# IV.A.5c First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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## Accomplishments

- Developed a method for quickly screening new complex hydride materials for the thermodynamics of reaction.
- Developed a method to screen doped materials for thermodynamic stability with respect to phase segregated compounds.
- Developed an automated approach to search for all possible reactions for a given set of reactants and products.
- Investigated initial reaction kinetics for hydrogenation-related reactions on surfaces of materials.

## Introduction

Complex metal hydrides such as alanates, amides and borohydrides of period 2 and 3 metals are promising materials for reaching high gravimetric and volumetric hydrogen densities for on-board fuel cell storage. A serious thermodynamic limitation of these materials is that high temperatures are often required to release $H_2$. The reaction free energy for decomposition of practical materials must lie in a narrow range of values to allow reversible hydrogenation and dehydrogenation at acceptable temperatures and pressures. In addition, the kinetics of hydrogenation and dehydrogenation must be acceptably facile

Research carried out at the University of Pittsburgh and Carnegie Mellon University has focused on using computer modeling to predict the thermodynamics of existing and novel complex hydrides. We have identified several new materials that are predicted to have favorable thermodynamics, some of which are currently being investigated experimentally. We have investigated the thermodynamics of doping as a means of tuning the energies of reaction for hydrides that are too stable or not stable enough. We have also initiated an investigation into the kinetics of selected hydride materials in an effort to understand the atomic-level phenomena that control the rate of hydrogenation of complex metal hydrides.

## Approach

We have collaborated with many Metal Hydride Center of Excellence (MHCoE) partners, including: John Vajo, Ping Liu, Bruce Clemens, Mark Allendorf, Sandia, Duane Johnson, Ursula Kattner, Eric Majzoub, Ewa Ronnebro, J.-C. Zhao, Brian Bowman, Craig Jensen, and Zak Fang.

We use quantum mechanical methods for computing the structural, electronic, energetic, and kinetic properties of complex hydrides and related materials. The specific method we use for most of our calculations is periodic plane wave density functional theory (DFT), which is an approach for computing the approximate solution to the Schrödinger equation for condensed phase (solids) materials. This method requires as input at least an initial guess for the crystal structure of material to be modeled. The DFT method can then be used to optimize the atomic coordinates of each atom in the unit cell, the volume, and the shape of the unit cell. More importantly, we have developed a DFT-based method that can be used to quickly and reliably estimate the enthalpies of reaction for complex hydrides. We have used this method to screen over 300 possible hydrogen storage reactions and have identified several promising materials that have not previously been investigated. We can also calculate the free energies of reaction, including computing the entropic contributions through the phonon density of states. This is a much more computationally demanding approach– we have performed such calculations for a subset of the most promising reaction schemes identified from our screening calculations. We have also used DFT methods

to compute kinetics for surface reactions as an initial approach for studying kinetics of reactions involving complex hydrides.

We have used the Vienna *Ab initio* Simulation Package (VASP) to perform most of the calculations in our work.  We have used the gradient corrected approximation with the Perdew-Wang 91 functional [1]. We have used both ultrasoft pseudopotentials (USPP) and the projector augmented wave (PAW) method [2].

## Results

One of the central goals of our calculations is to examine a large number of possible destabilized reaction schemes for $H_2$ storage.  To this end, we performed DFT calculations for over 150 solid compounds with known crystal structures comprised from Al, B, C, Ca, N, H, Li, Mg, Sc, Si, Ti and V that are listed in the Wyckoff [3], Pearson's Handbook [4], and the Inorganic Crystal Structure Database (ICSD) database [5].  The DFT-optimized structural parameters for these compounds are in generally good agreement with experimental data.

We have computed reaction enthalpies for over 350 reactions for which enthalpies were not previously known.  Most of these reactions are considered unpromising from the standpoint of hydrogen storage densities or reaction enthalpies, or both.  We note that reaction enthalpy, $\Delta H$, must lie in a narrow range for practical hydrogen storage materials.  If the enthalpy is too low then the material will not be easily reversible. If the enthalpy is too high then unacceptably high temperatures will be required to release the hydrogen. We have used the zero temperature enthalpy of reaction, $\Delta U_0$, as a surrogate for the actual enthalpy of reaction. We have shown that this metric is adequate for screening purposes [6].  Recognizing that $\Delta U_0$ provides only an approximation for $\Delta H$, we adopted an inclusive strategy for identifying promising reactions by including all reactions with $15 \leq \Delta U_0 \leq 75$ kJ/mol $H_2$ for further consideration.  While recognizing that this approach may yield some false positives, we feel it is more productive to list all the reactions identified in this way in detail rather than to exclude examples that might be rejected by a more conservative approach.

