A Density Functional Study of α-$Mg(BH_4)_2$

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Boranates (tetrahydroborates) are studied intensively because of their potential use as hydrogen storage materials. In this Article, we present a first-principles study of α-$Mg(BH_4)_2$ at the level of density functional theory. We optimize the complex structure of α-$Mg(BH_4)_2$, starting from the experimental crystal structures with 30 formula units per unit cell. From total energy calculations, incorporating vibrational contributions at finite temperature, we show that the hydrogen desorption reaction α-$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$ has a reaction enthalpy of 38 kJ/mol H_2 at room temperature. This makes $Mg(BH_4)_2$ an interesting candidate as a hydrogen storage material.

Introduction

Any future economy based on hydrogen as a fuel will require a safe, reliable, and cheap method for storing hydrogen. Solid-state hydrogen storage represents one of the most likely solutions.[1] Recently, a very promising material, magnesium tetrahydroborate or boranate, $Mg(BH_4)_2$, was studied experimentally in this context.[2,3] Although the material has been known for more than 50 years, the crystal structure was resolved only recently.[4,5] $Mg(BH_4)_2$ has a gravimetric hydrogen content of 14.9 wt % and, hence, is one of the few materials that might enable us to satisfy the long-term DOE requirement of 10 wt % of hydrogen with respect to the complete storage system.

Besides the gravimetric hydrogen storage capacity, the hydrogen desorption temperature is the most crucial parameter determining the usefulness of a material for hydrogen storage. The ideal material should have an equilibrium hydrogen pressure of 1 bar at room temperature. This would enable a combined storage–fuel cell system, where the residual heat of the fuel cell is used to drive the desorption reaction. To achieve this equilibrium pressure, the desorption enthalpy of a storage material should be close to 39.2 kJ/mol H_2.[1] Without the use of a catalyst, $Mg(BH_4)_2$ desorbs hydrogen at temperatures around 290 °C.[2] At present, it is unclear to what an extent this temperature can be lowered by decreasing the kinetic barriers. A fundamental lower limit of the desorption temperature is defined by thermodynamics. It is the temperature at which the change in Gibbs free energy $\Delta G = \Delta H - T\Delta S$ of the reaction is zero. Kinetic barriers, which increase the practical desorption temperature, can be modified by adding catalysts or changing the particle sizes, for instance. Calculating the reaction enthalpy from first principles may help assess the limits set by thermodynamics.

The decomposition of $Mg(BH_4)_2$ into the elemental solids and H_2 gas is the most elementary reaction:

$$Mg(BH_4)_2 \rightarrow Mg + 2B + 4H_2 \qquad (1)$$

Experimentally, the hydrogen desorption reaction of $Mg(BH_4)_2$ is likely to give magnesium diboride as a final reaction product:

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2 \qquad (2)$$

These two reactions have been studied by first principles calculations using model crystal structures of $Mg(BH_4)_2$.[6,7] This Article will focus on the effects of accurate crystal structures of all compounds involved in reactions 1 and 2. We will comment on possible alternative reaction schemes. In addition, the temperature dependence of the reaction enthalpies will be determined. In contrast to earlier findings,[6] we conclude from our calculations that the thermodynamics of $Mg(BH_4)_2$ is close to that of an ideal hydrogen storage material.

Theoretical Section

The first step in obtaining the enthalpies is to calculate the total energies of all of the compounds involved in the reactions. The energies are obtained from first-principles

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(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.

(2) Chłopek, K.; Frommen, C.; Léon, A.; Zabara, O.; Fichtner, M. *J. Mater. Chem.* **2007**, *17*, 3496.

(3) Matsunaga, T.; Buchter, F.; Mauron, P.; Bielman, M.; Nakamori, Y.; Orimo, S.; Ohba, N.; Miwa, K.; Towata, S.; Züttel, A. *J. Alloys Compd.* **2007**, *459*, 483.

(4) Černý, R.; Filinckuk, Y.; Hagemann, H.; Yvon, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5765.

