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A first principles study of the thermal stability of $A_m(MH_4)_n$ light complex hydrides

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Abstract

From the physical point of view, the cohesive energy of a reactant is preferable to its formation energy for characterizing its influence on the reaction processes from the reactants to the products. In fact it has been found that there is a certain correlation between the experimental hydrogen desorption temperature and the cohesive energy calculated by a first principles method for a series of $A_m(MH_4)_n$ ($A = \text{Li, Na, Mg}$; $M = \text{Be, B, Al}$) light complex hydrides (including Na_2BeH_4 , Li_2BeH_4 , NaAlH_4 , LiAlH_4 , $\text{Mg}(\text{AlH}_4)_2$, LiBH_4 and NaBH_4), which suggests that cohesive energy may be a useful physical quantity for evaluating the hydrogen desorption ability of complex hydrides, especially in cases when dehydrogenation products have unknown crystal structures, or may even be unknown. To understand this correlation more deeply, the ionic interaction between A and the MH_4 complex and the covalent interaction between M and H were calculated and their contributions to the cohesive energy evaluated quantitatively. The calculated results show that the covalent $M-H$ interaction in the MH_4 complex is the dominant part of the cohesive energy E_{coh} (up to more than 75%) and hardly changes during high-pressure structural transitions of $A_m(MH_4)_n$. It was also found that low electronegativity of M or high electronegativity of A is responsible for the weak covalent $M-H$ interaction and finally leads to the low thermodynamic stability of $A_m(MH_4)_n$, suggesting that complex hydrides $A_m(MH_4)_n$ can be destabilized by partial substitution of M (A) with an element with electronegativity lower (higher) than M s (A s). This conclusion has been confirmed by lots of experimental results and may be a useful guideline for the future design of new complex hydrides of the type $A_m(MH_4)_n$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Light complex hydrides of the type $A_m(MH_4)_n$ ($A = \text{Li, Na, Mg}$; $M = \text{Be, B, Al}$) as potential hydrogen storage materials have attracted much attention because of their high gravimetric hydrogen densities. However, their poor kinetics and lack of reversibility of hydrogen absorption/desorption reactions

are the most critical problems for practical applications. For example, LiBH_4 does not decompose and release hydrogen until it reaches an elevated temperature of about 320°C [1]. In 1997 Bogdanovic and Schwickardi reported that a Ti-based catalyst could accelerate the hydrogenation/dehydrogenation reactions of NaAlH_4 [2]; since then numerous experimental and theoretical efforts have focused on enhancing the kinetic properties of light complex hydrides by finding new catalysts [3–12]. It was reported that graphite, as a co-dopant,

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decreases the dehydrogenation temperature of Ti-doped NaAlH₄ by as much as 15 °C compared to hydrides without graphite [3] and that Sc-doped NaAlH₄ exhibits comparable kinetics with Ti-doped NaAlH₄ but a higher effective hydrogen storage [4]. Although the hydrogenation/dehydrogenation kinetics can be obviously improved by dopants/catalysts, the microscopic mechanism of destabilization is still ambiguous. Miwa *et al* [13] predicted that the suppression of charge transfer by partial substitution of an element having a higher electronegativity than Li is effective for lowering the hydrogen desorption temperature of LiBH₄.

Nakamori *et al* [14] reported that charge transfer from Aⁿ⁺ cations to (BH₄)⁻ anions is responsible for the thermodynamic stability of metal borohydride (M = B) series A(BH₄)_n (A = Li, Na, K, Cu, Mg, Zn, Sc, Zr, and Hf; n = 1–4). However, how or why dopant/catalyst atoms can destabilize complex hydrides is still an open problem.

This work aimed to assess the thermal stability of the A_m(MH₄)_n type (A = Li, Na, Mg; M = Be, B, Al) light complex hydrides from the viewpoint of their physical nature, based on which the microscopic mechanism of destabilization by dopants could be explained.

The hydrogenation enthalpy of complex hydrides is usually regarded as an index of their thermodynamic stability [13–15], but sometimes it does not reflect the actual thermal stability, which is critical for the hydrogen desorption capacity. For example, it was reported [14] that the calculated formation enthalpy of LiBH₄ is larger than that of NaBH₄s, while the decomposition temperature of LiBH₄ is lower than that of NaBH₄. This may be because an enthalpy difference between the initial reactants and final products indicates only that the system loses or gains energy as a result of the reaction. When chemical reactions take place, initial chemical bonds are firstly going to be broken in the reactants and then new chemical bonds will be formed in the products. The former process is more closely related to the cohesive energies of the reactants than to their formation energies. In fact, Hess's law is based on the fact that the total amount of energy for breaking all the bonds of the reactants and for building all the bonds of the products is independent of the route taken in going from the reactants to the products, provided that in each case the same initial and final states of temperature and pressure are applied to the reactants and products. In spite of a negative enthalpy difference between the final products and initial reactants, some reactants cannot react spontaneously when mixed and an input of energy is required to make the reaction start; therefore the influence of a reactant on the reaction processes from the reactants to the products could be better measured by its cohesive energy than its formation energy.

