

Nature of the chemical bond in complex hydrides, NaAlH₄, LiAlH₄, LiBH₄ and LiNH₂

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Abstract

The most stable crystal structures of complex hydrides, MXH_n (NaAlH₄, LiAlH₄, LiBH₄ and LiNH₂) were simulated by the plane-wave pseudopotential method. The local chemical bonds between constituent ions were simulated using the DV-X α molecular orbital method. As a result, it was found that the covalent interaction is operating between X and H ions to form a XH_n ion in MXH_n. In addition, the ionic interaction is operating between M and XH_n ions through the charge transfer from M to XH_n ions. On the basis of this understanding of the nature of the chemical bond between ions, a phase stability diagram of complex hydrides was proposed using two parameters. One is the bond energy of XH diatomic molecules and the other is electronegativity difference, $\Delta\Phi_{X-M}$, between M and X ions. The calculated stability change by doping into NaAlH₄ could be explained qualitatively following this diagram. This diagram will provide us a clue to the modification of hydrides to lower the hydrogen decomposition temperature.

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1. Introduction

Recently, special attention has been directed toward complex hydrides such as NaAlH₄, LiNH₂ and LiBH₄, because they are superior in both the mass and volume densities of hydrogen to conventional hydrogen storage alloys [1–5]. However, for these complex hydrides there are still some problems in the reversibility of hydrogenation and dehydrogenation reactions, and also in high decomposition temperatures and low reaction rates [1–4]. So, the proper control of their phase stability is crucial for making these complex hydrides fit for practical use of hydrogen storage.

Extensive experiments have been performed in order to reduce the decomposition temperature and to increase the reaction rate by using some catalysts [3,4]. Also, the reaction energies for formation, decomposition and mixing

with dopants have been calculated using the pseudopotential method to account for the stability of complex hydrides and also to modify the stability by doping [6,7]. However, it is still unclear how to consider the relationship between constituent elements and the stability in whole complex hydrides, because comprehensive explanation has not been given to these hydrides in view of chemical interactions.

In this study, the most stable structures in pure and doped complex hydrides, MXH_n (NaAlH₄, LiAlH₄, LiBH₄ and LiNH₂), were investigated in order to understand the dominant chemical interactions in them. The plane-wave pseudopotential method was used for the geometry optimization by the total energy minimization. The local ionic arrangements were also simulated around the dopants such as, Li, Na, K, B, Al, Ga, in NaAlH₄. Also, characteristics of the local chemical bonding between constituent ions were obtained by using the DV-X α molecular orbital method. On the basis of these calculations, the phase stability diagram of MXH_n hydrides was proposed using the bond energy of diatomic

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molecule, XH_n , and the electronegativity difference between M and X ions.

2. Calculation procedure

A complex hydride, MXH_n , consists of M ions and XH_n complex ions. However, according to previous study, the positions of hydrogen in the complex ion are sometimes difficult to be determined experimentally. So, in this study, the crystal structures of four complex hydrides, $NaAlH_4$, $LiAlH_4$, $LiBH_4$ and $LiNH_2$, were optimized by the total energy minimization.

For this purpose, the first-principles calculations based the density function theory (DFT) were performed with the generalized gradient approximation (GGA) by Perdew et al. [8]. The implementation of DFT employed here combines a plane-wave basis set with the total energy pseudopotential method, as is embodied in the CASTEP code [9]. The present calculations used are based upon the ultrasoft pseudopotentials proposed by Vanderbilt [10]. The plane-wave cutoff energy was chosen to be 380 eV. This cutoff energy was found to achieve the convergence of the total energies within 0.03 eV/atom relative to the results with the cutoff energies up to 600 eV. The sampling in the reciprocal space was done with k -points grids of $5 \times 5 \times 2$ for $NaAlH_4$, $3 \times 2 \times 2$ for $LiAlH_4$, $2 \times 3 \times 2$ for $LiBH_4$ and $6 \times 6 \times 7$ for $LiNH_2$. The optimized lattice parameters were comparable to the experimental values within the deviation of less than 2%. All the ions in the cell were allowed for full relaxation. The doping effect was investigated in $NaAlH_4$. The lattice parameters of the doped crystal supercells of $NaAlH_4$ were fixed to be equal to the calculated values of the perfect crystal. The Na and Al ions located in the positions of less than 0.4 nm distant from the doped ion, and also the H ions arranged around each Al ion were allowed for full relaxation. Further detailed explanation of the calculations is given elsewhere [11,12].

