



First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

J. Karl Johnson & David S. Sholl

University of Pittsburgh, Georgia Institute of Technology

12 June 2008



Project ID #
ST33

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 60%

Budget

- Requested total: \$1.05M (DOE)
- Cost sharing: \$0.33M
- FY06 \$175K (DOE)
- FY07 \$218K (DOE) requested

Barriers

- A. System weight and volume
- E. Charging/discharging rates (kinetics)
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- Cal Tech, GE, HRL, U. Hawaii, JPL, NIST, Sandia, Stanford, UIUC, U. Utah
- Coordination of theory work within MHCoe through the theory working group

Overall Objectives

- Compute thermodynamics of metal hydride systems
- Compute interfacial properties of hydrides
- Address fundamental processes in hydrogenation

Specific Objectives for FY07-FY08

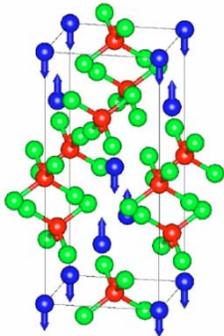
- Develop an automated approach for screening complex hydrides by gravimetric densities and heats of reaction, ΔH .
- Explore nanoparticle thermodynamics through calculation of surface energies and Wulff construction calculations.
- Screen doped hydrides for phase stability.
- Compute surface reactions as relating to poisoning and initial kinetics of hydrogenation/dehydrogenation.
- Investigate the structure and thermodynamics of $\text{Mg}(\text{BH}_4)_2$.

Milestones

Month/Year	Milestone or Go/No-Go Decision
Feb-07 	<p>Identify single-step reactions having acceptable hydrogen gravimetric densities and thermodynamics using the automated free energy search procedure. Paper has now been published: <i>J. Phys. Chem. C</i>, 112, 5258-5262 (2008).</p>
Jun-08	<p>Identify and classify multi-step and metastable reactions having acceptable hydrogen capacities and thermodynamics using the automated free energy search procedure. Interesting multi-step reactions have been identified. More calculations and analysis required.</p>
Sept-08	<p>Investigate dehydrogenation/hydrogenation pathways for Mg(BH₄)₂ in concert with experimental efforts. Experiments have identified Mg(B₁₂H₁₂) as a possible amorphous phase intermediate.</p>

Plane wave Density Functional Theory (DFT) is well suited to treating hydrogen interactions with metals^{1,2}

UASP
b-initio
package
simulation



Planewave PAW Pseudopotentials

- Gradient-corrected DFT (PW91)
- Convergence reached with energy cutoff and k -space sampling
- All solid state structures fully optimized within experimental space group

PHONON code³ direct lattice method for finite temperature thermodynamics

→ C_v and Entropy S



Changes in *Gibbs Free Energy* ΔG

Enthalpy Changes at $T=0$ K (neglecting zero point energies) ΔU_0

1. Kamakoti et al., *Science*, **307**, 569 (2005)
2. Wolverton et al., *Phys. Rev. B*, **69**, 144109 (2004)
3. K. Parlinski, Software PHONON (2005)

Alapati, Johnson, and Sholl, *J. Phys. Chem. C* **111**, 1584 (2007);
Phys. Chem. Chem. Phys. **9** 1438 (2007)

Previously,

DFT calculations used to give energies of ~200 potentially relevant crystal structures

Reaction enthalpies of hundreds of possible reactions calculated (but list of reactions developed in an ad-hoc manner)

Free energy calculations performed for most interesting reactions, predicting van't Hoff curves

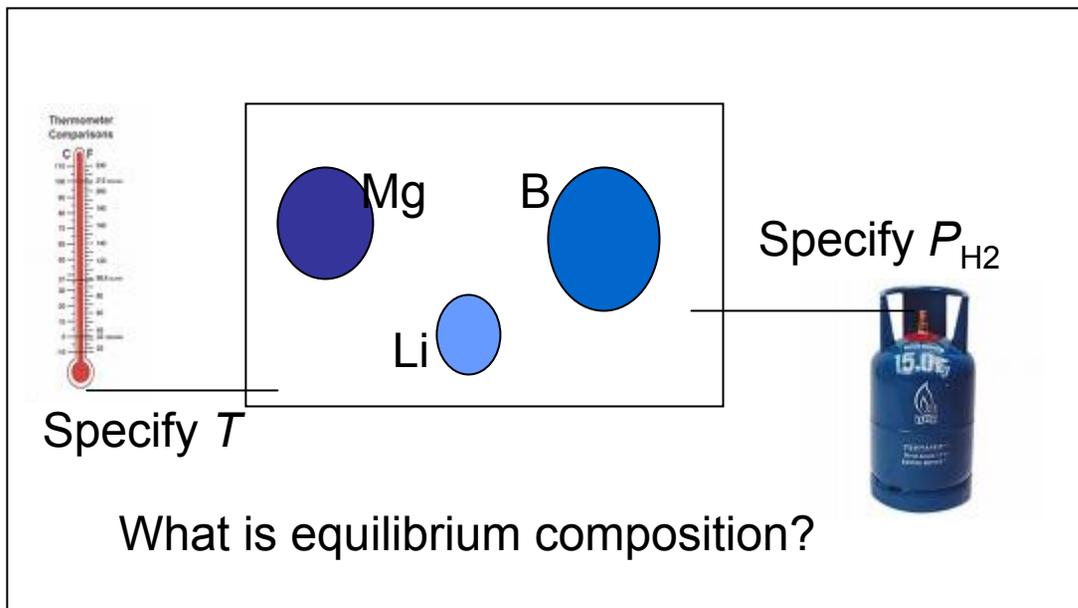
Multiple new reactions (not previously examined in literature) predicted to have favorable reaction thermodynamics

in response to feedback from Tech Team and DOE Reviewers.....