Both the cohesive energy (E_{coh}) and formation energy (E_{F}) of A_m(MH₄)_n complex hydrides (Mg(AlH₄)₂, LiAlH₄, NaAlH₄, Li₂BeH₄, Na₂BeH₄, LiBH₄ and NaBH₄) were calculated using a first principles method to find out their relations to thermal stability, according to the following definition:

$$E_{\text{coh}}[A_m(\text{MH}_4)_n] = \{E_{\text{total}}[A_m(\text{MH}_4)_n] - mE(A) - nE(M) - 4nE(H)\}/4n, \quad (1)$$

$$E_{\text{F}}[A_m(\text{MH}_4)_n] = \{E_{\text{total}}[A_m(\text{MH}_4)_n] - m\varepsilon(A) - n\varepsilon(M) - 4n\varepsilon(H)\}/4n, \quad (2)$$

where $E_{\text{total}}[A_m(\text{MH}_4)_n]$ (A = Na, Li and Mg; M = Al, Be and B) represents the total energy (corrected by zero point energy) for each formula unit of A_m(MH₄)_n; $E(A/M/H)$ is the energy of each free atom and $\varepsilon(A/M)$ is the energy of each atom in its crystal structure, which is the sum of the energy of a free A/M atom and the cohesive energy per A/M atom in its crystal structure; $\varepsilon(H)$ is half of the energy (corrected by zero point energy) of a hydrogen molecule. The ionic interaction between A and the MH₄ complex and the covalent interaction between M and H were calculated and their contributions to the cohesive energy were evaluated quantitatively. Based on these results, the relationship between the thermal stability and M–H bonding interaction is discussed for A_m(MH₄)_n.

2. Computational details

The present calculations were performed using the plane-wave ultra-soft pseudopotential (PW-USPP) method based on the density functional theory (DFT) as implemented in the CASTEP code. The PW91 form of the generalized gradient approximation (GGA) was applied as the exchange–correlation potential. The structure optimizations for the seven complex hydrides in this study were carried out using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm by allowing all atomic positions to vary but all cell parameters to be fixed at the lattice parameters given in [1, 3, 16–22]. Actually, we also tested the influence of the fixed (or relaxed) lattice parameters on the properties we were interested in, and the results show that there is no significant difference, e.g. the largest difference in cohesive energy is 0.01 eV/f.u. for Li₂BeH₄. In structural optimizations, the self-consistent loop terminated until the total energy was converged to 10⁻⁶ eV/atom, the forces on each unconstrained atom were smaller than 0.03 eV Å⁻¹, the stress was lower than 0.05 GPa and the displacement smaller than 0.001 Å. For these seven complex hydrides, the cutoff energy adopted was from 330 eV (for hydrides including lithium) to 410 eV (for hydrides including sodium). The *k*-point grid spacing for the Brillouin zone integration was smaller than 0.04 Å⁻¹. On the basis of the Mulliken population analysis, the average net charge (Q_A) of atom A and the bond overlap population (BOP_{M–H}) between M and H atoms were calculated using a projection of PW states onto molecular orbital basis:

$$Q_A = \sum_k (w_k) \sum_{\mu}^{\text{onA}} \sum_{\nu} P_{\mu\nu}(k) S_{\mu\nu}(k), \quad (3)$$

$$\text{BOP}_{A-B} = \sum_k (w_k) \sum_{\mu}^{\text{onA}} \sum_{\nu}^{\text{onB}} 2P_{\mu\nu}(k) S_{\mu\nu}(k), \quad (4)$$

where w_k is the weight associated with the employed *k* points in the Brillouin zone and $P_{\mu\nu}(k)$ and $S_{\mu\nu}(k)$ are the density matrix and overlap matrix, respectively; $\mu(\nu)$ represents an atom orbital of an A or B atom. According to the Mulliken population analysis, BOP_{M–H} could be used to evaluate the strength of the covalent bond between atoms M and H and the

Table 1. Experimental hydrogen desorption temperatures in references and the calculated formation energies and cohesive energies of these complex hydrides in the present study.

