

First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

J. Karl Johnson

University of Pittsburgh

David S. Sholl

Carnegie Mellon University

16 May 2007

Project ID #
ST17

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 40%

Budget

- Requested total: \$1.38M (DOE)
- Cost sharing: 20%
- FY06 \$175k (DOE)
- FY07 \$218k (DOE) requested

Barriers

- Identify materials with high gravimetric and volumetric densities
- Identify materials with favorable kinetics

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

Objectives

Overall Objectives

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

Specific Objectives for FY06-FY07

- Identify promising complex hydride materials through computational screening of the heat of reaction, ΔH
- Develop an automated approach for identifying all possible compounds from a given set of reactants and products
- Screen doped hydrides for phase stability
- Initiate calculations for ΔH of substituted (doped) complex hydrides, including $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$
- Compute surface reactions as relating to poisoning and initial kinetics of hydrogenation/dehydrogenation
- Contribute to the development of CALPHAD databases for metal hydrides

Approach

We use Plane wave Density Functional Theory (DFT) to calculate thermodynamic properties of candidate hydride materials—DFT is sufficiently accurate to be used for screening

b-initio
VASP
package
simulation

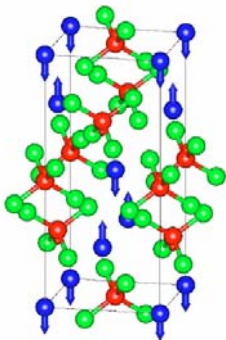


Planewave Pseudopotentials

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

Enthalpy Changes
(neglecting zero point energies)

$$\Delta U_0$$



PHONON code¹ direct lattice method

→ C_V and Entropy S



Changes in *Gibbs Free Energy* ΔG

Accomplishments: New Hydride Reactions Identified

DFT-based Database for Destabilized Hydrides

Alapati, Johnson, and Sholl, *J. Phys. Chem. B* **110** (2006) 8769;
J. Phys. Chem. C **111** (2007) 1584; *Phys. Chem. Chem. Phys.*, **9** (2007) 1438

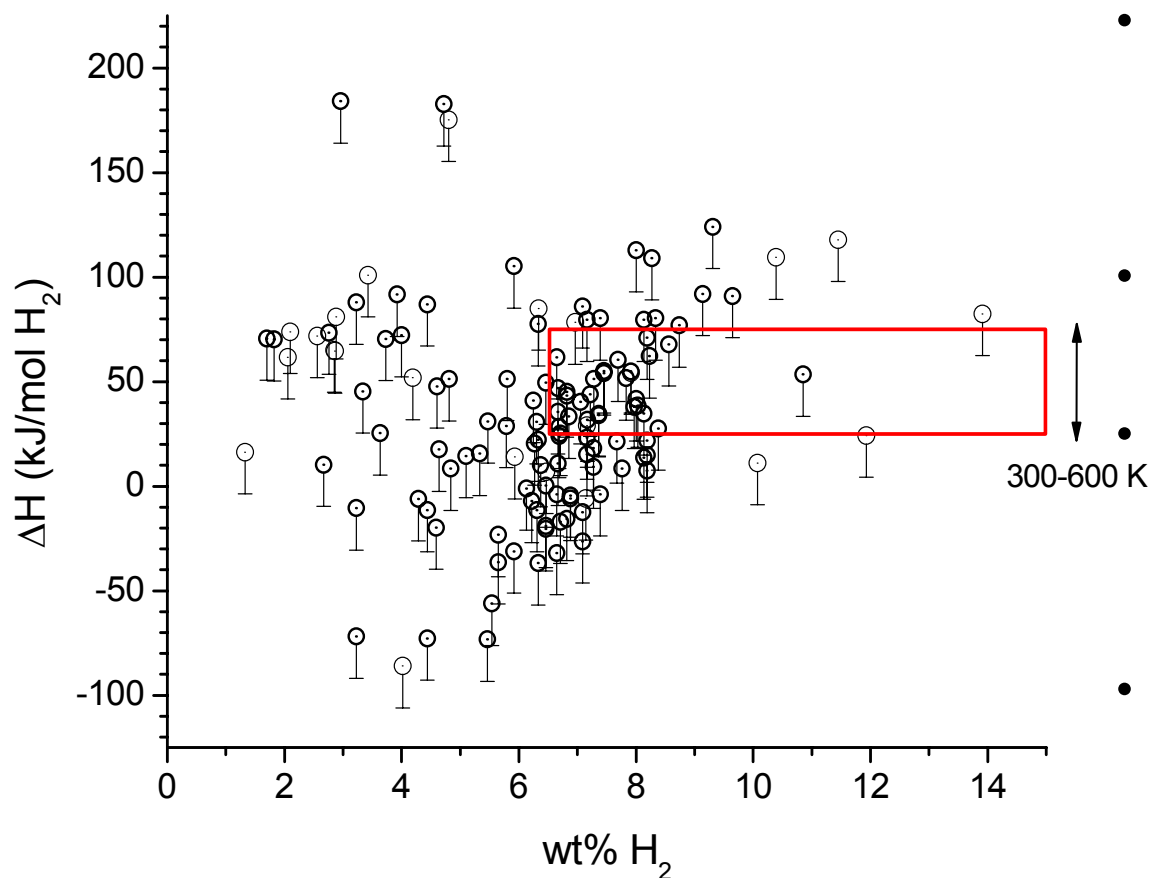
We have optimized the crystal structures of >160 solid materials listed
in Wyckoff, Pearson, or ICSD comprised of
Al, B, Ca, Li, Mg, Si, C, N, Sc, Ti, V or H