(5) Her, J.; Stephens, P. W.; Gao, Y.; Soloveichik, G. L.; Rijssenbeek, J.; Andrus, M.; Zhao, J. *Acta Crystallogr.* **2007**, *B63*, 561.

(6) Vajeeston, P.; Ravindran, P.; Kjekshus, A.; Fjellvåg, H. *Appl. Phys. Lett.* **2006**, *89*, 071906.

(7) Nakamori, Y.; Miwa, K.; Ninomiya, A.; Li, H.; Ohba, N.; Towata, S.; Züttel, A.; Orimo, S. *Phys. Rev. B* **2006**, *74*, 045126.

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calculations based on density functional theory (DFT). The projector augmented wave (PAW) method is applied in combination with a plane wave basis set, as incorporated in the Vienna Ab initio Simulation Package (VASP).[8–12] The total energies are obtained with a high plane wave kinetic energy cutoff of 700 eV for the wave functions and 1400 eV for the augmentation density. The PW91 generalized gradient approximation to the exchange correlation functional is adopted, and nonlinear core corrections are applied.[13,14] The Brillouin zone integrations are performed with the improved tetrahedron scheme using a sampling density of one **k**-point per 1.3×10^{-4} Å^{-3}.[15] The **k**-point mesh and plane wave kinetic energy cutoff are such that total energies are typically converged with respect to the basis set on a scale of 0.1 meV per formula unit. Structures are optimized until the forces on the atoms are less than 10 meV/Å. Unit cells are optimized until the pressure is smaller than 1 kbar, unless explicitly stated otherwise. With the computational parameters listed above, we estimate that reaction enthalpies are converged on a scale of 5 meV (0.5 kJ/mol H_2).

To calculate the zero point energies (ZPE) and phonon densities of state, we need the phonon frequencies of all of the compounds involved in the reactions. Vibrational frequencies are obtained from the dynamical matrix, whose matrix elements (the force constants) are calculated using a finite difference method.[16] The force constants are calculated from four displacements, $-2, -1, 1, 2 \times 0.005$ Å, for each atomic degree of freedom. For structures with small unit cells, one has to use supercells to minimize interaction between periodic images; $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells give converged ZPEs for bulk magnesium and magnesium diboride, respectively. To calculate the phonon spectrum of α-Mg(BH$_4$)$_2$, one does not need a supercell as the unit cell is sufficiently large. For crystalline boron, we use the phonon spectrum that has been reported before.[17]

To obtain enthalpies at a finite temperature, we calculate the phonon densities of states $g(\omega)$ within the harmonic approximation and occupy the phonon modes according to Bose−Einstein statistics. The phonon contribution to the enthalpy is given by:

$$H^{\mathrm{vib}}(T) = \int_0^\infty g(\omega)\left\{\frac{1}{2} + n(\omega)\right\}\hbar\omega \, \mathrm{d}\omega \qquad (3)$$

where $n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$ is the Bose−Einstein occupation number, and $\beta = (k_{\mathrm{B}}T)^{-1}$. The first term between the curly brackets in the integral of eq 3 gives the ZPE, and the second term gives the contribution from the finite temperature occupation of the phonon modes. The **q**-point meshes we use to calculate the phonon densities of state are such that the ZPE and temperature dependencies are converged on a scale of 1 meV per formula unit (0.1 kJ/mol). We do not make a correction for the nonanalytical term in the dynamical matrix. This term is important in obtaining the correct LO−TO phonon splitting at Γ ($\mathbf{q} = 0$), but it has only a minor effect on the total phonon density of states and on the phonon contribution to the enthalpy.[18]

