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Density functional study of Mg_2FeH_6 complex hydride

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Mg_2FeH_6, which has the highest volumetric hydrogen density, is considered a promising hydrogen storage material. Within the framework of the density functional theory, the crystal structure, physical properties, electronic structure and formation capacity of Mg_2FeH_6 complex hydride have been investigated. The optimized structural parameters correspond closely with the experimental data from X-ray and neutron powder diffraction measurements. A detailed study of the electronic structures, including the energy band, density of states (DOS) and charge density distribution, reveals the orbital hybridization and bonding characteristics within this hydride. It was shown that Mg_2FeH_6 is a semiconductor with the energy gap of ca. 2.3347 eV, and that a mixed ionic-covalent bond between Fe and H in FeH_6 complexes is embedded in the matrix of Mg^{2+} cations. The calculated formation enthalpies of Mg_2FeH_6 , based on the possible synthesis routes, indicate that optimum conditions are achieved if this hydride is fabricated from pure elements, and that the preparation of other compounds would lead to inferior synthesis.

Keywords: *hydrogen storage materials; density functional theory; electronic structure; enthalpy of formation*

1. Introduction

With the growing pressure of energy shortage and environmental contamination, a common issue becomes to develop sustainable and clean energy sources. Hydrogen has been viewed as a highly appealing energy carrier for renewable energy because of its abundance and environmental friendliness. In the exploitation of hydrogen energy, hydrogen storage is one of the key challenges influencing the success of the hydrogen economy. Great efforts have been made to develop advanced hydrogen storage tech-

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nology, and the solid state materials that chemically bind or physically adsorb hydrogen at volume densities higher than that of gas and liquid hydrogen are proved to be the most promising way of storing hydrogen. Mg and Mg based alloys have received great interest because of their high hydrogen volumetric-gravimetric capacity, light weight and low cost. However, a slow sorption kinetics and high dissociation temperature hamper their practical applications. Up to now, considerable research has been undertaken to identify a suitable material that absorbs hydrogen close to room temperature and desorbs it at temperatures low enough to use the waste heat of exhaust gas [1–3].

Complex hydrides are considered to be the most useful of all known hydrogen storage materials because they exhibit mixed ionic-covalent bonding between metal and the hydrogen complex, thereby making them adaptable and suitable for facilitating the hydrogenation/dehydrogenation process [4–6]. In particular, this makes them suitable for the storage of renewable fuel, which is used in both power cells as well as combustion engines. The ternary Mg_2FeH_6 hydride shows the highest volumetric hydrogen density, of 150 kg $H_2 \cdot m^{-3}$, among all the known transition metal complex hydrides and has a high gravimetric hydrogen density of 5.47 wt. %. Furthermore, this hydride is based on an inexpensive metallic element, Mg, and Fe, and its commercial price should be much lower than that of other complex hydrides, which makes it more appealing. However, this ternary hydride has the particularity that Mg and Fe do not form stable binary compounds themselves [7]. Therefore, the synthesis and study of Mg_2FeH_6 becomes difficult to carry out. Several investigations regarding Mg_2FeH_6 have been mainly focused on enhancing the hydride yield by adopting different preparation routes [8–12]. In order to improve effectively the performance of Mg_2FeH_6 involved in reversible hydrogenation/dehydrogenation processes for practical applications, beginning with an understanding of the fundamental physical properties of this complex hydride, is of key importance and great interest. Theoretical investigations into complex metal hydrides including calculations from first principles have been very common in recent years [13–15]. However, few studies on Mg_2FeH_6 as a potential hydrogen storage material have been reported. In the present work, first principle calculations based on density functional theory are conducted in a comprehensive study of the structural and electronic properties, as well as the formation ability, of Mg_2FeH_6 complex hydride. The results are expected to provide theoretical guidance for designing and improving this potential hydrogen storage material.

