First-principles calculations of the crystal structure, electronic structure, and thermodynamic stability of $\text{Be}(\text{BH}_4)_2$

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Alanates and boranates are intensively studied because of their potential use as hydrogen storage materials. In this paper, we present a first-principles study of the electronic structure and the energetics of beryllium boranate $[\text{Be}(\text{BH}_4)_2]$. From total energy calculations, we show that—in contrast to the other boranates and alanates—hydrogen desorption directly to the elements is likely and is at least competitive with desorption to the elemental hydride (BeH_2). The formation enthalpy of $\text{Be}(\text{BH}_4)_2$ is only -0.14 eV/ H_2 (at $T=0$ K). This low value can be rationalized by the participation of all atoms in the covalent bonding, which is in contrast to the ionic bonding observed in other boranates. From calculations of thermodynamic properties at finite temperature, we estimate a decomposition temperature of 162 K at a pressure of 1 bar.

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I. INTRODUCTION

In the past decade, the environmental importance of reducing the CO_2 exhaust has been widely accepted. The use of hydrogen based fuel cells is an important contribution to achieve this reduction. One major obstacle for this use is the development of a method for hydrogen storage with a high gravimetric and volumetric hydrogen density.¹

One way of storing hydrogen is in a (complex) metal hydride. The ideal hydrogen storage material should have the highest possible gravimetric hydrogen density. This obviously requires the use of lightweight materials. Moreover, the formation energy of the hydride has to be such that it is stable at atmospheric conditions; yet, it has to decompose at a moderate temperature to release the hydrogen. A further important point is that the reactions involved in hydrogen desorption and/or absorption must have fast kinetics.

Over the past decade, alanates and boranates have been extensively studied as potential hydrogen storage materials.^{1,2} Alanates and boranates consist of a lattice of metal cations and $[\text{AlH}_4]^-$ or $[\text{BH}_4]^-$ complex anions, respectively. Generally, these materials decompose by heating via intermediate complex hydrides into bulk metals, elemental hydrides, and hydrogen gas. In the past few years, the attention has gradually shifted from alanates toward boranates because of the high gravimetric hydrogen density in the latter. However, many boranates turn out to be too stable.

In principle, a large variety of boranates can be synthesized by changing the metal cations, which can be used to tune the formation energy.³ So far, most effort has been devoted to alkali boranates,^{4–10} and more recently, to mixtures of alkali boranates^{11,12} and to alkaline earth boranates.^{13–17} In order to understand the chemical trends, we have recently developed a simple model for the formation energies of these compounds.¹⁸ This model demonstrates that these boranates are ionic compounds (in the sense discussed above) and that

the difference in their formation energies can be understood on the basis of the electrostatic (Madelung) lattice energy. The basic stability of the $(\text{BH}_4)^-$ cation is not affected by substituting one alkali or alkaline earth cation by another.

The stability of $(\text{BH}_4)^-$ may be changed by adding an element that competes with boron in binding with hydrogen. To investigate this possibility, we study beryllium boranate¹⁹ $[\text{Be}(\text{BH}_4)_2]$ in this paper. Establishing the electronic structure and thermodynamic stability of $\text{Be}(\text{BH}_4)_2$ will assist us in understanding the chemical and physical trends in alkali, alkaline earth alanates, and boranates.²⁰

We present a first-principles study of the electronic structure and the thermodynamic properties of $\text{Be}(\text{BH}_4)_2$. The electronic structure in relation to the crystal structure is used to analyze the bonding in $\text{Be}(\text{BH}_4)_2$. We calculate total energies and phonon frequencies of all compounds involved in possible formation reactions of $\text{Be}(\text{BH}_4)_2$. From these data, we obtain the thermodynamic properties at finite temperature.

