a specific point of alloying content, the transition point is about 20% for transition metals.

B. MgH$_2$-M system hydrides

Calculated formation enthalpies of $Mg_{1-x}M_xH_2$ (M=Mg, Ca, Sr) are shown in Fig.3. It can be clearly found from Fig.3 that alloying with Ca will result in the increase of thermodynamic stabilities of $Mg_{1-x}Ca_xH_2$ hydride since the calculated formation enthalpies of the rutile and fluorite structure always decrease with the increase of alloying content. However, the alloying treatment with Sr can induce a slight decrease in the thermodynamic stabilities of rutile $Mg_{1-x}Sr_xH_2$, since the enthalpy of $Mg_{0.625}Sr_{0.375}H_2$ is 0.06 eV higher than that of MgH$_2$. Figure 3 also clearly indicates that the most obvious decrease in structural stability of both rutile and fluorite structure is from the alloying treatment with Ba. It can be observed that the enthalpy of rutile $Mg_{0.5}Ba_{0.5}H_2$ is 0.33 eV higher than that of MgH$_2$. In addition, the structural transition point from the rutile to fluorite structure is around 40% for $Mg_{1-x}M_xH_2$, which has a big delay compared with that of $Mg_{1-x}TM_xH_2$ hydrides (about 20%). At this point, its theoretical hydrogen-storage capacity is 3.1 wt%.

C. Electronic properties of Mg$_{0.5}$Ba$_{0.5}$H$_2$

As mentioned above, alloying with Ba will lead to an obvious decrease in the thermodynamic stability of $Mg_{1-x}M_xH_2$ and the fluorite $Mg_{0.5}Ba_{0.5}H_2$ has a high formation enthalpy, so here $Mg_{0.5}Ba_{0.5}H_2$ has been se-

lected to make a comparison with pure MgH$_2$. After structure optimization, the cubic fluorite structure of Ba doped MgH$_2$ is distorted, and the unit cell volume is obviously increased by 39.9%. The interatomic distance between Mg and H atoms also significantly increased from 1.94 Å to 2.24 Å. So the interaction between Mg and H will be weakened. Calculated DOS of rutile MgH$_2$ is shown in Fig.4. There is a wide band gap (about 2.73 eV) between the conduction band and valence band, revealing its insulating nature. The partial DOS of MgH$_2$ suggests that its valence bands are mainly contributed by H 1s states, while the contribution from the Mg 3s and 2p orbitals is not so much. The involvement of 2p electrons in the valence band is an evidence of hybridization of Mg 3s and 2p orbitals. The DOS of Ba-doped MgH$_2$ ($Mg_{0.5}Ba_{0.5}H_2$) is presented in Fig.5. With Ba-doping, the Ba 5p and 4d orbitals make a distinct contribution to the valence band. While a peak within the energy range from -10 eV to -15 eV is mainly ascribed to the hybridization of H 1s and Ba 5p orbitals, indicating that there exists a strong bonding between Ba and H atoms. Although $Mg_{0.5}Ba_{0.5}H_2$ still keeps its non-metallic nature, its metallization is obviously improved as suggested from the relative decrease of band gap.

IV. CONCLUSION

Based on two crystallographic modifications of MgH$_2$ (rutile-type and fluorite-type), the relative thermodynamic stabilities of MgH$_2$-TM and MgH$_2$-M (TM=Sc, Ti, Y, M=Ca, Sr, Ba) have been studied by first-principles calculations. Rutile structure of MgH$_2$ will transform into fluorite structure when alloying with these elements. For MgH$_2$-TM hydrides, the structure-transition point from rutile structure to fluorite structure is at around 20% substitution, which agrees very well with both experimental and previous calculated data. For MgH$_2$-M hydrides, this structural transition point is at around 40% substitution. Further-
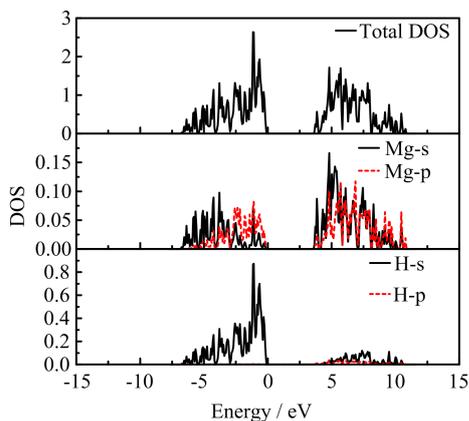
FIG. 4 Calculated DOS of rutile MgH$_2$.
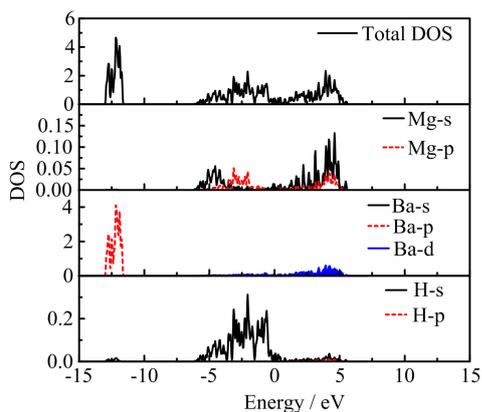
FIG. 5 Calculated DOS of fluorite Mg$_{0.5}$Ba$_{0.5}$H$_2$.

more, Ti Sr, and Ba substitution not only cause the structure transition, but also reduce its thermodynamic stabilities, especially in the case of Ba substitution. The formation enthalpy of fluorite Mg$_{0.5}$Ba$_{0.5}$H$_2$ is 0.33 eV higher than that of pure rutile MgH$_2$, suggesting that its hydrogen-desorption temperature at atmospheric pressure will be much lower compared to pure MgH$_2$. Mg$_{0.5}$Ba$_{0.5}$H$_2$ also has a reasonable theoretical hydrogen-storage capacity of about 3.1 wt%, which indicates that it would be a potential candidate of hydrogen storage materials.

V. ACKNOWLEDGMENTS

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