The reaction enthalpies $\Delta H(T)$ per H_2 released are obtained from the total energies E and vibrational enthalpies $H^{\mathrm{vib}}(T)$ of all of the compounds involved:

$$\Delta H(T) = H_{\mathrm{H_2gas}}(T) + \frac{1}{n}\sum_{\mathrm{P}} [E_{\mathrm{P}} + H_{\mathrm{P}}^{\mathrm{vib}}(T)] - \frac{1}{n}\sum_{\mathrm{R}} [E_{\mathrm{R}} + H_{\mathrm{R}}^{\mathrm{vib}}(T)] \qquad (4)$$

where n is the number of H_2 molecules in the reaction equation ($n = 4$ in reactions 1 and 2), and P, R label the product and reactant compounds, respectively. $H_{\mathrm{H_2gas}}(T)$ gives the enthalpy of the hydrogen gas: $H_{\mathrm{H_2gas}}(T) = E_{\mathrm{H_2}} + E_{\mathrm{H_2}}^{\mathrm{ZPE}} + H_{\mathrm{H_2gas}}^{\mathrm{exp}}(T)$, where the first two terms, the electronic total energy and the zero point energy, are calculated, and the final term, which contains the temperature dependency, is obtained from literature data.[19] We have tested the reliability of this procedure on the alkali boranates MBH$_4$, M = Li, Na, K. The reported values of ΔH at standard conditions of the decomposition reaction of these compounds into the elements (analogous to reaction 1) are 97, 96, and 115 kJ/mol H_2, respectively.[20] Our calculated values are 92, 89, and 110 kJ/mol H_2, which would indicate that our calculations typically underestimate such enthalpies by ~5 kJ/mol H_2.

Results and Discussion

Structure of α-Mg(BH$_4$)$_2$. To calculate the total energy of Mg(BH$_4$)$_2$, its crystal structure is needed. Two experimental crystal structures were published recently.[4,5] The structure of Černý et al.[4] is based on XRD (at room temperature) and neutron diffraction (at 173 K) of Mg(BD$_4$)$_2$, whereas that of Her et al.[5] is based on XRD (at room temperature) of Mg(BH$_4$)$_2$. The unit cell of both structures contains 330 atoms, that is, 30 Mg(BH$_4$)$_2$ formula units. In both cases, the space group is $P6_1$ (No. 169) with all atoms at Wyckoff 6a positions, which leads to a total of 165 symmetry-independent coordinates. Her et al.[5] report lattice parameters of $a = 10.3414$ Å and $c = 37.086$ Å, whereas Černý et al.[4] give slightly smaller lattice parameters, that is, $a = 10.3182$ Å and $c = 36.9983$ Å.

Starting from the structure given by Černý et al.,[4] we optimize the atomic positions while fixing the cell parameters at their experimental values. Full details of the optimized structure are given in the Supporting Information. The largest changes with respect to the experimental geometry were in the BH$_4$ tetrahedra surrounding the B9 and, to a lesser extent, the B6 and B10 atoms. The optimized B−H interatomic distances are in the range 1.22−1.23 Å. The spread is small, suggesting that all BH$_4$ tetrahedra in the crystal structure are similar. The Mg−H and Mg−B distances are in the ranges

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(8) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
(9) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15.
(10) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.
(11) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
(12) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
(13) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
(14) Louie, S.; Froyen, S.; Cohen, M. *Phys. Rev. B* **1982**, *26*, 1738.
(15) Blöchl, P. E.; Jepsen, O.; Anderson, O. *Phys. Rev. B* **1994**, *49*, 16223.
(16) Kresse, G.; Furthmüller, J.; Hafner, J. *Europhys. Lett.* **1995**, *32*, 729.
(17) van Setten, M. J.; Uijttewaal, M. A.; de Wijs, G. A.; de Groot, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 2458.
(18) Hector, L. G., Jr.; Herbst, J. F.; Wolf, W.; Saxe, P.; Kresse, G. *Phys. Rev. B* **2007**, *76*, 014121.
(19) Hemmes, H.; Driessen, A.; Griessen, R. *J. Phys. C* **1986**, *19*, 3571.
(20) Züttel, A; Borgschulte, A.; Orimo, S. *Scr. Mater.* **2007**, *56*, 823.