Major FY2008 Reaction Screening Accomplishments:

We can now screen reactions with account of multistep character, study reactions in a more comprehensive and rigorous way and provide more accurate prediction of single-step reactions.

Adapted from Akbarzede, Ozoliņš, Wolverton, *Adv. Mater.* **19**, 3233 (2007)



Library of possible compounds

Mg, B, Li, H_2
 MgH_2 , MgB_2 , MgB_4 , MgB_7
 LiH , $LiBH_4$, Li_5B_4 , $Mg(BH_4)_2$

- At fixed T , minimize grand potential, Ω , via linear programming to obtain equilibrium composition
- Ramp T to detect all possible reactions over a specified range

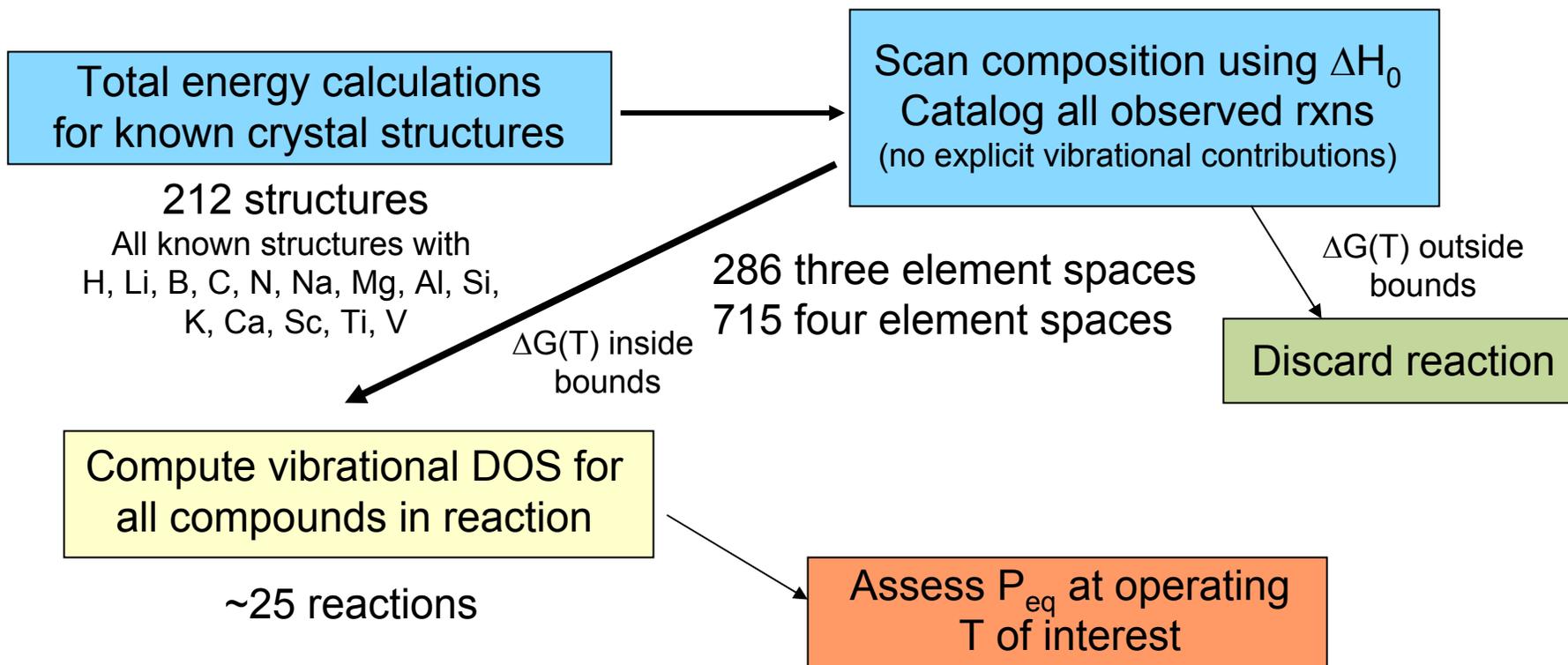
Example:



Step 1 T_1

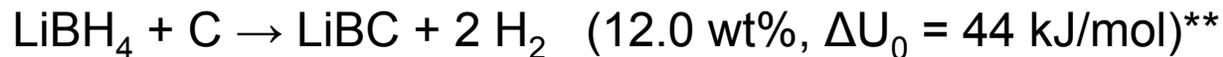
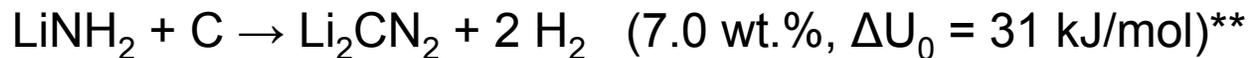
Step 2 T_2

Step 3 T_3



Over 16 million discrete compositions are screened in this way

A number of “interesting” reactions listed in our previous papers are still predicted to be viable single step processes