Al₁₀V, Al₁₂Mg₁₇, Al₂Ca, Al₂Ca₃N₄, Al₂Ca₃Si₂, Al₂CaSi₂, Al₂Li₃, Al₂Sc, Al₂Ti, Al₃Li, Al₃Li₁₂Si₄, Al₃Li₈Si₅, Al₃Sc,
Al₃Ti, Al₃V, Al₄Li₉, AlB₂, AlH₃, AlLi, AlLi₃N₂, AlLiSi, AlMg₄Si₆, AlN, AlSc, AlSc₂, AlSc₂Si₂, AlTi, AlTi₃,
AlV₃, B₃Ca₄LiN₆, BCa₃N₃, BLi₃N₂, BN, Ca(AIH₄)₂, Ca₁₁N₈, Ca₂HN, Ca₂LiSi₃, Ca₂N, Ca₂N₂BH,
Ca₂N₃V, Ca₃AlN₃, Ca₃N₂, Ca₃N₃V, Ca₅Si₃, CaB₂C₂, CaB₆, CaC₂, CaCN₂, CaH₂, CaLi₂,
CaLiN, CaLiSi₂, CaMg₂, CaMg₂N₂, CaMgSi, CaN₆, CaSi, CaSi₂, Li₁₂Mg₃Si₄, Li₂C₂,
Li₂CN₂, Li₂Si, Li₃AlH₆, Li₃BN₂, Li₃N, Li₃ScN₂, Li₄BN₃H₁₀, Li₄NH, Li₅B₄, Li₅N₃Si,
Li₇N₄V, Li₇Si₂, LiAl(NH₂)₄, LiAlH₄, LiBC, LiBH₄, LiCN, LiH, LiMgN, LiN₃, LiN₃Si₂,
LiNH₂, LiSi, Mg(AIH₄)₂, Mg(NCN), Mg(NH₂)₄, Mg₂C₃, Mg₂Si, Mg₃BN₃, Mg₃N₂, Mg₅Si₆,
MgB₂, MgB₂C₂, MgB₄, MgB₇, MgB₉N, MgC₂, MgCN₂, MgH₂, MgN₂Si, MgSiN₂, N(SiH₃)₃,
N₄Si₃-α, N₄Si₃-β, Sc₂BC₂, Sc₂C, Sc₂C₃, Sc₂V₃Si₄, Sc₃AlC, Sc₃C₄, Sc₄C₃, Sc₅Si₃, ScAl₃C₃,
ScAl₃C₃, ScB₁₂, ScB₂, ScB₂C, ScB₂C₂, ScC, ScH₂, ScN, ScSi, ScSi₂, SiB₆, Ti₂AlN, Ti₂C, Ti₂N,
Ti₃AlC, Ti₃AlC₂, Ti₃AlN, Ti₃SiC₂, Ti₄AlN₃, Ti₅Si₃, Ti₅Si₄, Ti₈C₅, TiB, TiB₂, TiC, TiH, TiH₂, TiN, TiSi, TiSi₂,
V₂B₃, V₂C, V₂H, V₃B₂, V₃Si, V₆C₅, V₆Si₅, VB, VB₂, VC, VH₂, VN, VSi₂