2.00−2.13 Å (average 2.06 Å) and 2.38−2.43 Å (average 2.41 Å), respectively. During the optimization, a decrease of about 65 kJ/mol in total energy is observed. Most of the energy decrease results from optimizing bond lengths that involve hydrogen atoms, whose positions are difficult to obtain experimentally. Our optimized B−H bond lengths are longer that those reported in ref 4. They are however very close to what is found in low temperature neutron diffraction experiments on alkali boranates.[19,20] As discussed in ref 21, XRD or neutron diffraction experiments at room temperature give a larger spread in B−H bond lengths. Within the uncertainties introduced by these temperature motions, our Mg−H and Mg−B distances agree with the experimental results.

When optimizing the atomic positions starting from the structure proposed by Her et al.,[5] we find that the interatomic distances are in the same ranges as those in the optimized Černý et al. structure.[4] In this case, a decrease of about 150 kJ/mol in total energy is observed during optimization. This rather large energy change mainly results from optimizing bond lengths involving hydrogen atoms, as before. It can be noted that a rather short B−H distance of 1.1 Å was used in ref 5. This might be a result of the fact that XRD measures the electronic charge distribution instead of the nuclear positions, as in neutron diffraction. For the positions of covalently bonded light atoms, such as hydrogen, XRD and neutron diffraction experiments can therefore yield slightly different results. In addition, the librational motions of the BH_4 tetrahedra, which are quite substantial at room temperature, lead to apparent shorter B−H distances.[21] In low temperature neutron diffraction, B−H bond lengths are typically in the range 1.21−1.23 Å,[21,22] in agreement with typical calculated values.

All atomic positions in the optimized Her et al. and Černý et al. structures differ by less than 0.1 Å. The unit cell volume of the Černý et al. structure is ∼0.7% smaller than that of the Her et al. structure, and all atoms shift somewhat to accommodate this volume difference while conserving the B−H and Mg−H bond lengths. The calculated external pressure for the optimized Her et al. structure is 0.00 kbar, indicating that it has the optimal volume. The optimized Černý et al. structure is 6.5 kJ/mol per unit cell higher in energy and it has an external pressure of 1.76 kbar, consistent with the smaller volume. The energy difference between the two structures amounts to 0.05 kJ/mol H_2, which is negligible when we consider the enthalpies of possible dehydrogenation reactions. We find that $Mg(BH_4)_2$ in the optimized $P6_1$ structure is 17.6 kJ/mol per formula unit lower in energy than the most stable ($Pmc2_1$) structure discussed in ref 6.

The electronic structure of $Mg(BH_4)_2$ is illustrated by the electronic density of states (DOS) shown in Figure 1. The DOS shows two peaks in the valence region and a large band gap, 6.64 eV, between the valence and conduction bands. Both features are also observed in other boranates.[7] The peaks in the valence region result from the covalent bonds between H and B atoms. Because the contribution of the Mg states is very small, the bonding in $Mg(BH_4)_2$ is mainly ionic between Mg^{2+} and $(BH_4)^-$ ions. The tetrahedral geometry of the $(BH_4)^-$ ions results in a characteristic splitting into two valence peaks, the lower one of s (A_1) symmetry and the upper one of p (T_2) symmetry with a relative weight 1:3. The interaction between the ions in the crystal lattice leads to a broadening of the peaks.[23] The broadening in the $P6_1$ structure is very similar to that in the simpler $Pmc2_1$ structure, as can be observed in Figure 1. The similarity between the DOSs of the $P6_1$ and the $Pmc2_1$ structures is consistent with the small energy difference between the two structures.

