First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Final Report
May 2011

Executive Summary

The objective of this project is to complement experimental efforts of MHoCE partners by using state-of-the-art theory and modeling to study the structure, thermodynamics, and kinetics of hydrogen storage materials. Specific goals include prediction of the heats of formation and other thermodynamic properties of alloys from first principles methods, identification of new alloys that can be tested experimentally, calculation of surface and energetic properties of nanoparticles, and calculation of kinetics involved with hydrogenation and dehydrogenation processes. Discovery of new metal hydrides with enhanced properties compared with existing materials is a critical need for the Metal Hydride Center of Excellence. New materials discovery can be aided by the use of first principles (ab initio) computational modeling in two ways: (1) The properties, including mechanisms, of existing materials can be better elucidated through a combined modeling/experimental approach. (2) The thermodynamic properties of novel materials that have not been made can, in many cases, be quickly screened with ab initio methods. We have used state-of-the-art computational techniques to explore millions of possible reaction conditions consisting of different element spaces, compositions, and temperatures. We have identified potentially promising single- and multi-step reactions that can be explored experimentally.

Introduction

Complex metal hydrides have been extensively studied as candidate materials for hydrogen storage in vehicular and other applications.[1-9] An important focus in this field has been to find complex metal hydride mixtures having thermodynamics that make using them under moderate temperatures and pressures feasible.[5,6,10-12] Controlling the reaction thermodynamics of complex metal hydrides via so-called destabilization reactions is one example of this kind.[4,13-15] Vajo et al. reported that $LiBH_4$ is destabilized by MgH_2,[4] and subsequent experiments showed that $LiBH_4$ can also be destabilized by CaH_2.[14] Although experiments are the final arbiter of a reaction's usefulness, it is not practical to systematically study every conceivable reaction mixture experimentally. Therefore, systematic thermodynamic calculations based on first-principles calculations have played a useful role in the search for desirable reaction mixtures. First-principles calculations have been shown to yield reaction free energies that are accurate within ± 10 kJ/mol H_2—a level of precision that is adequate for screening large numbers of

potentially interesting reactions.[16-18]

Several earlier efforts have been made to categorize metal hydride mixtures using the thermodynamic calculations based on density functional theory (DFT) calculations and a database of crystal compounds.[19-24] The methodological basis of these calculations is the grand canonical linear programming method introduced by Ozolins and co-workers.[19-22,24] This approach rigorously determines the thermodynamic state of a specified set of elements among a set of crystalline materials in equilibrium with gaseous H_2, subject to a number of caveats. Ozolins *et al.* systematically predicted the thermodynamics of possible metal hydride mixtures in the Li-Mg-Ca-B-H system using this method.[22] The same group has reported results for the Li-B-N-H, Li-Mg-N-H and Li-Mg-Al-H systems.[19-21,24] Calculations that explored a wider range of elements were performed by Alapati, Johnson, and Sholl, who analyzed the 715 four-element spaces available from thirteen solid elements plus H with the same method.[23] Alapati et al. performed calculations based on 0 K reaction enthalpies predicted by DFT, an approach that requires much less computational effort for each solid than the free energy calculations used by Ozolins et al. This approach allowed Alapati et al. to screen a much larger element and composition space than previously examined with an uncertainty of about ± 15 kJ/mol H_2. The 0 K approximation inherent in this approach can readily be removed for the most promising reactions by computing the DFT-based free energies of the solids involved in these reactions.[16-18,23]

A key limitation of the linear programming approach is that it cannot make predictions about reactions that involve compounds that are not included in the database of materials used for the calculations. Because of the large amount of research that has been performed on metal hydrides and related materials in recent years, the studies cited above were based on databases that did not include many materials that have been characterized in more recent experiments. For example, the earlier work of Alapati et al. did not include the metal closoboranes ($M_nB_{12}H_{12}$, for M=Li, Mg, Ca, or K), which since that time have been observed or predicted as intermediates in the decomposition reactions of the metal borohydrides.[22,25-29] One aim of the present work is to update the extensive calculations of Alapati et al. using a database of materials that includes a large number of these recently described compounds. Specifically, we performed the necessary DFT calculations to add 147 new crystalline compounds (including but not limited to $B_{12}H_{12}$-based materials) to the 212 materials that were used earlier by Alapati et al. We then analyzed the reactions thermodynamics for all reaction mixtures defined by the 715 four-element spaces mentioned above.

The earlier work of Alapati et al. categorized the large number of distinct reactions that can occur for mixtures involving metal hydrides by focusing exclusively on reactions that occur in a single step. However, there are well known examples of multi-step reactions that have properties that are interesting in H_2 storage applications that are not captured if one focuses solely on single step reactions. A second aim of our work is to analyze the large number of reactive mixtures listed above to identify multi-step reactions with useful thermodynamic properties.

Approach

All DFT calculations were performed with methods that are consistent with the earlier calculations of Alapati *et al.*[16-18,23,30] These DFT calculations used the Vienna *ab initio* Simulation Package (VASP) with the PW91 generalized gradient approximation (GGA) functional.[31-34] The projector augmented wave (PAW) method was used for describing the core electrons of each atom.[35] An energy cutoff of 425 eV was used for all calculations. Geometries were relaxed until the forces on all atoms were less than 0.03 eV/Å. Structural optimizations of all new crystal compounds in our database were performed by the conjugate gradient method. Calculations of compounds having cubic unit cells were performed with a Monkhorst-Pack mesh of 9×9×9 or 8×8×8 *k*-points. A smaller number of *k*-points were used for a few systems having the largest unit cells. The numbers of *k*-points for compounds having the non-cubic unit cells were determined by considering the shape of the unit cells so that the density of *k*-points in reciprocal space was similar to the value for materials with cubic unit cells.

We used a single unit cell to optimize the bulk crystal structure of each compound listed in Table 1. In general, the initial structures for geometry relaxations were obtained from the experimental data available from ICSD.[36] Optimization of $Li_2B_{12}H_{12}$ and $MgB_{12}H_{12}$ were started from the structures observed by Her *et al.*[25] and predicted by Ozolins *et al.*,[22] respectively. One heuristic way to examine the reliability of our optimized structures is to compare the volume of the optimized structure with the experimental volume. As expected, the agreement between the experimentally observed and DFT optimized volumes is in general very good. There are two compounds where the experimental and DFT optimized volumes differ by more than 10%: $Si_2C_7H_{18}N_2$ (14% error) and Ti_2AlC (11% error). It is not clear what the source of these relatively large discrepancies is.

For two reactions described below we computed the VDOS of every solid compound in order to compute the reaction free energy. For these VDOS calculations, we used the PHONON code developed by Parlinski.[37]

Table 1: List of the 147 crystalline compounds whose total energies were calculated with DFT in this work.

Two-element compounds				
AlB_{12}	Al_4C_3	Al_4Ca	$Al_{14}Mg_{13}$	$Al_{30}Mg_{23}$
$Al_{23}V_4$	$Al_{45}V_7$	B_4C	$B_{13}C_2$	$(B_{10}H_{13})_2$
$B_{13}N_2$	C_2Ca	C_2N_2	C_3N_4	C_5N_4
$C_{12}N_6$	CaB_4	Ca_2Si	KC_8	KSi
K_8Si_{46}	LiB	LiMg	$Li_{12}Si_7$	$Li_{13}Si_4$
$Li_{15}Si_4$	NaB_{15}	Na_3B_{20}	Na_4Si_4	Na_8Si_{46}
$Sc_{15}C_{19}$	SiB_3	SiC	TiV	V_2N
V_5Si_3				
Three-element compounds				
$Al(BH_4)_3$	Al_2MgC_2	$Al_{18}Mg_3Ti_2$	BC_2N	$C_2H_4N_4$

$C_2H_{18}N_{18}$	$C_2N_2(NH)$	Ca_4Al_3Mg	CaAlSi	$Ca(BH_4)_2$
$CaB_{12}H_{12}$	CaC_4N_6	$Ca_4N_2(CN_2)$	$Ca_{11}N_6(CN_2)_2$	$CaSiN_2$
$Ca_2Si_5N_8$	$Ca_5(Si_2N_6)$	Ca_4TiN_4	H_9CN_9	KBH_4
$KB_{21}H_{18}$	$K_2B_6H_6$	$K_2(B_{10}H_{10})$	$K_2B_{12}H_{12}$	KC_4N_3
KNH_2	$(K(NH_2))(NH_3)_2$	$LiAlB_{14}$	$LiB_{13}C_2$	$Li_2B_{12}C_2$
LiBH	$Li(BH_2)$	$Li_2B_{12}H_{12}$	$Li_3(BH_6)$	$Li_2B_{12}Si_2$
$LiMgH_3$	Li_2MgSi	LiN_3Si_2	$LiNa_2N$	$LiNa_5N_2$
$Li_2Na_4N_2$	Li_2NaN	$Li_3Na_3N_2$	$Li_4Na_2N_2$	Li_5NaN_2
Li_3NaSi_6	$MgAl_2Si_2$	$MgB_{12}C_2$	$Mg_2B_{24}C$	$MgB_{12}H_{12}$
$MgB_{12}Si_2$	MgC_4N_6	Mg_7TiH_{16}	N_2BH_7	$N_2B_{10}H_{18}$
$N_3B_3H_6$	$N_3B_3H_{12}$	$N_4B_9H_{11}$	$N_4B_{10}H_8$	$N_4B_{10}H_{22}$
NH_3BH_3	$(NH_4)_2B_{12}H_{12}$	$(NH_2)CN$	NH_4HCN_2	$Na_5Al_3H_{14}$
$NaBH_4$	$Na_2(B_{10}H_{10})$	$Na_3(BN_2)$	$Na_3C_6N_9$	Sc_2AlC
Ti_2AlC	Ti_6Si_2B	$V_{12}Al_3C_8$	V_5SiB_2	
Four-element compounds				
$AlNC_3H_{10}$	BCH_5N_2	$B_{10}C_6H_{30}N_2$	$B_{20}C_3H_{30}N_2$	BC_4KN_4
$CH_3NH_2BH_3$	$Ca(NH_2BH_3)_2$	$KAl(NH_2)_4$	$K_5C_2HN_4$	$KCaN_3H_6$
$K(HCN_2)$	K_2LiAlH_6	$KLi_3(NH_2)_4$	$KLi_7N_8H_{16}$	$K_2Li(NH_2)_3$
$K_2Mg(NH_2)_4$	K_2NaAlH_6	$K_2Na(NH_2)_3$	$K_3Si_6N_{11}H_6$	$LiAlMg_{10}H_{24}$
$Li(B(CN)_4)$	$Li_2Ca(NH)_2$	$LiK(BH_4)_2$	$Li(NH_2BH_3)$	$(Li(NH_3)_4)_2(B_6H_6)(NH_3)_2$
$LiNa_2AlH_6$	$LiNa_2(NH_2)_3$	$LiSc(BH_4)_4$	$Mg(BH_4)_2(NH_3)_2$	$(NH_4)B(CN)_4$
$NaAl(NH_2)_4$	$NaB(CN)_4$	$Si_2C_7H_{18}N_2$	$VC_8H_{24}N_4$	
Five-element compounds				
$LiAlC_4H_{16}N_4$	$LiSi_3C_9H_{27}N_2$	$Si_2B_2C_{12}H_{37}N_5$		

Results

Our thermodynamic calculations identified 74 promising single-step reactions that are predicted to have 15 kJ/mol $H_2 \leq \Delta U_0 \leq 75$ kJ/mol H_2 and that release ≥ 6.0 wt.% H_2. These 74 reactions are shown in Table 2. An initial way to consider this set of reactions is to compare them to the 43 single-step reactions that were identified in the earlier calculations by Alapati et al.[23] Only 17 of these 43 reactions appear among the 74 reactions listed in Table 2; 26 of the reaction mixtures identified by Alapati et al. are predicted by our more complete database to not satisfy the screening criteria listed above. Almost all of these 26 reactions involve either $LiBH_4$ or $Mg(BH_4)_2$, which are now predicted to react via $B_{12}H_{12}$-containing intermediates that were unknown at the time of Alapati et al.'s work. The importance of these intermediates has been discussed in a number of recent reports.[22,25,26,28] 57 of the reactions identified by our calculations were not encountered in the calculations of Alapati et al. because they include one or more compounds that were not included in the database used in those calculations.