We have identified multiple interesting reactions that had not previously been examined experimentally. Several of these examples are summarized in Table 1. One example is:

$$3 \text{ LiNH}_2 + 2 \text{ LiH Si } \rightarrow \text{ Li}_5\text{N}_3\text{Si} + 4 \text{ H}_2 \qquad (1)$$
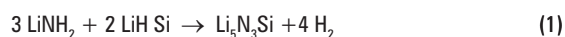
This reaction yields 7.16 wt% hydrogen on completion.  Our DFT calculations yield $\Delta U_0 = 23\text{-}34$ kJ/mol $H_2$ using the PAW approach.  The range of values for this reaction reflects the variants in the $\text{Li}_5\text{N}_3\text{Si}$ crystal structure that were employed in our calculations

[7].  A related reaction involves a mixture of $\text{LiNH}_2$ and $\text{MgH}_2$:

$$\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2 \text{ H}_2 \qquad (2)$$
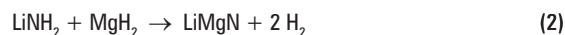
This reaction releases 8.19 wt% hydrogen on completion, with a DFT-predicted $\Delta U_0$ of 31.9 kJ/mol $H_2$.  The dehydrogenation properties of the mixture of $\text{LiNH}_2$ and $\text{MgH}_2$ in the molar ratio of 2:1

**TABLE 1.**  Reactions with $15 \leq \Delta U_0 \leq 75$ kJ/mol $H_2$ and gravimetric densities > 6.5 wt%** indicate results for final materials with varying Si loading.  For reactions involving $\text{LiBH}_4$, the enthalpy for the reaction with the hexagonal and orthorhombic polymorphs of $\text{LiBH}_4$ is denoted by (h) and (o), respectively.

| Reaction | wt% H$_2$ | $\Delta U_0$ |
|---|---|---|
| 3 LiNH$_2$ + 2 LiH + Si → Li$_5$N$_3$Si + 4 H$_2$ (10/11 Si atoms) | 7.16 | 34.2/23.3** |
| LiBH$_4$ + 2 LiNH$_2$ → Li$_3$BN$_2$ + 4 H$_2$ | 11.9 | 24.3 (o) 20.2 (h) |
| MgH$_2$ + 2 LiBH$_4$ → 2 LiH + MgB$_2$ + 4 H$_2$ | 11.56 | 66.8 (o) 58.6 (h) |
| LiNH$_2$ + MgH$_2$ → LiMgN + 2 H$_2$ | 8.19 | 31.9 |
| 4 LiBH$_4$ + MgH$_2$ → 4 LiH + MgB$_4$ + 7 H$_2$ | 12.46 | 69.2 (o) 59.9 (h) |
| 7 LiBH$_4$ + MgH$_2$ → 7 LiH + MgB$_7$ + 11.5 H$_2$ | 12.99 | 71.5-75.5 (o) 61.5-65.5 (h) |
| CaH$_2$ + 6 LiBH$_4$ → CaB$_6$ + 6 LiH + 10 H$_2$ | 11.69 | 62.7 (o) 52.9 (h) |
| ScH$_2$ + 2 LiBH$_4$ → ScB$_2$ + 2 LiH + 4 H$_2$ | 8.91 | 49.7 |
| TiH$_2$ + 2 LiBH$_4$ → 2 LiH + TiB$_2$ + 4 H$_2$ | 8.63 | 22.2 (o) 14.1 (h) |
| LiBH$_4$ + C → LiBC + 2 H$_2$ | 11.95 | 43.6(o) 35.3(h) |
| 2 LiNH$_2$ + C → Li$_2$CN$_2$ + 2 H$_2$ | 6.97 | 31.4 |
| ScH$_2$ + 2 LiBH$_4$ + C → ScB$_2$C + 2 LiH + 4 H$_2$ | 7.86 | 52.9(o) 44.8(h) |
| ScH$_2$ + 2 LiBH$_4$ + 2 C → ScB$_2$C$_2$ + 2 LiH + 4 H$_2$ | 7.04 | 52.4(o) 44.3(h) |
| MgH$_2$ + 2 LiBH$_4$ + 2 C → MgB$_2$C$_2$ + 2 LiH + 4 H$_2$ | 8.59 | 55.3(o) 47.2(h) |
| CaH$_2$ + 2 LiBH$_4$ + 2 C → CaB$_2$C$_2$ + 2 LiH + 4 H$_2$ | 7.35 | 59.7(o) 51.6(h) |
| 3 Ca(AlH$_4$)$_2$ + 2 Si → 2 Al$_2$Ca + Al$_2$CaSi$_2$ + 12 H$_2$ | 6.69 | 24.1 |
| 3 Ca(AlH$_4$)$_2$ + 2 Si → 4 Al + Al$_2$Ca$_3$Si$_2$ + 12 H$_2$ | 6.69 | 28.4 |
| 6 Ca(AlH$_4$)$_2$ + 17 MgH$_2$ → Al$_{12}$Mg$_{17}$ + 6 CaH$_2$ + 35 H$_2$ | 6.67 | 35.4 |
| Ca(AlH$_4$)$_2$ + 2 LiH → 2 AlLi + CaH$_2$ + 4 H$_2$ | 6.85 | 33.3 |
| 3 Ca(AlH$_4$)$_2$ + 4 LiH → 4 AlLi + Al$_2$Ca + 2 CaH$_2$ + 12 H$_2$ | 7.17 | 31.8 |