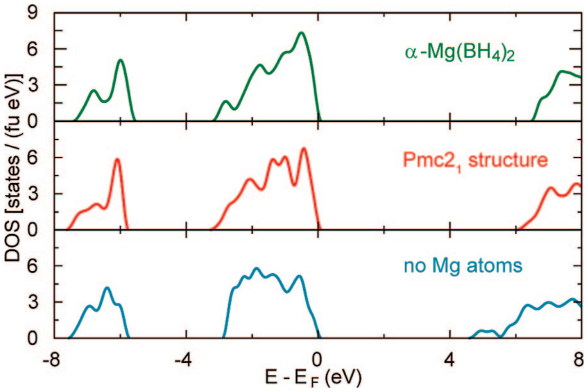

Figure 1. Electronic density of states of $Mg(BH_4)_2$ in the α-structure, in the $Pmc2_1$ structure (see text), and in the α-structure with the Mg atoms replaced by a homogeneous compensating background charge. The zero of energy (E_F) is set at the top of the valence band. In calculating the DOS, a Gaussian smearing with a smearing parameter of 0.1 eV was used.

The influence of the Mg^{2+} ions on the electronic structure is clarified from a comparison to the DOS calculated by replacing the Mg^{2+} ions by a homogeneous positive background charge; see Figure 1. The latter changes the shape of the valence peaks and reduces the gap between the valence and conduction bands by ∼2 eV. Following one's chemical intuition, one might expect that the conduction band would be composed of Mg^{2+} states. Removing the Mg^{2+} ions, one then expects an increase of the gap. We observe however a decrease, which indicates that the gap is not of a charge transfer character. Similar to the alanates, both the highest valence as well as the lowest conduction bands have primarily an anion character.[23] As discussed in ref 23, the increase of the gap upon inserting the Mg^{2+} ions into the structure can be understood as the stabilization of the more localized valence anion states relative to the more delocalized conduction anion states by the Madelung field of the cations.

We conclude that the chemical bonding in $Mg(BH_4)_2$ is qualitatively similar to that of other boranates. Unlike other boranates, however, $Mg(BH_4)_2$ has a remarkably complex crystal structure with 30 formula units per unit cell. This complexity is related to the geometry of the basic building block of the structure. All Mg atoms in $Mg(BH_4)_2$ are 8-fold coordinated by H atoms, in contrast to the 6-fold coordination of Mg observed, for instance, in MgH_2 and $Mg(AlH_4)_2$. The Mg−H bond distances in all of these compounds are fairly

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(21) Hartman, M. R.; Rush, J. J.; Udovic, T. J.; Bowman, R. C., Jr.; Hwang, S.-J. *J. Solid State Chem.* **2007**, *180*, 1298.

(22) Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K. *J. Alloys Compd.* **2004**, *375*, 98.

(23) van Setten, M. J.; de Wijs, G. A.; Popa, V. A.; Brocks, G. *Phys. Rev. B* **2007**, *75*, 035204.

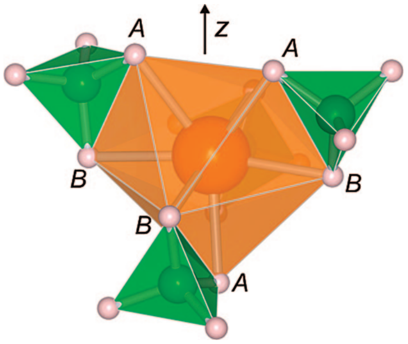

Figure 2. The basic building block of the $Mg(BH_4)_2$ crystal. Mg, B, and H atoms are indicated by orange, green, and gray balls.[30] Mg is 8-fold coordinated by H in a dodecahedron geometry, and B is 4-fold coordinated by H in a tetrahedron geometry, indicated in orange and green. Packing in the crystal distorts the dodecahedron and breaks the D_{2d} symmetry. The B−H and Mg−H distances are 1.22−1.23 and 2.01−2.13 Å; H_A−H_B distances along the tetrahedron edges and between tetrahedra: H_A−H_A and H_B−H_B distances are 2.06−2.09, 2.7−3.0, 2.2−2.4, and 2.7−3.1 Å, respectively (*m*, *g*, *a*, and *b* edges following the nomenclature of ref 22). For a BH_4 tetrahedron, the angles H_A−B−H_B and H_A−Mg−H_B are typically 115 ± 1° and 60 ± 1°. The angles between the Mg−H_A and Mg−H_B bonds and the *z*-axis are ∼35° and ∼95°.