The 74 reactions listed in Table 2 were found by calculations that consider systems that are able to reach perfect thermodynamic equilibrium in an environment where H_2 is the only possible gas species. To discuss these reactions, it is useful to divide them into several classes that are arranged by our expectations for how reasonable these assumptions are. We first consider reactions that involve species that include $B_{12}H_{12}$; 13 reactions include species of this type. These reactions do not include any refractory materials or carbon. The reaction mixtures found in our calculations are consistent with those already reported by Ozolins *et al.* for $LiBH_4$, $Ca(BH_4)_2$, $Mg(BH_4)_2$, $MgH_2/MgB_{12}H_{12}$, $LiBH_4/Mg(BH_4)_2$, and $Mg(BH_4)_2/Ca(BH_4)_2$[22] and Kim *et al.* for $LiSc(BH_4)_4$.[27] There are also several experimental reports related to the mixtures of $LiBH_4$, $Ca(BH_4)_2$, $Mg(BH_4)_2$, $MgH_2/MgB_{12}H_{12}$, and $LiBH_4/Mg(BH_4)_2$.[6,25,26,28,38-45] Unfortunately, most experimental studies indicate metal closoboranes are very kinetically stable, meaning that reactions involving any $B_{12}H_{12}$ species are typically not reversible.[22,46] This observation suggests that the 13 reactions involving $M_nB_{12}H_{12}$ (M = Li, Mg, Ca, and K) would be undesirable from a practical point of view.

The reactions involving $B_{12}H_{12}$ species illustrate one way in which a reaction that is thermodynamically feasible may be strongly limited by kinetic effects. It is reasonable to suspect that similar kinetic limitations could limit the viability of reactions whose reactants or products are known to be refractory. Among the materials we considered, BN, TiB_2, ScB_2, AlN, VN, CaB_6, and V_2N can all be characterized as refractory materials because they have melting temperatures ≥ 2000 °C.[47-53] Thirty-nine of the reactions listed in Table 2 involve one or more of these species. Ten of the 39 reactions were already predicted by Alapati, Johnson, and Sholl:[23] $2LiH+LiNH_2+BN$, $2LiBH_4+ScH_2$, $2LiBH_4+TiH_2$, $2LiBH4+Mg(NH_2)_2$, $ScH_2+Mg(BH_4)_2$, $3LiBH_4+TiN$, $12LiH+3Mg(NH_2)_2+4BN$, $2ScN+3Mg(BH_4)_2$, $2TiN+3Mg(BH_4)_2$ and, $4LiH+3LiNH_2+VN$. There are also relevant theoretical reports showing the same reaction schemes as our current prediction for $CaH_2/CaB_{12}H_{12}$, $ScH_2/Ca(BH_4)_2$, and $TiH_2/Ca(BH_4)_2$.[22,24,54] A few experimental reports support the idea that refractory materials make reactions involving them irreversible.[55,56] Purewal et al. experimentally examined hydrogen absorption and desorption behavior in the $LiBH_4/ScH_2$ system.[55] They did not observe any reaction between $LiBH_4$ and ScH_2, presumably due to the stability of ScH_2 and ScB_2. Yang et al. experimentally studied $LiBH_4/TiH_2$, another reaction system included in this category.[56] Similar to Purewal et al., they observed that $LiBH_4$ decomposed to release H_2 without reacting with TiH_2. They also examined the reversibility of the $LiBH_4/CaH_2$ system and concluded that the system was not reversible due to the kinetic stability of CaB_6.

The reactions we have discussed above are likely to be impractical because of kinetic limitations. It is also possible that some of the reactions predicted by our calculations may differ from experimental observations because of the formation of non-H_2 gases at equilibrium. This issue was discussed in detail in recent work that reported thermodynamic calculations for a small number of metal hydrides that included a wide range of potential gas species, not just H_2.[57] One class of chemical mixtures highlighted in that work was those that involve C. In these mixtures the thermodynamically stable states at low temperatures often involved high levels of CH_4. It

appears in general to be incorrect to assume that calculations that do not allow for the presence of CH_4 can predict the correct thermodynamic equilibrium states when carbon is present in the reaction mixture. For this reason, we have separated the 19 reactions in Table 2 that involve carbon either as graphitic C or as part of a compound such as KC_8.

The discussion of the potential role of methane in reaction mixtures involving C could lead to the conclusion that it would be better to simply exclude all C-containing materials from the materials considered in our calculations. We feel, however, that it is better to report the results involving these compounds because the kinetic implications of mixing metal hydrides and carbon experimentally are not yet clear. There are recent reports showing that nanoporous carbons can improve reaction kinetics in metal hydride systems.[58-62] Berseth et al., for example, examined the interaction between carbon nanostructures and $NaAlH_4$ and concluded that the carbon materials could improve the dehydrogenation reaction of $NaAlH_4$.[59] These experiments indicated that the nanostructured C did not react with the metal hydride. In interpreting experiments of this kind, however, it is important to be aware of the potential reactions that can occur between metal hydrides and carbon supports.

Table 2: Promising single-step reactions divided into six categories. ΔU_0 and ΔS_{conf} represent the changes of the reaction enthalpy at 0 K and the configurational entropy. The configurational entropy is only listed systems having partial occupancies. The enthalpy changes at 0 K for reactions involving $LiBH_4$ used the DFT total energy of ortho-$LiBH_4$.

Interesting reactions (3 reactions)	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**
$MgH_2 \rightarrow Mg+H_2$	7.66	64.7
$LiH+2LiNH_2+KBH_4 \rightarrow Li_3BN_2+KH+4H_2$	7.48	43.6 (-7.2)
$2MgH_2+Mg(NH_2)_2 \rightarrow Mg_3N_2+4H_2$	7.4	26
Reactions involving $B_{12}H_{12}$ species (13 reactions)	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**
$LiBH_4 \rightarrow (5/6)LiH+(1/12)Li_2B_{12}H_{12}+(13/12)H_2$	10.03	62.1
$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 5Mg_2Si+2Li_2B_{12}H_{12}+36H_2$	9.46	41
$5Si+12Mg(BH_4)_2 \rightarrow 5Mg_2Si+2MgB_{12}H_{12}+36H_2$	9.21	43.6
$5Si+10Mg(BH_4)_2+2Ca(BH_4)_2 \rightarrow 5Mg_2Si+2CaB_{12}H_{12}+36H_2$	8.85	41.2
$2LiBH_4+5Mg(BH_4)_2 \rightarrow 5MgH_2+Li_2B_{12}H_{12}+13H_2$	8.36	43.1
$5Si+10Mg(BH_4)_2+4KBH_4 \rightarrow 5Mg_2Si+2K_2B_{12}H_{12}+36H_2$	8.1	37.3 (-2.9)
$Mg(BH_4)_2 \rightarrow (5/6)MgH_2+(1/6)MgB_{12}H_{12}+(13/6)H_2$	8.09	47.1
$LiSc(BH_4)_4 \rightarrow (2/5)LiBH_4+ScH_2+(3/10)Li_2B_{12}H_{12}+(22/5)H_2$	7.97	24.1
$5Mg(BH_4)_2+Ca(BH_4)_2 \rightarrow 5MgH_2+CaB_{12}H_{12}+13H_2$	7.72	43.1
$5MgH_2+MgB_{12}H_{12} \rightarrow 6MgB_2+11H_2$	7.45	62.1
$5Mg(BH_4)_2+2KBH_4 \rightarrow 5MgH_2+K_2B_{12}H_{12}+13H_2$	6.94	38 (-4)
$Ca(BH_4)_2 \rightarrow (5/6)CaH_2+(1/6)CaB_{12}H_{12}+(13/6)H_2$	6.26	57.4

$LiH+3Ca(BH_4)_2 \rightarrow 3CaH_2+(1/2)Li_2B_{12}H_{12}+(13/2)H_2$	6.03	56.5
Reactions involving refractory materials (BN, TiB_2, ScB_2, AlN, VN, CaB_6, V_2N) (39 reactions)	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**
$27N_2BH_7+AlNC_3H_{10} \rightarrow AlN+27BN+(3/2)C_2H_{18}N_{18}+86H_2$	13.08	65.6
$(NH_4)_2B_{12}H_{12} \rightarrow 10B+2BN+10H_2$	11.33	44
$5LiSc(BH_4)_4+2(NH_4)_2B_{12}H_{12} \rightarrow 5ScB_2+4BN+(5/2)Li_2B_{12}H_{12}+45H_2$	9.95	15
$20SiC+19(NH_4)_2B_{12}H_{12} \rightarrow 38BN+20SiB_3+10B_{13}C_2+190H_2$	9.16	40.8
$2LiBH_4+ScH_2 \rightarrow 2LiH+ScB_2+4H_2$	8.91	49.7
$2LiBH_4+TiH_2 \rightarrow 2LiH+TiB_2+4H_2$	8.63	22.2
$ScB_2+(NH_4)_2B_{12}H_{12} \rightarrow ScB_{12}+2BN+10H_2$	8.25	41.5
$9ScH_2+Si+9Mg(BH_4)_2 \rightarrow 7MgH_2+Mg_2Si+9ScB_2+38H_2$	8.18	37.3
$2LiBH_4+Mg(NH_2)_2 \rightarrow MgH_2+2LiH+2BN+4H_2$	8.07	20.6
$ScH_2+Mg(BH_4)_2 \rightarrow MgH_2+ScB_2+4H_2$	7.99	37.5
$BN+LiSc(BH_4)_4 \rightarrow (1/5)LiBH_4+ScN+(2/5)Li_2B_{12}H_{12}+(26/5)H_2$	7.7	22.8
$3Mg(NH_2)_2+4NaBH_4 \rightarrow 4NaH+Mg_3N_2+4BN+12H_2$	7.55	34.4 (-8.8)
$11LiH+25LiNH_2+AlB_{12} \rightarrow AlN+12Li_3BN_2+(61/2)H_2$	7.51	56
$41ScH_2+4VB_2+40Mg(BH_4)_2 \rightarrow 40MgH_2+41ScB_2+2V_2B_3+161H_2$	7.42	37.2
$10Si+3(NH_4)_2B_{12}H_{12} \rightarrow 6BN+10SiB_3+30H_2$	7.42	38.7
$3LiBH_4+TiN \rightarrow 3LiH+TiB_2+BN+(9/2)H_2$	7.13	35.9
$NaAl(NH_2)_4 \rightarrow AlN+NaN_3+4H_2$	7.07	16.2
$ScH_2+Ca(BH_4)_2 \rightarrow CaH_2+ScB_2+4H_2$	6.91	46.8
$3LiNH_2+2KBH_4 \rightarrow Li_3BN_2+BN+2KH+6H_2$	6.84	41.6 (-9.7)
$56LiH+21Mg(NH_2)_2+4V_2N \rightarrow 8Li_7N_4V+7Mg_3N_2+70H_2$	6.75	47.9
$TiH_2+Ca(BH_4)_2 \rightarrow CaH_2+TiB_2+4H_2$	6.74	19.3
$12LiH+3Mg(NH_2)_2+4BN \rightarrow 4Li_3BN_2+Mg_3N_2+12H_2$	6.65	54.2
$LiNH_2+NaBH_4 \rightarrow LiH+NaH+BN+2H_2$	6.63	19.4 (-11.3)
$5LiSc(BH_4)_4+2MgB_{12}H_{12} \rightarrow 5ScB_2+2Mg(BH_4)_2+(5/2)Li_2B_{12}H_{12}+29H_2$	6.58	21.6
$ScH_2+2NaBH_4 \rightarrow 2NaH+ScB_2+4H_2$	6.58	67.5 (-19.8)
$39LiNH_2+2AlB_{12} \rightarrow 2AlN+13Li_3BN_2+11BN+39H_2$	6.5	59.5
$2ScN+3Mg(BH_4)_2 \rightarrow 3MgH_2+2ScB_2+2BN+9H_2$	6.48	43.1
$5NaBH_4+2(NH_4)_2B_{12}H_{12} \rightarrow 4BN+(5/2)Na_2(B_{10}H_{10})+(35/2)H_2$	6.47	26.7 (-6.7)
$TiH_2+2NaBH_4 \rightarrow 2NaH+TiB_2+4H_2$	6.42	40 (-15.1)
$Mg(NH_2)_2+Ca(BH_4)_2 \rightarrow MgH_2+CaH_2+2BN+4H_2$	6.39	17.7
$2TiN+3Mg(BH_4)_2 \rightarrow 3MgH_2+2TiB_2+2BN+9H_2$	6.35	19.5
$2LiH+LiNH_2+BN \rightarrow Li_3BN_2+2H_2$	6.33	49.1
$CaH_2+CaB_{12}H_{12} \rightarrow 2CaB_6+7H_2$	6.3	61.8

