

IV.I.8 Kinetics and Thermodynamics of Metal and Complex Hydride Nanoparticles

Christopher Wolverton (Principal Investigator)

Department of Materials Science and Engineering,
Northwestern University
2220 Campus Drive, Room 2036
Evanston, Illinois 60208-3108, USA
Phone: (734) 678-6319; Fax: (847) 491-7820
E-mail: c-wolverton@northwestern.edu

Vidvuds Ozolins (co-PI)

Department of Materials Science and Engineering,
University of California, Los Angeles
Los Angeles, California 90095-1595, USA
Phone: (310) 267-5538; Fax: (310) 206-7353
E-mail: vidvuds@ucla.edu

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Accomplishments

Predicted New Ground State and Polymorphism of Mg Borohydride

In collaboration with Eric Majzoub (UMSL), we have developed a method which can predict entirely new, unsuspected ground state structure types for complex ionic crystals. Physically, this approach is based on the observation that complex hydrides are characterized by an arrangement of positively charged cations (e.g., Mg^{2+}) and negatively charged complex anions (e.g., BH_4^-), with strong covalent bonds within each anionic complex and predominantly electrostatic interactions between the cations and anions. These considerations suggest that the type and symmetry of the ground state crystal structure can be determined by minimizing the total electrostatic energy for a given set of ionic charges, ionic radii, and fixed shapes of complex anions. The resulting ground states, henceforth called *prototype electrostatic ground states* (PEGS), are then used as input to DFT calculations to relax all structural parameters and obtain accurate total energies. In [1] we showed that this method can successfully predict the observed ground states of alkali and rare earth alanates, including currently unknown structures of several bi-alkali hexa-alanates, such as $LiCaAlH_6$, $NaCaAlH_6$, $KCaAlH_6$, $NaMgAlH_6$, and $KMgAlH_6$. Using the PEGS search strategy, we have predicted a new $T=0$ K ground state of $Mg(BH_4)_2$ of tetragonal $I\bar{4}m2$ symmetry (see Figure 1), which is lower than all other previously

predicted structures. Interestingly, it is also 5 kJ/mol lower in energy than the recently proposed $P6_1$ structure with 30 formula units per primitive cell. Our predicted structure represents a truly new prototype that has not been observed in any other systems, and demonstrates the effectiveness of the PEGS method. The calculated thermodynamic properties of magnesium borohydride are found to be ideal for reversible storage: its enthalpy $\Delta H=29.5$ kJ/(mol H_2) and entropy are $\Delta S=101$ J/(K mol H_2) for the thermodynamically favored decomposition pathway into $MgB_{12}H_{12}$, MgH_2 , and H_2 .

Hydrogen Storage in Li-Sc-B-H

In collaboration with Eric Majzoub (UMSL) and experimentalists from Caltech/JPL [2], we have conducted an in-depth study of crystal structures and thermodynamic properties of borohydrides with Li^+ and Sc^{3+} cations. For $LiSc(BH_4)_4$, a tetragonal structure in space group $I\bar{4}$ (#82) was predicted to be significantly (60 kJ/mol) lower in energy than the $P\bar{4}2c$ structure proposed from high-resolution X-ray data [3]. The predicted diffraction patterns of $I\bar{4}$ do not correspond to those obtained from crystalline ternary borohydride phases made by ball milling, suggesting that several metastable polymorphs may exist. Our thermodynamic calculations show that $LiSc(BH_4)_4$ is stable at low temperatures. We find that the formation energy for reaction, $LiBH_4 + Sc(BH_4)_3 \rightarrow LiSc(BH_4)_4$, is strongly

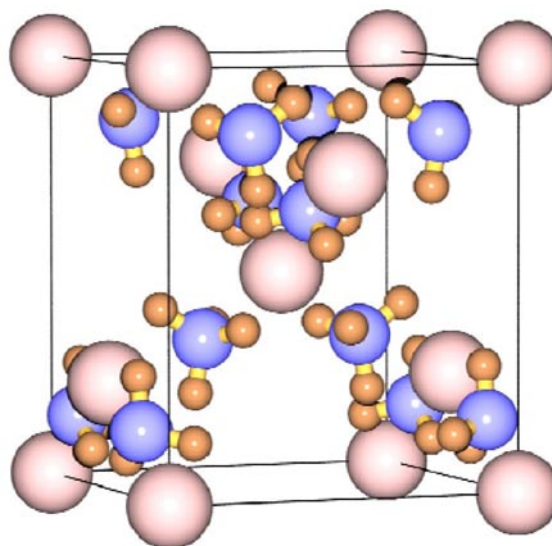
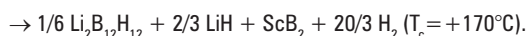
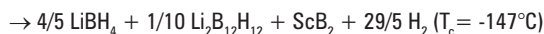
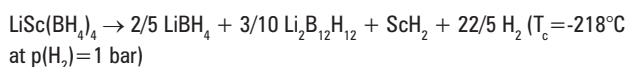