Screening Criteria for New Hydrides

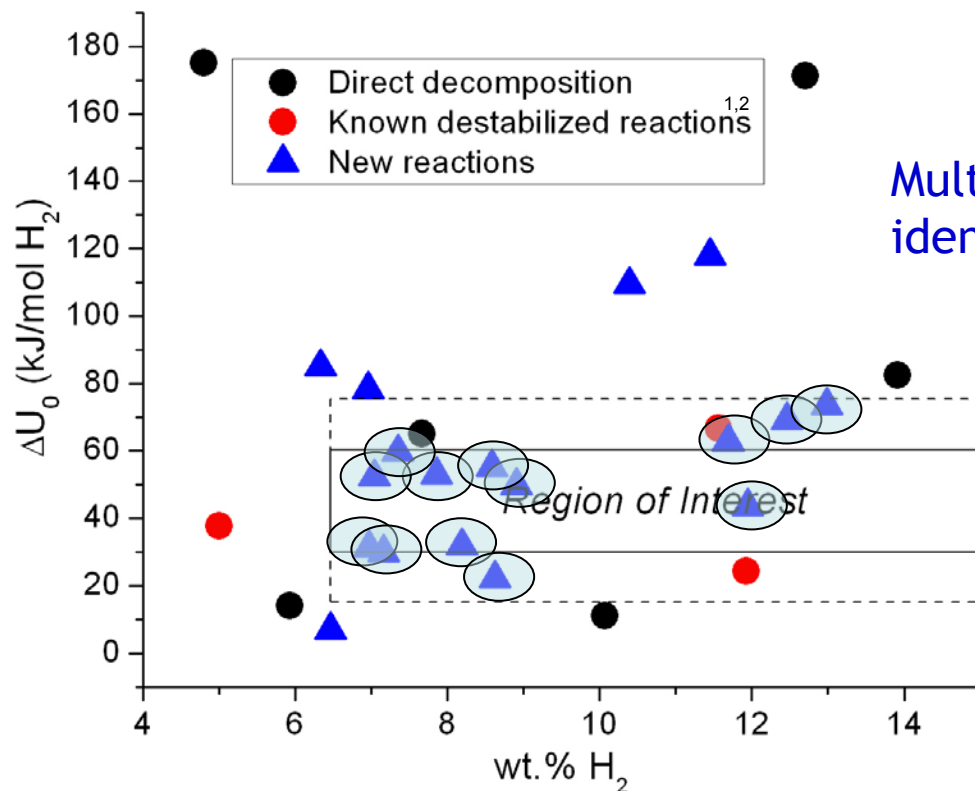
DFT-based Database for Destabilized Hydrides

Alapati, Johnson, and Sholl, *J. Phys. Chem. B* **110** (2006) 8769;
J. Phys. Chem. C **111** (2007) 1584; *Phys. Chem. Chem. Phys.*, **9** (2007) 1438



- We have computed the zero temperature heats of reaction for ~ 350 reactions from the set of ~ 160 solid materials
- The target range for ΔU_0 values is $15 \leq \Delta U_0 \leq 45$ kJ/mol H_2
- We expand the range to include $\Delta U_0 \leq 75$ kJ/mol H_2 in order to not miss potentially interesting reactions
- Error bars include estimate of zero-point and heat capacity effects