2. Models and method of calculations

X-ray and neutron powder diffraction experimental analysis showed that Mg_2FeH_6 has a K_2PtCl_6 type structure, as shown in Fig. 1a [8]. Its unit cell has the cubic symmetry, space group *Fm*3*m* (No. 225), and 36 atoms with the lattice constant $a = 6.443$ Å. Mg, Fe and H atoms occupy the 8*c*, 4*a* and 24*e* sites in the crystal, respectively. The

atomic coordinates in the unit cell are: Mg (8*c*) – (0.25, 0.25, 0.25); Fe (4*a*) – (0, 0, 0); H (24*e*): (*x*, 0, 0), $x \approx 0.24$.

Figure 1b presents the cluster model of Mg_2FeH_6. It is an octahedral FeH_6 complex, surrounded by 8 Mg atoms in a cubic configuration. These complexes are arranged on an fcc lattice such that each Mg atom is tetrahedrally surrounded by 4 FeH_6 complexes and has 12 H atoms as the nearest neighbours. The metal–hydrogen bond distances are d(Fe–H) = 1.556 Å and d(Mg–H) = 2.2739 Å, respectively. The shortest separations between the hydrogen atoms within (intra) and between (inter) the FeH_6 complexes are d^{intra}(H–H) = 2.201 Å and d^{inter}(H–H) = 2.346 Å, respectively. The primitive cell of Mg_2FeH_6 is used in the calculations as shown in Fig. 1c. It has 9 atoms, comprising 2 Mg atoms, 1 Fe atom and 6 H atoms.

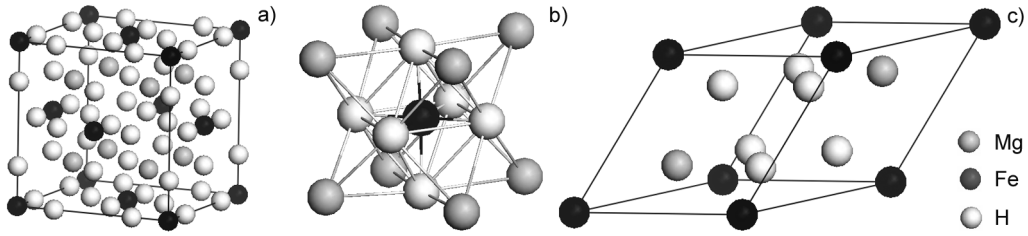

Fig. 1. Models of: a) a crystal cell, b) a cluster, c) primitive cell of Mg_2FeH_6

In the present work, the structural optimization and total energy calculations are performed with the DMol^3 package [16-18] which is based on the density functional theory (DFT) [19, 20], and the Perdew–Burke–Eruzerhof (PBE) exchange-correlation functional [21] is adopted for generalized gradient approximation (GGA) correction. All electron Kohn–Sham wave functions are expanded in a double numerical basis with a polarized orbital (DNP). The cell parameters, including lattice constants, and the atomic positions in the structure are fully relaxed to get the final structure with minimum total energy. The convergences criteria of optimization are 2.721×10^{-4} eV, 0.054eV/ Å and 0.005 Å for energy, gradient and atomic displacement, respectively.

3. Results and discussions

3.1. Parameters of crystal structure and physical properties

To assess the accuracy of the computational method, a series of preliminary calculations on crystal structure parameters and physical properties were performed on the related solids, such as hcp-Mg, bcc-Fe, rutile type α-MgH_2, and H_2 molecule. The corresponding results are listed in Table 1. It was found that their equilibrium lattice constants, atomic positions, interatomic distances and cohesive energies are all in good agreement with the experimental data. For example, the lattice constants *a*, *c* and

the c/a ratio of hcp-Mg are 3.1715 Å, 5.1504 Å and 1.6240, respectively, which are close to the experimental values [22] of $a = 3.21$ Å, $c = 5.21$ and $c/a = 1.623$, and the error of c/a ratio, calculated here relative to the experimental result, is about 0.06%. The calculated cohesive energy $E_{coh} = 1.4942$ eV/atom of hcp-Mg, which is close to the experimental value [22] of $E_{coh} = 1.51$ eV/atom, and the error of cohesive energy, calculated here relative to the experimental result, is about 1.05%. The lattice constant of bcc-Fe is 2.8619 Å, which is close to the experimental value [22] of $a = 2.87$ Å, and the error of the lattice constant calculated here relative to the experimental result, is about 0.28%.