*Reaction being studied experimentally by Ahn(Cal Tech)/Vajo(HRL)/Bowman(JPL)

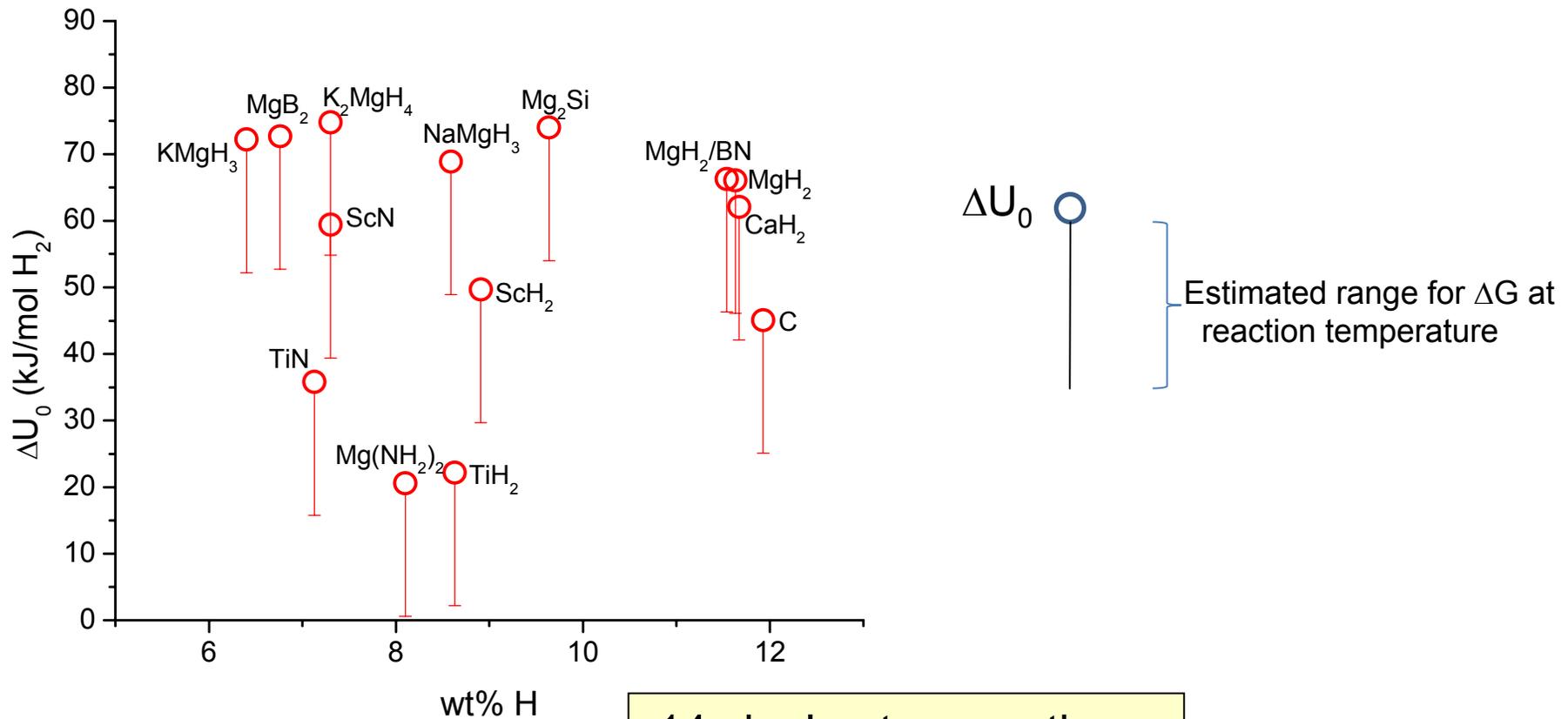
**Reactions being studied experimentally by Fang(Utah)

Results for Single-Step Reactions with LiBH_4

Alapati, Johnson, & Sholl, *J. Phys. Chem. C*, **112**, 5258 (2008).

Only reactions with $15 < \Delta U_0 < 75 \text{ kJ/mol H}_2$ and $> 6 \text{ wt.}\% \text{ H}$ retained

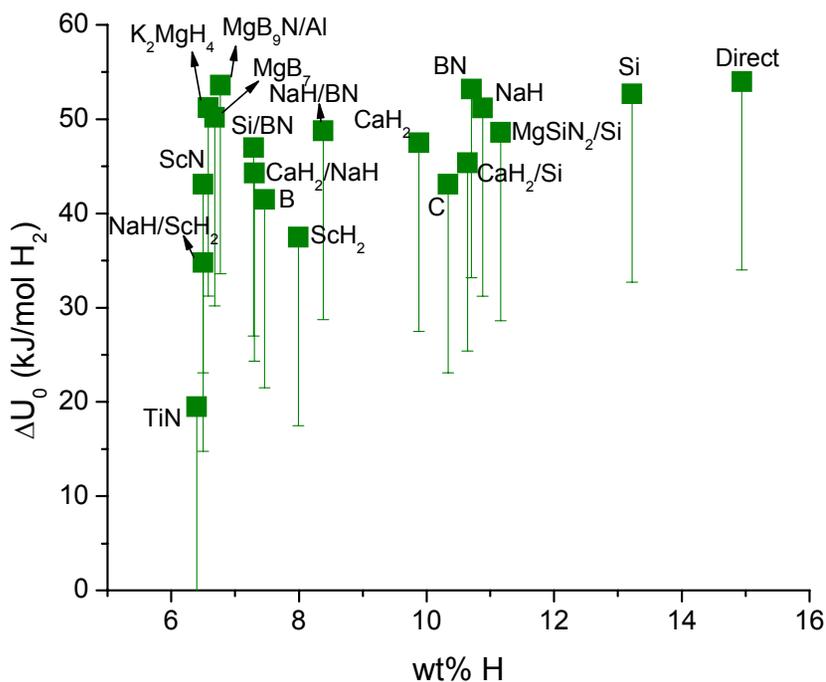
Example: $6 \text{ LiBH}_4 + 2 \text{ TiN} \rightarrow 6 \text{ LiH} + 2 \text{ TiB}_2 + 2 \text{ BN} + 9 \text{ H}_2$, 7.1 wt.% H, $\Delta U_0 = 36 \text{ kJ/mol}$