Multiple Promising Reactions Identified



Multiple interesting reaction schemes identified which have > 6.5 wt% H_2

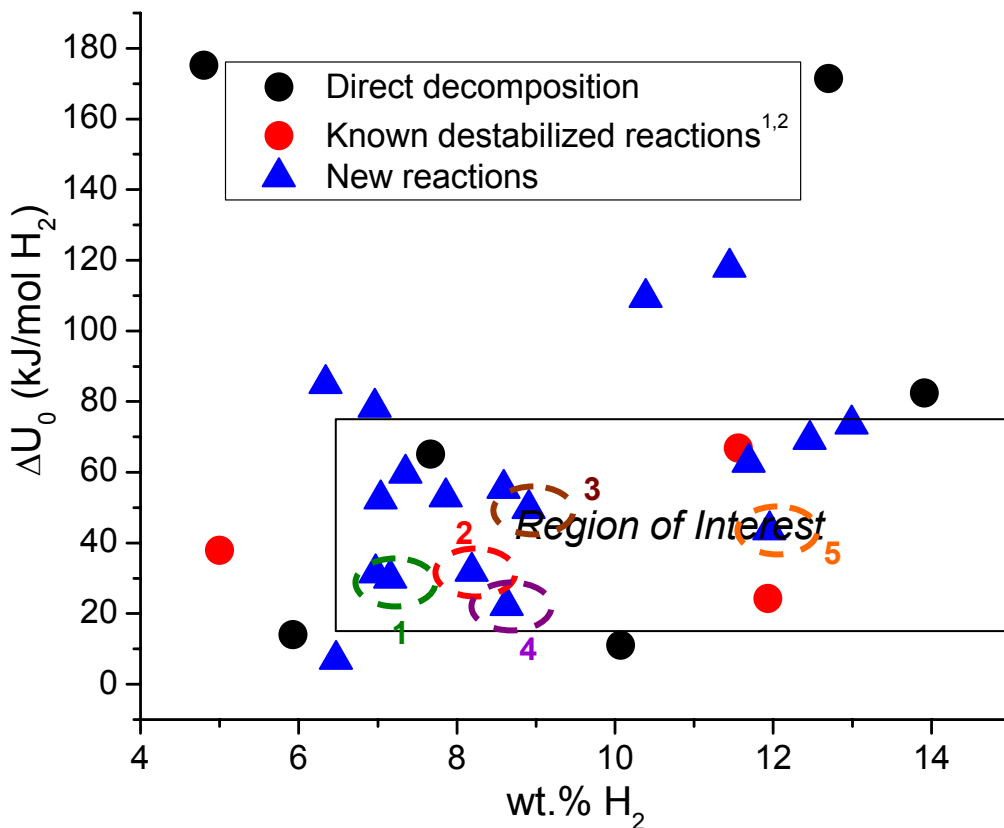
■ Several new promising destabilization reactions identified – all have high storage densities and promising thermodynamics.

■ A large number of reactions (not shown) are less promising for either storage density and/or thermodynamic reasons.

1. Vajo et al., *J. Phys. Chem. B* **2005**, 109, 3719; Vajo et al., *J. Phys. Chem. B* **2004**, 108, 13977

2. Pinkerton et al., *J. Phys. Chem. B* **2005**, 109, 6

Specific Promising Reactions



Rxn 1: $3 \text{LiNH}_2 + 2 \text{LiH} + \text{Si} \rightarrow \text{Li}_5\text{N}_3\text{Si} + 4 \text{H}_2$; 7.16 wt.% H_2 ; $\Delta U_0 = 24\text{-}30 \text{ kJ/mol H}_2$