The DV- $X\alpha$ cluster method [13,14] was used for investigating the nature of chemical bonds between ions in the complex hydrides. This is a molecular orbital method, assuming the Hartree–Fock–Slater (HFS) approximation. In this method, the exchange–correlation between electrons is given by the Slater’s $X\alpha$ potential. The matrix elements of Hamiltonian and the overlap integrals are calculated by a random sampling method. The molecular orbitals are constructed by a linear combination of numerically generated atomic orbitals (LCAO). The cluster models consisting of about 100 ions were constructed by using the optimized structure. For example, in case of $NaAlH_4$, the cluster model used was $[Na_{17}Al_{18}H_{72}]^{-1}$. For comparison, the calculations were repeated using the cluster models constructed by the experimental crystal data. For a characterization of the electronic structures and chemical bonding in the cluster, the bond order between ions and the ionicity of each element in the cluster were estimated according to the Mulliken population analysis

[15]. Here, the bond order is a measure to show the strength of the covalent bond between ions.

3. Results and discussion

3.1. Partial density of states in $NaAlH_4$

The partial density of states is shown in Fig. 1 for $NaAlH_4$. This was obtained after the geometry optimization using the pseudopotential method. It was found from this figure that the Fermi energy level, E_f , lay in the band gap between the valence band consisting mainly of the H 1s and Al 3s, 3p components and the conduction band consisting mainly of the Na 3s, 3p components and the Al 3p component. The H 1s component was overlapped greatly with the Al 3s, 3p components, resulting in the strong covalent interaction operating between H and Al ions to form an AlH_4 ion. On the other hand, the Na 3s, 3p components were distributed mostly over the energy region above the E_f , so the charge transfer occurred mainly from Na ion to AlH_4 ion and caused an ionic interaction between them. Similar trends were also seen in the other hydrides, $LiAlH_4$, $LiBH_4$ and $LiNH_2$.

From these results, it can be said that these complex hydrides, MXH_n (e.g., M = Na and X = Al in case of $NaAlH_4$), are characterized by the covalent interaction between the X and H ions and the ionic interaction between the M and XH_n ions. So, our attention was directed toward the covalent bond between the X and H ions, and the charge transfer from the M to XH_n ions.

3.2. Chemical bonding

The DV- $X\alpha$ molecular orbital calculations were performed using the cluster models with and without the geometry optimization. Following the Mulliken population analysis, the covalent bond strength was estimated from the bond order between the X and H ions. Also, the ionicity of M was esti-

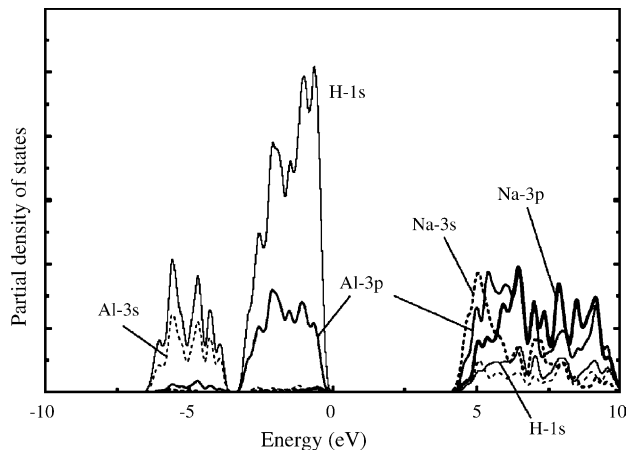


Fig. 1. Partial density of states for $NaAlH_4$.