similar, that is, 2.0 ± 0.1 Å. The nearest neighbor H−H distances in MgH_2 and $Mg(AlH_4)_2$ are larger than 2.5 Å, including those between H atoms bonded to one Al atom. In contrast, the distance between H atoms bonded to one B atom is only 2.0 Å. This smaller H−H distance facilitates an increase of the coordination of Mg to 8 H atoms. The H atoms in this coordination shell belong in pairs to BH_4's, so that each Mg is coordinated by 4 $(BH_4)^-$ ions. The geometry of the H coordination around Mg is that of a (slightly distorted) D_{2d} dodecahedron shown in Figure 2. This is one of the most commonly observed geometries for 8-fold coordination of metal ions, especially in case of bidentate ligands, such as $(BH_4)^-$ here. In a D_{2d} dodecahedron geometry, the Coulomb repulsion between the ligands is relatively small and the geometry is stabilized by the Coulomb interaction.[24,25]

In the $Mg(BH_4)_2$ crystal, each Mg dodecahedron is linked to 4 neighboring dodecahedra by BH_4 bridges, thus creating a network.[4] The basic building block of the network is shown in Figure 2. The tetrahedral shape of the BH_4 bridge introduces a torsion between nearest neighbor dodecahedra as illustrated by Figure 3. The geometries of the building block and the bridges do not allow for a network with a simple tetrahedral structure, such as in the Cu_2O structure discussed in the Supporting Information of ref 4. The torsion angles introduced by the bridges naturally lead to a strained network. The strain can be alleviated by spreading it over a number of building blocks in a large unit cell. More details can be found in the Supporting Information.

Reaction Enthalpies. Having obtained the total energy of α-$Mg(BH_4)_2$, we need the total energies of all compounds involved in reactions 1 and 2 to calculate the reaction enthalpies. The energies of bulk magnesium, bulk boron, and the H_2 molecule are calculated using the previously reported structural parameters.[17,23,26] For bulk boron, we use the lowest energy (*β* rhombohedral) structure.[17] The crystal structure of MgB_2 has the space group *P*6/*mmm* (No. 191), with Mg and B atoms at 1a and 2d Wyckoff positions, respectively. The calculated optimized lattice parameters are $a = 3.072$ Å and $c = 3.520$ Å, in good agreement with the experimental values $a = 3.086$ Å and $c = 3.524$ Å.[27]

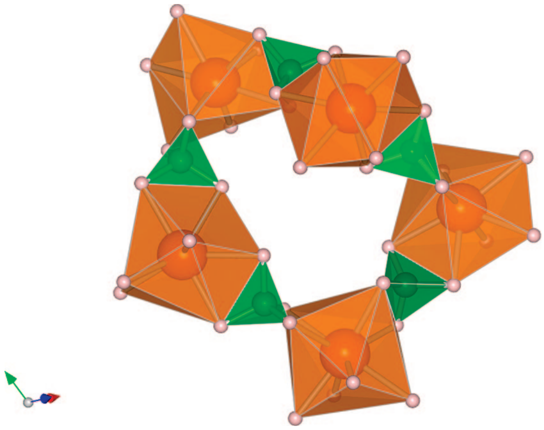

Figure 3. A substructure in the $Mg(BH_4)_2$ crystal illustrating MgH_8 dodecahedra (orange) linked by BH_4 tetrahedra (green).[30] Each dodecahedron is linked to other substuctures by two more tetrahedra (not shown), thus forming a tetrahedral network. Five-membered rings like the one shown here are quite common in this network.[4]

From the total energies, we obtain $\Delta E = 65$ kJ/mol H_2 for reaction 1 and $\Delta E = 53$ kJ/mol H_2 for reaction 2. From a simplified ionic model,[28] we obtain $\Delta E = 81$ kJ/mol H_2 for reaction 1, which gives a measure for the influence of the detailed crystal structure of α-$Mg(BH_4)_2$. Using the simple $Pmc2_1$ structure for $Mg(BH_4)_2$,[6] $\Delta E = 60$ kJ/mol H_2 is calculated for reaction 1. The enthalpies of the reactions listed in ref 6 change accordingly, because α-$Mg(BH_4)_2$ in the $P6_1$ structure is 17.6 kJ/mol per formula unit more stable than that in the $Pmc2_1$ structure used in ref 6.