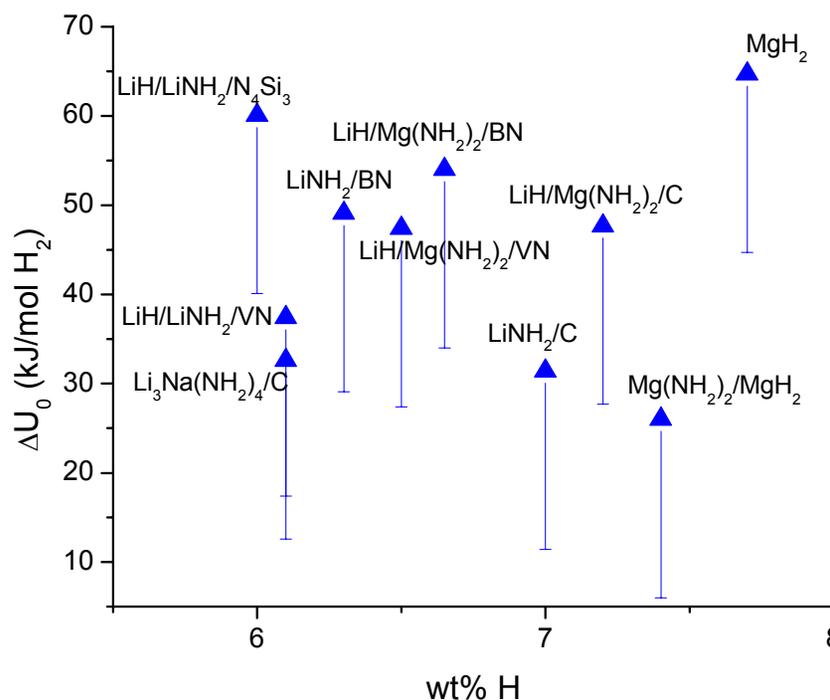
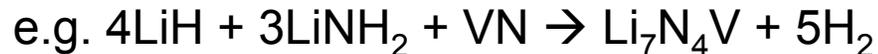
14 single-step reactions identified involving LiBH_4

Alapati, Johnson, & Sholl, *J. Phys. Chem. C*, **112**, 5258 (2008).

Mixtures including $\text{Mg}(\text{BH}_4)_2$

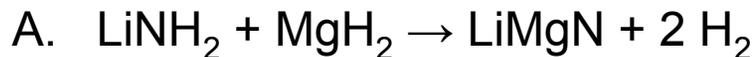


Mixtures not including LiBH_4 or $\text{Mg}(\text{BH}_4)_2$



Identified 43 single step reactions with
> 6 wt% H and $15 < \Delta U_0 < 75$ kJ/mol H_2

A number of “interesting” reactions listed in our previous papers are now known to proceed by more complicated multistep pathways....

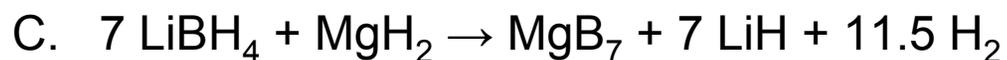
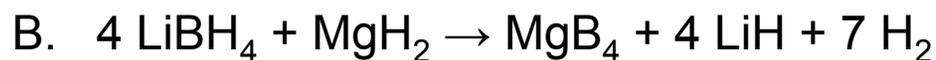


-- Forms $0.5 \text{Mg}(\text{NH}_2)_2 + 0.5 \text{MgH}_2 + \text{LiH}$ on rehydrogenation

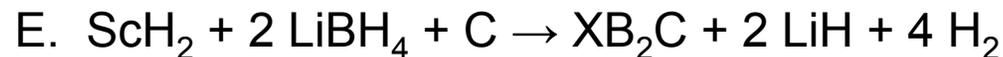
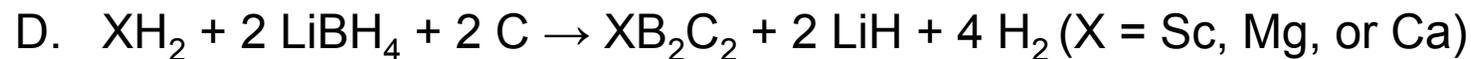
Predicted Possible Dehydrogenation Paths starting from LiH , $\text{Mg}(\text{NH}_2)_2$, LiNH_2



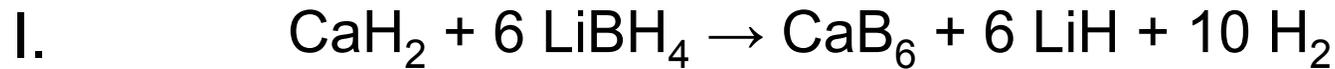
Similar multi-step pathway identified by Akbarzede, et al., Adv. Mater. 19, 3233 (2007)



} Both reactions proceed by multistep paths (this situation also identified by Ursula Kattner using CALPHAD)



Our predictions are motivating experimental studies outside MHCoE:



Experiments: Goudy et al. (unpublished), P_{eq}
Pinkerton et al. (*J. Alloys Compds.*, in press), ΔH

Theory predicts experimentally observed P_{eq} and ΔH with good accuracy



Experiments by Hanada, et al., *J. Phys. Chem. C*, **112** 131 (2008).