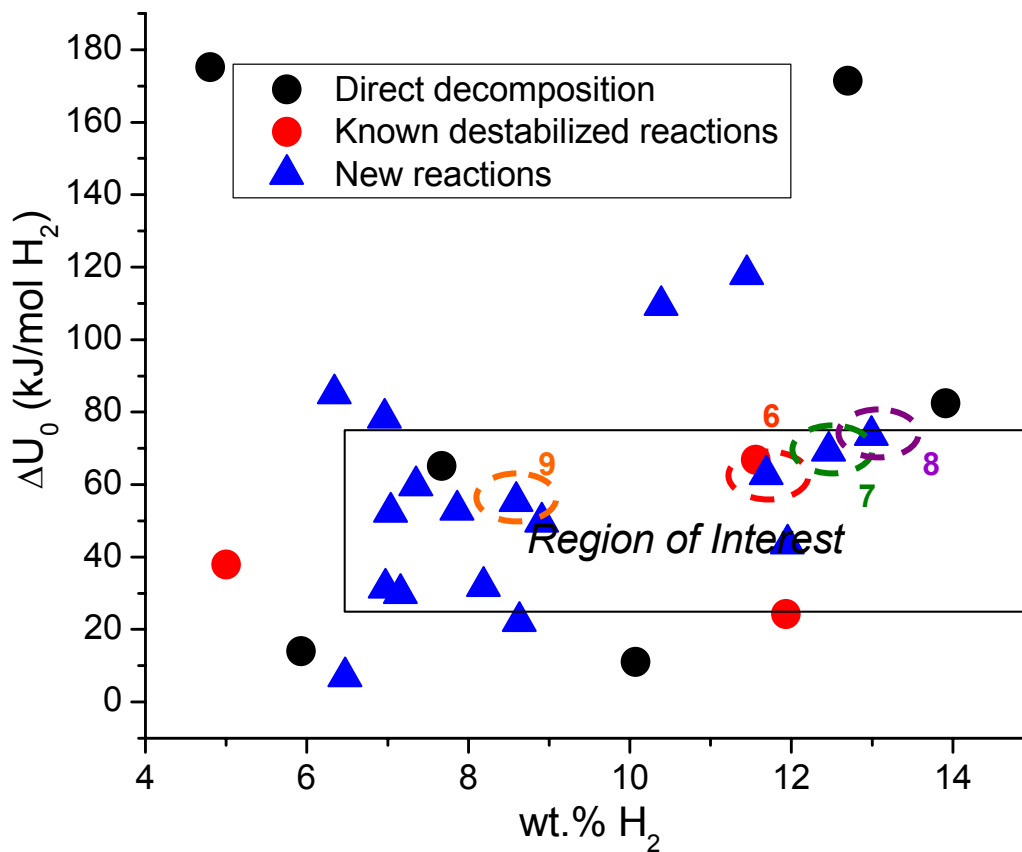
Rxn 2: $\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2 \text{H}_2$; 8.19 wt.% H_2 ; $\Delta U_0 = 32 \text{ kJ/mol H}_2$

Rxn 3: $2 \text{LiBH}_4 + \text{ScH}_2 \rightarrow 2 \text{LiH} + \text{ScB}_2 + 4 \text{H}_2$; 8.91 wt.% H_2 ; $\Delta U_0 = 49.7 \text{ kJ/mol H}_2$

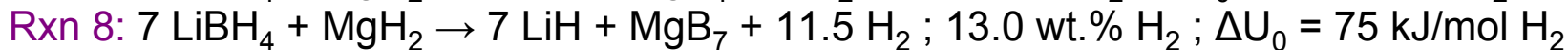
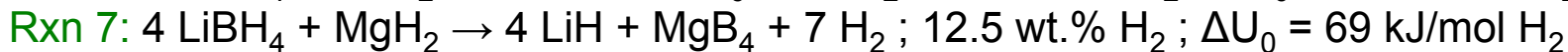
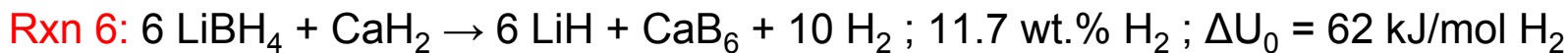
Rxn 4: $2 \text{LiBH}_4 + \text{TiH}_2 \rightarrow 2 \text{LiH} + \text{TiB}_2 + 4 \text{H}_2$; 8.63 wt.% H_2 ; $\Delta U_0 = 22.2 \text{ kJ/mol H}_2$

Rxn 5: $\text{LiBH}_4 + \text{C} \rightarrow \text{LiBC} + 2 \text{H}_2$; 11.95 wt% H_2 ; $\Delta U_0 = 43.6 \text{ kJ/mol H}_2$

Specific Promising Reactions



- Rnx 6 being investigated by Fang et al., but forms $\text{Mg}(\text{NH}_2)_2$ (see also Ozoliņš et al.)
- Rnx 7 and 8 Analogous to Vajo et al. reaction:
 $2 \text{LiBH}_4 + \text{MgH}_2 \rightarrow 2 \text{LiH} + \text{MgB}_2 + 4 \text{H}_2$