$3Mg(NH_2)_2+4KBH_4 \rightarrow Mg_3N_2+4BN+4KH+12H_2$	6.29	46.9 (-10.3)
$8ScH_2+2V_2B_3+9Mg(BH_4)_2 \rightarrow 9MgH_2+8ScB_2+4VB_2+35H_2$	6.24	37.1
$13CaH_2+CaSi_2+14CaB_{12}H_{12} \rightarrow 2Si+28CaB_6+97H_2$	6.13	60.6
$4LiH+3LiNH_2+VN \rightarrow Li_7N_4V+5H_2$	6.09	37.4
$ScB_2+4BN+3LiSc(BH_4)_4 \rightarrow 4ScN+(3/2)Li_2B_{12}H_{12}+15H_2$	6.05	21.9
$MgH_2+3BN+2MgB_{12}H_{12} \rightarrow 3MgB_9N+13H_2$	6.05	58.6
Reactions involving C (19 reactions)	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**
$LiBH_4+C \rightarrow LiBC+2H_2$	11.93	45.1
$2C+Mg(BH_4)_2 \rightarrow MgB_2C_2+4H_2$	10.34	43.1
$20C+13(NH_4)_2B_{12}H_{12} \rightarrow 26BN+10B_{13}C_2+130H_2$	10.27	35.2
$2C+Ca(BH_4)_2 \rightarrow CaB_2C_2+4H_2$	8.6	56.8
$VC_8H_{24}N_4 \rightarrow 7C+VN+NH_4HCN_2+(19/2)H_2$	8.42	22.8
$214C+607Mg(BH_4)_2+100Ca(BH_4)_2 \rightarrow 500MgH_2+107MgB_2C_2+100CaB_{12}H_{12}+1728H_2$	8.23	42.4
$C+KBH_4+K(NH_2)(NH_3)_2 \rightarrow BN+K_2CN_2+6H_2$	7.8	26.8 (-3.8)
$2LiH+2C+Ca(BH_4)_2 \rightarrow CaH_2+2LiBC+4H_2$	7.35	42.2
$4LiH+3Mg(NH_2)_2+2C \rightarrow 2Li_2CN_2+Mg_3N_2+8H_2$	7.17	47.8
$2C+K(NH_2)(NH_3)_2 \rightarrow (1/3)K_3C_6N_9+4H_2$	7.12	68.4
$LiH+C+NaBH_4 \rightarrow NaH+LiBC+2H_2$	6.98	62.9 (-19)
$2LiNH_2+C \rightarrow Li_2CN_2+2H_2$	6.96	31.4
$266C+100KBH_4+383Ca(BH_4)_2 \rightarrow 250CaH_2+133CaB_2C_2+50K_2B_{12}H_{12}+1182H_2$	6.75	53.4 (-2.6)
$MgH_2+2C+Ca(BH_4)_2 \rightarrow CaH_2+MgB_2C_2+4H_2$	6.71	52.4
$14Li_3Na(NH_2)_4+5Na_2CN_2+16NH_4HCN_2 \rightarrow 21Li_2CN_2+24NaN_3+96H_2$	6.71	64.6
$2C+MgB_{12}H_{12} \rightarrow MgB_{12}C_2+6H_2$	6.36	64.3
$16LiNH_2+KC_8 \rightarrow 8Li_2CN_2+KH+(31/2)H_2$	6.22	31.7
$7NaNH_2+2NH_4HCN_2 \rightarrow 2Na_2CN_2+3NaN_3+12H_2$	6.18	62.8
$Li_3Na(NH_2)_4+2C \rightarrow (3/2)Li_2CN_2+(1/2)Na_2CN_2+4H_2$	6.11	32.6

The discussion above described how 71 of the 74 single step reactions identified by our thermodynamic calculations are unlikely to be of practical interest for reversible H_2 storage. Of the remaining 3 reactions that meet our screening criteria, one is the direct decomposition of MgH_2. It is well known that the reaction enthalpy of this reaction is too high to allow H_2 release at the temperatures desirable in a mobile storage device.[13,63-65] The observation that the DFT-predicted reaction enthalpy lies towards the upper bound of the range of reaction enthalpies we used in our screening is consistent with this fact. This leaves two single-step reactions that do not

suffer from any of the possible disadvantages listed above, one with a 2:1:1 mixture of $LiNH_2$, LiH, and KBH_4, and the other with a 2:1 mixture of MgH_2 and $Mg(NH_2)_2$. Both of these reactions release ~7.4 wt.% H_2 at completion.

The reaction between MgH_2 and $Mg(NH_2)_2$ forming Mg_3N_2 with H_2 release has been analyzed in several previous computational studies.[19,23,66] Akbarzadeh, Ozolins, and Wolverton computed the free energy for this reaction using DFT.[19] We performed similar calculations after computing the VDOS for each solid compound in the reaction, and our results are entirely consistent with those of Akbarzadeh, Ozolins, and Wolverton. A van't Hoff plot based on our DFT-calculated free energies is shown in Fig. 1. The predicted reaction temperature for the $MgH_2/Mg(NH_2)_2$ mixture at a H_2 pressure of 1 bar is 160 K, in good agreement with the value (130 K) reported by Akbarzadeh, Ozolins, and Wolverton.[19] An important feature of Fig. 1 is that is indicates the (large) range of H_2 pressures that are associated with an uncertainty of ±10 kJ/mol H_2. This is the typical uncertainty that is associated with DFT-calculated reaction free energies for metal hydride decomposition reactions where comparisons with detailed experimental data have been possible.[4,13,17]

The 2:1 mixture of MgH_2 and $Mg(NH_2)_2$ was studied in ball milling experiments by Hu et al.[66] As predicted by computational studies, they observed that Mg_3N_2 was produced with the release of a stoichiometric amount of H_2 (7.4 wt.%). Very low levels of NH_3 (~1 ppm) were detected. Hu et al. described the thermodynamics of this process using tabulated thermodynamic data, and estimated that the heat of reaction at 298 K was 3.5 kJ/mol H_2. This is in reasonable agreement with our DFT-calculated result ($\Delta H_{298\,K}$ = 15.6 kJ/mol H_2). No experimental information appears to be available regarding the reversibility of this reaction. Figure 1 indicates that large H_2 pressures would be necessary to reverse the reaction at room temperature or above.

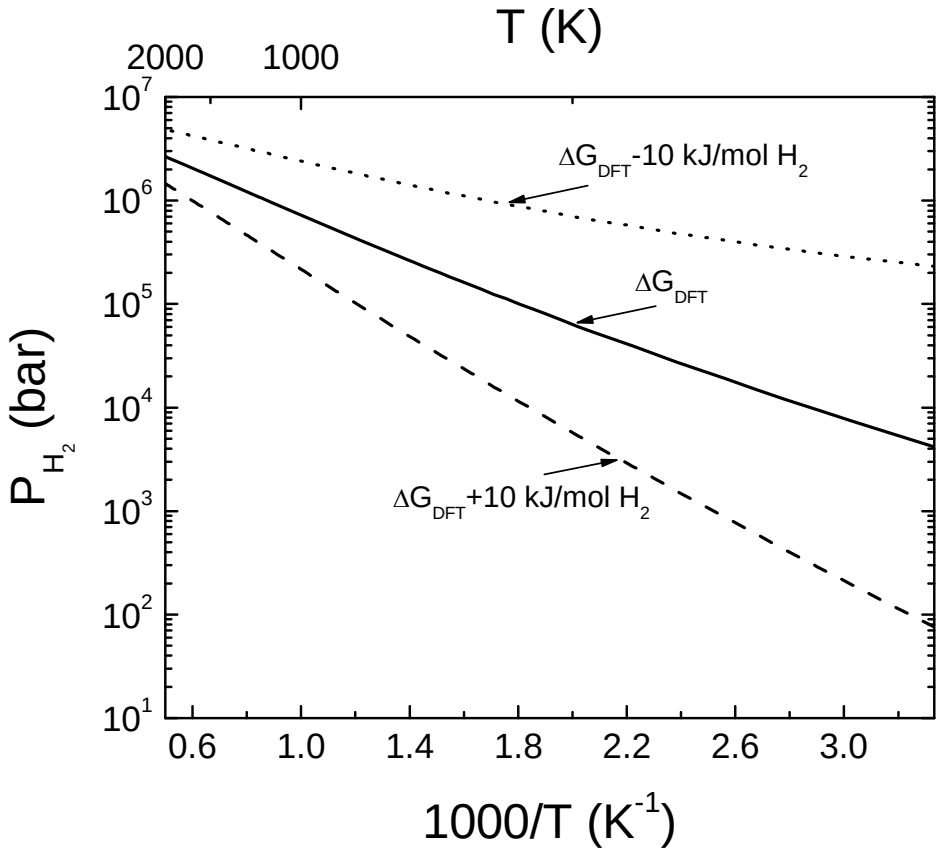

Figure 1: A van't Hoff plot for $2MgH_2 + Mg(NH_2)_2 \rightarrow Mg_3N_2 + 4H_2$. The dotted (dashed) line represents the upper (lower) bound of the van't Hoff plot when an uncertainty of ±10 kJ/mol H_2 in the DFT-calculated reaction free energy is considered.

The other promising single-step reaction is the reaction of a 2:1:1 mixture of $LiNH_2$, LiH, and KBH_4, which is predicted to react in a single step forming solid Li_3BN_2 and KH along with gaseous H_2. This reaction has, to the best of our knowledge, not been considered in any earlier experimental or computational studies. This calculated 0 K reaction enthalpy change for this reaction is 43.6 kJ/mol H_2. We computed the VDOS for each solid compound in this reaction in order to analyze the free energy for the reaction. When we consider the vibrational and entropic contributions, our calculation predicts $\Delta H_{300\,K}$ = 28.1 kJ/mol H_2 and $\Delta S_{vib,300\,K}$ (the reaction vibrational entropy change at 500 K) = 116.3 J/K/mol H_2, giving $\Delta G_{300\,K}$ = -6.8 kJ/mol H_2. As discussed above, the partial disorder of H atoms in α-KBH_4 means that the configurational entropy (S_{conf}) associated with this disorder should be considered to completely describe the reaction thermodynamics. If we use an estimate for the configurational entropy based on complete disorder among the partially occupied sites,[29] TS_{conf} at 300 K is -3.5 kJ/mol H_2. As

discussed in our earlier work on KBH_4, this approach is likely to overestimate the entropy associated with site disorder in KBH_4.[29] Therefore, the resulting reaction free energy change including the configurational entropy effect would be -3.3 kJ/mol H_2. The van't Hoff plot based on these calculations is shown in Fig. 2. This figure shows that this reaction has the reaction temperatures of 300 ~ 420 K at H_2 pressures of 1 ~ 100 bar, indicating that H_2 would be released at the appropriate temperatures and H_2 pressures for reversible hydrogen storage applications. As with Fig. 1, we show uncertainty estimates in Fig. 2 that emphasize how the imprecision associated with DFT calculations leads to a rather large uncertainty in predicted H_2 pressures. Despite this unavoidable uncertainty, the thermodynamic properties of this reaction suggest that it is a good candidate for experimental studies.

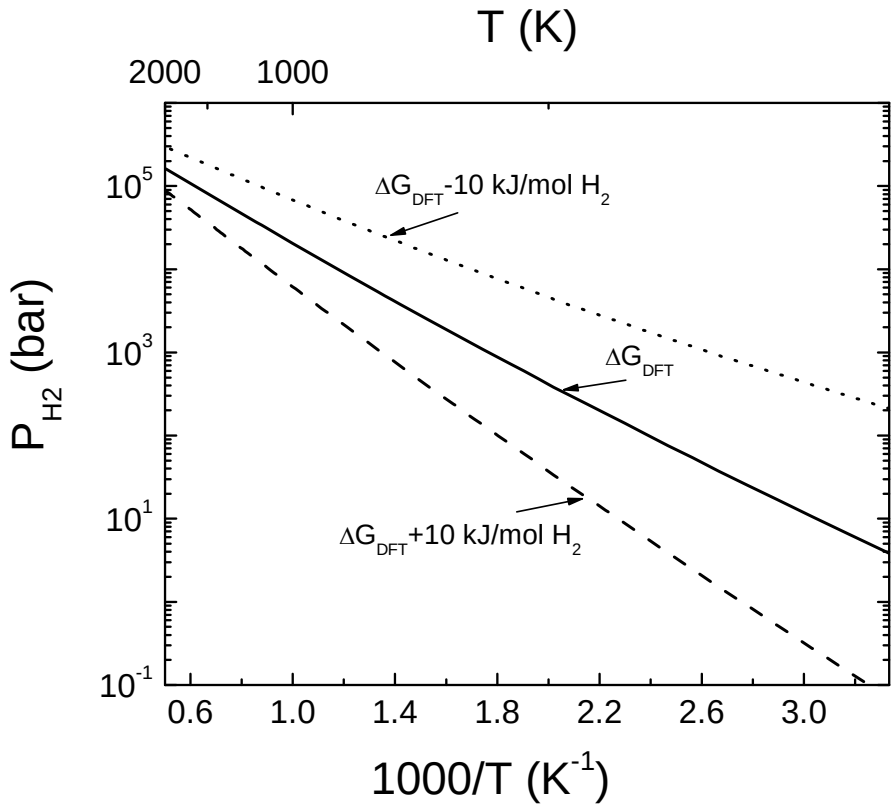

Figure 2: Similar to Fig. 1, but for $2LiNH_2 + LiH + KBH_4 \rightarrow Li_3BN_2 + KH + 4H_2$.