was studied by Luo [8].  The decomposition enthalpy for the 2 $LiNH_2$+$MgH_2$ mixture was found to be 34 kJ/mol of $H_2$.

It has been observed from studies on the $Mg(NH_2)_2$ and LiH systems that different products can be obtained depending upon the starting stoichiometry of the reactants, e.g., Nakamori et al [9] studied $Mg(NH_2)_2$ + 4 LiH → 1/3 $Mg_3N_2$ + 4/3 $Li_3N$ + 4 $H_2$; $Mg(NH_2)_2$ + 8/3 LiH → 1/3 $Mg_3N_2$ + 4/3 $Li_2NH$ + 8/3 $H_2$ was studied by Leng et al [10] and Ichikawa et al [11]. Nakamori et al [9] have observed that increasing the LiH content in the mixture is an effective way to prevent ammonia release; however, the trade off is that the amount of desorbed hydrogen is reduced. The observation that changing the molar ratios of the reactants gives rise to different products lends credence to our prediction that LiMgN may be obtained as a product of $LiNH_2$ and $MgH_2$, as given in (2) and also justifies the reactions given below in reactions (3) and (4).

Two other examples identified by our calculations are:

$$4 \text{ LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_4 + 4 \text{ LiH} + 7 \text{ H}_2 \qquad (3)$$

$$7 \text{ LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_7 + 7 \text{ LiH} + 11.5 \text{ H}_2 \qquad (4)$$

Our DFT calculations predict that $\Delta U_0$ is 69.2 (71.5-75.5) kJ/mol $H_2$ using the orthorhombic form of $LiBH_4$ for the reaction forming $MgB_4$ ($MgB_7$).  The range of enthalpies for the latter reaction is due to the different structures of $MgB_7$ used to account for the vacancies in the crystal structure.

A fifth example involves $CaH_2$:

$$\text{CaH}_2 + 6 \text{ LiBH}_4 \rightarrow \text{CaB}_6 + 6 \text{ LiH} + 10 \text{ H}_2 \qquad (5)$$

Upon completion, this reaction releases 11.7 wt% hydrogen and the DFT-predicted $\Delta U_0$ is 63 kJ/mol of $H_2$.