Complex hydrides	E_F (kJ/mol H)	E_{coh} (kJ/mol H)	T_{Des} (°C) [ref]
Mg(AIH ₄) ₂	−10.47	445.80	115 [24]
LiAlH ₄	−27.37	487.42	150 [23], 160 [26], 150 [27]
NaAlH ₄	−27.18	498.87	210 [2], 212 [23], 185 [26], 165 [32]
Li ₂ BeH ₄	−56.60	559.94	270 [25]
LiBH ₄	−44.05	581.06	420 [14], 380 [31], 320 [1], 340 [29]
NaBH ₄	−43.76	592.39	500 [14], 490 [30], 565 [28]

average net charge difference between atom A and the MH₄ complex to estimate the ionic interaction.

In addition, the zero point vibrational energy of these complex hydrides was calculated using a basis set of a linear combination of atomic orbitals (LCAOs) in Dmol3 code, with the PW91 form of GGA adopted as the exchange–correlation potential. All the electrons are included in the calculation, and the DNP (double numerical plus a polarization p-function on all hydrogen atoms) form of the basis set was adopted. The cutoff orbital was 4.9 Å, and the *k*-point sampling was about 0.04 Å^{−1}. The calculated zero point energy is 18.54 kJ/mol H (kJ per mol of hydrogen atom) for Mg(AIH₄)₂, 20.04 kJ/mol H for LiAlH₄, 19.00 kJ/mol H for NaAlH₄, 23.00 kJ/mol H for Li₂BeH₄, 19.99 kJ/mol H for Na₂BeH₄, 26.67 kJ/mol H for LiBH₄ and 24.42 kJ/mol H for NaBH₄, coinciding well with the calculated zero point energy 21.93 kJ/mol H for Na₂BeH₄ and 24.69 kJ/mol H for NaBH₄ given in [14, 16]. The calculated zero point energy of H₂ is 27.01 kJ/mol H₂ (kJ per mol of hydrogen molecules).

3. Results and discussions

3.1. Relationship between cohesive energy and thermal stability for A_m(MH₄)_n

The thermal stability of complex hydrides can be characterized experimentally by the temperature at which the complex hydrides start to decompose and simultaneously release hydrogen. In the present study, the experimental hydrogen desorption temperatures (T_{Des}) of selected complex hydrides are compared with their calculated formation energies (E_F) and cohesive energies (E_{coh}), as listed in table 1. It can be found that the hydrogen desorption temperature and the cohesive energy, rather than the formation energy, have the same order as Mg(AIH₄)₂ < LiAlH₄ < NaAlH₄ < Li₂BeH₄ < LiBH₄ < NaBH₄, although the hydrogen desorption temperature might be different for the same complex hydride in different experiments. This fact suggests that cohesive energies of these complex hydrides could well describe their thermal stability, which maybe a useful physical quantity for evaluating the hydrogen desorption ability of complex hydrides, especially in the cases that the crystal structures of dehydrogenation products are unknown or the products may even be unknown.

3.2. The relationship between bonding interaction and cohesive energy

Nakatsuka *et al* [33–36] suggested that the chemical interaction play a dominant role in the stability of alloyed hydrides.

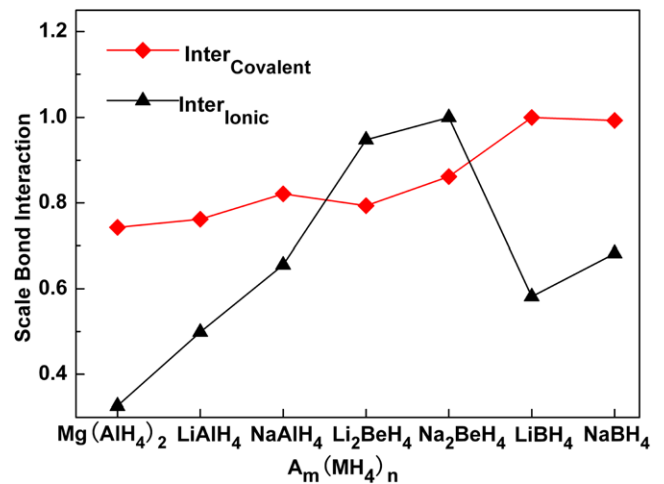


Figure 1. Variation in Inter_{Covalent}^S and Inter_{Ionicity}^S with A_m(MH₄)_n complex hydrides.