FIGURE 1. New low-energy $I\bar{4}m2$ structure of $Mg(BH_4)_2$ predicted using Monte Carlo electrostatic energy optimization [1].

negative, $\Delta H = -30$ kJ/mol at $T = 27^\circ\text{C}$, indicating that this compound readily forms upon ball-milling. Hydrogen release from $\text{LiSc}(\text{BH}_4)_4$ is predicted to occur via a series of steps:



Since hydrogen release from borohydrides typically has high kinetic barriers and requires temperatures of at least a few hundred $^\circ\text{C}$, it is likely that the first two steps will remain “kinetically frozen” until the temperature of the third step ($+170^\circ\text{C}$). Thus, the formation of LiBH_4 may be by-passed altogether and the decomposition process may go directly into $\text{Li}_2\text{B}_{12}\text{H}_{12}$, LiH , ScB_2 , and H_2 , in good agreement with experimental data.

In addition to $\text{LiSc}(\text{BH}_4)_4$, we have predicted the currently unknown crystal structures of $\text{Sc}(\text{BH}_4)_3$ and $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$ (see Figure 2); the former is marginally unstable at $T = 0$ K w.r.t. hydrogen release, while $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$ is predicted to be thermodynamically stable up to $T_c = 214^\circ\text{C}$ at 1 bar H_2 pressure. Overall, we conclude that the Li-Sc-B-H system is not an attractive candidate for hydrogen storage.

New Entropically Optimized Hydrogen Storage Reactions in Li-Mg-Ca-B-H

Metal borohydrides [LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$] are attractive candidates for onboard storage because they contain high densities of hydrogen by weight and by volume. We have applied the recently developed prototype electrostatic ground state (PEGS) search method [4] and the DFT-based grand-canonical linear programming approach (GCLP) [5] to predict currently

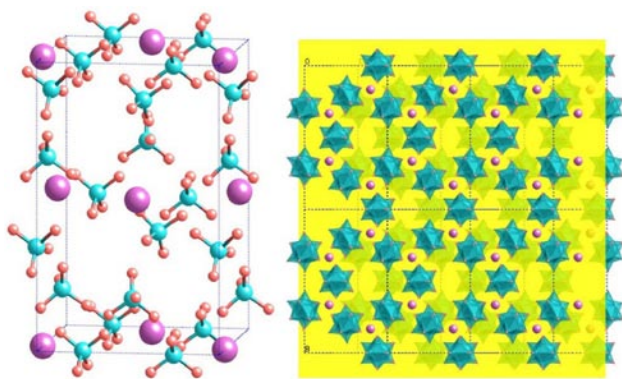


FIGURE 2. Left panel: Orthorhombic $C222$, crystal structure of $\text{Sc}(\text{BH}_4)_3$. Right panel: Planar projection of the predicted Cm crystal structure of $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$. Semitransparent yellow plane marks the (001) lattice plane, Sc^{3+} ions are violet, and $[\text{B}_{12}\text{H}_{12}]^{2-}$ groups are cyan.

unknown crystal structures and hydrogen storage reactions in the quinary Li-Mg-Ca-B-H system. We show how the *combination* of these two methods provides a powerful theoretical framework for predicting new high capacity hydrogen storage reactions with excellent thermodynamic properties. In particular, we use PEGS to predict the crystal structures of $\text{X}_n\text{B}_{12}\text{H}_{12}$ compounds. For $\text{LiB}_{12}\text{H}_{12}$, we find a new phase of $C2/m$ symmetry that is 7 kJ/mol lower in energy than the recently proposed $Pa\bar{3}$ phase obtained in solution-grown samples of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ [6]. For $\text{MgB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ we propose crystal structures of $C2/m$ and $C2/c$ symmetry, respectively. We find that LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ are thermodynamically favored to release H_2 by forming $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{MgB}_{12}\text{H}_{12}$, respectively, while $\text{Ca}(\text{BH}_4)_2$ has two thermodynamically degenerate decomposition pathways, one of which involves an intermediate $\text{CaB}_{12}\text{H}_{12}$ phase, while the other goes directly into CaB_6 and CaH_2 . Surprisingly, we also find that the classical destabilized $\text{LiBH}_4 + \text{MgH}_2$ reaction is thermodynamically favored to proceed via an intermediate $\text{Li}_2\text{B}_{12}\text{H}_{12}$ compound.