II. COMPUTATIONAL METHODS

First-principles calculations are carried out within the density functional theory (DFT) approach by applying a generalized gradient approximation (GGA) for the exchange correlation functional.²¹ We use a plane wave basis set and the projector augmented wave (PAW) method,^{22,23} as implemented in the Vienna *ab initio* simulation package (VASP),^{24–26} and apply nonlinear core corrections.²⁷

Brillouin zone integrations are performed with a tetrahedron method²⁸ for calculating total energies. A Gaussian smearing method is used for calculating densities of states, with a smearing parameter of 0.1 eV. The k -point meshes are such that total energies are converged within 0.1 meV/f.u. The total energies used in the calculations of the reaction enthalpies are obtained with a high plane wave kinetic en-

FIG. 3. (Color online) Total energy per unit cell of $\text{Be}(\text{BH}_4)_2$ as a function of the cell volume.

The optimized B-H and Be-H bond lengths are given in Fig. 1. As references, the B-H bond length in a $(\text{BH}_4)^-$ anion is 1.21 Å, whereas a B-H bond length in a typical three center B-H-B bond is 1.34 Å.³⁴ A comparison with these numbers indicates that the B-H bonding in $\text{Be}(\text{BH}_4)_2$ is closer to that in the $(\text{BH}_4)^-$, although there is some distortion due to the presence of the Be atom, in particular, on the $\text{B}_d\text{-H}_c$ bond. This could indicate some competition between B and Be for bonding to hydrogen. For comparison, the B-H bond lengths in alkali boranates are all very close to 1.21 Å. However, the Be-H bond lengths are still quite large, which indicates a significant ionic contribution to the bonding.

We have also optimized the structure of BeH_2 (see Table II). It agrees well with the experimental structure³⁷ and with that obtained in a previous calculation,^{30,38} the largest difference being that our calculated bulk modulus (21.4 GPa) is $\sim 10\%$ smaller than that calculated in Ref. 38 (23.8 GPa). For elemental boron, we use the β -rhombohedral structure, as given in Ref. 33. For elemental beryllium [space group $P\bar{3}m1$ (No. 164)], we find lattice parameters $a=2.260$ Å and $c=3.567$ Å, which compare well with the experimental values of 2.29 and 3.60 Å, respectively.³⁹

IV. ELECTRONIC STRUCTURE

As discussed above, the crystal structure of $\text{Be}(\text{BH}_4)_2$ indicates a weak bonding between polymer chains and a stron-

TABLE II. Optimized crystal structure of BeH_2 . The space group is $Ibam$ (No. 72) and the optimized lattice parameters are $a, b, c=8.967, 4.141, 7.643$ Å. The experimental lattice parameters are $a, b, c=9.082, 4.160, 7.707$ Å (Ref. 37).

Atom	Wyckoff	x	y	z
Be	4a	0	0	0.25
Be	8j	0.1677	0.1200	0
H	16k	0.0882	0.2241	0.1520
H	8j	0.3102	0.2771	0

FIG. 4. (Color online) Charge density difference plots ($e/\text{\AA}^3$) of $\text{Be}(\text{BH}_4)_2$ with respect to the isolated atoms. The top picture gives a cut through a plane containing B_b , H_b , and Be atoms of the polymer backbone, the middle picture a cut through B_d and H_c side chain plane, and the bottom right picture a cut through B_d and H_d side chain plane. Electrons are transferred from regions close to the Be atoms to regions close to the H atoms and the B-H bonds.

ger bonding within a polymer chain. The charge displacement upon bond formation can be visualized by plotting the charge density difference, i.e., the charge density of $\text{Be}(\text{BH}_4)_2$ minus that of the individual isolated atoms. Cuts through the charge density difference in various planes along a polymer backbone are shown in Fig. 4. They clearly indicate the formation of B-H covalent bonds, which are polarized somewhat toward the H atoms. The character of the Be-H bonds is much less clear from these plots. In any case, these bonds are strongly polarized in the direction of the H atoms.