What role does it play in the thermal stability of A_m(MH₄)_n? As pointed out by many researchers, A_m(MH₄)_n complex hydrides can be considered to cohere mainly by the ionic bonding between atom A and the MH₄ complex and the covalent bonding between M and H atoms [14, 16–18, 21]. According to the definition of bond energy of a covalent bond [37], the energy of the bond between M and H atoms can be calculated by

$$E_{MH} = \alpha BOP_{M-H}\xi + \beta, \quad (5)$$

where ξ is the average energy of atomic overlap orbits between M and H, and β is close to zero. Thus the covalent bond interaction (Inter_{Covalent}) between M and H characterized by E_{MH} is proportional to the BOP value. The ionic interaction (Inter_{Ionicity}) between an A atom and a MH₄ complex, according to [38], can be approximated by q/R_{A-M} , where q represents half of the difference between average net charges of Q_A and Q_{MH_4} ($Q_{MH_4} = Q_M + 4Q_H$) and R_{A-M} is the distance between A and MH₄. To quantitatively evaluate the contributions of Inter_{Ionicity} and Inter_{Covalent} to the thermal stability of these complex hydrides, they are normalized by the following equations, and the results are shown in figure 1:

$$\text{Inter}_{\text{Covalent}}^S = \text{BOP}/\text{BOP}_{\text{max}}, \quad (6)$$

$$\text{Inter}_{\text{Ionicity}}^S = (Nq/R)/(Nq/R)_{\text{max}}, \quad (7)$$

where BOP_{max} (or $(Nq/R)_{\text{max}}$) is the maximum one among the BOP (or the (Nq/R)) values of the seven complex hydrides;

Table 2. Parameters for calculating equations (6) and (7).

Materials	Structure	E_{coh} (kJ/mol H)	$\text{BOP}_{\text{M-H}}$	Q_{A}	Q_{M}	Q_{H}	$R_{\text{A-M}}$ (Å)	N
Mg(AIH ₄) ₂	$P\bar{3}m1$	445.80	0.778	2.31	0.98	-0.534	3.483	3
LiAlH ₄	$P21/c$	487.42	0.798	1.27	0.74	-0.503	3.340	6
NaAlH ₄	$I41/a$	498.87	0.86	1.36	0.49	-0.463	3.626	8
Li ₂ BeH ₄	$P21/c$	559.94	0.831	1.02	-0.46	-0.395	2.822	8
Na ₂ BeH ₄	$P21/m$	574.27	0.903	1.16	-0.87	-0.363	3.042	8
LiBH ₄	$Pnma$	581.06	1.048	1.67	-0.94	-0.183	2.510	4
NaBH ₄	$F\bar{4}3m$	592.39	1.04	1.6	-0.82	-0.195	3.075	6

Table 3. $\text{BOP}_{\text{B-H}}$, Q_{Na} , Q_{B} , Q_{H} , $\text{BL}_{\text{B-H}}$ (Å) (bond length of B-H bond), $R_{\text{Na-B}}$ (Å), N and $V/\text{f.u.}$ (Å³) of NaBH₄.

Materials	Structure	$\text{BOP}_{\text{B-H}}$	Q_{Na}	Q_{B}	Q_{H}	$\text{BL}_{\text{B-H}}$	$R_{\text{Na-B}}$	N	$V/\text{f.u.}$
αNaBH_4	$F\bar{4}3m$	1.04	1.6	-0.82	-0.19	1.215	3.075	6	58.169
βNaBH_4	$P\bar{4}21c$	1.07	1.74	-0.84	-0.22	1.204	2.860	6	46.729
γNaBH_4	$Pnma$	1.1	1.76	-0.81	-0.24	1.201	2.808	8	43.353

the ‘ N ’ in equation (7) is the number of first-neighbor A atoms of MH₄. $R_{\text{A-M}}$ adopted here is the average distance between M and its first-neighbor A atoms. All these values, together with Q_{M} , Q_{H} (used to calculate Q_{MH_4}) and the bond length between M and H atoms ($B_{\text{M-H}}$), are listed in table 2. We combine $\text{Inter}_{\text{Covalent}}^{\text{S}}$ and $\text{Inter}_{\text{Ionicity}}^{\text{S}}$ as the total interaction in a complex hydride by the weighted average method as