Table 1. The equilibrium lattice constants a and c [Å], cohesive energy E_{coh} [eV/formula unit], bulk modulus B_0 [GPa], atomic positions and interatomic distance d [Å] for hcp-Mg, bcc-Fe, rutile type α-MgH_2, and H_2 molecule

Material	Property	This work	Experimental	Reference
hcp-Mg	a	3.1751	3.21	[22]
	c	5.1504	5.21	
	E_{coh}	1.4942	1.51	
	B_0	32.4579	35.4	
bcc-Fe	a	2.8619	2.87	[22]
	E_{coh}	5.4088	4.28	
	B_0	248.3762	168.3	
H_2	d(H–H)	0.7490	0.741	[23]
	E_{coh}	4.5502	4.74	
α-MgH_2	a	4..5124	4.501	[24]
	c	3.0240	3.010	
	E_{coh}	6.6185	-	
	B_0	47.7486	51	[25]
	u_H	0.3040	0.304	
Mg_2FeH_6	a	6.3977	6.443	[8]
	E_{coh}	24.9536	-	
	B_0	77.1010	-	
	Mg(8c)			
	x	0.2501	0.25	
	y	0.2500	0.25	
	z	0.2484	0.25	
	Fe(4a)			
	x	0	0	
	y	0	0	
	z	0	0	
	H(24e)			
	x	0.2456	0.24	
	y	0	0	
	z	0	0	
	d (Mg-H)	2.2667	2.2739	
	d (Mg-Fe)	2.7717	–	
	d (Fe-H)	1.5720	1.5560	
	d^{intra}(H-H)	2.2165	2.2010	
	d^{inter}(H-H)	2.3178	2.3460	

The bond length of a free H_2 molecule is 0.7490 Å, which is close to the experimental value [23] of $d_{H–H}$ = 0.741 Å, and the error of the bond length, calculated here related to the experimental result, is about 1.08%. The lattice constants a, c and c/a ratio of α-MgH_2 are 4.5124 Å, 3.0240 Å and 0.6702, respectively, which are close to the experimental values [24, 25] of a = 4.501 Å, c = 3.010 Å and c/a = 0.6687, the error of the c/a ratio, calculated here related to the experimental result, being about 0.22%. Evidently, a good agreement exists between the predictions based on calculations and experimental values. Although the calculated bulk moduli of solids such as Fe have larger errors relative to the experimental results [22], they are sufficiently acceptable for the purpose of the verifying calculations.

Next, the lattice constants, atomic positions and interatomic distances of Mg_2FeH_6 primitive cell are estimated from the minimized total energy. The final results are also listed in Table 1. It is found that the optimized structure of a Mg_2FeH_6 primitive cell maintains *Fm*3*m* symmetry, which is in good agreement with the experimental structure revealed by X-ray and neutron powder diffraction data [8]. The lattice constant of Mg_2FeH_6 is 6.3977 Å (the value is obtained by conversion of the lattice constant 4.5311 Å of the Mg_2FeH_6 primitive cell), which is close to the experimental value [8] of a = 6.443 Å, and the error of the lattice constant, calculated here with respect to the experimental result, is about 0.70%. The present positions of Mg, Fe, H atoms as well as interatomic distances in the Mg_2FeH_6 primitive cell are also in good agreement with the experimental results [8]. In particular, the hydrogen positions in Mg_2FeH_6 are precisely determined as to be (0.2456, 0, 0), which are very close to the deuterium positions (0.2420, 0, 0) in Mg_2FeD_6 obtained in the neutron diffraction measurement [8]. In addition, we also present the cohesive energy E_{coh} and bulk modulus B_0 of Mg_2FeH_6, and they are 24.9536eV per formula unit and 77.1010 GPa, respectively. Since no experimental values of E_{coh} and B_0 of Mg_2FeH_6 are available, no comparisons can be made with either of their theoretically computed values. However, the results of this paper are expected to be useful as a reference for future investigations into this complex hydride.