Yet our calculated value for the enthalpy of $Mg(BH_4)_2$ in the $Pmc2_1$ structure is considerably lower than the 71 kJ/mol H_2 reported in ref 6 for reaction 1. The origin of this difference lies in the reference point chosen for elemental boron. We choose the most stable (*β*-rhombohedral) structure for boron as a reference, whereas in ref 6 one of the metastable (α-tetragonal) forms is used. The difference in energy between these two structures is 21 kJ/mol per B atom. Experimentally, it may be that boron emerges from the dehydrogenation reaction in amorphous form. Our choice of the most stable structure then represents a unique reference point. As a consequence, the enthalpies of all reactions listed in ref 6 involving elemental B change by 21 kJ/mol per B atom, if the most stable *β*-rhombohedral is used.

Following eq 3, we calculate the phonon densities of states of all solids involved in the reactions and occupy the phonon modes according to Bose−Einstein statistics to obtain the vibrational contributions to the reaction enthalpies. The H_2

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(24) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(25) King, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 6455.

(26) van Setten, M. J.; de Wijs, G. A.; Popa, V. A.; Brocks, G. *Phys. Rev. B* **2005**, *72*, 073107.

(27) Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. *Nature* **2001**, *410*, 63.

(28) van Setten, M. J.; de Wijs, G. A.; Brocks, G. *J. Phys. Chem. C* **2007**, *111*, 9592.

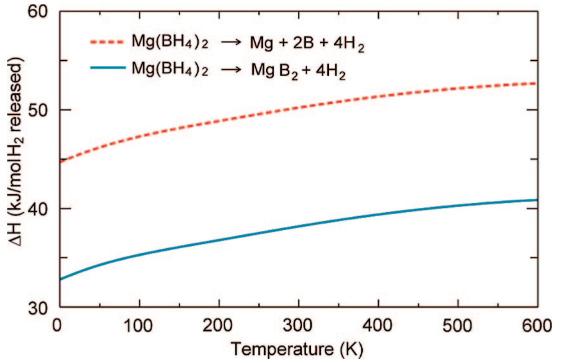

Figure 4. Temperature dependence of the reaction enthalpies of reactions 1 and 2.

gas is modeled using the thermodynamic data given by Hemmes et al.[19] Applying eq 3 at $T = 0$ K gives the zero point energy corrections. Reaction enthalpies $\Delta H(0\ \mathrm{K}) =$ 45 and 33 kJ/mol H_2 are obtained for reactions 1 and 2, respectively. The value for reaction 1 corresponds very well with the value of 46 kJ/mol H_2 predicted by the empirical correlation between electronegativities and formation enthalpies proposed by Nakamori et al.[7]

The temperature dependence of the reaction enthalpies calculated is shown in Figure 4. The temperature dependence is small, but not negligible. At room temperature, enthalpies $\Delta H(298\ \mathrm{K})$ of 51 and 38 kJ/mol H_2 are obtained for reactions 1 and 2, respectively. In particular, the latter value is close to what is needed for a hydrogen storage material. An alternative to reaction 2 would be the hydrogen desorption of $Mg(BH_4)_2$ to MgH_2, that is, $Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2$. Using a value of 75 kJ/mol H_2 for the decomposition enthalpy of MgH_2,[29] this gives an enthalpy of 44 kJ/mol H_2 for this reaction, which indicates that it is thermodynamically unfavorable as compared to reaction 2.