The electronic projected density of states (PDOS) of $\text{Be}(\text{BH}_4)_2$, with projections on s, p components of the individual atoms, is shown in Fig. 5. Tetrahedrally bonded $(\text{BH}_4)^-$ generates a characteristic pattern in the valence band part of the PDOS, which is qualitatively similar to that observed for $(\text{AlH}_4)^-$ tetrahedra in the aluminates.^{40–45} The tetrahedral geometry of $(\text{BH}_4)^-$ results in a splitting into two valence peaks, i.e., the lower one of s (A_1) symmetry and the upper one of p (T_2) symmetry, with a relative weight ratio of 1:3. Projected on atomic states, the s peak then has contributions from H s and B s orbitals and the p peak has contributions from H s and B p orbitals. The p peak can be split due to symmetry breaking caused by the crystal field. This is clearly observed in the lowest two panels of Fig. 5, showing

FIG. 5. (Color online) The PDOS of $\text{Be}(\text{BH}_4)_2$. The Fermi level E_F at the top of the valence band is the zero of energy. The upper (red) and lower curves (black) give projections on p and s atomic states, respectively. Atomic radii of 0.7, 0.5, and 1.1 Å are used for Be, B, and H, respectively.

the PDOS on the B_d and H_d atoms with the s peak at ~ -7 eV and a p doublet around ~ -1 eV. The splitting between s and p peaks is large (~ 6 eV), and the crystal field splitting is much smaller (~ 1 eV).

The interaction between the BH_4 units in the crystal lattice leads to a broadening of the peaks due to band formation. The interaction is strongest along the $\text{B}_b(\text{H}_b)_4$ – Be – $\text{B}_b(\text{H}_b)_4$ polymer backbone (see Figs. 1 and 2). This leads to an s -type band in the range of ~ -9 to ~ -7.5 eV, involving contributions from H_b , B_b , and Be s orbitals, whose DOS has the characteristic shape of a one-dimensional structure (see the upper three panels of Fig. 5). In the range of ~ -5 to ~ -2 eV, we find a set of p -type bands. The bandwidths are smaller than the sp splitting, but they are not negligible, reflecting the covalent bonding along the polymer backbone.

The involvement of the Be atoms can be clarified by calculating the DOS for a $\text{Be}(\text{BH}_4)_2$ structure, in which the Be atoms are replaced by a homogeneous background with a charge of $2+$. The result is shown in Fig. 6. The s and p valence bands discussed above are replaced by much narrower peaks that reflect electron localization on $(\text{BH}_4)^-$ ions in this artificial structure. In other words, the Be atoms in $\text{Be}(\text{BH}_4)_2$ are involved in the covalent bonding. This is in contrast to alkali or alkaline earth boranates and alanates, where the DOS changes little if the cations are replaced by a background charge. The bonding in the latter compounds can

FIG. 6. (Color online) The total DOS of $\text{Be}(\text{BH}_4)_2$. The Fermi level E_F at the top of the valence band is the zero of energy. In the lower curve, the beryllium atoms are replaced by an homogeneous background with a charge of $2+$.

be described as an ionic bonding between $(\text{BH}_4)^-$ or $(\text{AlH}_4)^-$ anions and M^+ (alkali) or M'^{2+} (alkaline earth) cations.⁴⁵

V. REACTION ENTHALPIES

For light elements, such as hydrogen, beryllium, and boron, the quantum character of their atomic vibrations is important. This leads to vibrational energies at zero temperature that are not negligible. For each compound involved in the reaction, we calculate its zero point vibrational energy (ZPVE) from the frequencies of the vibrational modes in the optimized structure. For hydrogen molecules, the zero point rotational energy (ZPRE) is also not entirely negligible. Reaction enthalpies ΔH_0 at $T=0$ K are then calculated from

$$\Delta H_0 = \sum_p (E_p^{\text{tot}} + E_p^{\text{ZPVE}}) + E_{\text{H}_2}^{\text{ZPRE}} - \sum_r (E_r^{\text{tot}} + E_r^{\text{ZPVE}}), \quad (1)$$

where $E_{p/r}^{\text{tot}}$ denotes the total energy of the reaction products p or reactants r , $E_{p/r}^{\text{ZPVE}}$ are the corresponding ZPVEs, and $E_{\text{H}_2}^{\text{ZPRE}}$ is the ZPRE of the hydrogen molecules involved in the reaction. At $T=0$ K, reaction enthalpies with neglected ZPEs will be denoted by ΔE .