$Ca(AlH_4)_2$ has high enough gravimetric density to be used for hydrogen storage applications.  Hence, many of the new reactions we considered in Figure 2(a) involve $Ca(AlH_4)_2$.  The predicted DFT reaction enthalpy for the decomposition of $Ca(AlH_4)_2$ via

$$\text{Ca(AlH}_4)_2 \rightarrow \text{CaH}_2 + 2 \text{ Al} + 3 \text{ H}_2 \qquad (6)$$
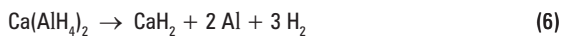
is only $\Delta U_0$=14 kJ/mol $H_2$.  Thus, even though many reactions with superficially attractive reaction enthalpies can be constructed using $Ca(AlH_4)_2$, they are all likely to be metastable pathways with respect to the direct decomposition reaction.  Experimental studies for $Ca(AlH_4)_2$ dehydrogenation show that this compound does not decompose and release $H_2$ until temperatures in excess of 200°C are reached [12].  Even allowing for uncertainties in our DFT calculated reaction enthalpies, the high decomposition temperature suggests that the

decomposition of $Ca(AlH_4)_2$ is kinetically rather than thermodynamically limited.  If the reaction is kinetically limited, it is at least conceivable that more facile reaction pathways with slightly higher reaction enthalpies may exist and therefore be experimentally observable.  This rather speculative concept indicates that it is at least worthwhile identifying a number of these metastable reactions.  Some of these reactions $Ca(AlH_4)_2$ that have reaction enthalpies in the range of 15-40 kJ/mol $H_2$ and release more than 6.5 wt% $H_2$ on completion have been listed in Table 1.  It is important to reiterate that on purely thermodynamic grounds we do not expect these reactions to be observable.  Nevertheless, experiments with $Ca(AlH_4)_2$ may be worthwhile, as there is a small probability of identifying interesting metastable reactions.

Hydrides of transition metals are usually not considered for hydrogen storage applications owing to their low gravimetric densities.  We have applied our computational methods to reactions involving the hydrides of Sc, Ti, and V, and this process has yielded some interesting reactions.  The hydrides of Sc are known to exist in the form of $ScH_2$ and $ScH_3$, but the structure of $ScH_3$ is not known exactly [13].  As a result, we have used the dihydride in our calculations.  The hydrides of Ti exist as mono- and dihydrides [14,15]. For V, hydrides exist in the form of $VH_2$ and $V_2H$ [16-20].  Experimentally, $V_2H$ is known to exist in two different crystal structures [18,19].  We have considered both of these in our calculations.

The potential destabilization schemes we have considered involving hydrides of Sc, Ti and V using combinations of the materials typically release relatively small amount of $H_2$ at completion, but there are several that involve more than 6.5 wt% $H_2$.  Almost all the reactions involving $ScH_2$ we have considered hold little promise for high capacity reversible storage of $H_2$.  The positive outcome of this screening exercise, however, is that two reactions are predicted to have favorable properties.  The first of these [21] is:

$$\text{ScH}_2 + 2 \text{ LiBH}_4 \rightarrow \text{ScB}_2 + 2 \text{ LiH} + 4 \text{ H}_2 \qquad (7)$$

a reaction that releases 8.91 wt% $H_2$ on completion.  On a volumetric basis, this reaction stores 98.9 kg $H_2$/m³. This reaction is analogous to the destabilization of $LiBH_4$ with $MgH_2$ that has been studied experimentally by Vajo et al [22].  The calculated heat of reaction for reaction (7) is $\Delta U_0$ = 49.7 kJ/mol $H_2$ based on ortho-$LiBH_4$.  The reaction free energy as a function of temperature has been computed using the phonon density of states approach.  The resulting van't Hoff plot for this reaction is shown in Figure 1.  We estimate that the accuracy in the free energy calculations is ±10 kJ/mol $H_2$.  We, therefore, plot the predicted vapor pressures as the solid symbols and the estimated pressures based on the estimated errors as open symbols.
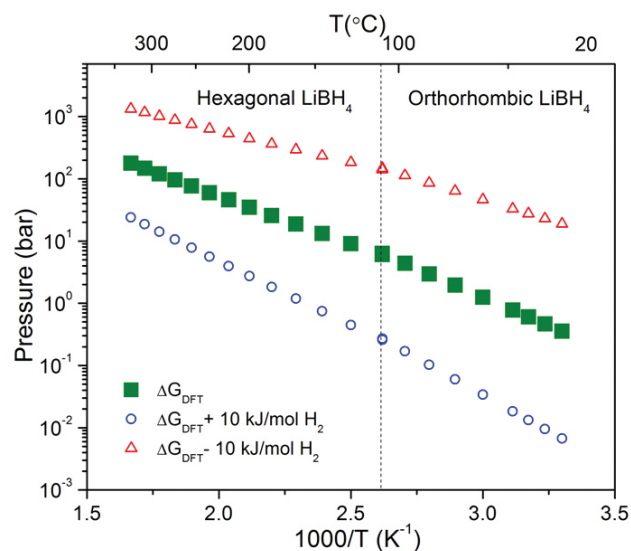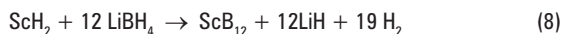
**FIGURE 1.** van't Hoff Plot from DFT Calculations for $ScH_2 + 2\ LiBH_4 \rightarrow ScB_2 + 2\ LiH + 4\ H_2$ (The open symbols represent estimates for the uncertainty in the calculations. For details, see the text.)