More importantly, we predict two new and previously unsuspected reactions (see Table 1), belonging to a qualitatively new class of entropically optimized reactions that use fully hydrogenated high-entropy borohydrides as reactants and lead to the formation of low-entropy $\text{X}_n\text{B}_{12}\text{H}_{12}$ phases as end products. Low reaction enthalpies [~ 25 kJ/(mol H_2)], which should significantly simplify heat management during on-board recharging, are compatible with nearly ideal thermodynamics (hydrogen release is predicted to occur around -20°C at $p = 1$ bar H_2 pressure) due to the exceptionally low vibrational entropies of the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ product phases. We formulate a guideline for designing new complex hydride reactions with *low entropies* – use reactants that have complex anions constituted by a small number of atoms (such as NH_2 , BH_4 , etc., resulting in a high number of low frequency phonon modes per atom) and products that are either tightly bound bulk phases or materials with large complex anions (e.g., $\text{B}_{12}\text{H}_{12}$), exhibiting few low-frequency phonon branches. Low entropies have a highly beneficial effect since they allow the use of materials with lower reaction enthalpies while

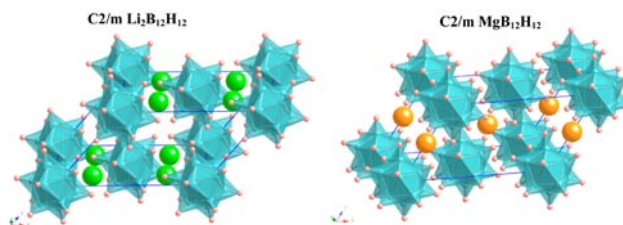


FIGURE 3. Predicted crystal structures of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (left) and $\text{MgB}_{12}\text{H}_{12}$ (right) See ref. [7].

TABLE 1. Predicted new hydrogen storage reactions for borohydrides. Enthalpies and entropies are given in kJ/(mol H₂) and J/(K mol H₂), respectively. ΔH^{300K} are the calculated enthalpies at T= 300 K, including vibrational energies. T_c gives the temperature of hydrogen release at p=1 bar of hydrogen pressure.

Reaction	Wt% (kg H ₂ /kg)	Vol. density (g H ₂ /l)	ΔH^{300K}	ΔS^{300K}	T _c (°C)
5Mg(BH ₄) ₂ + 2LiBH ₄ → Li ₂ B ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	8.4	46 (64)	24.4	100.0	-29
5Mg(BH ₄) ₂ + CaBH ₄ → CaB ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	7.7	51 (70)	25.7	100.5	-18

maintaining the same equilibrium H₂ pressure. Other things being equal, lower enthalpy reactions are always better due to a smaller amount of heat released during exothermic regeneration of these hydrides. These results demonstrate the power of the combined theoretical framework for structure prediction and linear programming-based reaction prediction, showing that previously unsuspected reactions can be found even in extensively studied materials systems.

Crystal Structure and Phonon Instability of High-Temperature β -Ca(BH₄)₂

Ca(BH₄)₂ is an interesting candidate for high-density hydrogen storage since it contains a large amount of hydrogen by weight and volume, and has been shown to reversibly release and absorb hydrogen, albeit at moderately high temperatures. Ca(BH₄)₂ undergoes a polymorphic transformation around 400–440 K from a low-temperature α -Ca(BH₄)₂ phase to a high-temperature β -Ca(BH₄)₂ phase. The crystal structure of β -Ca(BH₄)₂ has only recently been resolved, and its thermodynamic phase stability is still not well understood. Using a combined experimental and theoretical approach, we have independently determined the structure of β -Ca(BH₄)₂ and assessed its thermodynamic stability in the quasiharmonic approximation. The space-group *P42/m* gives an excellent agreement between experiment and theory, confirming the result of a recent study [Buchter *et al.*, J. Phys. Chem. B **112**, 8042 (2008)]. Using density-functional theory (DFT), we obtained a value of 10.9 kJ/mol for the static total-energy difference between the α -Ca(BH₄)₂ and the β -Ca(BH₄)₂ phases at T=0 K (without vibrations). Using DFT linear-response calculations, we find that the $[\frac{1}{2} \frac{1}{2} \xi]$ acoustic phonon branch of β -Ca(BH₄)₂ is dynamically unstable on the Brillouin-zone boundary at the T=0 K lattice parameters predicted from static DFT calculations. This phonon branch is very sensitive to the lattice parameters and can be stabilized by including lattice expansion due to zero-point vibrational contributions in the quasiharmonic approximation. This expanded stable β -Ca(BH₄)₂ structure has a room-temperature vibrational entropy that is 16 J/mol K higher than that of the α -Ca(BH₄)₂ phase, qualitatively consistent with the observed stabilization of the former at elevated temperatures. The main contribution to the entropy difference between the α -Ca(BH₄)₂ and β -Ca(BH₄)₂ phases comes from the