For the hydrogen molecules, we calculate a vibrational frequency of 4356 cm^{-1} , which is in good agreement with the experimental value of 4401 cm^{-1} .⁴⁶ The ZPVE, i.e., 0.266 eV, is then calculated from the energy levels of a Morse potential,

$$E(n) = \hbar \omega \left(n + \frac{1}{2} \right) - \frac{1}{4D_e} \left[\hbar \omega \left(n + \frac{1}{2} \right) \right]^2, \quad (2)$$

where ω is the vibration eigenfrequency and $D_e = 4.57$ eV is the dissociation energy. Assuming that *ortho*- and *para*-hydrogen molecules are produced in a proportion of 3:1, the average ZPRE of a hydrogen molecule is 0.011 eV by using the energy levels given in Ref. 46.

The calculated total energies and ZPEs of all compounds involved in the reactions are listed in Table III. We consider

TABLE III. Total energies (with respect to nonspin polarized model atoms), ZPVEs, and ZPREs in eV/f.u. in the relaxed structures.

	E^{tot}	E^{ZPVE}	E^{ZPRE}
$\text{Be}(\text{BH}_4)_2$	-45.868	2.450	
BeH_2	-10.797	0.542	
H_2	-6.803	0.266	0.011
B	-6.687	0.126	
Be	-3.729	0.091	

two possible reaction paths for the formation of $\text{Be}(\text{BH}_4)_2$. In the first path, $\text{Be}(\text{BH}_4)_2$ is directly formed from the elements, as follows:

The second path involves the formation of an intermediate compound BeH_2 , as follows:

The enthalpies of these reactions are calculated using Eq. (1) and the values are given in Table III.

Equation (3) gives a reaction enthalpy $\Delta E = -0.39$ eV/ H_2 if ZPEs are neglected. If ZPEs are included, the reaction enthalpy becomes $\Delta H_0 = -0.14$ eV/ H_2 , which indicates the importance of ZPE corrections for these light-weight compounds. In principle, these values are in a range that is useful for hydrogen storage.

Can these enthalpies be understood as an extrapolation of reaction enthalpies of similar boranate systems? Recently, Nakamori *et al.*³ observed a linear dependence of the (calculated) formation enthalpies of boranates $M(\text{BH}_4)_n$ on the Pauling electronegativity χ_{ps} of the cation M . Smaller χ_{ps} correspond to more stable boranates. Using their linear fit and $\chi_P = 1.57$ for Be, we obtain $\Delta H_0 = 0.00$ eV/ H_2 . The deviation between this and our first-principles number (-0.14 eV/ H_2) is somewhat larger than the mean square deviation of 0.05 eV/ H_2 that Nakamori *et al.*³ obtained for their fit. In another recent study, we employed an ionic model with a modified Born–Haber cycle to analyze the formation energies of alanates and boranates.¹⁸ This model gives a reaction enthalpy $\Delta E = -0.02$ eV/ H_2 . This number is also higher than the value we obtain from first-principles calculation (-0.39 eV/ H_2). Both the analyses of Nakamori *et al.*³ and van Setten *et al.*¹⁸ were based on an ionic picture. However, in the previous section, we already concluded that the bonding in $\text{Be}(\text{BH}_4)_2$ is not purely ionic. The Be atoms are (partially) covalently bonded to BH_4 , which gives an additional stabilization, resulting in a higher dehydrogenation enthalpy.