Calculation of Reaction Free Energies

Previous DFT calculations gave the $T = 0$ enthalpy— $G(T)$ required for computing van't Hoff (vapor pressure) plots

$$G \cong U_0 + U_{ZP} + U'_{vib}(T) - TS_{vib}(T) + PV$$

DFT total energy

Ideal gas law

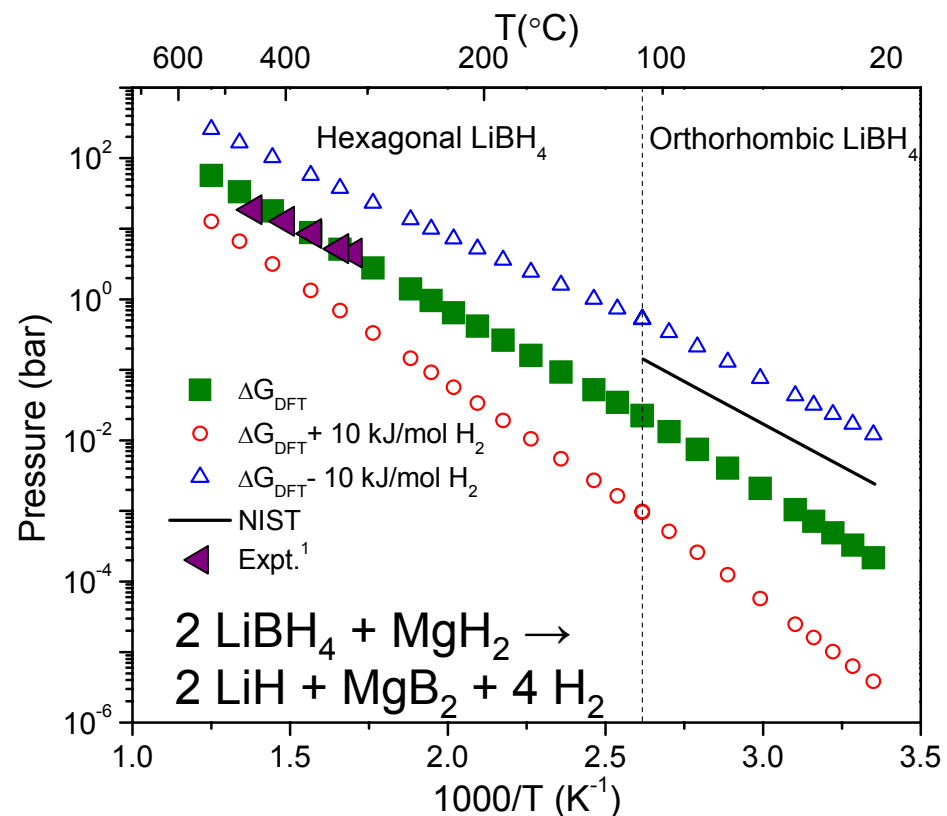
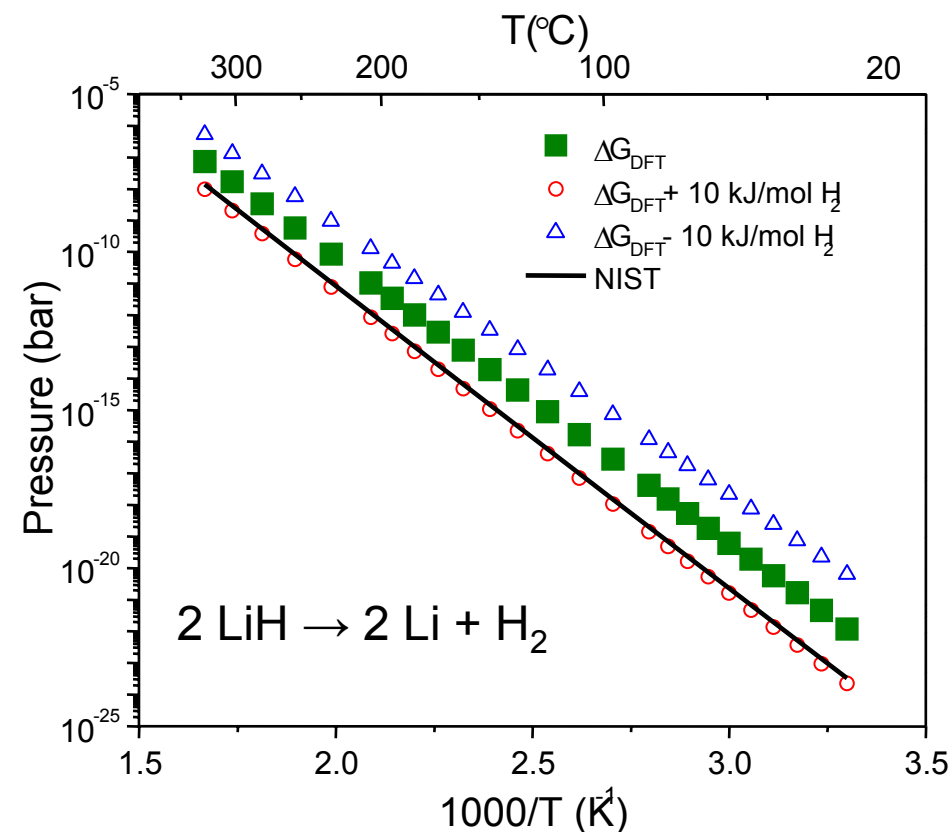
harmonic approximation using
PHONON code (Parlinski)