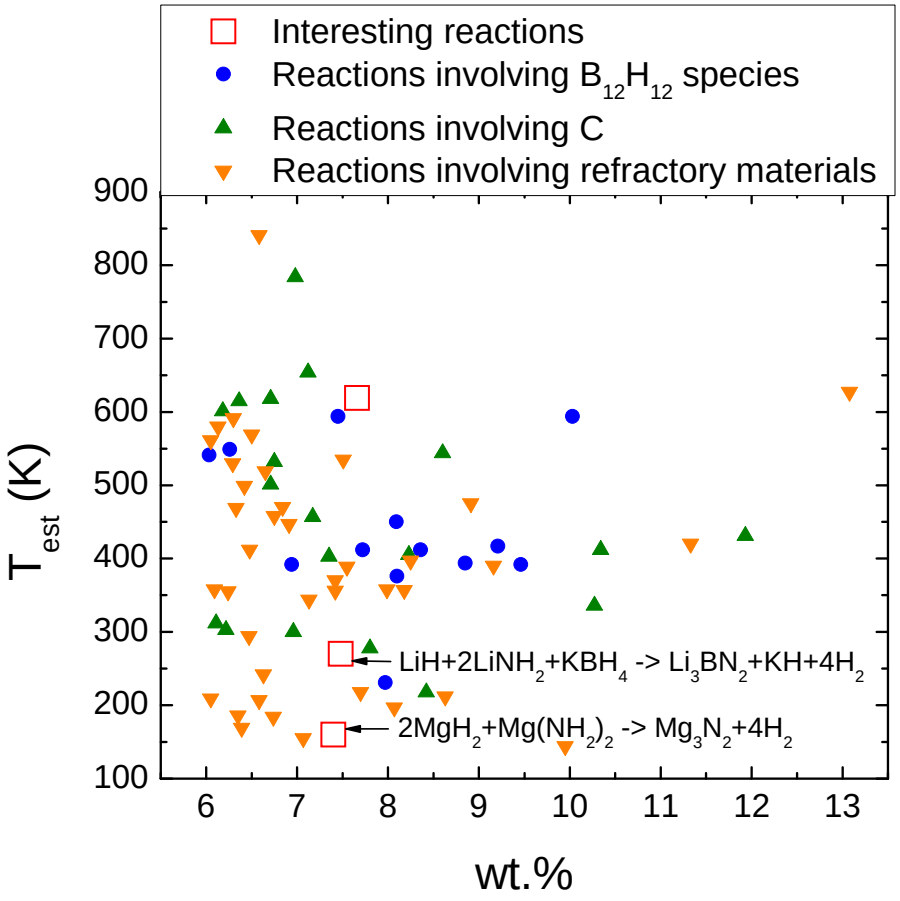

Figure 3: The estimated temperature required to generate a partial pressure of H_2 of 1 bar (T_{est}) as a function of H_2 capacity (wt.%) for the 74 promising single-step reactions described in Table 2.

We summarize the main results from visually in Fig. 3 by plotting the estimated reaction temperature for a H_2 pressure of 1 bar as a function of the H_2 capacity of each single step reaction. For all of the reactions except the two shown in Figs. 1 and 2, the reaction temperature, T_{est}, was estimated using

$$T_{est}\ (\mathrm{K}) = \Delta U_0/(\Delta S - R) \qquad (3)$$

ΔU_0 and ΔS are the reaction enthalpy at 0 K and reaction entropy associated with site disorder when this phenomenon is relevant and R is the gas constant. The equation neglects the contributions of the vibrational energies and PV term to the free energies of solid compounds.[17,18,67] The reaction temperatures of $MgH_2/Mg(NH_2)_2$ and $LiNH_2/LiH/KBH_4$ mixtures for a H_2 pressure of 1 bar were taken from the van't Hoff plots in Figs. 1 and 2.

We now turn to the possibility of finding multi-step reactions with useful properties for reversible H_2 storage. We examined all of the reaction mixtures defined in section 2 to detect

multi-step reactions in which every step satisfied $15 \leq \Delta U_0 \leq 75$ kJ/mol H_2 and the total H_2 release from the combined reaction steps was > 6.0 wt.% H_2. This initially generated more than 10^5 candidate reaction mixtures, but this large number contains a much smaller number of distinct reaction schemes. To illustrate this concept, consider the reaction of a mixture of *x* moles of Li_3AlH_6 and *y* moles of MgH_2. For a range of *x* and *y*, our thermodynamic calculations show that this mixture reacts in two steps as follows:

$$x\ Li_3AlH_6 \rightarrow 3x\ LiH + x\ Al + 1.5x\ H_2 \quad (4)$$

$$y\ MgH_2 + x\ Al \rightarrow (x/30)\ Al_{30}Mg_{23} + (y - 23x/30)\ MgH_2 + (23x/30)\ H_2 \quad (5)$$

The overall H_2 capacity of this pair of reactions varies depending on how much MgH_2 remains unreacted in the second step. In all families of reactions like this, we chose the net stoichiometry of the mixture to maximize the H_2 capacity. Applying this approach reduces the number of distinct multi-step reactions to ~1000.

In the two step reaction above, the second reaction uses a product from the first reaction as a reactant. We will refer to this situation as a reaction that is linked by an intermediate compound. Examples also exist where two or more independent reactions can be combined to increase the overall H_2 capacity relative to one reaction alone. An example of this concept is that reaction of a 10:1:6:2 mixture of MgH_2:$NaMgH_3$:$Mg(NH_2)_2$:$KMgH_3$. This mixture evolves via three reactions that do not use reactants from lower temperature reactions in the higher temperature reactions. The first step, in which a 10:5 ratio of MgH_2 and $Mg(NH_2)_2$ react, releases 5.14 wt.% H_2 relative to the overall mixture. The two additional steps both release 0.514 wt.% H_2, meaning that the net H_2 release from the multi-step process is > 6 wt.%.

The individual reactions that are predicted to take place within multi-step reactions could suffer from practical drawbacks for the same reasons discussed in the preceding section. To reflect these issues, we further filtered the multi-step reactions to exclude any reactions that involve carbon in any form or the refractory materials BN, TiB_2, ScB_2, AlN, VN, CaB_6, V_2N, VB_2, and V_5Si_3. In addition, we excluded multi-step reactions including any step with reaction enthalpy at 0 K higher than 60 kJ/mol H_2. This filtering of our results led to 23 distinct multi-step reactions, which are listed in Tables 3 and 4. Table 3 (4) lists the examples that are (are not) linked by intermediate compounds. In general, $LiBH_4$ undergoes the phase transition from the low temperature orthorhombic phase to the high temperature hexagonal phase at 381 K,[68-70] so that the orthorhombic phase has lower DFT total energy than the hexagonal phase. It implies that if a reaction involving $LiBH_4$ as a reactant occurs at a temperature higher than 381 K, the 0 K reaction enthalpy change calculated using the DFT energy of the orthorhombic phase will be overestimated. If a low temperature step in a multi step reaction corresponds to the case just described, the step may have higher 0 K reaction enthalpy change than a high temperature step in the same multi step reaction. Because all the reaction steps involving $LiBH_4$ listed in these tables correspond to this case, we used the DFT total energy of hexagonal $LiBH_4$ to calculate 0 K reaction enthalpy changes.

Table 3: Multi-step reactions with one or more single step reactions linked via

intermediate compounds. ΔG_{max} - ΔG_{min} is the difference between $\Delta U_0 - T\Delta S_{conf}$ for the final step and the first step in a multi-step reaction. The enthalpy changes at 0 K for reactions involving $LiBH_4$ used the DFT total energy of the hexagonal phase of $LiBH_4$. The $T\Delta S_{conf}$ term is given only for compounds known to have partial occupancy.

Class I **(reactions having (ΔG_{max}- ΔG_{min}) ≤ 30 kJ/mol H_2 and not involving $B_{12}H_{12}$ species)**				
No.	**Reaction**	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**	**ΔG_{max}- ΔG_{min} (kJ/mol H_2)**
1	Entire reaction $36MgH_2+19Mg(NH_2)_2+2KMgH_3 \rightarrow 19Mg_3N_2+2KH+76H_2$	7.12		21.2
	1st step $36MgH_2+18Mg(NH_2)_2 \rightarrow 18Mg_3N_2+72H_2$	6.748	26	
	2nd step $0.5Mg(NH_2)_2+2KMgH_3 \rightarrow 0.5Mg_3N_2+K_2MgH_4+2H_2$	0.187	38.6	
	3rd step $0.5Mg(NH_2)_2+K_2MgH_4 \rightarrow 0.5Mg_3N_2+2KH+2H_2$	0.187	47.2	
2	Entire reaction $13MgH_2+NaMgH_3+9Mg(NH_2)_2+4KMgH_3 \rightarrow NaH+9Mg_3N_2+4KH+36H_2$	6.23		21.2
	1st step $13MgH_2+6.5Mg(NH_2)_2 \rightarrow 6.5Mg_3N_2+26H_2$	4.498	26	
	2nd step $NaMgH_3+0.5Mg(NH_2)_2 \rightarrow NaH+0.5Mg_3N_2+2H_2$	0.346	31.3	
	3rd step $Mg(NH_2)_2+4KMgH_3 \rightarrow Mg_3N_2+2K_2MgH_4+4H_2$	0.692	38.6	
	4th step $Mg(NH_2)_2+2K_2MgH_4 \rightarrow Mg_3N_2+4KH+4H_2$	0.692	47.2	
3	Entire reaction $1.58Li_3AlH_6+1.2MgH_2 \rightarrow 4.75LiH+0.02Al+0.05Al_{30}Mg_{23}+3.58H_2$	6.17		28.1
	1st step $1.58Li_3AlH_6 \rightarrow 4.75LiH+1.58Al+2.38H_2$	4.097	28.8	
	2nd step $1.2MgH_2+1.56Al \rightarrow 0.05Al_{30}Mg_{23}+1.2H_2$	2.07	56.9	
Class II				

(reactions having (ΔG_{max}- ΔG_{min}) ≥ 30 kJ/mol H_2 and not involving $B_{12}H_{12}$ species)				
1	Entire reaction $5.67Li_3AlH_6+8MgH_2 \rightarrow 17LiH+0.47Al_{12}Mg_{17}+16.5H_2$	6.45		30.3
	1st step $5.67Li_3AlH_6 \rightarrow 17LiH+5.67Al+(17/2)H_2$	3.323	28.8	
	2nd step $4.34MgH_2 +3.67Al \rightarrow 0.19Al_{30}Mg_{23}+4.34H_2$	1.698	56.9	
	3rd step $3.66MgH_2 +0.19Al_{30}Mg_{23} \rightarrow 0.47Al_{12}Mg_{17}+3.66H_2$	1.429	59.1	
2	Entire reaction $9Li_3AlH_6+Al+Si+12MgH_2 \rightarrow 27LiH+Mg_2Si+0.22Al_{30}Mg_{23} +0.3Al_{12}Mg_{17}+25.5H_2$	6.01		30.8
	1st step $0.33Li_3AlH_6+0.67Al+Si \rightarrow AlLiSi+H_2$	0.236	28.3	
	2nd step $8.67Li_3AlH_6 \rightarrow 26LiH+8.67Al+13H_2$	3.063	28.8	
	3rd step $2MgH_2+AlLiSi \rightarrow LiH+Al+Mg_2Si+1.5H_2$	0.353	40.7	
	4th step $7.67MgH_2+10Al \rightarrow 0.33Al_{30}Mg_{23}+7.67H_2$	1.806	56.9	
	5th step $2.33MgH_2+0.12Al_{30}Mg_{23} \rightarrow 0.3Al_{12}Mg_{17}+2.33H_2$	0.55	59.1	
3	Entire reaction $10Li_3AlH_6+9MgH_2+ScH_2 \rightarrow 30LiH+Al_3Sc+0.05Al_{30}Mg_{23} +0.47Al_{12}Mg_{17}+25H_2$	6.13		31.9
	1st step $3Li_3AlH_6+ScH_2 \rightarrow 9LiH+Al_3Sc +5.5H_2$	1.348	27.2	
	2nd step $7Li_3AlH_6 \rightarrow 21LiH+7Al +10.5H_2$	2.574	28.8	
	3rd step $5.37MgH_2+7Al \rightarrow 0.24Al_{30}Mg_{23}+5.37H_2$	1.316	56.9	
	4th step $3.64MgH_2+0.19Al_{30}Mg_{23} \rightarrow 0.47Al_{12}Mg_{17}+3.64H_2$	0.891	59.1	
4	Entire reaction	6		42.4