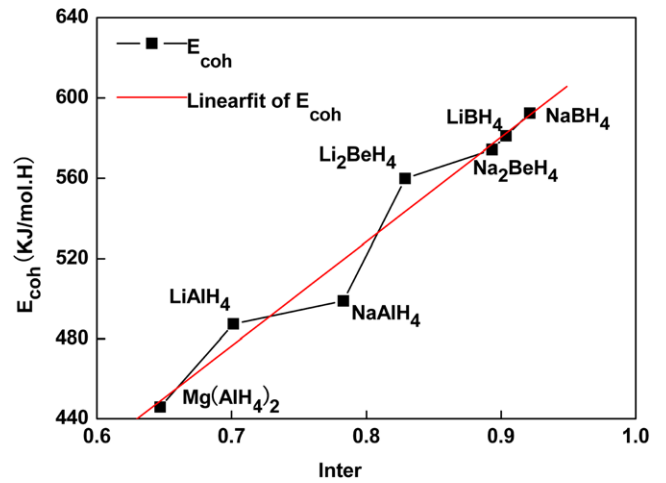
$$\text{Inter} = a\text{Inter}_{\text{Covalent}}^{\text{S}} + b\text{Inter}_{\text{Ionicity}}^{\text{S}}, \quad (8)$$

where ‘ a ’ and ‘ b ’ in equation (8) are the weighted factors of the covalent and ionic interaction in an $A_m(\text{MH}_4)_n$. ‘Inter’ is a dimensionless quantity and proportional to its corresponding cohesive energy (E_{coh}) of $A_m(\text{MH}_4)_n$. E_{coh} is the sum of bond energies of all the bonds in this complex hydride.

Figure 1 shows the variation in $\text{Inter}_{\text{Covalent}}^{\text{S}}$ and $\text{Inter}_{\text{Ionicity}}^{\text{S}}$ calculated from equations (6) and (7) with $A_m(\text{MH}_4)_n$. According to $E = k(a\text{Inter}_{\text{Covalent}}^{\text{S}} + b\text{Inter}_{\text{Ionicity}}^{\text{S}}) + C$, the constants k , a , b and C can be obtained by making the sum of $(E - E_{\text{coh}})^2$ of the seven complex hydrides minimum subject to $a + b = 1$, where E_{coh} are the calculated cohesive energies for the seven complex hydrides. As a result, when $a=0.77$ and $b=0.23$, a line $E = 519.73 \times \text{Inter} + 112.63$, as shown in figure 2, fits well with each E_{coh} of the seven complex hydrides. The largest deviation of 20.70 kJ/mol H (about 5% of E_{coh}) for NaAlH₄ may originate from the approximation that the ξ in equation (5) are assumed to be same for all the seven $A_m(\text{MH}_4)_n$. Although the exact ξ is not taken into account, the conclusion could be drawn from the well-fit E_{coh} line that M-H bonding is mainly responsible for the E_{coh} of $A_m(\text{MH}_4)_n$; that is, the covalent M-H interaction plays a dominant role in their thermal stability, and the values of $\text{BOP}_{\text{M-H}}$ can even be used to represent the degree of stability to some extent. As a result, it is necessary to investigate the potential factors affecting covalent bond interaction.

3.3. Crystal structure effects the covalent interactions

Most complex hydrides with the same components have more than one crystal structure under different external

**Figure 2.** Dependence of E_{coh} on Inter for $A_m(\text{MH}_4)_n$.

conditions [1, 3, 16–22]. To investigate the effects of crystal structure on bond interactions, BOP , Q_{Na} , Q_{B} , Q_{H} , $\text{BL}_{\text{B-H}}$ (bond length of B-H bond), $R_{\text{Na-B}}$, N and the volume per formula unit ($V/\text{f.u.}$) of the three crystal structures of NaBH₄ observed by experiments [20], are listed in table 3. As shown in this table, as the structure transits from $F\bar{4}3m$ to $Pnma$ at pressure of 8.9 GPa, BOP values of B-H bonds ($\text{BOP}_{\text{B-H}}$) increase by only about 6% (from 1.04 to 1.1), and $\text{BL}_{\text{B-H}}$ decreases by less than 1% (from 1.215 to 1.201 Å), while the volume of each formula unit ($V/\text{f.u.}$) decreases by about 25% (from 58.169 to 43.353 Å³).

These facts reveal that the volume reduction is mainly caused by a reduction of average distance (from 3.075 to 2.808 Å) between the MH₄ complex and the Na ion or by an increase in number N (from 6 to 8) of the first-neighbor Na ions of a MH₄ complex. Similar results can be obtained for other complex hydrides. It could be concluded from the above results that MH₄ is almost an invariable structural element in $A_m(\text{MH}_4)_n$ during structural transition, and plays a key role in cohesion; in other words, the covalent interaction between M and H in the MH₄ tetrahedron is hardly sensitive to structural transition.

Table 4. BOP_{M-H} , Q_{Li} , Q_M , Q_H , Q_{MH_4} , Nq/R , the hydrogen desorption temperatures (T_{Des} (°C)) of $Li_m(MH_4)_n$ [1, 23, 25], and the electronegativity of M (EN_M) in [38].

