First-principles study on the intermediate compounds of LiBH$_4$

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We report the results of the first-principles calculation on the intermediate compounds of LiBH$_4$. The stability of Li$_3$B$_n$H$_{12}$ and Li$_3$B$_n$H$_n$$_{12}$($n = 5-12$) has been examined with the ultrasoft pseudopotential method based on the density functional theory. Theoretical prediction has suggested that monoclinic Li$_3$B$_{12}$H$_{12}$ is the most stable among the candidate materials. We propose the following hydriding/dehydriding process of LiBH$_4$ via this intermediate compound: LiBH$_4$ $\leftrightarrow$ $\frac{12}{7}$Li$_3$B$_{12}$H$_{12}$ + $\frac{8}{7}$LiH + $\frac{18}{7}$H$_2$ $\leftrightarrow$ LiH + B + $\frac{2}{3}$H$_2$. The hydrogen content and enthalpy of the first reaction are estimated to be 10 mass% and 56 kJ/mol H$_2$, respectively, and those of the second reaction are 4 mass% and 125 kJ/mol H$_2$. They are in good agreement with experimental results of the thermal desorption spectra of LiBH$_4$. Our calculation has predicted that the bending modes for the $\Gamma$-phonon frequencies of monoclinic Li$_3$B$_{12}$H$_{12}$ are lower than that of LiBH$_4$, while stretching modes are higher. These results are very useful for the experimental search and identification of possible intermediate compounds.

I. INTRODUCTION

Hydrogen is the most promising environmentally clean energy carrier to replace fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Complex hydrides including the light metal lithium (Li) have sufficient gravimetric hydrogen storage capacity, and many researches and development about the lithium complex hydride such as LiBH$_4$ and LiNH$_2$ have been done recently. Particularly, LiBH$_4$ can desorb about 14 mass% of hydrogen by the following thermal decomposition:

$$\text{LiBH}_4 \rightarrow \text{LiH} + B + \frac{3}{2} \text{H}_2. \quad (1)$$

However, the experimental value of enthalpy of this reaction is 69 kJ/mol H$_2$ and LiBH$_4$ is too stable to release hydrogen at ambient condition. High temperature and high pressure are needed for rehydriding reaction, so its reversibility becomes a problem for practical use.

Züttel et al. investigated the hydrogen desorption from LiBH$_4$ in details, and reported that the thermal desorption spectra of LiBH$_4$ mixed with SiO$_2$ powder exhibited three hydrogen desorption peaks. These peaks were observed around 500 K, 550 K and 600 K, and the products corresponded to “LiBH$_3$” , “LiBH$_2$” and “LiBH$_2$” , respectively. The compounds in quotes were nominal compositions estimated from amount of desorbed hydrogen. This is a strong evidence for the existence of the intermediate compounds , and the hydrogen desorption reaction takes place in at least two steps not a single step like in Eq. (1). Although low temperature release of hydrogen and improvement of reversibility can be expected by use of the intermediate compound, little attention has been paid yet.

In this study, the stability of the intermediate compounds of LiBH$_4$ has been investigated theoretically and we clarify a hydriding/dehydriding process of LiBH$_4$. The thermal desorption experiment observed a structural transition around 380 K and the melting of the compound at 550 K. The stability of the solid phases at absolute zero temperature is mainly discussed here. In Sec. II we describe the details of the computational method and the possible intermediate compounds of LiBH$_4$. Section III reports the calculated results on the stability of some candidate compounds. And then, we discuss the hydriding/dehydriding reaction via the intermediate compounds. Furthermore, the electronic structures and $\Gamma$-phonon frequencies on the most stable compound are studied. We also investigate the stability of the borane complex anions, and then compare with the solid compounds.

II. COMPUTATIONAL DETAILS

First-principles calculations have been performed by the ultrasoft pseudopotential methods based on the density functional theory. The generalized gradient approximation (GGA) formula is applied to the exchange-correlation energy.