3.2. Electronic structure

The energy band structure and electronic density of states (DOS) of Mg_2FeH_6 are calculated and shown in Figs. 2, 3, respectively. Both of these figures exhibit an energy gap of about 2.3347 eV between valence and conduction bands, indicating that Mg_2FeH_6 hydride exhibits a semiconducting behaviour. The eight valence bands in Fig. 2 have a width of about 9.2519eV. From these figures it can be seen that the first valence band in the low energy range between –9.2519 and –6.1226eV mainly originates from the contribution of H(s), a few Mg(s) and a few Fe(s) orbitals, while the next seven interlapping valence bands in the higher energy range between –5.4423 and 0 eV are mainly from H(s) , Fe(p) and Fe (d) states. This suggests that there is a strong hybridization between H and Fe orbitals, while there is a weak one between H and Mg

orbitals. The conduction bands are mainly from Mg (and to lesser extent Fe and H) empty states. Mg has hardly any projection in the occupied states, as is shown in Fig. 3, indicating that each Mg donates two electrons to the FeH_6 complex [13]. Based on the analysis, it can be concluded that significant charge transfer leads to the formation of Mg^{2+} ions and a negatively charged FeH_6 complex, which constitutes the ionic bonding between them. At the same time, there exists a strong covalent bonding interaction between hydrogen and iron within the FeH_6 complex. The covalent bonding plays a comparatively more dominant role than ionic bonding in this complex hydride.

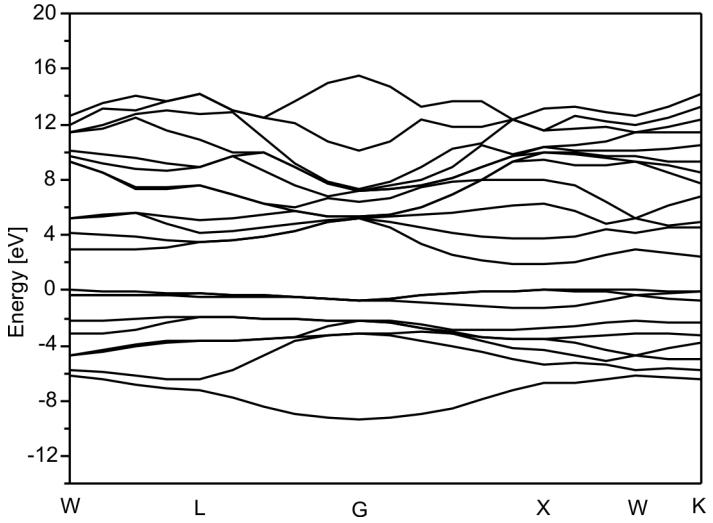

Fig. 2. Energy band structure of Mg_2FeH_6

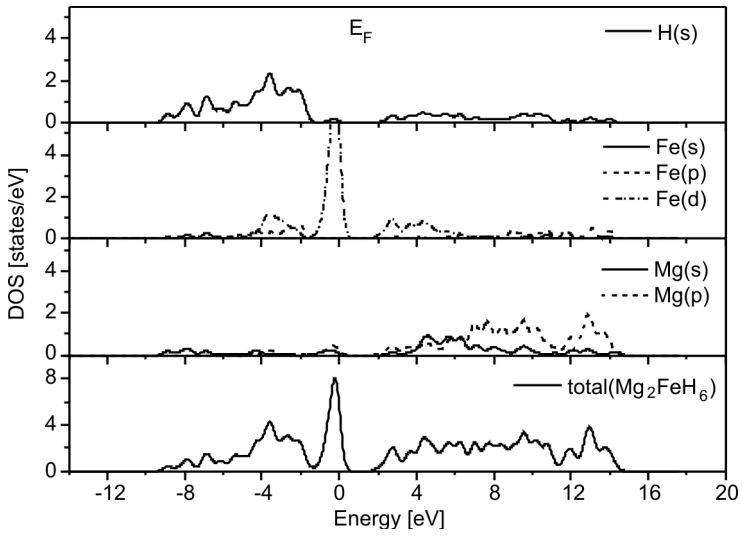

Fig. 3. Total and partial densities of states of Mg_2FeH_6

Further analysis of the charge distribution of Mg_2FeH_6 and the charge transfer in the FeH_6 complexes is performed. The total charge density $\rho(r)$ and the difference charge density $\Delta\rho(r)$ in the plane containing Mg, Fe, H atoms are shown in Figs. 4a, b. The difference charge density $\Delta\rho(r)$ [26] is defined as the difference between the total charge density of the solid and a superposition of atomic charge densities with the same spatial coordinates as in the solid. In Figure 4a, the total charge density plot shows that there is a strong bond between Fe and H atoms in FeH_6 complexes, while weak bonding interactions exist between Mg and FeH_6 complexes. The electron density is highest in the vicinity of FeH_6 complexes, which are consistent with the analytical results obtained from electronic density of states (DOS).