Materials	BOP_{M-H}	Q_{Li}	Q_M	Q_H	Q_{MH_4}	Nq/R	T_{Des}	EN_M
LiAlH ₄	0.798	1.27	0.74	-0.503	-1.27	2.28	150	1.714
Li ₂ BeH ₄	0.831	1.02	-0.46	-0.395	-2.04	4.34	250	1.81
LiBH ₄	1.048	1.67	-0.94	-0.183	-1.67	2.66	320	2.275

Table 5. BOP_{M-H} , Q_A , Q_{Al} , Q_H , Q_{AlH_4} , Nq/R , the hydrogen desorption temperatures (T_{Des} (°C)) of $A_m(AlH_4)_n$ [23, 24, 26], and the electronegativity of A (EN_A) in [38].

Materials	BOP_{M-H}	Q_A	Q_{Al}	Q_H	Q_{AlH_4}	Nq/R	T_{Des}	EN_A
Mg(AlH ₄) ₂	0.778	2.31	0.98	-0.534	-1.155	1.493	115	1.318
LiAlH ₄	0.798	1.27	0.74	-0.503	-1.27	2.283	150	0.67
NaAlH ₄	0.86	1.36	0.49	-0.463	-1.36	3.003	185	0.56

3.4. The effects of elements M and A on the covalent interaction between M and H

To investigate the effects of elements M and A on the covalent bonding interaction between M and H in $A_m(MH_4)_n$, the calculated BOP_{M-H} , Q_{Li} , Q_M , Q_H , Q_{MH_4} and Nq/R for LiAlH₄, Li₂BeH₄, LiBH₄, Mg(AlH₄)₂ and NaAlH₄, together with their experimental hydrogen desorption temperatures (T_{Des} (°C)) in [1, 23–26] and the electronegativity of M (EN_M) in [38], are divided into two categories: one listed in table 4 keeping A as Li, and the other in table 5 with the same M as Al.

As shown in tables 4 and 5, there are three noticeable common points. Firstly, the average net charge of A is always positive ($Q_A > 1$) and that of the MH₄ subunit is negative ($Q_{MH_4} < -1$), consistent with the hypothesis of ionic bonding between them. Secondly, the values of BOP_{M-H} are in of same order as their corresponding hydrogen desorption temperatures; this confirms again our conclusion that the covalent M–H interaction has a dominant influence on the thermal stability of $A_m(MH_4)_n$. Thirdly, higher BOP_{M-H} value correspond to smaller negative value of Q_H and smaller value of Q_M . For $Li_m(MH_4)_n$ in table 4, with EN_M increasing as Al < Be < B, Q_M is decreasing in the order: $Q_{Al}(0.74) > Q_{Be}(-0.46) > Q_B(-0.94)$, indicating that Al is an electron donor while Be and B are acceptors in $Li_m(MH_4)_n$. For $A_m(AlH_4)_n$ in table 5, with EN_A decreasing as Mg > Li > Na, Q_{Al} is in a decreasing order of Mg(AlH₄)₂ (0.98) > LiAlH₄ (0.74) > NaAlH₄ (0.49), suggesting that Al will lose fewer and fewer valence electrons to H with EN_A decreasing.

Whether or not M is able to obtain electrons from A and how many electrons an MH₄ complex can acquire from A are mainly determined by the relative electron-attracting ability of M compared with A and H, which can be understood from two respects: (1) higher EN_M than EN_A could cause more electrons to be transferred from an A atom to each MH₄ complex and to be shared by M and H atoms, finally leading to larger BOP_{M-H} ; (2) higher EN_M means a greater competition between M and H atoms in attracting electrons, the closer EN_M to EN_H , the larger the BOP_{M-H} , i.e. the higher the thermal stability of $A_m(MH_4)_n$. In other words, we could destabilize these complex hydrides by adjusting the valence distribution using partial substitution of M (or A) with an

element with its electronegativity lower (higher) than EN_M (or EN_A), i.e. doping an element with an electronegativity lower than EN_M and higher than EN_A will degrade the thermal stability of $A_m(MH_4)_n$. This conclusion is consistent with (1) the results given by Nakamori *et al* [14] that the thermal stability of A(BH₄)_n decreases with increasing EN_A ; and (2) the experimental results [2, 4] that both Sc and Ti, with electronegativity 1.36 and 1.54 in Pauling scale [39] higher than EN_{Na} (0.93) but lower than EN_{Al} (1.61), can improve the dehydrogenation kinetics of NaAlH₄.