	$9Li_3AlH_6+7MgH_2+VH_2 \rightarrow 27LiH+0.69Al_3V+0.05Al_{45}V_7+0.41Al_{12}Mg_{17}+21.5H_2$			
	1st step $3Li_3AlH_6+VH_2 \rightarrow 9LiH+Al_3V+5.5H_2$	1.536	15.1	
	2nd step $3.43Li_3AlH_6+Al_3V \rightarrow 10.29LiH+0.15Al_{45}V_7+5.15H_2$	1.436	27.2	
	3rd step $2.57Li_3AlH_6 \rightarrow 7.72LiH+2.57Al+3.86H_2$	1.077	28.8	
	4th step $1.97MgH_2+2.57Al \rightarrow 0.09Al_{30}Mg_{23}+1.97H_2$	0.551	56.9	
	5th step $5.03MgH_2+0.09Al_{30}Mg_{23}+0.1Al_{45}V_7 \rightarrow 0.41Al_{12}Mg_{17}+0.69Al_3V+5.03H_2$	1.404	57.5	
Class III (reactions involving $B_{12}H_{12}$ species)				
1	Entire reaction $24LiBH_4+KBH_4 \rightarrow 20.84LiH+1.59Li_2B_{12}H_{12}+0.5K_2B_{12}H_{12}+27.09H_2$	9.47		13.9
	1st step $24LiBH_4 \rightarrow 20LiH+2Li_2B_{12}H_{12}+26H_2$	9.088	47.2	
	2nd step $KBH_4+0.42\ Li_2B_{12}H_{12} \rightarrow 0.84LiH+0.5K_2B_{12}H_{12}+1.09H_2$	0.379	31.7 (-29.4)	
2	Entire reaction $178LiBH_4+10Ca(BH_4)_2+42KBH_4+Li_2B_{12}H_{12} \rightarrow 180LiH+10CaH_2+21K_2B_{12}H_{12}+260H_2$	7.49		13.9
	1st step $178LiBH_4 \rightarrow 148.35LiH+14.85Li_2B_{12}H_{12}+192.85H_2$	5.556	47.2	
	2nd step $3.35LiH+10Ca(BH_4)_2 \rightarrow 10CaH_2+1.65Li_2B_{12}H_{12}+21.65H_2$	0.624	56.5	
	3rd step $42KBH_4+17.5Li_2B_{12}H_{12} \rightarrow 35LiH+21K_2B_{12}H_{12}+45.5H_2$	1.311	31.7 (-29.4)	

Table 4: Similar to Table 3 but for multi-step reactions in which individual reactions are not linked by intermediate compounds.

Class I **(reactions having (ΔG_{max}- ΔG_{min}) ≤ 10 kJ/mol H_2)**				
No.	**Reaction**	**wt.%**	**ΔU_0 ($T\Delta S_{conf}$) (kJ/mol H_2)**	**ΔG_{max}- ΔG_{min} (kJ/mol H_2)**
1	Entire reaction $6LiBH_4+15Mg(BH_4)_2+MgH_2+8Si \rightarrow 8Mg_2Si+3Li_2B_{12}H_{12}+55H_2$	9.31		1.6
	1st step $MgH_2+0.5Si \rightarrow 0.5Mg_2Si+H_2$	0.169	37.6	
	2nd step $6LiBH_4+15Mg(BH_4)_2+7.5Si \rightarrow 7.5Mg_2Si+3Li_2B_{12}H_{12}+54H_2$	9.136	39.2	
2	Entire reaction $18.33Si+40Mg(BH_4)_2+4Ca(BH_4)_2 \rightarrow 18.33Mg_2Si+3.33MgB_{12}H_{12}+4CaB_{12}H_{12}+132H_2$	9.01		2.4
	1st step $10Si+20Mg(BH_4)_2+4Ca(BH_4)_2 \rightarrow 10Mg_2Si+4CaB_{12}H_{12}+72H_2$	4.914	41.2	
	2nd step $8.33Si+20Mg(BH_4)_2 \rightarrow 8.33Mg_2Si+3.33MgB_{12}H_{12}+60H_2$	4.095	43.6	
3	Entire reaction $5MgH_2+10Si+15Mg(BH_4)_2+6KBH_4 \rightarrow 10Mg_2Si+3K_2B_{12}H_{12}+59H_2$	7.69		2.6
	1st step $5MgH_2+2.5Si \rightarrow 2.5Mg_2Si+5H_2$	0.652	37.6	
	2nd step $7.5Si+15Mg(BH_4)_2+6KBH_4 \rightarrow 7.5Mg_2Si+3K_2B_{12}H_{12}+54H_2$	7.042	37.3 (-2.87)	
4	Entire reaction $35Si+80Mg(BH_4)_2+8KBH_4 \rightarrow 35Mg_2Si+10MgB_{12}H_{12}+4K_2B_{12}H_{12}+252H_2$	8.86		3.5
	1st step $10Si+20Mg(BH_4)_2+8KBH_4 \rightarrow 10Mg_2Si+4K_2B_{12}H_{12}+72H_2$	2.532	37.3 (-2.9)	
	2nd step $25Si+60Mg(BH_4)_2 \rightarrow 25Mg_2Si+10MgB_{12}H_{12}+180H_2$	6.329	43.6	
5	Entire reaction	9.38		4.5

	$16LiBH_4+28.33Si+60Mg(BH_4)_2 \rightarrow 28.33Mg_2Si+8Li_2B_{12}H_{12}+3.33MgB_{12}H_{12}+204H_2$			
	1^{st} step $16LiBH_4+20Si+40Mg(BH_4)_2 \rightarrow 20Mg_2Si+8Li_2B_{12}H_{12}+144H_2$	6.622	39.2	
	2^{nd} step $8.33Si+20Mg(BH_4)_2 \rightarrow 8.33Mg_2Si+3.33MgB_{12}H_{12}+60H_2$	2.759	43.62	
6	Entire reaction $25MgH_2+NaMgH_3+13Mg(NH_2)_2 \rightarrow NaH+13Mg_3N_2+52H_2$	7.28		5.3
	1^{st} step $25MgH_2+12.5Mg(NH_2)_2 \rightarrow 12.5Mg_3N_2+50H_2$	6.996	26	
	2^{nd} step $NaMgH_3+0.5Mg(NH_2)_2 \rightarrow NaH+0.5Mg_3N_2+2H_2$	0.28	31.3	
7	Entire reaction $4MgH_2+47Si+108Mg(BH_4)_2 \rightarrow 47Mg_2Si+18MgB_{12}H_{12}+328H_2$	9.11		6.1
	1^{st} step $4MgH_2+2Si \rightarrow 2Mg_2Si+4H_2$	0.111	37.6	
	2^{nd} step $45Si+108Mg(BH_4)_2 \rightarrow 45Mg_2Si+18MgB_{12}H_{12}+324H_2$	9.002	43.6	
8	Entire reaction $2LiBH_4+MgH_2+7Mg(BH_4)_2+3.83Si \rightarrow 3.83Mg_2Si+Li_2B_{12}H_{12}+0.33MgB_{12}H_{12}+25H_2$	9.07		6.1
	1^{st} step $MgH_2+0.5Si \rightarrow 0.5Mg_2Si+H_2$	0.363	37.6	
	2^{nd} step $2LiBH_4+5Mg(BH_4)_2+2.5Si \rightarrow 2.5Mg_2Si+Li_2B_{12}H_{12}+18H_2$	6.533	39.2	
	3^{rd} step $2Mg(BH_4)_2+0.83Si \rightarrow 0.83Mg_2Si+0.33MgB_{12}H_{12}+6H_2$	2.178	43.6	
9	Entire reaction $MgH_2+6Mg(BH_4)_2+Ca(BH_4)_2+3.42Si \rightarrow$	8.6		6.1

	$3.42Mg_2Si+0.17MgB_{12}H_{12}$ $+CaB_{12}H_{12}+22H_2$			
	1st step $MgH_2+0.5Si \rightarrow 0.5Mg_2Si+H_2$	0.391	37.6	
	2nd step $5Mg(BH_4)_2+Ca(BH_4)_2+2.5Si \rightarrow$ $2.5Mg_2Si+CaB_{12}H_{12}+18H_2$	7.033	41.2	
	3rd step $Mg(BH_4)_2+0.42Si \rightarrow$ $0.42Mg_2Si+0.17MgB_{12}H_{12}+3H_2$	1.172	43.62	
10	Entire reaction $46LiBH_4+10Mg(BH_4)_2+5Si \rightarrow$ $35LiH+5Mg_2Si+5.5Li_2B_{12}H_{12}+81.5H_2$	9.77		8
	1st step $4LiBH_4+10Mg(BH_4)_2+5Si \rightarrow$ $5Mg_2Si+2Li_2B_{12}H_{12}+36H_2$	4.314	39.2	
	2nd step $42LiBH_4 \rightarrow 35LiH+3.5Li_2B_{12}H_{12}+45.5H_2$	5.452	47.2	
11	Entire reaction $12LiBH_4+MgH_2+Mg(BH_4)_2+Si \rightarrow$ $9.67LiH+Mg_2Si+1.17Li_2B_{12}H_{12}+17.17H_2$	9.36		9.6
	1st step $MgH_2+0.5Si \rightarrow 0.5Mg_2Si+H_2$	0.545	37.6	
	2nd step $0.4LiBH_4+Mg(BH_4)_2+0.5Si \rightarrow$ $0.5Mg_2Si+0.2Li_2B_{12}H_{12}+3.6H_2$	1.963	39.2	
	3rd step $11.6LiBH_4 \rightarrow$ $9.67LiH+0.97Li_2B_{12}H_{12}+12.57H_2$	6.851	47.16	
12	Entire reaction $10LiBH_4+2MgH_2+Si \rightarrow$ $8.33LiH+Mg_2Si+0.83Li_2B_{12}H_{12}+12.83H_2$	8.67		9.6
	1st step $2MgH_2+Si \rightarrow Mg_2Si+2H_2$	1.35	37.6	
	2nd step $10LiBH_4 \rightarrow$ $8.33LiH+0.83Li_2B_{12}H_{12}+10.83H_2$	7.315	47.2	
Class II **(reactions having 10 kJ/mol $H_2 \leq (\Delta G_{max}- \Delta G_{min}) \leq$ 20 kJ/mol H_2)**				
1	Entire reaction	7		12.6

	$33MgH_2+17Mg(NH_2)_2+2KMgH_3 \rightarrow 17Mg_3N_2+K_2MgH_4+68H_2$			
	1^{st} step $33MgH_2+16.5Mg(NH_2)_2 \rightarrow 16.5Mg_3N_2+66H_2$	6.791	26	
	2^{nd} step $0.5Mg(NH_2)_2+2KMgH_3 \rightarrow 0.5Mg_3N_2+K_2MgH_4+2H_2$	0.206	38.6	
2	Entire reaction $10MgH_2+NaMgH_3+6Mg(NH_2)_2+2KMgH_3 \rightarrow NaH+6Mg_3N_2+K_2MgH_4+24H_2$	6.17		12.6
	1^{st} step $10MgH_2+5Mg(NH_2)_2 \rightarrow 5Mg_3N_2+20H_2$	5.14	26	
	2^{nd} step $NaMgH_3+0.5Mg(NH_2)_2 \rightarrow NaH+0.5Mg_3N_2+2H_2$	0.514	31.3	
	3^{rd} step $0.5Mg(NH_2)_2+2KMgH_3 \rightarrow 0.5Mg_3N_2+K_2MgH_4+2H_2$	0.514	38.6	

For convenience, the multi-step reactions in Table 3 are divided into three classes. Class I contains three multi-step reactions that do not involve any $B_{12}H_{12}$ species in which the difference in the calculated reaction energies between the first step and final step, $\Delta G_{max} - \Delta G_{min}$, is lower than 30 kJ/mol H_2. This free energy includes entropy effects associated with site disorder in KBH_4 and $NaBH_4$ only, not entropy associated with the VDOS. Class II contains four multi-step reactions that do not involve any $B_{12}H_{12}$ species for which $\Delta G_{max} - \Delta G_{min}$ is larger than 30 kJ/mol H_2. Class I is thermodynamically more desirable for hydrogen storage than Class II because when $\Delta G_{max} - \Delta G_{min}$ is large, a broad range of temperatures would be required for all steps in the multi-step mechanism to be relevant. Class III contains two multi-step reactions that include $B_{12}H_{12}$ species and satisfy the screening criteria stated early. These reactions release relatively large amounts of H_2 compared to the previous classes.