Ackland, *J. Phys. Condens. Matt.*, **14** (2002) 2975

Equilibrium pressure for decomposition reaction given by

$$\frac{P}{P_0} = \exp\left(\frac{-\Delta G(T)}{RT}\right).$$

Test Calculations for Reaction Free Energies

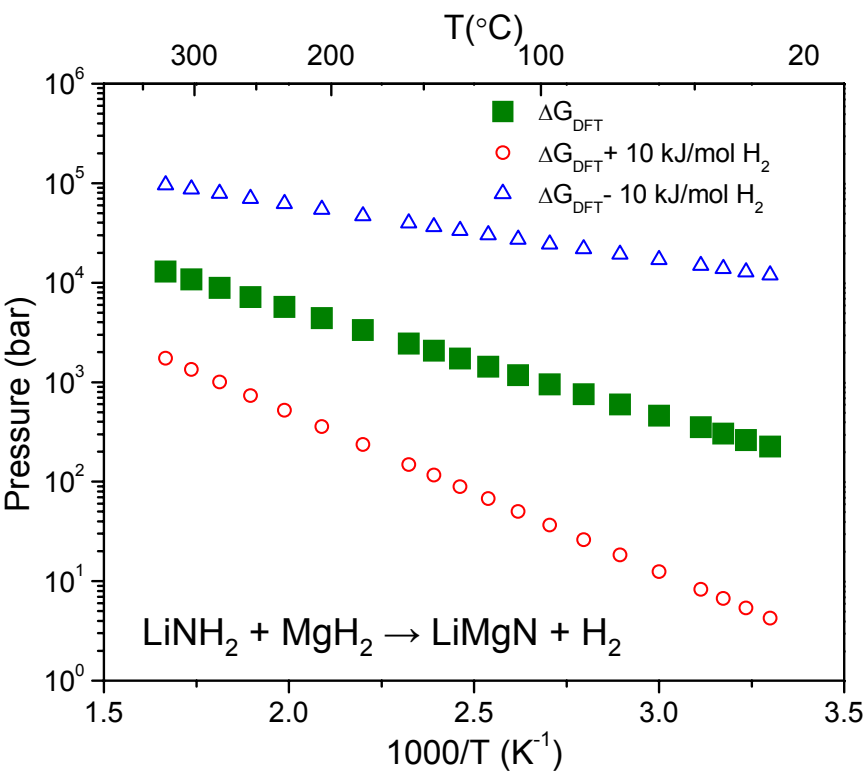