The interaction between the ion cores and electrons is described by the ultrasoft pseudopotential, and the norm-conservation constraint is imposed on Li for the calculation efficiency improvement. The scalar-relativistic all-electron calculations are first carried out on the free atoms(ions). We chose 2s and 2p states for
both Li and B pseudopotential as the reference states with the cutoff radii of 2 a.u. (Li) and 1.5 a.u. (B), respectively. A single projector function is used for each angular momentum component. The 3d state is treated as the local part of pseudopotential. The hydrogen pseudopotential is constructed from 1s, 2s and 2p states with the cutoff radii of 1.1 a.u.(s) and 1.2 a.u. (p). We use double projector functions for the s component and a single projector function for the p component. For all pseudopotentials, the pseudo-wave functions and the pseudo-charge-augmentation functions are optimized by a method similar to that proposed by Rappe et al. Also, the partial core correction is taken into account for Li and B pseudopotentials.

In the solid-state calculations, the pseudo-wave functions are expanded by plane waves with a cutoff energy equal to 15 hartrees. The cutoff energy for the charge density and potential is set to be 120 hartrees. The integral over the Brillouin zone is approximated by the summation on the k-grid elements of which the edge lengths closer to the target value of 0.15Å⁻¹ as possible. We confirmed that these calculation conditions gave a good convergence of energy within 0.002 eV/atom. The preconditioned conjugate-gradient technique is employed to minimize the Kohn-Sham energy functional. A procedure based on the iterative diagonalization scheme and the Broyden charge mixing method is adopted in this study. Optimization of crystal structures is performed till the atomic forces and the macroscopic stresses become less than 5 × 10⁻⁴ hartree/bohr and 0.1 GPa, respectively. During the structural optimization process, the partial occupation numbers near the Fermi level are determined by the Fermi-Dirac distribution function with \( k_B T = 3 \times 10^{-3} \) hartrees. The Helmholtz free-energy functional including the entropy term, is minimized instead of the Kohn-Sham energy functional. Then, the improved tetrahedron method is used in order to minimize the Kohn-Sham energy functional in the optimized structure. The dynamical matrix is calculated by the force-constant method to obtain the \( \Gamma \) phonon frequencies. The atomic displacement is set to be 0.02 Å. The further details of calculation are described in Refs. 2, 13 and references therein.

As the candidates of the intermediate compounds, the existing alkali metal-B-H materials are used. For example, it is well known that boron (B) and hydrogen (H) form inorganic compounds called ‘borane’ and the compounds of Cs₁₂B₁₂H₁₂, K₂B₁₂H₁₂ and K₂B₁₂H₁₂ are reported. The space group of crystal structure for the compound Cs₂B₁₂H₁₂ is \( \text{Am} \overline{2} \) (No.40) and cation Cs⁺ and anion \([\text{B}_3\text{H}_8]^-\) are arranged same as the NaCl-type structure with an orthorhombic distortion. The crystal structures of K₂B₁₂H₁₂ and K₂B₁₂H₁₂ are best described as an anti-CaF₂-type arrangement with K⁺ cation in the center of a tetrahedron formed by \([\text{B}_n\text{H}_m]^{2-}\) dianions. We first assumed that Li₂B₁₂H₁₈, Li₂B₁₂H₁₂ and Li₂B₁₂H₁₂ compounds, which had the same crystal structures as existing CsB₁₂H₈, K₂B₁₂H₁₂ and K₂B₁₂H₁₂, respectively. The stability of these candidates was evaluated using the first-principles calculations. Since the existence of a series of closo-type dianions \([\text{B}_n\text{H}_m]^{2-}\) (\( n = 5 \) - 12) is also well known, our calculation have been expanded to Li₂B₁₂H₈ (\( n = 5 \) - 12) compounds. Although Li atom and \([\text{B}_n\text{H}_m]^-\) cluster are arranged in the anti-CaF₂-type structure and the unit cell parameters are supposed to be a face-centered-cubic symmetry (\( a = b = c, \alpha = \beta = \delta = 90^\circ \)) as starting points for the structural optimization, the output relaxed compounds have different symmetry depending on the structure of \([\text{B}_n\text{H}_m]^-\) clusters. The alkali metal salt of monoclinic \( K_2B_{12}(OH)_{12} \) with closo-\([\text{B}_12(\text{OH})_{12}]^{2-}\) dianions has been reported, and monoclinic Li₂B₁₂H₁₂ with similar crystal structure is also examined.