Most alanates and boranates form a simple alkali and/or alkaline earth hydride when hydrogen is released in a first step. The dehydrogenation of this simple hydride then occurs as a separate second step. Usually, the enthalpies are such that only the first step is considered useful for hydrogen stor-

TABLE IV. Calculated reaction enthalpies at 0 K without ZPVE (ΔE), at 0 K including ZPVE (ΔH_0), and at 298 K (ΔH_{298}). All entries are in eV/ $\text{H}_2(\text{g})$.

	ΔE	ΔH_0	ΔH_{298}
$\text{Be} + 2\text{B} + 4\text{H}_2(\text{g}) \rightarrow \text{Be}(\text{BH}_4)_2$	-0.39	-0.14	-0.21
$\text{Be} + \text{H}_2(\text{g}) \rightarrow \text{BeH}_2$	-0.27	-0.09	-0.16
$\text{BeH}_2 + 2\text{B} + 3\text{H}_2(\text{g}) \rightarrow \text{Be}(\text{BH}_4)_2$	-0.43	-0.15	-0.22

age. For $\text{Be}(\text{BH}_4)_2$, these two steps correspond to the reverse reactions of Eqs. (5) and (4). The calculated reaction enthalpies of Eqs. (4) and (5) are $\Delta E = -0.27$ and -0.43 eV/ $\text{H}_2(\text{g})$ and $\Delta H_0 = -0.09$ and -0.15 eV/ $\text{H}_2(\text{g})$ with ZPE corrections, respectively. By comparing these numbers to those of reaction (3), we see that (per H_2) $\text{Be}(\text{BH}_4)_2$ is slightly more stable than BeH_2 . This would indicate that a one-step reaction directly from the elements [Eq. (3)] is more favorable than the two-step reaction via the simple hydride [Eqs. (4) and (5)]. However, the enthalpy difference is very small. In addition, kinetic barriers may influence the relative importance of the two reaction paths.

We will now focus on finite temperature properties. For solids, we calculate the Gibbs free energy $G(T)$ in the harmonic approximation as

$$G(T) = E^{\text{tot}} + H^{\text{vib}}(T) - TS^{\text{vib}}(T), \quad (6)$$

with

$$H^{\text{vib}}(T) = \int_0^\infty d\omega g(\omega) \left\{ \frac{1}{2} \hbar \omega + \hbar \omega n(\omega) \right\} \quad (7)$$

and

$$S^{\text{vib}}(T) = k_B \int_0^\infty d\omega g(\omega) \{ \beta \hbar \omega n(\omega) - \ln[1 - e^{-\beta \hbar \omega}] \}, \quad (8)$$

where $g(\omega)$ is the phonon density of states, $n(\omega) = [\exp(\beta \hbar \omega) - 1]^{-1}$ is the Bose–Einstein occupation number, and $\beta = 1/k_B T$. The first term in the integral of Eq. (7) gives the ZPVE and the second term gives the finite temperature contribution. Note that we neglect the PV term (i.e., the distinction between energy and enthalpy), which is a good approximation for solids. For the Gibbs free energy, the enthalpy, and the entropy of the hydrogen gas, we use the values given in Ref. 47.

By using the above expressions, we obtain the enthalpies at 298 K and 1 bar. All enthalpies are summarized in Table IV. The calculated reaction enthalpy $\Delta H_{298} = -0.16$ eV/ H_2 of Eq. (4) is in good agreement with $\Delta H_{298} = -0.15$ eV/ H_2 , which was obtained by Hector *et al.*³⁰ in a similar DFT study. It is also in reasonable agreement with the experiment (for amorphous BeH_2) of Senin *et al.*,⁴⁸ who obtained $\Delta H_{298} = -0.20$ eV/ H_2 . (For deuteride, the formation enthalpy for the crystalline state is available: $\Delta H_{298}(\text{BeD}_2) = -0.32$ eV/ H_2 .⁴⁸ By combining our ΔE with the temperature corrections from Ref. 30, we find $\Delta H_{298}(\text{BeD}_2) = -0.20$ eV/ H_2 , which is very close to the result of Ref. 30.)