The seven multi-step reactions in Class I and Class II of Table 3 can be summarized by the two kinds of reaction schemes. The first scheme combines the destabilization reactions of $Mg(NH_2)_2$ by MgH_2, $NaMgH_3$, $KMgH_3$, or K_2MgH_4. Two of the multi-step reactions in Table 3 are of this type. In these two reactions, the first step involves the combination of $Mg(NH_2)_2$ and MgH_2. This single step reaction was identified above and in previous experimental and computational work.[19,24,66,71,72] K_2MgH_4 is the only compound connecting separate reaction steps in this scheme. In the second scheme, which accounts for five multi-step reactions, the first reaction is the decomposition and/or destabilization reaction of Li_3AlH_6, followed by destabilization reactions of MgH_2. For example, the net reaction predicted from the initial

mixture of Li_3AlH_6 and MgH_2 with a ratio of 17:24 in Table 3 produces LiH and $Al_{12}Mg_{17}$ with a H_2 release of 6.45 wt.% and ΔG_{max} - ΔG_{min} of 30.3 kJ/mol H_2 via three single step reactions. The first step is the decomposition reaction of Li_3AlH_6 forming LiH and Al with a H_2 release of 3.323 wt.%. The second step is the destabilization reaction of MgH_2 by Al which is produced from the first step, forming $Al_{30}Mg_{23}$ with a H_2 release of 1.698 wt.%. The third step is the destabilization reaction of MgH_2 by $Al_{30}Mg_{23}$ which is produced from the second step, forming $Al_{12}Mg_{17}$ with a H_2 release of 1.429 wt.%.

The multi-step reactions in Table 4 are divided into two classes. Class I contains twelve multi-step reactions in which ΔG_{max} - ΔG_{min} is lower than 10 kJ/mol H_2. Class II contains two multi-step reactions in which ΔG_{max} - ΔG_{min} is between 10 kJ/mol H_2 and 20 kJ/mol H_2. They have the relatively low values of ΔG_{max} - ΔG_{min} compared to the multi-step reactions in Table 3, but most of them involve $B_{12}H_{12}$ species which appear to be undesirable for reversible hydrogen storage applications because of their kinetic stability. Basically, the multi-step reactions in Table 4 are the combination of two or more initial mixtures that have separate reaction paths. For example, the net reaction of the initial mixture of $LiBH_4$, MgH_2, and Si with the ratio of 10:2:1 in Table 4 produces LiH, Mg_2Si, and $Li_2B_{12}H_{12}$ with a H_2 release of 8.67 wt.% and ΔG_{max} - ΔG_{min} of 9.6 kJ/mol H_2 via two single step reactions. The first step is the reaction between MgH_2 and Si to form Mg_2Si with a H_2 release of 1.35 wt.% and the second step is the decomposition reaction of $LiBH_4$ to form LiH and $Li_2B_{12}H_{12}$ with a H_2 release of 7.315 wt.%.

Recommendations

Several promising reactions have been identified in our computational approach. The reaction $LiH+2LiNH_2+KBH_4 \rightarrow Li_3BN_2+KH+4H_2$ appears to be especially promising and should be investigated experimentally. In addition, several multi-step reactions should be investigated experimentally.

Lessons learned from the Center approach

The MHCoE has provided a unique opportunity for close collaboration between experimental and theory groups. This free exchange of information has given rise to better work than could be accomplished by groups working individually. Free and frequent communication is essential for success.

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Appendix A
List of Peer Reviewed Publications

1. The role of interstitial H2 in hydrogen diffusion in light metal borohydrides, Shiqiang Hao and David S. Sholl, Phys. Chem. Chem. Phys., **11**, 11106-11109 (2009)
2. Crystal structures and thermodynamic investigations of LiK(BH4)2, KBH4, and NaBH4 from first-principles calculations, Ki Chul Kim and David S. Sholl, J. Phys. Chem. C, **114**, 678-686 (2010)
3. Predicting Impurity Gases and Phases During Hydrogen Evolution from Complex Metal Hydrides using Free Energy Minimization Enabled by First-principles Calculations, Ki Chul Kim, Mark D. Allendorf, Vitalie Stavila, and David S. Sholl, submitted to PCCP.
4. Ki Chul Kim, Anant D. Kulkarni, J. Karl Johnson, and David S. Sholl, "Large-scale screening of promising metal hydrides for hydrogen storage system from first-principles calculations based on equilibrium reaction thermodynamics", *Journal of Physical Chemistry C*, submitted, (2010).
5. Anant D. Kulkarni, Lin-Lin Wang, Duane D. Johnson, David S. Sholl, and J. Karl Johnson, "First-Principles Characterization of Amorphous Phases of $MB_{12}H_{12}$, M=Mg, Ca", *Journal of Physical Chemistry C*, **114**, 14601-14605, (2010).
6. Ki Chul Kim, Bing Dai, J. Karl Johnson and David S. Sholl, "Assessing nanoparticle size effects on metal hydride thermodynamics using the Wulff construction", *Nanotechnology*, **20**, 204001 (2009).
7. Bing Dai, Rees B. Rankin, J. Karl Johnson, Mark D. Allendorf, David S. Sholl, Nikolai A. Zarkevich and Duane D. Johnson, "Influence of Surface Reactions on Complex Hydride Reversibility", *Journal of Physical Chemistry C*, **112**, 18270–18279 (2008).
8. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Large-Scale Screening of Metal Hydride Mixtures for High-Capacity Hydrogen Storage from First-Principles Calculations", *Journal of Physical Chemistry C*, **112**, 5258-5262 (2008).
9. Bing Dai, David S. Sholl, and J. Karl Johnson, "First Principles Study of Experimental and Hypothetical $Mg(BH_4)_2$ Crystal Structures", *Journal of Physical Chemistry C*, **112**, 4391-4395 (2008).
10. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Stability analysis of doped materials for reversible hydrogen storage in destabilized metal hydrides", *Physical Review B,* **76**, 104108 (2007).
11. Bing Dai, David S. Sholl, and J. Karl Johnson, "First Principles Investigation of Adsorption and Dissociation of Hydrogen on Mg_2Si Surfaces", *Journal of Physical Chemistry C*, **111**, 6910-6916 (2007).
12. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Using First Principles Calculations To Identify New Destabilized Metal Hydride Reactions for Reversible Hydrogen Storage", *Phys. Chem. Chem. Phys.* **9**, 1438-1452 (2007).
13. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "First principles screening of

destabilized metal hydrides for high capacity H_2 storage using scandium", *Journal of Alloys and Compounds* **446-447**, 23-27 (2007).
14. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl, "Predicting Reaction Equilibria for Destabilized Metal Hydride Decomposition Reactions for Reversible Hydrogen Storage", *Journal of Physical Chemistry C* **111**, 1584—1591 (2007).
15. Sudhakar V. Alapati, J. Karl Johnson, and David S. Sholl "Identification of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations", *Journal of Physical Chemistry B*, **110**, 8769-8776 (2006).

Appendix B
Final data tables for all materials investigated

Table A1. List of 359 compounds included in our database.

One-element compounds				
Al	B	C	Ca	K
Li	Mg	Na	Sc	Si
Ti	V			
Two-element compounds				
AlB_2	AlB_{12}	Al_4C_3	Al_2Ca	Al_4Ca
AlH_3	AlLi	Al_2Li_3	Al_3Li	Al_4Li_9
$Al_{12}Mg_{17}$	$Al_{14}Mg_{13}$	$Al_{30}Mg_{23}$	AlN	AlSc
$AlSc_2$	Al_2Sc	Al_3Sc	AlTi	$AlTi_3$
Al_2Ti	Al_3Ti	AlV	AlV_3	Al_3V
$Al_{10}V$	$Al_{23}V_4$	$Al_{45}V_7$	B_4C	$B_{13}C_2$
$B_3Ca_4LiN_6$	$(B_{10}H_{13})_2$	BN	$B_{13}N_2$	C_2Ca
C_2N_2	C_3N_4	C_5N_4	$C_{12}N_6$	CaB_4
CaB_6	CaH_2	$CaLi_2$	$CaMg_2$	CaN_6
Ca_2N	Ca_3N_2	$Ca_{11}N_8$	CaSi	$CaSi_2$
Ca_2Si	Ca_5Si_3	KB_6	KC_8	K_2C_2
KH	KN_3	K_3N	KSi	K_4Si_4
K_8Si_{46}	LiB	Li_5B_4	Li_2C_2	LiH
LiMg	LiN_3	Li_3N	LiSi	Li_2Si
Li_7Si_2	$Li_{12}Si_7$	$Li_{13}Si_4$	$Li_{15}Si_4$	MgB_2
MgB_4	MgB_7	MgC_2	Mg_2C_3	MgH_2
Mg_3N_2	MgSc	Mg_2Si	Mg_5Si_6	N_4Si_3
NaB_{15}	Na_3B_{20}	Na_2C_2	NaH	NaN_3
Na_3N	NaSi	Na_4Si_4	Na_8Si_{46}	ScB_2
ScB_{12}	ScC	Sc_2C	Sc_2C_3	Sc_3C_4
Sc_4C_3	$Sc_{15}C_{19}$	ScH_2	ScN	ScSi

$ScSi_2$	Sc_5Si_3	SiB_3	SiB_6	SiC
SiH	TiB	TiB_2	TiC	Ti_2C
Ti_8C_5	TiH	TiH_2	TiN	Ti_2N
TiSi	$TiSi_2$	Ti_5Si_3	Ti_5Si_4	TiV
VB	VB_2	V_2B_3	V_3B_2	VC
V_2C	V_6C_5	V_8C_7	VH_2	V_2H
VN	V_2N	VSi_2	V_3Si	V_5Si_3
V_6Si_5				
Three-element compounds				
$Al(BH_4)_3$	Al_5C_3N	$Al_6C_3N_2$	$Al_7C_3N_3$	$Al_8C_3N_4$
$Al_2Ca_3N_4$	Al_2CaSi_2	$Al_2Ca_3Si_2$	$AlLi_3N_2$	AlLiSi
$Al_3Li_8Si_5$	$Al_3Li_{12}Si_4$	Al_2MgC_2	$AlMg_4Si_6$	$Al_{18}Mg_3Ti_2$
$AlSc_2Si_2$	BC_2N	$C_2H_4N_4$	$C_2H_{18}N_{18}$	$C_2N_2(NH)$
$CaAlH_5$	$Ca(AlH_4)_2$	Ca_4Al_3Mg	Ca_3AlN_3	CaAlSi
CaB_2C_2	$Ca(BH_4)_2$	$CaB_{12}H_{12}$	Ca_3BN_3	$CaCN_2$
CaC_4N_6	Ca_2HN	CaLiN	$CaLiSi_2$	Ca_2LiSi_3
$CaMg_2N_2$	CaMgSi	$Ca_4N_2(CN_2)$	$Ca_{11}N_6(CN_2)_2$	Ca_2N_3V
Ca_3N_3V	$CaSiN_2$	$Ca_2Si_5N_8$	$Ca_5(Si_2N_6)$	Ca_4TiN_4
H_9CN_9	$KAlH_4$	K_3AlH_6	KBH_4	$KB_{21}H_{18}$
$K_2B_6H_6$	$K_2(B_{10}H_{10})$	$K_2B_{12}H_{12}$	KCN	KC_2N_3
KC_4N_3	K_2CN_2	$K_3C_6N_9$	K_3LiSi_4	K_7LiSi_8
$KMgH_3$	K_2MgH_4	KNH_2	$(K(NH_2))(NH_3)_2$	$KSiH_3$
$LiAlB_{14}$	$LiAlH_4$	Li_3AlH_6	LiBC	$LiB_{13}C_2$
$Li_2B_{12}C_2$	LiBH	$Li(BH_2)$	$LiBH_4$	$Li_2B_{12}H_{12}$
$Li_3(BH_6)$	Li_3BN_2	$Li_2B_{12}Si_2$	LiCN	Li_2CN_2
$LiMgH_3$	LiMgN	Li_2MgSi	$Li_{12}Mg_3Si_4$	$LiNH_2$
Li_2NH	Li_4NH	LiN_3Si_2	Li_5N_3Si	Li_7N_4V
$LiNa_2N$	$LiNa_5N_2$	$Li_2Na_4N_2$	Li_2NaN	$Li_3Na_3N_2$
$Li_4Na_2N_2$	Li_5NaN_2	Li_3NaSi_6	Li_3ScN_2	$MgAlH_5$
$Mg(AlH_4)_2$	MgAlSi	$MgAl_2Si_2$	MgB_2C_2	$MgB_{12}C_2$
$Mg_2B_{24}C$	$Mg(BH_4)_2$	$MgB_{12}H_{12}$	MgB_9N	Mg_3BN_3
$MgB_{12}Si_2$	MgC_4N_6	Mg(NCN)	$Mg(NH_2)_2$	$MgSiN_2$
Mg_7TiH_{16}	N_2BH_7	$N_2B_{10}H_{18}$	$N_3B_3H_6$	$N_3B_3H_{12}$
$N_4B_9H_{11}$	$N_4B_{10}H_8$	$N_4B_{10}H_{22}$	NH_3BH_3	$(NH_4)_2B_{12}H_{12}$
$(NH_2)CN$	NH_4HCN_2	$N(SiH_3)_3$	$NaAlH_4$	Na_3AlH_6
$Na_5Al_3H_{14}$	NaAlSi	$NaAlSi_4$	$NaBH_4$	$Na_2(B_{10}H_{10})$
$Na_3(BN_2)$	NaCN	NaC_4N_3	Na_2CN_2	$Na_3C_6N_9$
$NaMgH_3$	NaN_3C_2	$NaNH_2$	$ScAl_3C_3$	Sc_2AlC
Sc_3AlC	ScB_2C	ScB_2C_2	Sc_2BC_2	$Sc_2V_3Si_4$