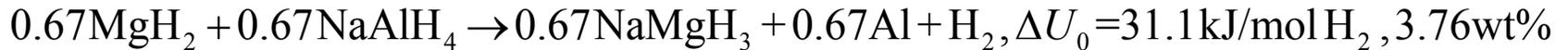
Experiments and theory both show a multistep process:



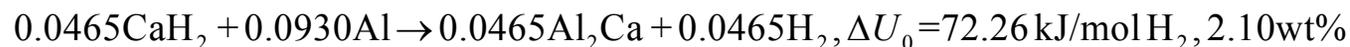
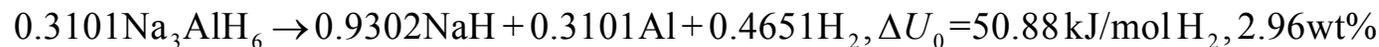
Theory predicts one more reaction at higher T:



Two examples shown below – many others identified

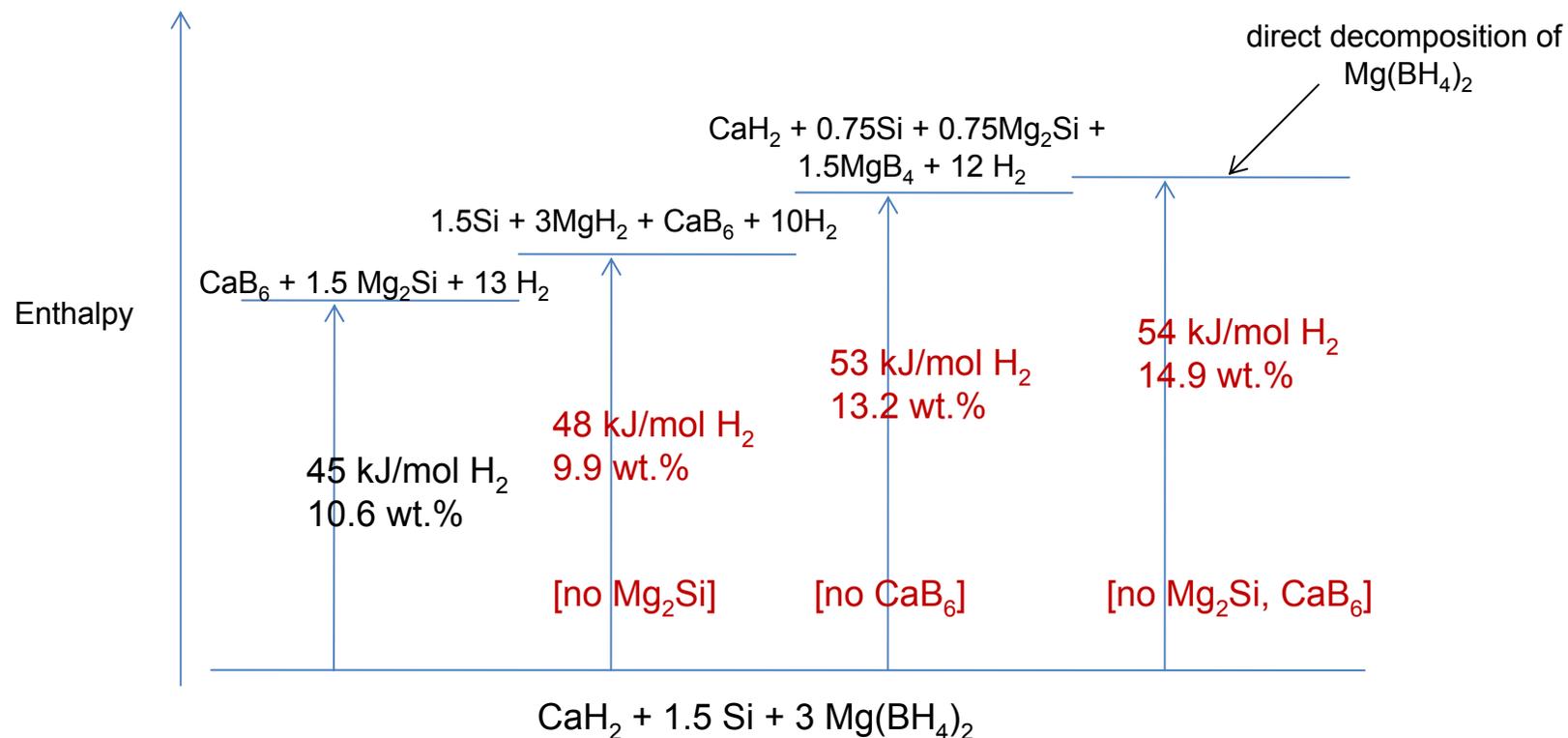


**Thermodynamically reasonable
steps 6.67 wt% total**



**All three steps within thermodynamic
criterion; 8.8 wt% total**

We have extended our thermodynamic analysis to consider metastable paths



These results are with 0 K enthalpies – ordering could change when full free energy is considered (“entropic stabilization”). Of 43 single-step reactions, 25 have one (or more) alternate pathways within 10 kJ/mol H_2 other than direct decomposition of one reactant

Multiple pathways need to be considered!