3.5. Electronic structure

To understand more deeply the thermal stability of $A_m(MH_4)_n$, the partial density of states (PDOS) and total density of states (DOS) of the five complex hydrides investigated in this paper are shown in figure 3. Their conspicuous characteristics are: (1) each of them exhibits a nonmetallic feature with an energy band gap (E_g) between valence band (VB) and conduction band (CB); (2) the VB mainly originates from energetically degenerate M s, p and H s, which indicates the formation of covalent bonds in the anionic MH₄ complex [16–18]; (3) the total DOS of atom A are mainly in the CB, and such a electronic structure as shown in the total DOS suggests that the interaction between atom A and the MH₄ complex is mainly ionic.

To compare the polarity of M–H bond interactions of the five complex hydrides, the numbers of valence electrons were calculated by integrating their PDOS curves within their VB regions. The numbers of valence electron of M decrease: 4.03 for LiBH₄ > 2.54 for NaAlH₄ > 2.49 for Li₂BeH₄ > 2.26 for LiAlH₄ > 2.06 for Mg(AlH₄)₂, with M s, p (especially M p) increasing in the CB region and H s antibonding with M increasing in this region, which indicate an increasing polarity of the M–H bond. This is consistent with the variation trend of their BOP_{M-H} values discussed in section 3.4: 1.045 for LiBH₄ > 0.86 for NaAlH₄ > 0.831 for Li₂BeH₄ > 0.798 for LiAlH₄ > 0.778 for Mg(AlH₄)₂. These results confirm again that the stronger the electron-attracting ability of M is compared with A, the more covalent the M–H bond is.

Further analysis of charge distribution of $Li_m(MH_4)_n$ was performed, and the total charge densities $\rho(r)$ in the plane containing one M atom and two H atoms are shown in figure 4.

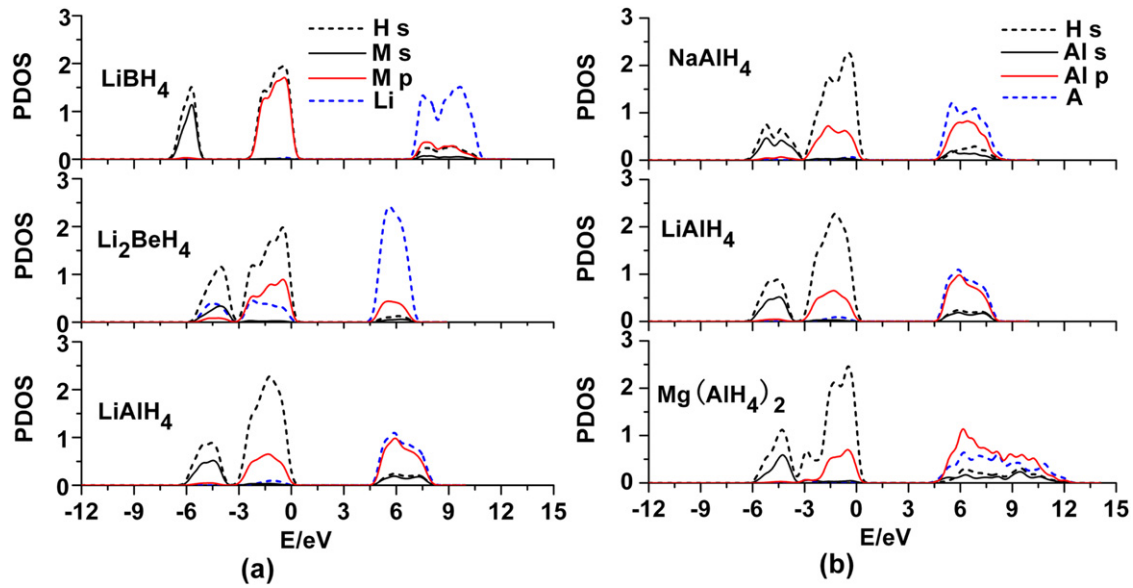


Figure 3. (a) The calculated partial density of states (PDOS) for $\text{Li}_m(\text{MH}_4)_n$ with M as B/Be/Al. (b) The PDOS of $\text{A}_m(\text{AlH}_4)_n$ with A as Na/Li/Mg. The black and dark gray (red) solid lines denote s orbits of an M atom, and p orbits of an M atom; the black, and dark gray dashed (blue) lines denote the s orbits of 4 H atoms, and the total DOS of an A atom, respectively. The Fermi energy is set as zero.