### III. Results and Discussions

#### A. Stability of candidate compounds : LiB₂H₉

Table I shows the calculated results on the structural parameters and the cohesive energies of LiB₂H₈ and Li₂B₁₂H₈ (\( n = 5 \) - 12). We denote the cubic Li₂B₁₂H₁₂ based on \( K_2B_{12}H_{12} \) with type-1 and monoclinic Li₂B₁₂H₁₂ based on \( K_2B_{12}(OH)_{12} \) with type-2, respectively. Compared with the cohesive energy of two type of \( \text{Li}_2\text{B}_{12}\text{H}_{12} \), the value of monoclinic \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) (type-2) is larger than that of type-1. Therefore, the type-2 \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) is easy to form. After the next paragraph, the only result concerning monoclinic \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) (type-2) is shown.

The enthalpy of formation for hydriding reactions including LiBH₄ from LiH (NaCl-type), \( \alpha \)-B (rhombohedral), and H₂ molecule are given in Table I where the zero-point energy corrections are not taken into consideration. They are provided using calculated cohesive energies of 2.3609 eV/atom for LiH, 6.2013 eV/atom for \( \alpha \)-B, 2.2689 eV/atom for H₂ molecule, and 3.1501 eV/atom for LiBH₄ (orthorhombic \( Pnma \) symmetry), respectively. The enthalpies of formation for \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) (\( n = 10, 11, 12 \)) are more negative than that for LiBH₄. Therefore these compounds have a great potential for generating in hydriding reactions from LiH and \( \alpha \)-B as the intermediate phase of LiBH₄.

In order to understand the stability of each compound intuitively, we represent the enthalpy of formation corresponding to the following reaction with hydrogen of \( \delta \) mole in Fig. I:

\[
(1-\delta)[\text{LiH}+\text{B}]+\delta \text{H}_2 \rightarrow \frac{1-\delta}{x} \text{LiB}_2\text{H}_y + \frac{(1-\delta)(x-1)}{x} \text{LiH}
\]

where \( \delta = (y-1)/(2x + y - 1) \) shows the mole fraction of H₂ and \( x \geq 1 \). From Fig. I monoclinic \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) is formed as the intermediate compound of the hydriding/dehydriding reaction of LiBH₄, because the actual reaction goes along the lowest state of enthalpy. Therefore, following hydriding/dehydriding process is proposed...
| Compound          | Space group | Unit cell parameters | Atoms | Atomic position | $E_{coh}$ (eV/atom) |
|-------------------|-------------|----------------------|-------|-----------------|-------------------|
| LiB$_2$H$_8$      | $Ama2$      | ($N.o.40$)           | Li    | $a=9.188\ \AA$  | 0.0595, 0.6321    |
|                   |             | $b=8.813\ \AA$      | B     | $0.1372, 0.1335$|
|                   |             | $c=5.763\ \AA$      | H     | $0.0909, 0.2507$|
| Li$_2$B$_3$H$_6$  | $R3m$       | ($N.o.160$)          | Li    | $a=5.599\ \AA$  | 0.0684, 0.1666    |
|                   |             | $c=16.763\ \AA$     | B     | $0.1386, 0.5149$|
| Li$_2$B$_4$H$_6$  | $Fm\bar{3}m$| ($N.o.225$)         | Li    | $a=7.968\ \AA$  | 0.25, 0.25        |
|                   |             | $b=9.836\ \AA$      | B     | $0.25, 0.25$     |
| Li$_2$B$_4$H$_7$  | $I2$        | ($N.o.5$)            | Li    | $a=5.691\ \AA$  | 0.25, 0.25        |
|                   |             | $b=9.835\ \AA$      | B     | $0.25, 0.25$     |
| Li$_2$B$_5$H$_9$  | $I\bar{4}m$ | ($N.o.121$)         | Li    | $a=10.687\ \AA$ | 0.01032, 0.1032   |
|                   |             | $c=15.062\ \AA$     | B     | $0.01032, 0.1032$|
| Li$_2$B$_9$H$_9$  | $R3$        | ($N.o.146$)         | Li    | $a=7.044\ \AA$  | 0.01631, 0.1631   |
|                   |             | $c=15.062\ \AA$     | B     | $0.01631, 0.1631$|
| Li$_2$B$_{10}$H$_{10}$ | $I42d$ | ($N.o.97$)          | Li    | $a=6.196\ \AA$  | 0.0807, 0.9031    |
|                   |             | $c=10.356\ \AA$     | B     | $0.0807, 0.9031$|
| Li$_2$B$_{11}$H$_{11}$ | $I2$ | ($N.o.5$)           | Li    | $a=7.083\ \AA$  | 0.01942, 0.0809   |
|                   |             | $b=11.028\ \AA$     | B     | $0.01942, 0.0809$|
| Li$_2$B$_{12}$H$_{12}$ (type-1) | $Fm\bar{3}$ | ($N.o.202$)       | Li    | $a=10.083\ \AA$ | 0.02133, 0.1471   |
|                   |             | $b=11.028\ \AA$     | B     | $0.02133, 0.1471$|
| Li$_2$B$_{12}$H$_{12}$ (type-2) | $P2_1/n$ | ($N.o.14$)           | Li    | $a=7.358\ \AA$  | 0.06747, 0.6250   |
|                   |             | $b=9.556\ \AA$      | B     | $0.06747, 0.6250$|
|                   |             | $c=6.768\ \AA$      | B     | $0.06747, 0.6250$|