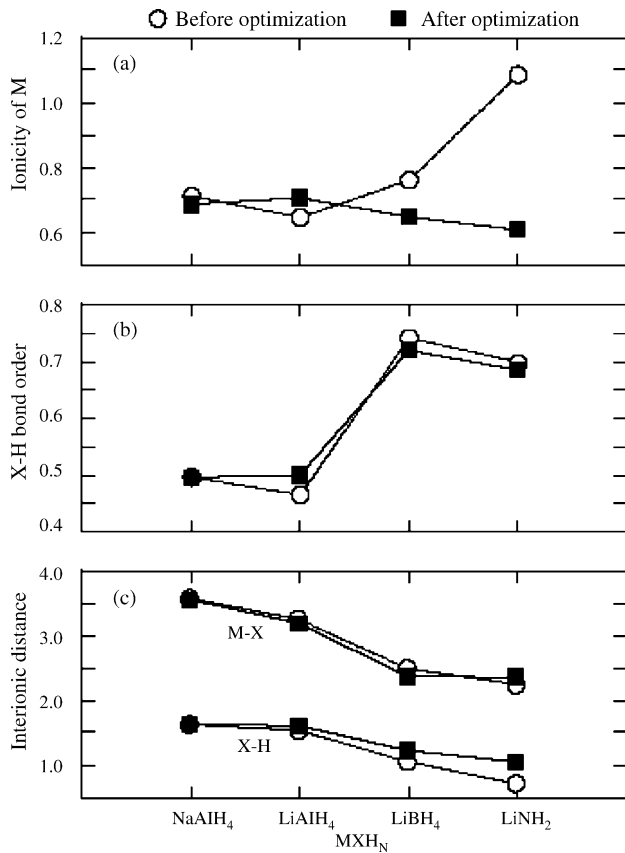


Fig. 2. (a) The ionicities of M, (b) the bond orders between X and H ions and (c) the M–X and X–H interionic distances in MXH_n .

mated as a measure to show the magnitude of the transferred charges from the M to XH_n ions.

The calculated results are shown in Fig. 2(a) for the ionicities of M and in (b) for the bond orders between the X and H ions. Here, the results from the optimized and non-optimized structures are indicated by solid squares and open circles, respectively. As shown in Fig. 2(a), there was the less change in the ionicity of M before and after the geometry optimization in any hydrides except for LiNH_2 . The large change in LiNH_2 was attributable to the large structural change by the geometry optimization. Namely, as shown in Fig. 2(c), the experimentally determined interionic distances of Li–N and N–H are shorter than the calculated ones. In particular, the experimental N–H distance, 0.07 nm, is much shorter than the calculated one, 0.103 nm, being comparable to the distance, 0.105 nm, in a diatomic NH molecule [16]. On the other hand, as shown in Fig. 2(b), the bond orders between the N and H ions are not sensitive to such a geometry optimization despite the large difference in the interionic distances.

As shown in Fig. 2(a), the ionicities of M (i.e., Na and Li) obtained after the geometry optimization were similar among four hydrides. Therefore, by taking account of the M–X interionic distances shown in Fig. 2(c), it was supposed that the ionic interactions between the M and XH_n ions are larger in LiBH_4 and LiNH_2 than in NaAlH_4 and LiAlH_4 , although this discussion may be modified in some ways due to the dif-

ference in the crystal structures among them. Also, as shown in Fig. 2(b), the B–H bond order in LiBH_4 and the N–H bond order in LiNH_2 are larger than the Al–H bond order in NaAlH_4 and LiAlH_4 . So, the covalent interactions between X and H ions, are larger in LiBH_4 and LiNH_2 than in NaAlH_4 and LiAlH_4 . By combining these results of the ionic interaction and the covalent interaction, we may see that NaAlH_4 and LiAlH_4 possess weaker chemical bonds than LiBH_4 and LiNH_2 . In other words, the former two hydrides are more unstable than the latter two hydrides, in agreement with the measured hydrogen decomposition temperatures, T_{dec} [2]. It is 398 K for LiAlH_4 and 483 K for NaAlH_4 , which are lower than 653 K for LiBH_4 and (563 ± 110) K for LiNH_2 [4].