The second promising reaction identified based on our initial calculations also involves $ScH_2$ and $LiBH_4$:

$$ScH_2 + 12\ LiBH_4 \rightarrow ScB_{12} + 12LiH + 19\ H_2 \tag{8}$$

In this case, we calculated $\Delta U_0 = 74.1$ kJ/mol $H_2$ using ortho-$LiBH_4$. This enthalpy is only marginally smaller than the DFT-computed enthalpy for direct decomposition of $LiBH_4$ [7, 23, 24]. More importantly, this result suggests that these reaction products are more likely to initially react to form $ScB_2$ via reaction (7) until the $ScH_2$ is consumed. On this basis, we exclude the reaction forming $ScB_{12}$ from further consideration.

Most reactions we have considered including hydrides of Ti also do not satisfy the gravimetric density requirements. Our DFT calculations indicate that direct decomposition of $TiH_2$ requires $\Delta U_0 = 142.7$ kJ/mol $H_2$. Using $TiH_2$ to destabilize $LiBH_4$ can give rise to two types of reactions: the first one has TiB and LiH as products along with $H_2$ and the second one is again analogous to reaction studies by Vajo et al [22] giving $TiB_2$ and LiH as products. For the reaction,

$$TiH_2 + 2\ LiBH_4 \rightarrow 2\ LiH + TiB_2 + 4\ H_2 \tag{9}$$
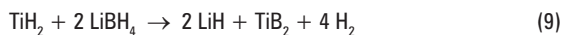
$\Delta U_0$ using the orthorhombic form of $LiBH_4$ is 22.2 kJ/mol $H_2$, while for the reaction

$$TiH_2 + LiBH_4 \rightarrow LiH + TiB + 2.5\ H_2 \tag{10}$$
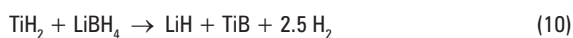
$\Delta U_0$ is 43.7 and 162 kJ/mol $H_2$ for the orthorhombic and cubic forms of TiB, respectively. As reasoned above for the case of $ScH_2$ we suggest that the reaction of $TiH_2$ and $LiBH_4$ would proceed via pathway of reaction shown in

reaction (9). Using TiH as a reactant also does not yield any promising reactions.

Considering the reactions with hydrides of V with other elements and hydrides do not yield any promising reactions. Although in this set of reactions there are a few which satisfy our screening gravimetric and thermodynamic requirements, we always also observed a lower energy pathway to form more stable alternative products. This is similar to the $Ca(AlH_4)_2$ systems discussed above. An example can be seen with the reaction:

$$VH_2 + 4\ LiNH_4 + 3\ LiH \rightarrow Li_7N_4V + 6.5\ H_2 \tag{11}$$

A $\Delta U_0$ value of ~28 kJ/mol $H_2$ and gravimetric density of 7.78% makes it a possible candidate for further thermodynamic analysis. But our database of reactions suggests that $VH_2$ and $LiNH_2$ can also react via $VH_2 + LiNH_4 \rightarrow VN + LiH + 1.5\ H_2$. This reaction has $\Delta U_0$ of -5.4 kJ/mol $H_2$ which makes it thermodynamically more favorable than reaction (11). This indicates that all of the $VH_2$ would initially react with $LiNH_2$ and we would be left with excess $LiNH_2$ and LiH in the system if this reaction were attempted.