Our calculations are based on a catalog of known compounds. If a reaction involves a previously unknown compound, our methods cannot describe it.

-- Implication: Aggressive efforts to identify crystal structures of new compounds are vital

Our results are for thermodynamic equilibrium only. They give no information about reaction kinetics or choice of catalysts.

-- Implication: New insights and experiments are needed to understand which reactions may be kinetically feasible or promoted by catalysts

Our methods do not consider gas-phase products other than H₂.

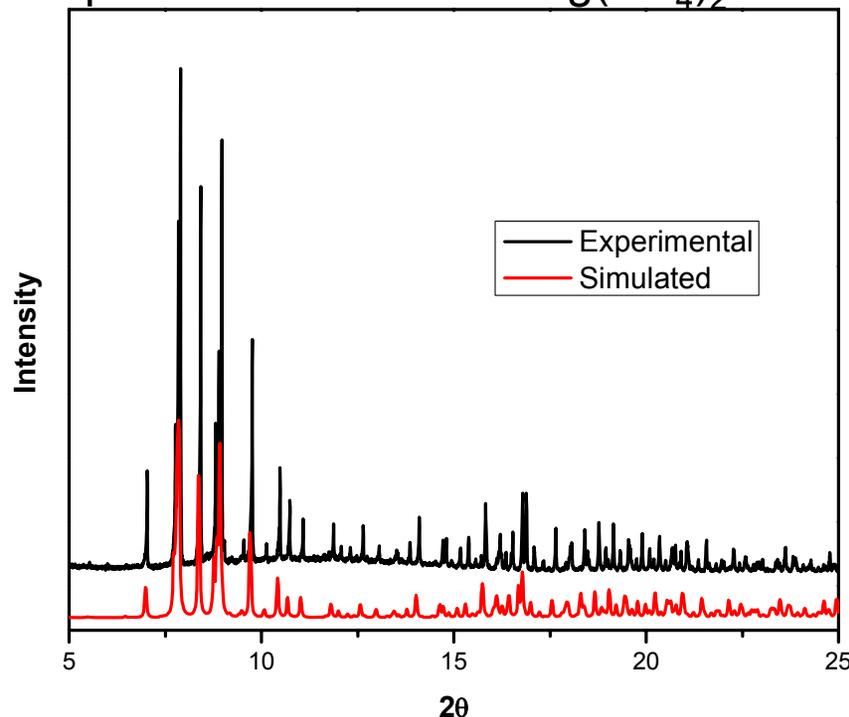
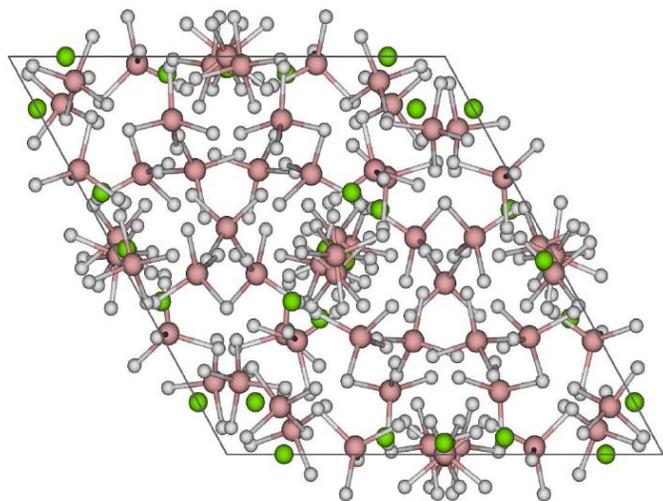
-- Implication: Methods should be extended to allow consideration of gas-phase contaminants (NH₃, CH₄, B₂H₆...)

These results include only stoichiometric compounds, so doped materials are not included as candidate materials.

-- Implication: CALPHAD and detailed DFT approaches should be used to assess possible doping strategies for promising systems

See Alapati, Johnson, & Sholl, *Phys. Rev. B* **76**, 104108 (2007)