$SiCN$	SiC_2N_4	Si_2CN_4	Ti_2AlC	Ti_3AlC
Ti_3AlC_2	Ti_2AlN	Ti_3AlN	Ti_4AlN_3	Ti_6Si_2B
Ti_3SiC_2	$V_{12}Al_3C_8$	V_5SiB_2		
Four-element compounds				
$AlNC_3H_{10}$	BCH_5N_2	$B_{10}C_6H_{30}N_2$	$B_{20}C_3H_{30}N_2$	BC_4KN_4
$CH_3NH_2BH_3$	Ca_2N_2BH	$Ca(NH_2BH_3)_2$	$KAl(NH_2)_4$	$K_5C_2HN_4$
$KCaN_3H_6$	$K(HCN_2)$	K_2LiAlH_6	$KLi_3(NH_2)_4$	$KLi_7N_8H_{16}$
$K_2Li(NH_2)_3$	$K_2Mg(NH_2)_4$	K_2NaAlH_6	$K_2Na(NH_2)_3$	$K_3Si_6N_{11}H_6$
$LiAlMg_{10}H_{24}$	$LiAl(NH_2)_4$	$Li(B(CN)_4)$	$Li_4BN_3H_{10}$	$Li_2Ca(NH)_2$
$LiK(BH_4)_2$	$Li_2Mg(NH)_2$	$Li(NH_2BH_3)$	$(Li(NH_3)_4)_2(B_6H_6)(NH_3)_2$	$LiNa_2AlH_6$
$LiNa_2(NH_2)_3$	$Li_3Na(NH_2)_4$	$LiSc(BH_4)_4$	$Mg(BH_4)_2(NH_3)_2$	$(NH_4)B(CN)_4$
$NaAl(NH_2)_4$	$NaB(CN)_4$	NaN_2CH	$Si_2C_7H_{18}N_2$	$VC_8H_{24}N_4$
Five-element compounds				
$LiAlC_4H_{16}N_4$	$LiSi_3C_9H_{27}N_2$	$Si_2B_2C_{12}H_{37}N_5$		

Table A2. Comparison of the experimental and the DFT calculated structural parameters for the 147 compounds listed in Table 1, with all distances in Å and angles in degrees.

Compound	Space group	Structural parameters (Å, degree)	
		Experimental	Calculated
AlB_{12}	$P4_12_12$	a = 10.17 c = 14.28	a = 11.41 c = 13.86
Al_4C_3	R-3mH	a = 3.335 c = 24.967 γ = 120	a = 3.349 c = 25.109 γ = 120
Al_4Ca	I4/mmm	a = 4.354 c = 11.18	a = 4.368 c = 11.19
$Al_{14}Mg_{13}$	Im-3m	a = 10.44	a = 10.2
$Al_{30}Mg_{23}$	R-3H	a = 12.825	a = 12.787
$Al_{23}V_4$	P63/mmc	a = 7.6928 c = 17.04 γ = 120	a = 7.6809 c = 17.04 γ = 120
$Al_{45}V_7$	C2/m	a = 25.604 b = 7.6213 c = 11.081 β = 128.92	a = 25.655 b = 7.6076 c = 11.086 β = 128.88
B_4C	R-3mH	a = 5.6 c = 12.12 γ = 120	a = 7.4 c = 8.77 γ = 120
$B_{13}C_2$	R-3mH	a = 5.633	a = 5.656

		c = 12.164 γ = 120	c = 12.12 γ = 120
$(B_{10}H_{13})_2$	Pbca	a = 10.66 b = 10.55 c = 14.56	a = 10.83 b = 10.69 c = 14.78
$B_{13}N_2$	R-3m	a = 5.45 c = 12.26	a = 5.49 c = 12.41
C_2Ca	C2/m	a = 7.2076 b = 3.8283 c = 7.3677 β = 107.193	a = 7.1698 b = 3.8325 c = 7.4162 β = 106.961
C_2N_2	Pcab	a = 6.31 b = 7.08 c = 6.19	a = 6.72 b = 6.38 c = 6.06
C_3N_4	P-6m2	a = 4.742 c = 6.7205 γ = 120	a = 4.766 c = 6.4004 γ = 120
C_5N_4	R3cH	a = 9.062 c = 11.625 γ = 120	a = 8.912 c = 11.416 γ = 120
$C_{12}N_6$	Pa-3	a = 10.781	a = 10.746
CaB_4	P4/mbm	a = 7.1 c = 4.14	a = 7.17 c = 4.1
Ca_2Si	Pnma	a = 7.69 b = 4.82 c = 9.05	a = 7.65 b = 4.83 c = 9.09
KC_8	Fddds	a = 4.92 b = 8.51 c = 21.39999	a = 4.97 b = 8.61 c = 21.36525
KSi	P-43n	a = 12.62	a = 12.72
K_8Si_{46}	Pm-3n	a = 10.3	a = 10.36
LiB	PNMA	a = 6.4 b = 3 c = 5.6	a = 6.2251 b = 3.0727 c = 5.589
LiMg	Im-3m	a = 3.484	a = 3.434
$Li_{12}Si_7$	Pnma	a = 8.6 b = 19.755 c = 14.336	a = 8.54 b = 19.631 c = 14.32
$Li_{13}Si_4$	Pbam	a = 7.99 b = 15.21	a = 7.902 b = 15.022

		c = 4.43	c = 4.432
$Li_{15}Si_4$	I-43d	a = 10.69	a = 10.6
NaB_{15}	Imam	a = 5.847 b = 8.415 c = 10.298	a = 5.848 b = 8.426 c = 10.295
Na_3B_{20}	Cmmm	a = 18.695 b = 5.701 c = 4.151	a = 18.636 b = 5.693 c = 4.158
Na_4Si_4	C2/c	a = 12.1534 b = 6.545 c = 11.1323 β = 118.9	a = 12.1512 b = 6.5632 c = 11.1085 β = 90
Na_8Si_{46}	Pm-3n	a = 10.19	a = 12.31
$Sc_{15}C_{19}$	P-42_1c	a = 7.5 c = 15	a = 7.51 c = 14.612
SiB_3	Imma	a = 8.3915 b = 12.568 c = 6.2134	a = 8.381 b = 12.588 c = 6.2233
SiC	F-43m	a = 4.36	a = 4.38
TiV	Im-3m	a = 3.159	a = 3.103
V_2N	P-31m	a = 4.917 c = 4.568 γ = 120	a = 4.899 c = 4.522 γ = 120
V_5Si_3	I4/mcm	a = 9.429 c = 4.756	a = 9.393 c = 4.715
$Al(BH_4)_3$	Pna2_1	a = 18.02 b = 6.14 c = 6.2	a = 17.99 b = 6.12 c = 6.2
Al_2MgC_2	P-3m	a = 3.377 c = 5.817 γ = 120	a = 3.385 c = 5.82 γ = 120
$Al_{18}Mg_3Ti_2$	Fd-3ms	a = 14.7875	a = 14.775
BC_2N	Pmm2	a = 2.528 b = 2.5024 c = 3.5871	a = 2.56 b = 2.5327 c = 3.6373
$C_2H_4N_4$	P21/c	a = 3.7913 b = 12.4117 c = 9.1125 β = 91.49	a = 3.6509 b = 12.0116 c = 9.1886 β = 91.32
$C_2H_{18}N_{18}$	P-1	a = 4.6208	a = 4.5006

		b = 8.5854 c = 9.2705 α = 108.486 β = 95.29 γ = 102.991	b = 8.415 c = 9.1743 α = 109.353 β = 95.17 γ = 103.087
$C_2N_2(NH)$	$Cmc2_1$	a = 7.57 b = 4.44 c = 4	a = 7.63 b = 4.48 c = 4.04
Ca_4Al_3Mg	Pbcm	a = 6.1792 b = 24.2113 c = 5.8864	a = 6.1906 b = 24.2483 c = 5.9045
CaAlSi	P-6m2	a = 4.2 c = 4.4	a = 4.21 c = 4.41
$Ca(BH_4)_2$	F2dd	a = 8.78 b = 13.02 c = 7.41	a = 8.75 b = 12.94 c = 7.37
$CaB_{12}H_{12}$	C2/c	a = 14.3283 b = 7.1642 c = 11.017 α = β = 89.8353 γ = 122.0687	a = 14.3069 b = 7.1522 c = 11.0012 α = β = 89.8472 γ = 122.0691
CaC_4N_6	C2/c	a = 12.446 b = 6.08 c = 7.898 β = 145.2	a = 12.855 b = 6.261 c = 7.674 β = 149.86
$Ca_4N_2(CN_2)$	Pnma	a = 11.44 b = 3.58 c = 13.84	a = 11.51 b = 3.58 c = 13.92
$Ca_{11}N_6(CN_2)_2$	P42/MNM	a = 14.523 c = 3.6083	a = 14.5506 c = 3.6221
$CaSiN_2$	Pbca	a = 5.123 b = 10.207 c = 14.823	a = 5.163 b = 10.279 c = 14.933
$Ca_2Si_5N_8$	Pbca	a = 10.584 b = 9.652 c = 13.663	a = 10.6163 b = 9.6748 c = 13.6685
$Ca_5(Si_2N_6)$	C12/C1	a = 9.836 b = 6.0519 c = 12.757 β = 100.2	a = 9.899 b = 6.094 c = 14.736 β = 121.155

Ca_4TiN_4	P-1	*a* = 5.98 *b* = 6.01 *c* = 8.99 α = 71.57 β = 79.47 γ = 68.26	*a* = 6.01 *b* = 6.04 *c* = 9.02 α = 71.62 β = 79.32 γ = 68.07
H_9CN_9	$P2_1/c$	*a* = 6.679 *b* = 7.722 *c* = 13.143 β = 95.44	*a* = 6.555 *b* = 7.546 *c* = 12.901 β = 95.71
KBH_4	Fm-3m	*a* = 6.71	*a* = 6.69
KBH_4	$P4_2/nmc$	*a* = 4.68 *c* = 6.57	*a* = 4.71 *c* = 6.61
$KB_{21}H_{18}$	C2	*a* = 12.49 *b* = 7.11 *c* = 16.94 β = 93.81	*a* = 12.71 *b* = 7.22 *c* = 17.04 β = 94.1
$K_2B_6H_6$	Fm-3m	*a* = 8.839	*a* = 8.897
$K_2(B_{10}H_{10})$	P121/n1	*a* = 12.8554 *b* = 11.1784 *c* = 6.8227 β = 93.357	*a* = 11.9928 *b* = 9.7475 *c* = 9.0276 β = 91.93
$K_2B_{12}H_{12}$	Fm-3	*a* = 10.629	*a* = 10.639
KC_4N_3	P-1	*a* = 8.665 *b* = 8.873 *c* = 3.89 α = 86.7 β = 90.1 γ = 105	*a* = 8.827 *b* = 9.296 *c* = 4.009 α = 83.8 β = 90.9 γ = 104.3
KNH_2	$P2_1/m$	*a* = 4.586 *b* = 3.904 *c* = 6.223 β = 95.8	*a* = 4.458 *b* = 3.745 *c* = 6.111 β = 94.958
$(K(NH_2))(NH_3)_2$	$C222_1$	*a* = 6.8386 *b* = 9.9525 *c* = 6.5903	*a* = 6.8342 *b* = 9.6806 *c* = 6.5711
$LiAlB_{14}$	Imam	*a* = 5.8469 *b* = 8.1429 *c* = 10.3542	*a* = 5.852 *b* = 8.142 *c* = 10.353
$LiB_{13}C_2$	Imma	*a* = 5.6677	*a* = 5.842

		b = 10.8201 c = 8.0399	b = 9.661 c = 8.923
$Li_2B_{12}C_2$	AMM2	a = 4.706 b = 5.318 c = 5.318 α = 115.798	a = 4.663 b = 5.5534 c = 5.5534 α = 100.47
LiBH	PNMA	a = 6.2 b = 3 c = 6.3	a = 5.6458 b = 3.0758 c = 6.5051
$Li(BH_2)$	PNMA	a = 8.1 b = 3 c = 5.9	a = 8.3217 b = 3.0367 c = 5.4851
$Li_2B_{12}H_{12}$	Pa3	a = 9.5771	a = 9.5804
$Li_3(BH_6)$	R3-H	a = 5.1824 α = β = γ = 91.1141	a = 5.3562 α = β = γ = 94.1637
$Li_2B_{12}Si_2$	Cmce	a = 6.106 b = 10.979 c = 8.405	a = 6.118 b = 11.012 c = 8.43
$LiMgH_3$	R3c	a = 4.96 c = 13.34	a = 4.94 c = 13.24
Li_2MgSi	Fm-3m	a = 12.83	a = 12.748
LiN_3Si_2	$Cmc2_1$	a = 9.222 b = 5.296 c = 4.78	a = 9.277 b = 5.329 c = 4.812
$LiNa_2N$	P6/mmm	a = 4 c = 4.2 γ = 120	a = 4.37 c = 3.838 γ = 120
$LiNa_5N_2$	C_2	a = 6.731 b = 5.944 c = 6.383 β = 91.18	a = 6.735 b = 5.949 c = 6.389 β = 91.15
$Li_2Na_4N_2$	P4/nmm	a = 3.895 c = 6.114	a = 4.066 c = 6.099
Li_2NaN	P6/nmm	a = 3.65 c = 4.6 γ = 120	a = 3.62 c = 4.716 γ = 120
$Li_3Na_3N_2$	Pm	a = 3.854 b = 3.676 c = 6.32 β = 90.31	a = 3.853 b = 4.208 c = 7.272 β = 89.85