We present the van't Hoff plot for a destabilized reaction involving graphite as the destabilizing agent in Figure 2. The reaction is:

$$LiBH_4 + C \rightarrow LiBC + 2\ H_2 \tag{12}$$

It has a gravimetric density of 11.95 wt% and an estimated reaction enthalpy of 43.6 (35.3) kJ/mol $H_2$ for the orthorhombic (hexagonal) $LiBH_4$ phase.
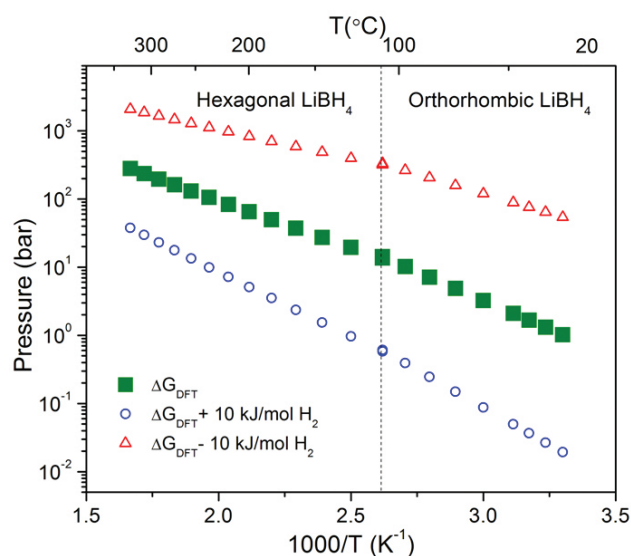


**FIGURE 2.** van't Hoff Plot for the Destabilization Reaction $LiBH_4 + C \rightarrow LiBC + 2\ H_2$ from DFT Calculations

We have computed the change in reaction enthalpy for selected hydride systems upon doping with different elements.  Doping can produce either an increase or a decrease in the reaction enthalpy.  This is illustrated in Figure 3 for the reaction

$$Sc_{1-x}X_xH_2 + 2\,LiBH_4 \rightarrow Sc_{1-x}X_xB_2 + 2\,LiBH + 4\,H_2 \qquad (13)$$
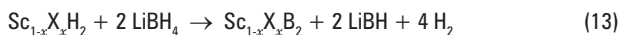
where X is a dopant atom of either Mg or Ti.  As can be seen in Figure 3, doping with Mg always results in an increase of reaction enthalpy, whereas doping with Ti decreases the enthalpy.  The first criterion for a successful dopant material is that the dopant must affect a favorable change in the reaction enthalpy.  That is, the dopant must decrease the reaction enthalpy for materials that are too stable or must increase the enthalpy for materials that are not sufficiently stable.  This is a necessary but not sufficient condition.  The doped materials must also be thermodynamically stable with respect to phase segregation.  For example, $Sc_7H_{16}Ti$ must be thermodynamically stable with respect to segregation into $ScH_2$ and $TiH_2$ phases.  At the same time, $Sc_7B_{16}Ti$ must be stable with respect to segregation into $ScB_2$ and $TiB_2$ phases.  We have computed the configurational and vibrational entropies associated with all components for several systems [25].  For screening purposes, inclusion of only the configurational entropy is sufficient.  The configurational entropy is very easy to compute, whereas vibrational entropic contributions are extremely computationally demanding.  We have found that most doped systems we have investigated are not stable with respect to phase segregation.  Ti doped $ScH_2$ is predicted to be stable, however.  But this material is not of practical interest because of the very high cost of Sc.
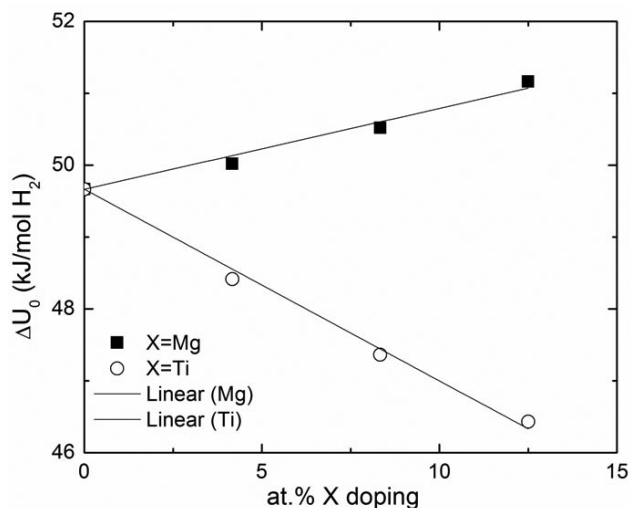
The kinetics of hydrogenation and dehydrogenation reactions are of critical importance for practical storage of hydrogen onboard fuel cell vehicles.  The study of solid-phase kinetics is an extremely challenging task.  Gas phase reactions have been studied extensively with *ab initio* methods and catalytic reactions on solid surfaces are now routinely investigated with DFT methods.  True solid-phase reactions involving phase transformations and material transport, however, have not been studied to any appreciable extent using first principles methods.  We have begun to study reaction kinetics by examining initial reactions on surfaces.  Our efforts have been directed at two different problems so far.  We have examined the initial hydrogenation of $Mg_2Si$ surfaces to form $MgH_2$ [26].  We have also begun to study the differences in reactivities of LiH, NaH, and KH surfaces.  In both of these cases we begin by finding the surfaces with the lowest surface free energies and then study reactions of various atoms or molecules on these surfaces.