FIG. 7. (Color online) Gibbs free energy of $\text{Be}(\text{BH}_4)_2$ (solid line), $\text{Be} + 2\text{B} + 4\text{H}_2(\text{g})$ (dashed red line), and $\text{BeH}_2 + 2\text{B} + 3\text{H}_2(\text{g})$ (dash dot blue line). All lines pertain to the same net composition of 1 f.u. $\text{Be}(\text{BH}_4)_2$.

Figure 7 gives the free energies $G(T)$ of $\text{Be}(\text{BH}_4)_2$, the products of the dehydrogenation reaction [i.e., the left and right hand sides of Eq. (3)], and the possible intermediate with BeH_2 [the left hand side of Eq. (5)] at a standard pressure of 1 bar. At 162 K, the free energy of the products drops below that of the hydride phase, whereas the “intermediate” with BeH_2 remains above the most stable curve throughout most of the temperature range. It therefore seems unlikely that hydrogen desorption goes via an intermediate stage with BeH_2 . However, as previously noted above for the enthalpies, the Gibbs free energy curves come very close. Moreover, kinetic effects might play a role.

The predicted desorption temperature relies only on the thermodynamics of the reaction. From the fact that experimentally $\text{Be}(\text{BH}_4)_2$ seems to be stable at room temperature, one may conclude that kinetic barriers play an important role in stabilizing $\text{Be}(\text{BH}_4)_2$. In this respect, $\text{Be}(\text{BH}_4)_2$ is similar to other boranates and alanates, where decomposition temperatures are much higher than what is expected on the basis of thermodynamics, and catalysts have to be applied in order to overcome kinetic barriers.

VI. CONCLUSIONS

We use DFT electronic structure calculations at the GGA level to study the crystal structure, electronic structure, and

thermodynamics of $\text{Be}(\text{BH}_4)_2$. We optimize the atomic positions and lattice parameters of all compounds involved in possible formation and dehydrogenation reactions. Both the crystal structure and the electronic structure indicate that the bonding between B and H atoms is covalent and that the bonding between Be and has a covalent as well as an ionic contribution. The crystal structure and the electronic density of states give evidence for $[-\text{BH}_4-\text{Be}-]_n$ (helical) polymers.

The enthalpies of possible formation reactions are calculated including zero point energy corrections. The latter are obtained by calculating the phonon frequencies of all compounds involved in the reactions. Since not only hydrogen but also boron and beryllium are relatively light elements, the zero point energies are relatively large for these compounds. The enthalpy of formation of $\text{Be}(\text{BH}_4)_2$ from the elements is $\Delta E = -0.39$ eV/ H_2 and $\Delta H_0 = -0.14$ eV/ H_2 .

$\text{Be}(\text{BH}_4)_2$ differs from other boranates and alanates in that its dehydrogenation to the elements is thermodynamically slightly more favorable than dehydrogenation via the simple hydride BeH_2 . In alkali or alkaline earth boranate and alanate, dehydrogenations always occur via the alkali or alkaline earth simple hydride. The different behaviors of $\text{Be}(\text{BH}_4)_2$ are mainly caused by the high stability of bulk beryllium metal.

$\text{Be}(\text{BH}_4)_2$ follows the general trends in the formation energies that have been observed in alkali and alkaline earth alanates and boranates. Boranates are more stable than the corresponding alanates, lighter cations give compounds that are more unstable, and alkaline earth compounds are more unstable than alkali compounds.⁴⁵ Indeed, $\text{Be}(\text{BH}_4)_2$ is less stable than LiBH_4 or $\text{Mg}(\text{BH}_4)_2$. We have not come across a mention of beryllium alanate in the literature, which might indicate that this compound would be too unstable.

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