3.3. Substitution energy and local geometry around dopant ion in NaAlH_4

The optimized geometries around substitutional ions in NaAlH_4 were calculated using the pseudopotential method. Here, either Al ion or Na ion was replaced by the same group element in the periodic table. Namely, B, Ga and In, all of which are the 3B group elements, were substituted for the Al ion. Li and K, both of which are the 1A group elements, were substituted for the Na ion. In case of the substitution for the Al ion, the optimized geometries are illustrated in Fig. 3(a) for B and (b) for Ga, respectively. In each figure, B_{Al} (or Ga_{Al}) means the B ion (or Ga ion) at the Al site. For comparison, the ionic arrangements in the undoped crystal are indicated by dotted circles, in each figure. It was found from Fig. 3(a) that only the positions of H ions around a substitutional B ion and its surrounding Al ions were relaxed largely, while keeping the other ions nearly unchanged. On the other hand, the relaxation was much smaller in the Ga substitution as shown in Fig. 3(b).

The results of the substitution for the Na ion are illustrated in Fig. 4(a) for Li and in (b) for K. In either case, the positions of H ions were relaxed to some extent. In the case of Li_{Na} , some H ions around the Al ions neighboring the Li_{Na} tended to move toward a central Li_{Na} ion, because the ionic radius is smaller in Li than in Na. In the case of K_{Na} , the direction of the movement was reverse, because the ionic radius is larger in K than in Na. Thus, the doping affected the neighboring H ion positions greatly.

Then, the substitution energies are calculated using the total energies of the supercells. For example, the substitution energy of A' ion on an a ion site, E_{sub} , is defined as follows,

$$E_{\text{sub}} = E_{\text{total}}(A') + \mu_A - E_{\text{total}}(\text{perfect}) - \mu_{A'} \quad (1)$$

where $E_{\text{total}}(A')$ is the total energy for a supercell containing one A' on the a site, and $E_{\text{total}}(\text{perfect})$ is the total energy for a perfect crystal supercell. μ_A and $\mu_{A'}$ are the atomic chemical potentials, and here, the total energies per atom for the bulk a and A' are chosen, respectively. There is no Fermi energy term involving in this equation, since a and A' are the same group elements with the same valence.

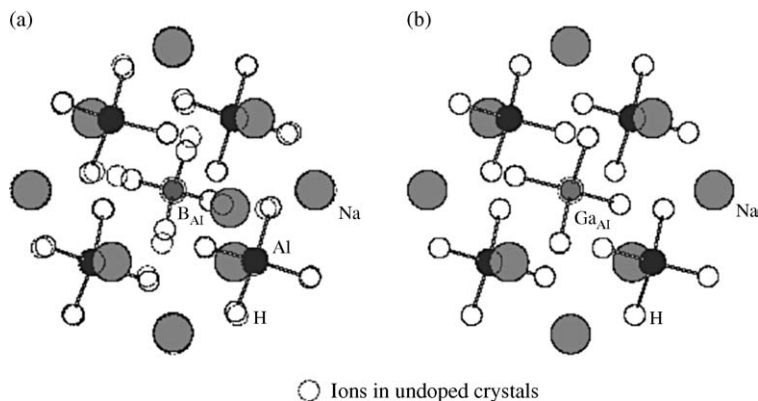


Fig. 3. Optimized geometries around (a) B ion and (b) Ga ion, both substituted for Al ion. The ionic arrangements in the undoped crystal are indicated by dotted lines.

Table 1
Substitution energies of elements for Al ion and Na ion in NaAlH₄

Site	Al			Na	
Substitute ion	B	Ga	In	Li	K
Substitution (eV)	-0.33	0.50	1.34	0.25	-0.25

The calculated results are listed in Table 1. From these results, it was found that the substitution energies of a B ion on the Al site and of a K ion on the Na ion site are negative and lowest among the elements sitting on each site. In other words, the doping of such ions could stabilize the NaAlH₄ phase. By contraries, the doping of the other elements (i.e., Ga, In, Li) made it unstable.

3.4. Stability of complex hydrides and phase stability diagram

The experimentally determined bond energy in a diatomic XH molecule is a good measure of the X–H chemical bonding. The relationship between the bond energy and the calculated X–H bond orders for four hydrides is shown in Fig. 5(a). It was evident from this figure that there was a clear

correlation between them. This is another confirmation that the covalent interaction is dominant between X and H ion in these hydrides. In addition, as might be expected from this correlation, the X–H distances in diatomic molecules are comparable to those in complex hydrides. For example, the calculated Al–H interionic distance was about 0.16 nm in NaAlH₄ and LiAlH₄, being close to the value, 0.165 nm, in a diatomic AlH molecule. Similarly, the B–H interionic distance was about 0.121 nm in LiBH₄ which is nearly same as the value, 0.124 nm in a diatomic BH molecule. Also, the calculated N–H interionic distance in LiNH₂ was very close to the value in a diatomic NH molecule as mentioned before.