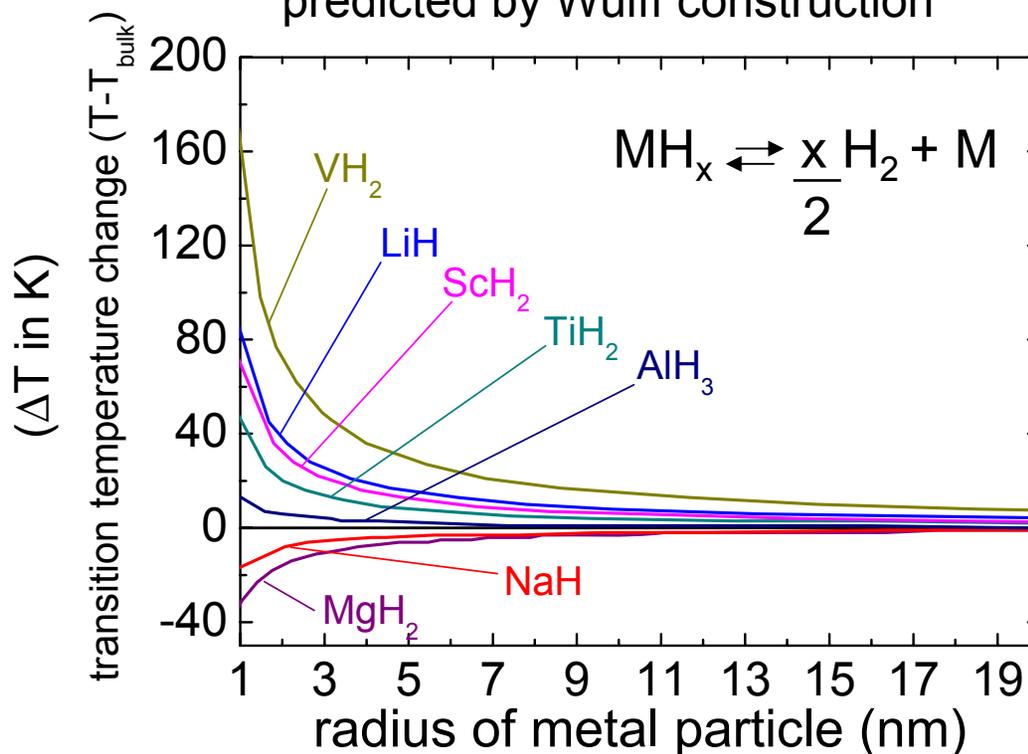
The unit cell of the optimized low temperature structure of Mg(BH₄)₂ with P6₁22 space group.



- Calculations complement experimental work by MHCoe partner GE. Zhao et al., *Acta Crystallogr., Sect. B: Struct. Sci*, **B63**, 561 (2007).
- DFT optimization of crystal structure identified a higher symmetry structure, slightly lower in energy. Computed XRD patterns in good agreement with experiments. Dai et al., *J. Phys. Chem. C*, **112**, 4391-4395 (2008).
- Calculations provide insight into energetics of competing structures.

Kim, Dai, Johnson & Sholl, in preparation

DFT used to predict surface energy contributions to reaction thermodynamics of simple hydrides for nanosized particles with equilibrium crystal shape predicted by Wulff construction



Small particles having
increased ΔT ,
 \therefore increased rxn ΔH

Small particles having
decreased ΔT ,
 \therefore decreased rxn ΔH

Thermodynamic effects are small for free particles with radius > 5 nm

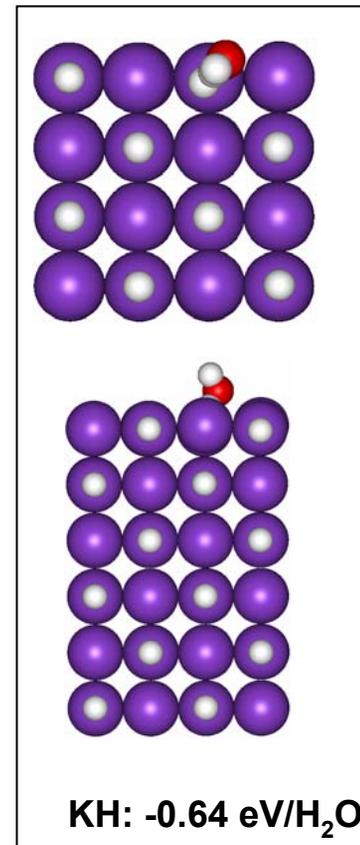
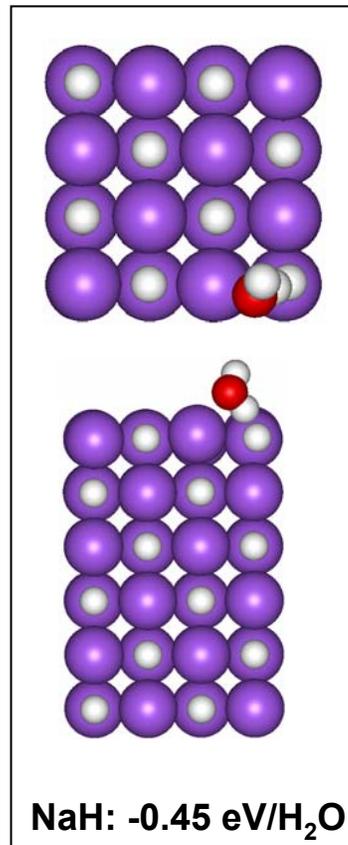
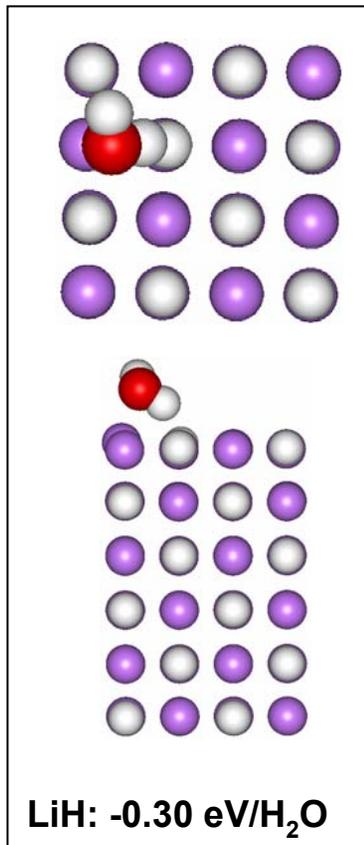
Metal alanates: MAIH_4 (M = Li, Na, K)