low-frequency region dominated by translational and rotational phonon modes.

First Principles Molecular Dynamics Study of the Structure and Dynamic Behavior of Liquid Li₄BN₃H₁₀

Recent experimental and computational studies have shown ‘complex hydrides’ to be promising hydrogen storage materials. Some of these materials are known to release hydrogen from the liquid state, such as Li₄BN₃H₁₀, however no experimental nor computational studies on its liquid structure have been reported. We have applied density functional theory based ab initio molecular dynamics to examine Li₄BN₃H₁₀ at temperatures both above and below the experimental melting point [8]. We examined the structure of the liquid, vibrational spectra, diffusivity and compared to experiments and the solid state. We found that the liquid state, like the solid state, is a mixture of Li⁺, BH₄⁻ and NH₂⁻ with ionic interactions between the BH₄⁻ and NH₂⁻ anions and the Li⁺ cations; however, the liquid demonstrates wide bond angle distributions in the anionic units, indicating that these units are not merely rigid. Our study also found that the Li⁺ sub-lattice disorders more readily than the other species. We calculated the activation energy and pre-exponential factor for Li⁺ diffusivity to be ~20 kJ/mol

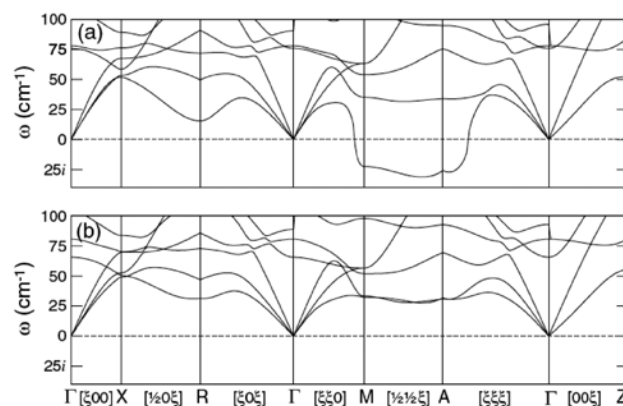


FIGURE 4. (a) Phonon dispersion of β -Ca(BH₄)₂ at the static total-energy minimum. Negative values correspond to unstable phonon branches with imaginary frequencies. (b) The same as (a), but after 2% expansion along the a and b lattice parameters, and 1% expansion along the c lattice parameter. Note that the instability vanishes for this geometry.

and 15×10^4 cm²/s, respectively. Finally, by computing the power spectrum, we find that the liquid contains the major internal vibrational modes of the solid, however the low frequency modes become more prominent with increasing temperature.

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8. D.E. Farrell, A. Thompson, D. Shin, and C. Wolverton, “*First Principles Molecular Dynamics Study of the Structure and Dynamic Behavior of Liquid Li₄BN₃H₁₀*,” (in preparation, 2009).

Publications

1. C. Kim, S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J.A. Zan, J.G. Kulleck, H. Kabbour, E.H. Majzoub, and V. Ozolins, “*LiSc(BH₄)₄ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density-Functional Theory Studies*,” to appear in *Journal of Physical Chemistry C* (2009).
2. Y.-S. Lee, Y. Kim, Y.W. Cho, D. Shapiro, C. Wolverton, and V. Ozolins, “*Crystal structure and phonon instability of high-temperature β-Ca(BH₄)₂*,” *Physical Review B* **79**, 104107 (2009).
3. V. Ozolins, E.H. Majzoub, and C. Wolverton, “*First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H system*,” *Journal of the American Chemical Society* **131** (1), 230-237 (2009).
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6. D.E. Farrell, A. Thompson, D. Shin, and C. Wolverton, “*First Principles Molecular Dynamics Study of the Structure and Dynamic Behavior of Liquid Li₄BN₃H₁₀*,” (in preparation, 2009).

Supported Personnel

Christopher Wolverton (PI, 1 month summer annually)
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