*TABLE I: Structural parameters and cohesive energies ($E_{coh}$) of the candidate compounds: LiB$_2$H$_y$. It is denoted that the cubic Li$_2$B$_{12}$H$_{12}$ based on K$_2$B$_{12}$H$_{12}$ with type-1 and monoclinic Li$_2$B$_{12}$H$_{12}$ based on K$_2$B$_{12}$(OH)$_{12}$ with type-2, respectively.*
TABLE II: The enthalpies of formation for the hydriding reaction of various compounds LiB

| Hydriding reaction                        | Enthalpy of formation (kJ/mol H₂) |
|------------------------------------------|-----------------------------------|
| LiH + 3B + 7/2H₂ → LiB₂H₈               | −36                               |
| 2LiH + 5B + 3/2H₂ → Li₂B₂H₃            | 113                               |
| 2LiH + 6B + 2 H₂ → Li₂B₆H₆             | −42                               |
| 2LiH + 7B + 5/2H₂ → Li₂B₂H₇           | −45                               |
| 2LiH + 8B + 3 H₂ → Li₂B₈H₈            | −32                               |
| 2LiH + 9B + 7/2H₂ → Li₂B₂H₉           | −42                               |
| 2LiH + 10B + 4 H₂ → Li₂B₁₀H₁₀          | −87                               |
| 2LiH + 11B + 9/2H₂ → Li₂B₁₁H₁₁         | −79                               |
| 2LiH + 12B + 5 H₂ → Li₂B₁₂H₁₂         | −125                              |
| LiH + B + 3/2H₂ → LiBH₄                | −75                               |

We also calculated other possible crystal structures such as Cu₂B₁₀H₁₀-type and [Li(thp)₃][B₁₁H₁₁]-type. Moreover, we performed the calculation for the Γ-phonon frequencies of the candidate materials. If there was a soft-mode, we lowered crystal structure symmetry with moving the atoms along the direction of the soft-mode eigenvectors. The maximum gain of cohesive energy was 0.03 eV/atom for Li₂B₁₂H₁₂, however, no compound or crystal structure more stable than monoclinic Li₂B₁₂H₁₂ was found. The present calculation result on the energy of monoclinic Li₂B₁₂H₁₂ provides the upper limit value for the thermodynamic stability. In conclusion, the existence of the intermediate compound of LiBH₄ was predicted theoretically.