If we assume that the curves shown in Figure 4 are still reasonable at higher temperatures (i.e., neglecting anharmonic effects and phase transitions), the hydrogen desorption enthalpy at the experimental temperature associated with reaction 2 is $\Delta H(563\ \mathrm{K}) = 41$ kJ/mol H_2. This value differs significantly from the experimental value of 16.8 kJ/mol H_2 reported by Chłopek et al.,[2] which was obtained by high-pressure differential scanning calorimetry. Combined with the experimental decomposition enthalpy for MgB_2, 40 kJ/mol, this would give 26.8 kJ/mol H_2 for reaction 1. On the other hand, Matsunaga et al. report a value of 39.3 kJ/mol H_2 for the hydrogen desorption reaction of $Mg(BH_4)_2$ to MgH_2.[3] Again, combining this value with the decomposition enthalpy of MgH_2, 75 kJ/mol H_2, this would give a reaction enthalpy of 48 kJ/mol H_2 for reaction 1. This value is in reasonable agreement with the calculated $\Delta H(563\ \mathrm{K}) = 53$ kJ/mol H_2 for reaction 1. The difference between the two figures for reaction 1 extracted from the experimental data indicates the difficulty in measuring the dehydrogenation enthalpy of $Mg(BH_4)_2$.

Conclusion

We have studied α-$Mg(BH_4)_2$ by first-principles calculations at the level of density functional theory. Optimizing the atomic positions starting from the two recently published experimental $P6_1$ crystal structures with 30 formula units per unit cell[4,5] gives essentially one unique structure. This structure is 17.6 kJ/mol lower in energy than the simpler $Pmc2_1$ structure used in theoretical calculations, which has 2 formula units per unit cell.[6]

The electronic structure and chemical bonding resemble those of other alkali and alkaline earth boranates. The H atoms are covalently bonded in tetrahedral $(BH_4)^-$ ions, which are ionically bonded to Mg^{2+} ions. Similar to other boranates, $Mg(BH_4)_2$ has a large band gap, $E_g = 6.6$ eV, and both the top of the valence band and the bottom of the conduction band are dominated by states derived from the $(BH_4)^-$ ions. Unlike other boranates, $Mg(BH_4)_2$ has a remarkably complex structure. The relative sizes of the ions allow for an 8-fold coordination of Mg^{2+} by H atoms, supplied in pairs by 4 $(BH_4)^-$ ions, resulting in a coordination shell that has the shape of a dodecahedron. Each of these is linked to 4 neighboring dodecahedra by $(BH_4)^-$ bridges generating a tetrahedral network. The shape of the dodecahedra and the torsions introduced by the bridges do not allow for a simple, high symmetry network and lead to a complex structure.

Total energy calculations including vibrational zero point energies give a dissociation enthalpy $\Delta H(0\ \mathrm{K}) = 45$ kJ/mol H_2 of $Mg(BH_4)_2$ to the elements. Incorporating the vibrational enthalpy within the harmonic approximation gives a dissociation enthalpy $\Delta H(298\ \mathrm{K}) = 51$ kJ/mol H_2. For the hydrogen desorption reaction α-$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$, the corresponding numbers are $\Delta H(0\ \mathrm{K}) = 33$ kJ/mol H_2 and $\Delta H(298\ \mathrm{K}) = 38$ kJ/mol H_2.

The latter value indicates that the thermodynamics of the hydrogen desorption reaction of $Mg(BH_4)_2$ is close to that of an ideal hydrogen storage material. This gives hope for a possible decrease of the presently observed high hydrogen desorption temperature of $Mg(BH_4)_2$ by means of catalysts or nanostructuring. Together with the high gravimetric hydrogen content, this makes $Mg(BH_4)_2$ a material having a high potential for solid-state hydrogen storage.

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Supporting Information Available: Details and a discussion of the optimized structures of α-$Mg(BH_4)_2$ as used in the calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Bogdanović, B.; Bohmhammel, K.; Christ, B.; Reiser, A.; Schlichte, K.; Vehlen, R.; Wolf, U. *J. Alloys Compd.* **1999**, *282*, 84.

(30) The images were created with the visualization program VESTA, see: Momma, K.; Izumi, F. *Commission Crystallogr. Comput., IUCr Newsletter* **2006**, *7*, 106.