Our calculations have helped to identify possible reasons for the experimentally observed difficulty in hydrogenating bulk $Mg_2Si$.  MHCoE colleagues have studied the reaction

$$Mg_2Si + 2\,H_2 \rightarrow 2\,MgH_2 + Si \qquad (14)$$

and have not been able to observe formation of $MgH_2$, although this phase is thermodynamically favored.  Our calculations indicate two problems with this reaction.  Firstly, we have found that the $Mg_2Si$ surface is extremely susceptible to oxidation.  Moreover, the oxidized surface is resistant to hydrogenation.  We have computed the dissociation pathway for $H_2$ on the surface of clean $Mg_2Si$ and also on the oxidized $Mg_2Si$ surface.  Our calculations indicate that $H_2$ can readily dissociate on the clean $Mg_2Si$ surface at room temperature, having a reaction barrier of about 40 kJ/mol.  Dissociation of $H_2$ on the oxidized surface, however, has a barrier of about 180 kJ/mol.  Moreover, the dissociation leads to Si-O-H bonds, which are not related to formation of a $MgH_2$ phase.  The dissociation pathway for $H_2$ on the oxidized $Mg_2Si$ surface is plotted in Figure 4.  Insets in the figure show initial, intermediate, transition, and final states along the reaction pathway.  The second insight gained from our DFT calculations is that hydrogenation of the clean $Mg_2Si$ surface may result in a passivated surface, comprised of Si-H bonds rather than Mg-H bonds.

## Conclusions and Future Directions

Plans for future work include the following:

- **Thermodynamics of confined metal hydrides.** MHCoE partners at HRL and Stanford are experimentally studying the effect of confinement on the thermodynamics and kinetics of complex
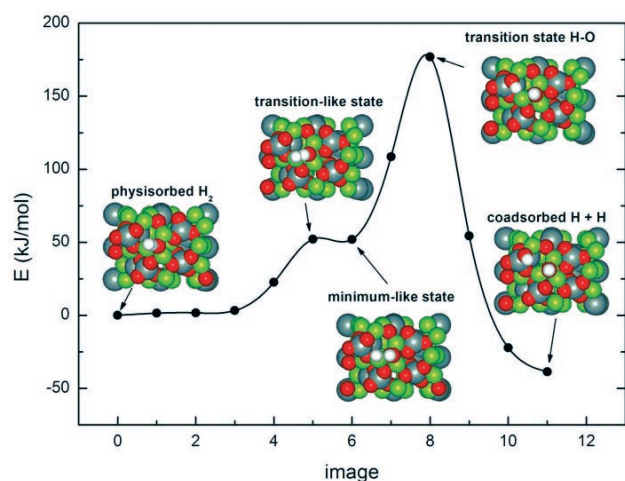
**FIGURE 3.** $\Delta U_0$ for $Sc_{1-x}X_xH_2 + 2\,LiBH_4 \rightarrow Sc_{1-x}X_xB_2 + 2\,LiH + 4\,H_2$ with X = Mg or Ti.  Straight lines are least squares fits to the DFT data.