Recently Kang et al. have reported that LiBH and LiB are the intermediate phases of LiBH₄, and propose the dehydriding reaction of LiBH₄ through LiBH as follows:

$$\text{LiBH}_4 \rightarrow \text{LiBH} + \frac{3}{2} \text{H}_2.$$  \hspace{1cm} (5)

We also performed the first-principles calculation of the orthorhombic phase of Pnma LiBH. The reaction enthalpy for Eq. (5) is 1.30 eV per LiBH₄ formula unit (84 kJ/molH₂), which is in good agreement with reported value of 1.28 eV per LiBH₄ formula unit in Ref.24. On the other hand, the reaction enthalpy of Eq. (3) is 0.63 eV per LiBH₄ formula unit. Therefore, the dehydriding reaction via the intermediate compound Li₂B₁₂H₁₂ is energetically more preferable one.

B. Intermediate compound: Li₂B₁₂H₁₂

Here we describe the fundamental properties, such as the crystal structure, the electronic structure, and the Γ-phonon frequencies, on Li₂B₁₂H₁₂ which is expected as intermediate compound of LiBH₄.

Optimized crystal structure model of monoclinic Li₂B₁₂H₁₂ is shown in Fig. 2. The bond lengths between B and H atom of Li₂B₁₂H₁₂ are 1.20 – 1.21 Å, and they are very close to those for LiBH₄ (1.23 – 1.24 Å) reported in Ref.2. As for the B-B bond lengths of intra-icosahedron, the values of 1.779 – 1.811 Å for Li₂B₁₂H₁₂ are comparable to the experimental ones for the α-rhombohedral boron (α-B) of 1.751 – 1.806 Å too. Since boron crystal has the icosahedral B₁₂ cluster as a common structural component, the decomposition of [B₁₂H₁₂]²⁻ anion into B₁₂ cluster and hydrogen molecule is easy to understand.

Figure 3 shows the total and partial density of states (DOS) for Li₂B₁₂H₁₂, which denotes that it has the energy gap of 5.60 eV. Since there is little contribution of Li orbital for occupied states, Li₂B₁₂H₁₂ consists of Li⁺ and [B₁₂H₁₂]²⁻ ions. The orbitals of B and H hybridize each other and the feature of occupied states in DOS is analogous with the distribution of the computed energies of the bonding molecular orbitals in [B₁₂H₁₂]²⁻.
The Γ-phonon mode frequencies of monoclinic Li$_2$B$_{12}$H$_{12}$ have been calculated so that the vibrational properties can be compared with experiments easily and directly. The phonon density of states is shown in Fig. 4. It is divided into three regions in the same case as LiBH$_4$. The first region is less than 300 cm$^{-1}$ where the displacements of Li atoms are dominant. The second region is between 450 cm$^{-1}$ and 1100 cm$^{-1}$ where the B-H bond of [B$_{12}$H$_{12}$]$^{2-}$ dianions vibrates with changing in angle between them (bending modes), and the third region is between 2400 cm$^{-1}$ and 2600 cm$^{-1}$ where the interatomic distance of B-H bond is changing along bond axis (stretching modes). The frequencies of bending modes are lower than LiBH$_4$ described in Ref. 2, while stretching modes are higher.

The investigation using in situ Raman spectroscopy is effective for the confirmation of the short-range order or bonding of LiBH$_4$. We examine the atomistic vibrations of LiBH$_4$ during heating by in situ Raman spectroscopy, and the identification of spectra modes originating from Li$_2$B$_{12}$H$_{12}$ is now in progress.

C. Stability of complex anions: [B$_n$H$_n$]$^{2-}$

Finally, we consider the relation between the stability of the compounds Li$_2$B$_n$H$_n$ and those of complex anions [B$_n$H$_n$]$^{2-}$. The energies of the isolated [B$_n$H$_n$]$^{2-}$ are obtained using a face-centered-cubic supercell with $a = 20$ Å. The single Γ point is used for the k-point sampling. The energies for the charged systems are computed by adding uniform background charges and improved with Makov and Payne correction for the interaction between periodic image charges.