Thus, the chemical bond strength between X ion and H ion in complex hydrides, MXH_n, is proportional to the bond energy in a diatomic XH molecule. So, the bond energies in diatomic XH molecules can be used as a measure of the X–H bond strength in complex hydrides. Also, the difference in the electronegativity between M and X, $\Delta\Phi_{X-M}$, can be used as a measure of the charge transfer from the M ion to the complex ion, XH_n, and hence $\Delta\Phi_{X-M}$ is a measure of the ionic interaction between them.

In the coordinate of these two parameters, representative hydrides are plotted in Fig. 5(b). For comparison, Mg₂NiH₄

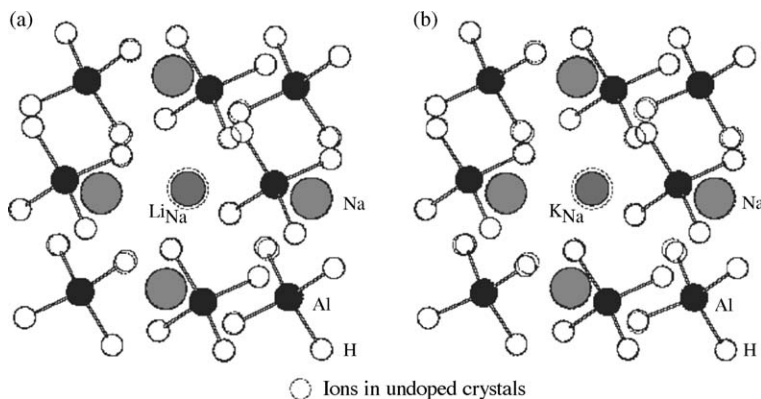


Fig. 4. Optimized geometries around (a) Li ion and (b) K ion, both substituted for Na ion. The ionic arrangements in the undoped crystal are indicated by dotted lines.

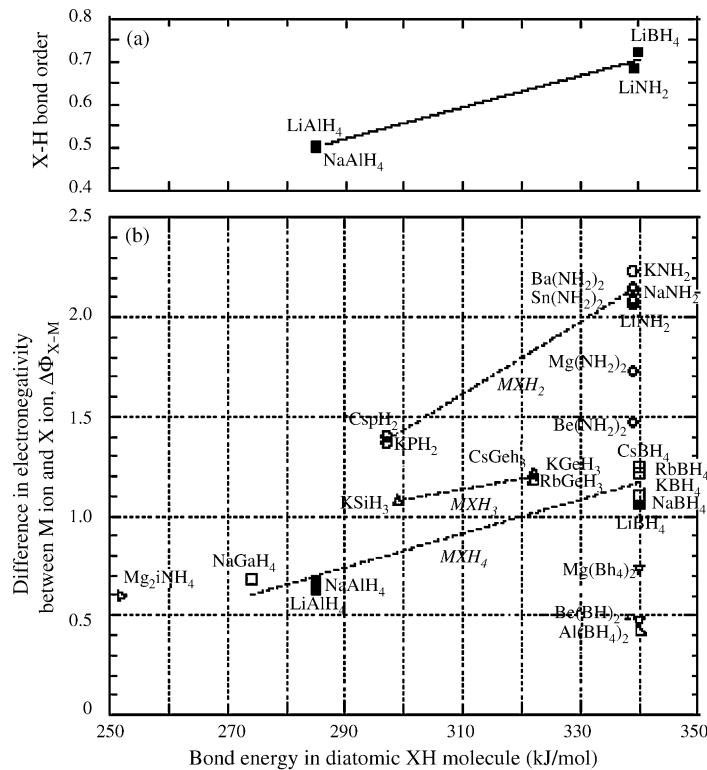


Fig. 5. (a) Correlation between X–H bond order and bond energy in diatomic molecules, XH and (b) phase stability diagram made by using the electronegativity difference, $\Delta\Phi_{X-M}$, between M and X ions and the bond energy in diatomic XH molecules.