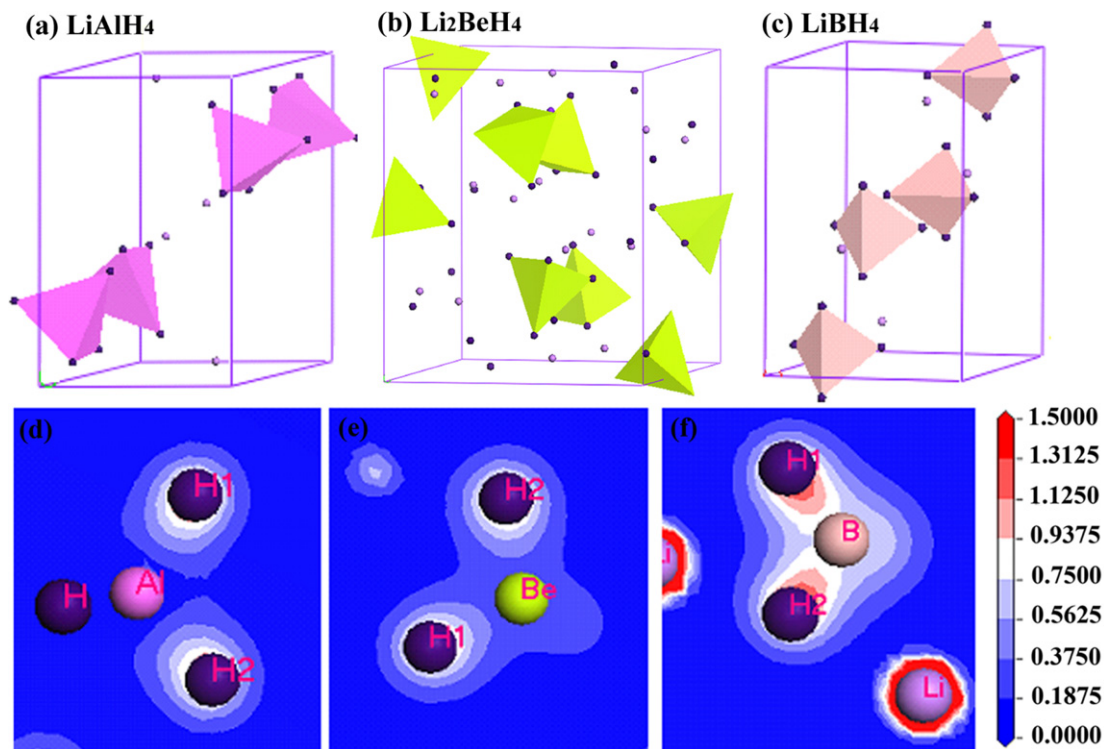


Figure 4. (a)–(c) The structures of LiAlH_4 , Li_2BeH_4 and LiBH_4 , the dark balls on the vertex of the tetrahedra are hydrogen atoms, other balls with lighter color are the lithium atoms, and the M atoms are at the centers of the tetrahedra. (d)–(f) The total charge density of LiAlH_4 , Li_2BeH_4 and LiBH_4 on the plane containing one M atom and two of its adjacent H atoms.

Apparently, along the M–H direction in LiAlH_4 , the $\rho(r)$ in the neighborhood of the Al atom is lower than 0.1875 \AA^{-3} , whereas that of the B atom is higher than 0.75 \AA^{-3} for LiBH_4 , and the situation for Li_2BeH_4 is between the above two. These results are consistent with the analysis of the polarity of the M–H bond on the basis of PDOS.

4. Conclusions

From the physical point of view, the cohesive energy of a reactant is preferable to its formation energy for characterizing its influence on the reaction processes from the reactants to the products. In the present study, a certain correlation between

the experimental hydrogen desorption temperature and the calculated cohesive energy of $A_m(\text{MH}_4)_n$ type metal complex hydrides has been found. This suggests that a high cohesive energy (E_{coh}) of $A_m(\text{MH}_4)_n$ corresponds to its high thermal stability. The contribution of the ionic interaction between A and the MH_4 complex and the covalent interaction between M and H to the cohesive energy E_{coh} reveals that the covalent interaction between M–H is the dominant part of E_{coh} and $\text{BOP}_{\text{M-H}}$ could be used to evaluate approximately the thermal stability of $A_m(\text{MH}_4)_n$. MH_4 is hardly an invariable structural element in $A_m(\text{MH}_4)_n$ complex hydrides during structural transition, i.e. the covalent interaction between M and H is insensitive to its structural transition. Either higher EN_A or lower EN_M will lead to less a covalent or more polar M–H bond; furthermore it will lower thermal stability of $A_m(\text{MH}_4)_n$. These conclusions provide a convenient and effective way to estimate to some extent the thermal stability of $A_m(\text{MH}_4)_n$, and a criterion for destabilizing $A_m(\text{MH}_4)$ by doping with an element.

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