Figure 5 shows the comparison of the formation energies, $E_{f\text{total}}$ and $E_{f\text{complex}}$, corresponding to the following reactions:

\begin{equation}
2\text{LiH} + n\text{B} + \frac{n-2}{2}\text{H}_2 \leftrightarrow \text{Li}_2\text{B}_n\text{H}_n, \quad (6)
\end{equation}

and

\begin{equation}
n\text{B} + \frac{n}{2}\text{H}_2 + 2e^- \leftrightarrow [\text{B}_n\text{H}_n]^{2-}, \quad (7)
\end{equation}

where the energies are normalized by the number of B-H pairs for comparison purposes. We can find a fairly good agreement between calculated and experimental values.
FIG. 5: Comparison of the formation energies, $E_f^{\text{solid}}$ and $E_f^{\text{complex}}$, corresponding to the reactions Eq. (6) and Eq. (7) in text, respectively, where the energies are normalized by the number of B-H pairs.

The correlation between both energies. This is probably due to the fact that the electrostatic interaction between Li$^+$ and [B$_n$H$_n$]$^{2-}$ is not sensitive to $n$ and a large part of this energy cancels out with that of LiH in Eq. (6). Among the closo-type dianions considered here, [B$_{12}$H$_{12}$]$^{2-}$ is the most stable one.

LiBH$_4$ desorbs hydrogen at temperatures above the melting point. The latent heat of fusion has been reported to be 0.078 eV/formula-unit for LiBH$_4$ and similar values are expected for Li$_2$B$_n$H$_n$, which is considerably smaller than the energy difference between [B$_{12}$H$_{12}$]$^{2-}$ and other close-type dianions. The stability of the [B$_{12}$H$_{12}$]$^{2-}$ anion supports our main conclusion in this study, that is, the intermediate phase suggested by the experiment is Li$_2$B$_{12}$H$_{12}$.

**IV. SUMMARY**

We have examined the stability of LiB$_3$H$_8$ and Li$_2$B$_n$H$_n$ ($n = 5 - 12$), which are the possible intermediate compounds of LiBH$_4$, by the first-principles calculation. Our computational results for enthalpy of the hydriding reactions provide that monoclinic Li$_2$B$_{12}$H$_{12}$ is the most stable one among the candidates. The following hydriding/dehydriding process of LiBH$_4$ is proposed:

$$\text{LiBH}_4 \leftrightarrow 1/12\text{Li}_2\text{B}_{12}\text{H}_{12} + 5/6\text{LiH} + 13/12\text{H}_2 \leftrightarrow \text{LiH} + \text{B} + 3/2\text{H}_2.$$  

The hydrogen content of the first and the second reaction are 10 mass% and 4 mass%, respectively, which agree well with the thermal desorption spectra (TDS) experiment on LiBH$_4$.

The heat of formation without zero point energy corrections for the first reaction, which is estimated from the solid state LiBH$_4$ with $Pnma$ symmetry (not liquid LiBH$_4$), is 56 kJ/molH$_2$. This value is lower than that for the direct reaction (LiBH$_4$ $\leftrightarrow$ LiH $+$ B $+$ 3H$_2$). Therefore, low-temperature release of hydrogen can be expected by use of this intermediate compound.

We have calculated the electronic structure and the Γ-phonon frequencies of monoclinic Li$_2$B$_{12}$H$_{12}$. This compound has the energy gap of 5.60 eV and consists of Li$^+$ and [B$_{12}$H$_{12}$]$^{2-}$ ions. From the phonon density of states, it is predicted that its bending modes have lower frequencies than that of LiBH$_4$, while stretching modes are higher. The identification of the experimental Raman spectra modes originating from Li$_2$B$_{12}$H$_{12}$ is now in progress.

The stability of closo borane complex anions [B$_n$H$_n$]$^{2-}$ was also examined. We found a fairly good correlation between the formation energies of the solid phases and the isolated dianions. This result supports the validity of the intermediate compound indicated in the TDS experiment being Li$_2$B$_{12}$H$_{12}$.