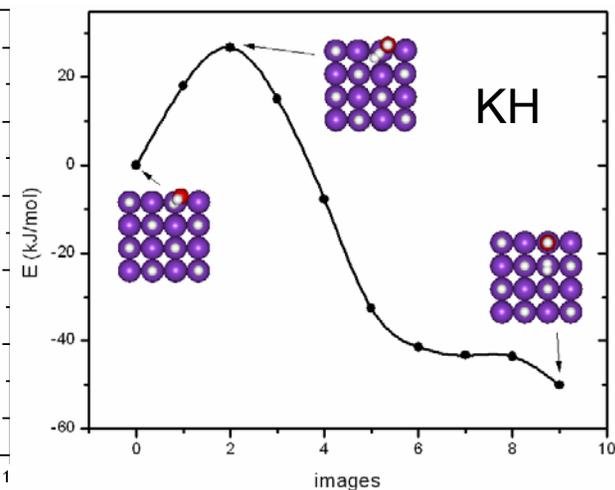
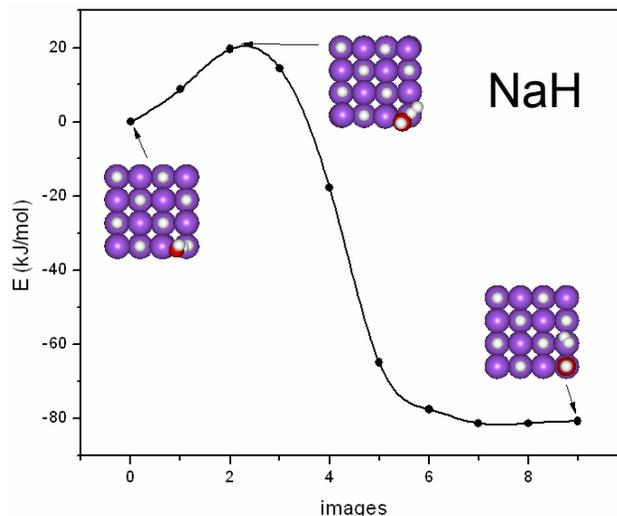
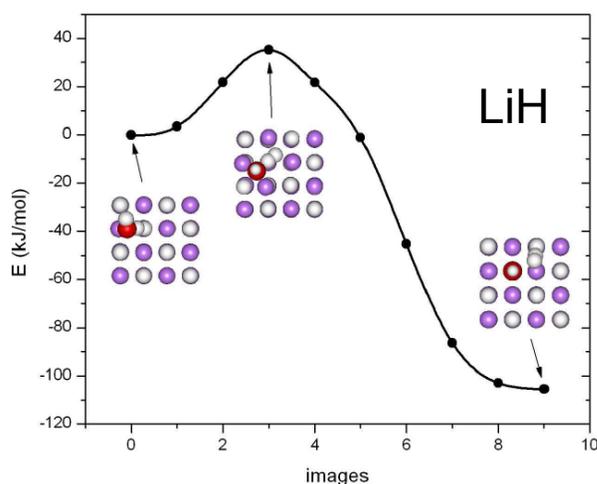
The experimental consensus is that second reaction is reversible without catalyst for M = K, reversible with catalyst for M = Na, and not reversible for M = Li.

Our hypothesis is that Al plays a similar role in each system, so differences in reversibility of second reaction are linked to MH/H₂ reactions.

Do differences in poisoning of MH surfaces with O₂ and/or H₂O lead to differences in hydrogenation of MH (+2 Al)?



- H₂O weakly adsorbs on LiH, NaH, KH surfaces, but does not dissociate without a barrier.
- DFT MD at 600-700 K shows that H₂O will dissociate on the LiH, NaH and KH surface to form bound OH and H₂ in the gas phase.



Turnover frequency (300 K, including ZPE, s⁻¹site⁻¹)

9.9×10^8

4.0×10^{10}

6.3×10^9

Do differences in poisoning of MH surfaces with O₂ and/or H₂O lead to differences in hydrogenation of MH (+2 Al)?

Our results do not support this idea – theory indicates that reaction of H₂O with every material is rapid

Future Work

- **FY 2008**
 - Finalize reaction screening including multistep and metastable reactions
 - Prioritize with experimental input plan for action on identified reactions
 - Continue work on surface/nanosize effects to complement experiments
- **FY 2009**
 - Extend thermodynamic screening activities to include minority gas-phase contaminants
 - Continue support of experimental efforts in interpretation of structures and kinetics for most promising reactions

- **Relevance:** Theory is a powerful tool for screening candidate materials
- **Technical Accomplishments:**
 - Thermodynamics of millions of possible reaction compositions have been predicted
 - Most reactions discarded as thermodynamically impractical
 - A set of >40 promising reactions have been identified for experimental exploration
 - Nanoscale surface effects on thermodynamics
- **Future work:**
 - Metastable/multi-step reaction identification
 - Nanosize effects
 - Kinetics and surface reactions
- **Personnel:** Sudhakar Alapati, Bing Dai, Ki Chul Kim, Anant Kulkarni