**FIGURE 4.**  A Dissociation Pathway for $H_2$ on the Oxidized $Mg_2Si$ Surface as Computed by Density Functional Theory

metal hydrides.  They are currently encapsulating $LiBH_4$ within carbon aerogels.  We can use DFT to compute thermodynamic information that will complement this experimental work.  We can study the thermodynamics of thin films as a way to mimic the nanophase confined systems being studied experimentally.

- **Fundamental kinetic studies.**  We plan to continue our work with the MHCoE Theory Group to study the kinetics of hydrogenation and dehydrogenation of selected systems.  It is critical that we make some fundamental progress on this difficult topic because it is ultimately insufficient to consider only thermodynamics of complex hydrides.

- **Thermodynamics of doping.**  We plan to continue our recent work on using DFT to screen dopants for thermodynamic stability relative to phase segregation and for the changes in the heat of reaction for dehydrogenation.  These calculations will provide specific predictions that can be tested by MHCoE experimental partners.

- **Automated screening of reactions.**  We will use our newly developed tool for identifying all possible reaction pathways to identify new reaction schemes.  We will perform detailed free energy calculations on the most promising candidate reactions and encourage experimental partners to test those that have the greatest potential.

- **Project support.**  We will continue to provide support for specific projects as collaborations with experimental groups continue to develop.  Specific projects that we are or may be involved with are listed below:

  - Doping of $Mg(BH_4)_2$ being investigated by J.-C. Zhao at GE.

  - Doping of $Ca(BH_4)_2$ being studied by Ewa Ronnebro at Sandia.

  - Collaborate with Zak Fang to help him identify materials involved in the LiMgN system he is investigating.

  - Alane regeneration project, collaboration with Craig Jensen and others, and in collaboration with Mark Allendorf in the MHCoE theory group.

## Special Recognitions & Awards/Patents Issued

**1.**  One of the papers that appeared in print in 2007, 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), was chosen by the editors of Science Magazine as one of their "Editors' Choice" articles.  See *Science*, Volume 315, Number 5819, 23 March 2007, page 1638.

This same paper was one of the 10 most viewed articles for March in Phys. Chem. Chem. Phys.

## FY 2007 Publications/Presentations

**1.**  S. V. Alapati, J. K. Johnson, and D. S. Sholl, "Stability Analysis of Doped Materials for Reversible Hydrogen Storage in Destabilized Metal Hydrides,"submitted to *Physical Review B*, (2007).

**2.**  B. Dai, D. S. Sholl, and J. K. Johnson, "First Principles Investigation of Adsorption and Dissociation of Hydrogen on $Mg_2Si$ Surfaces," *Journal of Physical Chemistry C*, 111(18), 6910-6916 (2007).

**3.**  S. V. Alapati, J. K. Johnson, and D. 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).

**4.**  S. V. Alapati, J. K. Johnson, and D. S. Sholl, "First principles screening of destabilized metal hydrides for high capacity $H_2$ storage using scandium," *Journal of Alloys and Compounds*, in press (2007).

**5.**  S. V. Alapati, J. K. Johnson, and D. S. Sholl, "Predicting Reaction Equilibria for Destabilized Metal Hydride Decomposition Reactions for Reversible Hydrogen Storage," *Journal of Physical Chemistry C*, 111, 1584-1591 (2007).

**6.**  S. V. Alapati, J. K. Johnson, and D. S. Sholl, "Identification of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations," *Journal of Physical Chemistry B*, 110, 8769-8776 (2006).

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**6.**  S. V. Alapati, J. K. Johnson,  D. S. Sholl, *Phys. Chem. Chem. Phys.*  *9*, 1438, (2007).

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**26.**  B. Dai, D. S. Sholl, J. K. Johnson, *J. Phys. Chem. C*, *111*, 6910 (2007).