There are various kinds of borane, such as nido-type [B$_n$H$_{n+4}$] and arachno-type [B$_n$H$_{n+6}$], in addition to closo-type borane [B$_n$H$_{n+2}$]. The nido and arachno borane are derived from closo borane by removing one and two vertices, respectively. These generate the salts in the ionized state as well as closo-type dianions. These alkali metal salts are also the candidates of the intermediate compound of LiBH$_4$. We will study the details of the hydriding/dehydriding process for LiBH$_4$ including the stability of these materials in future.

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1. A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, and Ch. Emmenegger, J. Power Sources 118, 1 (2003).
2. K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, Phys. Rev. B 69, 245120 (2004).
3. S. Orimo, Y. Nakamori, and A. Züttel, Mater. Sci. Eng. B 108, 51 (2004).
4. P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, Nature 420, 302 (2002).
5. Y. Nakamori and S. Orimo, Mater. Sci. Eng. B 108, 48 (2004).
6. K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, Phys. Rev. B 71, 195109 (2005).
7. D. Vanderbilt, Phys. Rev. B 41, R7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt,
ibid. 47, 10 142 (1993).
8 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964);
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
9 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev.
Lett. 77, 3865 (1996); 78, 1396 (E) (1997).
10 D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev.
Lett. 43, 1494 (1979).
11 A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D.
Joannopoulos, Phys. Rev. B 41, 1227 (1990).
12 S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B 26,
1738 (1982).
13 A. Fukumoto and K. Miwa, Phys. Rev. B 55, 11 155
(1997).
14 V. Eyret, J. Comput. Phys. 124, 271 (1996).
15 N. D. Mermin, Phys. Rev. 137, A1441 (1965).
16 P. E. Blochl, O. Jepsen, and O. K. Andersen, Phys. Rev.
B 49, 16223 (1994).
17 K. Kunc and R. M. Martin, Phys. Rev. Lett. 48, 406
(1982).
18 H. J. Deiseroth, O. Sommer, H. Binder, K. Wolfer, and B.
Frei, Z. anorg. Allg. Chem. 571, 21 (1989).
19 I.Y. Kuznetsov, D.M. Vinitskii, K.A. Solntsev, N.T.
Kuznetsov, and L.A. Butman, Russian J. Inorg. Chem. 32, 1803
(1987).
20 I. Tiritiris and T. Schleid, Z. anorg. Allg. Chem. 629, 1390
(2003).
21 T. Peymann, C. B. Knobler, S. I. Khan, and M. F.
Hawthorne, J. Am. Chem. Soc. 123, 2182 (2001).
22 R. D. Dobrott and W. N. Lipscomb, J. Chem. Phys. 37,
1779 (1962).
23 O. Volkov, W. Dirk, U. Englert, and P. Paetzold, Z. Anorg.
Allg. Chem. 625, 1193 (1999).
24 J. K. Kang, S. Y. Kim, Y. S. Han, R. P. Muller, and W.
A. Goddard III, Appl. Phys. Lett. 87, 111904 (2005).
25 B. Morosin, A. W. Mullendore, D. Emin, and G. A. Slack,
in Boron-Rich Solids, edited by D. Emin, T. L. Aselage, C. L.
Beckel, I. A. Howard, and C. Wood, AIP Conf. Proc.
No. 140 (AIP, New York, 1986), p. 70.
26 R. B. King, I. Silaghi-Dumitrescu, and A. Lupan, Inorg.
Chem. 44, 7819 (2005).
27 S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba,
S. Towata, and A. Züttel, J. Alloys Comp. 404-406, 427
(2005).
28 S. Orimo, Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, S.
Towata, and A. Züttel, Appl. Phys. Lett. C, to be published.
29 G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995).
30 M. B. Smith and G. E. Bass Jr., J. Chem. Eng. Data 8,
342 (1963).
31 G. A. Olah, K. Wade, and R. E. Williams, Electron
Deficient Boron and Carbon Clusters (JOHN WILEY & SONS, 1991).