$Li_4Na_2N_2$	Fm-3m	a = 5.265	a = 5.404
Li_5NaN_2	P4/mmm	a = 3.965 c = 5.504	a = 3.705 c = 5.186
Li_3NaSi_6	Pnma	a = 17.972 b = 3.788 c = 10.299	a = 18.021 b = 3.804 c = 10.331
$MgAl_2Si_2$	P-3m1	a = 4.05 c = 6.74	a = 4.08 c = 6.69
$MgB_{12}C_2$	C2/c	a = 7.27 b = 8.78 c = 7.28 β = 105.33	a = 7.26 b = 8.77 c = 7.25 β = 105.32
$Mg_2B_{24}C$	P-4n2	a = 8.94 c = 5.07	a = 8.96 c = 5.09
$MgB_{12}H_{12}$	C2/m	a = 11.689 b = 8.712 c = 6.907 β = 122.47	a = 11.687 b = 8.711 c = 6.905 β = 122.5
$MgB_{12}Si_2$	Pnma	a = 10.98 b = 6.11 c = 8.36	a = 11.03 b = 6.13 c = 8.39
MgC_4N_6	Pnnm	a = 6.171 b = 7.17 c = 7.404	a = 6.443 b = 7.289 c = 7.429
Mg_7TiH_{16}	Fm3m	a = 9.564	a = 9.341
N_2BH_7	Pbcn	a = 9.53 b = 5.12 c = 13.01	a = 9.768 b = 5.237 c = 12.672
$N_2B_{10}H_{18}$	Pnma	a = 18.096 b = 7.373 c = 7.223	a = 18.237 b = 7.528 c = 7.284
$N_3B_3H_6$	$P4_32_12$	a = 5.428 c = 16.279	a = 5.63 c = 17.223
$N_3B_3H_{12}$	Pbcm	a = 4.403 b = 12.21 c = 11.227	a = 4.442 b = 12.382 c = 11.272
$N_4B_9H_{11}$	$P2_1/c$	a = 8.318 b = 5.951 c = 19.265 β = 95.3	a = 8.611 b = 6.263 c = 20.044 β = 94.6

$N_4B_{10}H_8$	C2/c	*a* = 11.411 *b* = 6.658 *c* = 13.058	*a* = 11.945 *b* = 7.373 *c* = 15.268 α = 91.09
$N_4B_{10}H_{22}$	C2/c	*a* = 7.7 *b* = 7.7 *c* = 9.772 α = 83.872 β = 83.872 γ = 82.307	*a* = 7.813 *b* = 7.229 *c* = 9.473 α = 77.29 β = 76.99 γ = 82.3
NH_3BH_3	Pmn21	*a* = 5.395 *b* = 4.887 *c* = 4.986	*a* = 5.356 *b* = 4.796 *c* = 4.921
$(NH_4)_2B_{12}H_{12}$	Fm-3	*a* = 10.88	*a* = 10.79
$(NH_2)CN$	Pbca	*a* = 6.856 *b* = 6.628 *c* = 9.147	*a* = 6.726 *b* = 6.597 *c* = 8.916
NH_4HCN_2	$P2_12_12$	*a* = 6.44 *b* = 6.58 *c* = 7.4	*a* = 6.38 *b* = 6.5 *c* = 7.3
$Na_5Al_3H_{14}$	P4/mnc	*a* = 6.769 *c* = 10.289	*a* = 6.7 *c* = 10.2
$NaBH_4$	Fm-3m	*a* = 6.15	*a* = 6.02
$NaBH_4$	P-42_1c	*a* = 4.35 *c* = 5.86	*a* = 4.31 *c* = 5.82
$Na_2(B_{10}H_{10})$	P121/n1	*a* = 10.2828 *b* = 13.0218 *c* = 6.6734 β = 93.754	*a* = 9.846 *b* = 12.153 *c* = 8.104 β = 93.074
$Na_3(BN_2)$	$P2_1$/c	*a* = 5.717 *b* = 7.931 *c* = 7.883 β = 111.32	*a* = 5.737 *b* = 7.966 *c* = 7.9 β = 111.29
$Na_3C_6N_9$	$P2_1$/c	*a* = 11.048 *b* = 23.381 *c* = 3.516 β = 97.913	*a* = 11.397 *b* = 24.101 *c* = 3.937 β = 97.913
Sc_2AlC	P63/MMC	*a* = 3.2275 *c* = 14.8729 γ = 120	*a* = 3.2849 *c* = 15.0425 γ = 120

Ti_2AlC	$P6_3/mmc$	$a = 2.97$ $c = 13.22$	$a = 3.07$ $c = 13.71$
Ti_6Si_2B	P-62m	$a = 6.802$ $c = 3.338$ $\gamma = 120$	$a = 6.777$ $c = 3.312$ $\gamma = 120$
$V_{12}Al_3C_8$	P63/MCM	$a = 5.0882$ $c = 22.9830$ $\gamma = 120$	$a = 5.0651$ $c = 22.6375$ $\gamma = 120$
V_5SiB_2	I4/mcm	$a = 5.81$ $c = 10.79$	$a = 5.774$ $c = 10.762$
$AlNC_3H_{10}$	$P2_1/c$	$a = 5.428$ $b = 9.9076$ $c = 9.9632$ $\beta = 99.254$	$a = 5.379$ $b = 11.302$ $c = 10.271$ $\beta = 99.2$
BCH_5N_2	$Pna2_1$	$a = 7.973$ $b = 6.445$ $c = 6.976$	$a = 7.986$ $b = 6.515$ $c = 7.103$
$B_{10}C_6H_{30}N_2$	$P2_1/c$	$a = 8.369$ $b = 16.663$ $c = 11.989$ $\beta = 100.34$	$a = 8.586$ $b = 17.002$ $c = 12.249$ $\beta = 100.67$
$B_{20}C_3H_{30}N_2$	$P2_12_12_1$	$a = 10.334$ $b = 10.873$ $c = 17.524$	$a = 10.449$ $b = 11.199$ $c = 17.78$
BC_4KN_4	$I4_1/a$	$a = 6.976$ $c = 14.21$	$a = 7.151$ $c = 14.563$
$CH_3NH_2BH_3$	Pnma	$a = 11.1$ $b = 6.58$ $c = 4.92$	$a = 11.07$ $b = 6.35$ $c = 4.88$
$Ca(NH_2BH_3)_2$	C121	$a = 9.10$ $b = 4.37$ $c = 6.44$ $\beta = 93.19$	$a = 9.12$ $b = 4.29$ $c = 6.34$ $\beta = 93.1$
$KAl(NH_2)_4$	$C222_1$	$a = 10$ $b = 5.8$ $c = 10.14$	$a = 10.2$ $b = 5.82$ $c = 10.142$
$K_5C_2HN_4$	P4/ncc	$a = 9.095$ $c = 11.029$	$a = 9.225$ $c = 11.202$
$KCaN_3H_6$	$P2_1/c$	$a = 6.767$ $b = 11.68$	$a = 6.797$ $b = 11.834$

		c = 6.624 β = 106.7	c = 6.797 β = 106.82
$K(HCN_2)$	$P2_12_12_1$	a = 7.087 b = 9.09 c = 9.014	a = 7.229 b = 9.172 c = 9.158
K_2LiAlH_6	R-3m	a = 5.62 c = 27.4	a = 5.62 c = 27.31
$KLi_3(NH_2)_4$	$I4_1/amd$	a = 7.238 c = 23.956	a = 8.208 c = 23.699
$KLi_7N_8H_{16}$	$I4_1/a$	a = 7.18 c = 44.39	a = 7.678 c = 46.545
$K_2Li(NH_2)_3$	P42/m	a = 6.872 c = 11.706	a = 6.866 c = 11.726
$K_2Mg(NH_2)_4$	$P2_1/c$	a = 7.455 b = 7.024 c = 13.545 β = 105.6	a = 7.255 b = 7.255 c = 13.626 β = 105.25
K_2NaAlH_6	$P2_1/c$	a = 5.733 b = 5.754 c = 8.128 β = 89.97	a = 5.743 b = 5.7492 c = 8.0934 β = 89.99
$K_2Na(NH_2)_3$	P42/m	a = 7.3514 c = 13.1285	a = 7.5143 c = 13.3144
$K_3Si_6N_{11}H_6$	$P4_332$	a = 10.789	a = 10.797
$LiAlMg_{10}H_{24}$	P121	a = 8.9885 b = 8.9848 c = 4.4846 β = 89.655	a = 8.9147 b = 8.9417 c = 4.4493 β = 89.65
$Li(B(CN)_4)$	P43m	a = 7.8494 α = β = γ = 60	a = 7.7822 α = β = γ = 60
$Li_2Ca(NH)_2$	P-3m1	a = 3.57 c = 5.95	a = 3.58 c = 5.84
$LiK(BH_4)_2$	Pnma	a = 7.91 b = 4.49 c = 13.84	a = 7.78 b = 4.43 c = 13.72
$Li(NH_2BH_3)$	Pbca	a = 7.11 b = 13.93 c = 5.15	a = 6.92 b = 13.52 c = 5.07
$(Li(NH_3)_4)_2(B_6H_6)(NH_3)_2$	P21/c	a = 7.483 b = 11.871	a = 7.3965 b = 11.649

		c = 10.6047 β = 95.371	c = 10.4489 β = 95.21
$LiNa_2AlH_6$	P21/c	a = 5.165 b = 5.251 c = 7.339	a = 4.777 b = 4.715 c = 6.613
$LiNa_2(NH_2)_3$	$P4_2/m$	a = 6.28 c = 11.15	a = 6.17 c = 10.90
$LiSc(BH_4)_4$	P-42c	a = 6.08 c = 12.03	a = 6.45 c = 11.95
$Mg(BH_4)_2(NH_3)_2$	Pbca	a = 17.49 b = 9.41 c = 8.73	a = 17.73 b = 9.35 c = 8.68
$(NH_4)B(CN)_4$	I41/a	a = 7.132 c = 14.745	a = 7.453 c = 14.617
$NaAl(NH_2)_4$	$P2_1/c$	a = 7.328 b = 6.047 c = 13.151 β = 94.04	a = 6.565 b = 6.353 c = 15.362 β = 94.3
$NaB(CN)_4$	Fd-3mZ	a = 11.68	a = 11.874
$Si_2C_7H_{18}N_2$	$P2_1/c$	a = 9.71 b = 11.11 c = 11.88 β = 102.3	a = 10.143 b = 11.599 c = 12.422 β = 103.1
$VC_8H_{24}N_4$	P-1	a = 8.29 b = 12.016 c = 13.835 α = 75.662 β = 79.404 γ = 84.966	a = 8.637 b = 12.503 c = 14.479 α = 75.89 β = 79.47 γ = 85.3
$LiAlC_4H_{16}N_4$	$I4_1$	a = 14 c = 9.275	a = 14.128 c = 9.571
$LiSi_3C_9H_{27}N_2$	P-1	a = 8.776 b = 9.579 c = 21.949 α = 100.84 β = 92.18 γ = 115.67	a = 9.077 b = 9.875 c = 22.544 α = 101.16 β = 91.95 γ = 115
$Si_2B_2C_{12}H_{37}N_5$	$P2_1/c$	a = 15.785 b = 11.966 c = 11.804	a = 16.2 b = 12.212 c = 12.205

		$\beta = 102.19$	$\beta = 102.3$