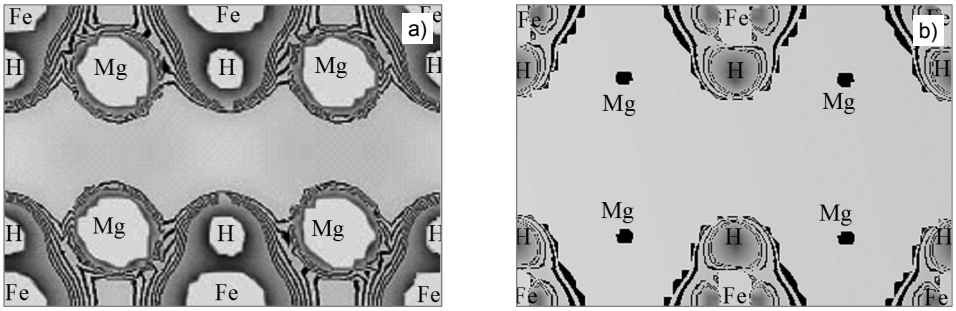

Fig. 4. Total (a) and difference (b) charge density plots of Mg_2FeH_6 in the (110) plane

From the difference density plot shown in Fig. 4b, it can be seen that there is significant charge transfer, leading to positively charged Mg and negatively charged FeH_6 complexes. For FeH_6 complexes, it was found that there is partial charge transfer from Fe to H, indicating that, besides the covalent bonding, there is also a weak ionic bonding interaction between Fe and H in FeH_6 complexes. These features are highly conducive to mixed ionic-covalent bonding between Fe and H in FeH_6 complexes embedded in the matrix of Mg^{2+} cations.

3.3. Enthalpy of formation

The enthalpy of formation is the most important thermodynamic parameter used to identify and classify hydrogen storage materials, since it determines the heat of the overall hydriding reaction, which, in turn, affects the temperatures of the reversible hydrogenation/dehydrogenation processes. It is the best aid to establish whether theoretically predicted phases are likely to be stable, and also such data may serve as guides for possible synthesis routes of materials. Commonly, the enthalpy of formation is negative, and the lower the enthalpy of formation, the greater the phase stability and the easier the synthesis of the material is [27]. As far as Mg_2FeH_6 is concerned, due to the absence of the binary Mg_2Fe compound, the synthesis of this complex hydride becomes very difficult. Experimentally, Mg_2FeH_6 are usually fabricated by ball

milling pure elements such as Mg and Fe or ball milling of other mixtures such as MgH_2 and Fe in an hydrogen atmosphere. In order to investigate the formation ability of Mg_2FeH_6 under various conditions of syntheses, it is necessary to calculate the enthalpy of formation. In the present work, three possible synthesis routes are considered as follows [8, 13]:

$$2MgH_2 + Fe + H_2 \rightarrow Mg_2FeH_6 \tag{1}$$

$$Mg + MgH_2 + Fe + 2H_2 \rightarrow Mg_2FeH_6 \tag{2}$$

$$2Mg + Fe + 3H_2 \rightarrow Mg_2FeH_6 \tag{3}$$

The corresponding enthalpy of formation (ΔH) is calculated according to the following expressions [28]:

$$\Delta H_1 = \frac{1}{3}\left(E_{\text{tot}}(Mg_2FeH_6) - 2E_{\text{tot}}(MgH_2) - E_{\text{tot}}(Fe_{\text{bcc}}) - E_{\text{tot}}(H_2)\right) \tag{4}$$