is also plotted in the figure, because Mg₂Ni is one of the promising hydrogen storage alloys. From this figure, it was found that those complex hydrides, MXH_n, which have the same hydrogen number, *n*, in the formula, are located along a line, as is indicated by the dotted line in the figure. There are three lines, each corresponding to MXH₂, MXH₃ and MXH₄. The difference, $\Delta\Phi_{X-M}$, in the electronegativity between M and X increases proportionally with the X–H bond energy in each line. In other words, the ionic interaction between M and XH₄ keeps balancing in some ways with the X–H covalent interaction to form stable complex hydrides. As a result, $\Delta\Phi_{X-M}$ becomes large when the X–H bond energy is high, and vice versa. In this meaning, these two interactions are indeed well-balanced in the hydrides.

For example, as shown in Fig. 5(b), in the cases of NaAlH₄ and NaBH₄, the bond energy of B–H is larger than that of Al–H, and $\Delta\Phi_{B-Na}$ is also larger than $\Delta\Phi_{Al-Na}$. Also, for the BH₄-containing system, $\Delta\Phi_{X-M}$ changes in the order, KBH₄ > NaBH₄ > LiBH₄, so that the stability will change in this order. This order agrees well with the order of the hydrogen decomposition temperature, $T_{dec.}$; 773 K for KBH₄, 673 K for NaBH₄ and 653 K for LiBH₄ [2]. As the X–H bond strength generally changes in the order, XH₂ > XH₃ > XH₄, the location of the dotted lines in the $\Delta\Phi_{X-M}$ coordinate changes in the order, MXH₂ > MXH₃ > MXH₄. There is another rule of controlling the stability of the hydrides with the same (XH_n)_m ion but the different number, *m*. For example, in case

of the hydrides containing a BH₄ ion, the values of $\Delta\Phi_{B-M}$ change in the order, LiBH₄ > Mg(BH₄)₂ > Be(BH₄)₂ > Al(BH₄)₃, as shown in Fig. 5(b). The location shifts toward the low $\Delta\Phi_{X-M}$ region with increasing *m* in (XH_n)_m. The same trend can be seen in the (NH₂)_m system, since LiNH₂ > Mg(NH₂)₂ > Be(NH₂)₂.

In this diagram, the difference in the phase stability due to the crystal structure is not expressed explicitly. So, the applicability of the phase stability diagram may be limited, but according to the present results, it may be said that the hydride located in the lower $\Delta\Phi_{X-M}$ region or in the lower X–H bond energy region, appears to be more unstable and has the possibility of releasing hydrogen at lower temperature. This discussion also supports the calculated results of the substitution energy in NaAlH₄ listed in Table 1. For example, if a B ion is substituted for the Al ion, the hydride might be stabilized because the B–H bond energy is larger than the Al–H bond energy. This agrees with the calculation, since the substitution of B ion for Al ion decreases the total energy, and hence stabilizes the hydride. This is also the case in the substitution of Ga ion for Al ion, because the Ga–H bond energy is smaller than the Al–H bond energy and the Ga substitution increases the total energy of the hydride as shown in Table 1. In addition, the decrease in the total energy with the substitution of K ion for Na ion might correspond to the increase in the stability, since $g\Delta\Phi_{Al-K}$ is larger than $\Delta\Phi_{Al-Na}$.

4. Summary

The most stable crystal structures in pure and doped complex hydrides, MXH_n (NaAlH_4 , LiAlH_4 , LiBH_4 and LiNH_2), were investigated by the pseudopotential method and the DV-X α cluster method. It was found that there is the strong covalent interaction operating between H and X ions to form a XH_n ion. On the other hand, the charge transfer occurred mainly from M to XH_n and yielded an ionic interaction between them. It was shown that there was a resemblance in the X–H distance between the complex hydrides and the diatomic XH molecule. A phase stability diagram was proposed using two parameters. One is the bond energy in diatomic XH molecules and the other is the difference in the electronegativity between M ion and X ion. This diagram was found to give a good clue to the phase stability of complex hydrides, and hence useful for modification of the hydrides by doping.

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