$$\Delta H_2 = \frac{1}{3}\left(E_{\text{tot}}(Mg_2FeH_6) - E_{\text{tot}}(Mg_{\text{hcp}}) - E_{\text{tot}}(MgH_2) - E_{\text{tot}}(Fe_{\text{bcc}}) - 2E_{\text{tot}}(H_2)\right) \tag{5}$$

$$\Delta H_3 = \frac{1}{3}\left(E_{\text{tot}}(Mg_2FeH_6) - 2E_{\text{tot}}(Mg_{\text{hcp}}) - E_{\text{tot}}(Fe_{\text{bcc}}) - 3E_{\text{tot}}(H_2)\right) \tag{6}$$

Here $E_{\text{tot}}(Mg_2FeH_6)$ refers to the total energy of the Mg_2FeH_6 primitive cell at the equilibrium lattice constant, $E_{\text{tot}}(Mg_{\text{hcp}})$, $E_{\text{tot}}(Fe_{\text{bcc}})$, $E_{\text{tot}}(MgH_2)$ are the single atomic energies of hcp-Mg, bcc-Fe in the solid states and α-MgH_2 in the primitive cell, respectively, and $E_{\text{tot}}(H_2)$ refers to the total energy of the gaseous H_2 molecule. In this paper, we calculate the single atomic energy of hcp-Mg and fcc-Fe by the following method: firstly, the energy of a pure metal crystal in the solid state is calculated, then the energy is divided by the number of atoms belonging to the crystal, and the result from the above calculation is just the energy of a single atom in the pure metal. The calculated values of $E_{\text{tot}}(Mg_2FeH_6)$, $E_{\text{tot}}(Mg_{\text{hcp}})$, $E_{\text{tot}}(Fe_{\text{bcc}})$, $E_{\text{tot}}(MgH_2)$ and $E_{\text{tot}}(H_2)$ are –45368.3726eV, –5442.5222eV, –34385.1223eV, –5474.8548eV and –31.6795eV, respectively. From Eqs. (1)–(3), the formation enthalpies of Mg_2FeH_6 based on various synthesis routes are estimated as ΔH_1 = –0.6204eV per H_2 molecule (i.e., –59.8200kJ/mol H_2), ΔH_2 = –0.8381eV per H_2 molecule (i.e., –80.9065kJ/mol H_2), ΔH_3 = –1.0558eV per H_2 molecule (i.e., –101.9929kJ/mol H_2). The calculated formation enthalpies are all negative, which indicates that these reactions are favourable from the thermodynamic point of view. By further comparing the values of ΔH, it is obvious that the route having the lowest reaction energy is the one that starts with pure elements. Hence, for the three considered synthesis routes, reaction (3) is clearly the optimum one. However, it should be noted that the kinetic aspects of these reaction pathways are not considered in the present calculation and this picture may be changed in a practical procedure. If there is no other compelling reason such as kinetics, the preparation of Mg_2FeH_6 the pure elements

should be the best synthesis route. This result is expected to be the guidance for enhancing the yield of Mg_2FeH_6 complex hydride.

4. Conclusions

The structural, electronic and formation ability of Mg_2FeH_6 complex hydride were investigated by using the first principles calculation based on density functional theory (DFT). The calculated structural parameters and physical properties are in good agreement with the experimental results, the hydrogen positions in Mg_2FeH_6 are precisely determined as (0.2456, 0, 0), being very close to the deuterium positions in Mg_2FeD_6 obtained in the neutron diffraction measurement. Detailed calculations of electronic structures suggest that the complex Mg_2FeH_6 hydride is a semiconductor with the energy band gap of about 2.3347 eV. The total and partial densities of states as well as the charge density plots indicate a significant charge transfer to Mg^{2+} ions and negatively charged FeH_6 complex. The bonding within the FeH_6 complex mainly involves the hybridization between Fe(p), Fe(d) and H(s) orbitals but exhibits a little ionic character for partial charge transfer from Fe to H. The calculations of formation enthalpy are used to estimate the heat change in hydrogenation process according to three possible synthesis routes. It is found that without considering the influence of kinetic aspects, the preparation of Mg_2FeH_6 is likely to perform via pure elements.

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