1. J. J. Vajo et al., *J. Phys. Chem. B* **2005**, 109, 3719

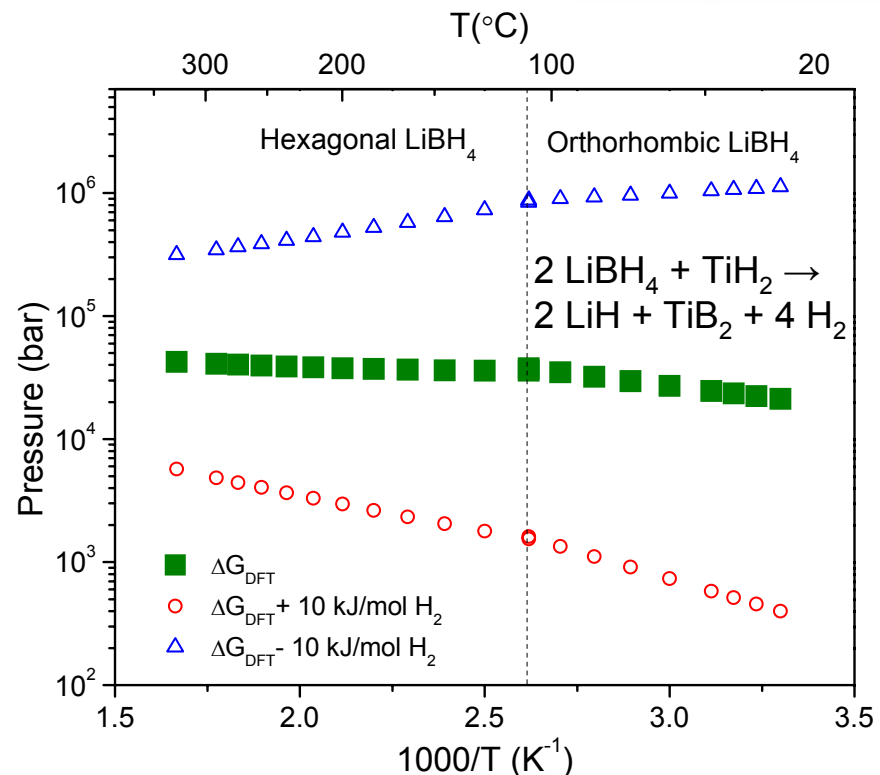
Good agreement with available data

Uncertainty of $\pm 10 \text{ kJ/mol H}_2$ is an *empirical* estimate of uncertainty in DFT

Free Energies of New Hydrides



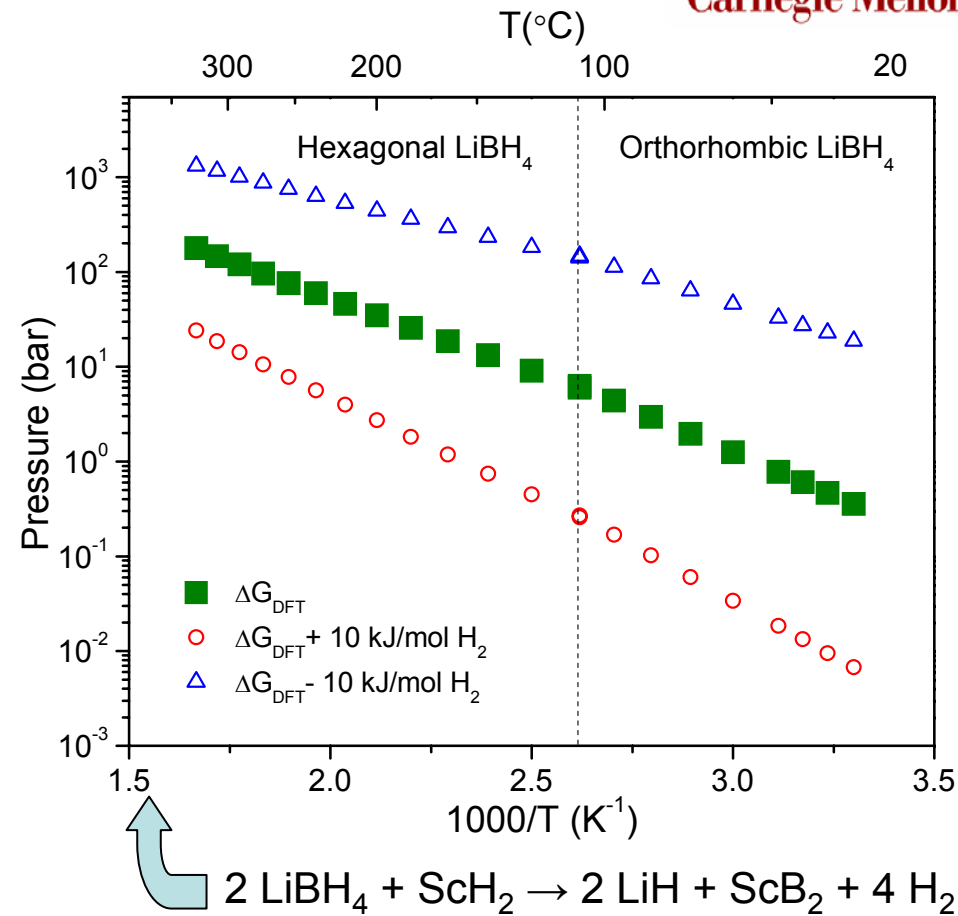
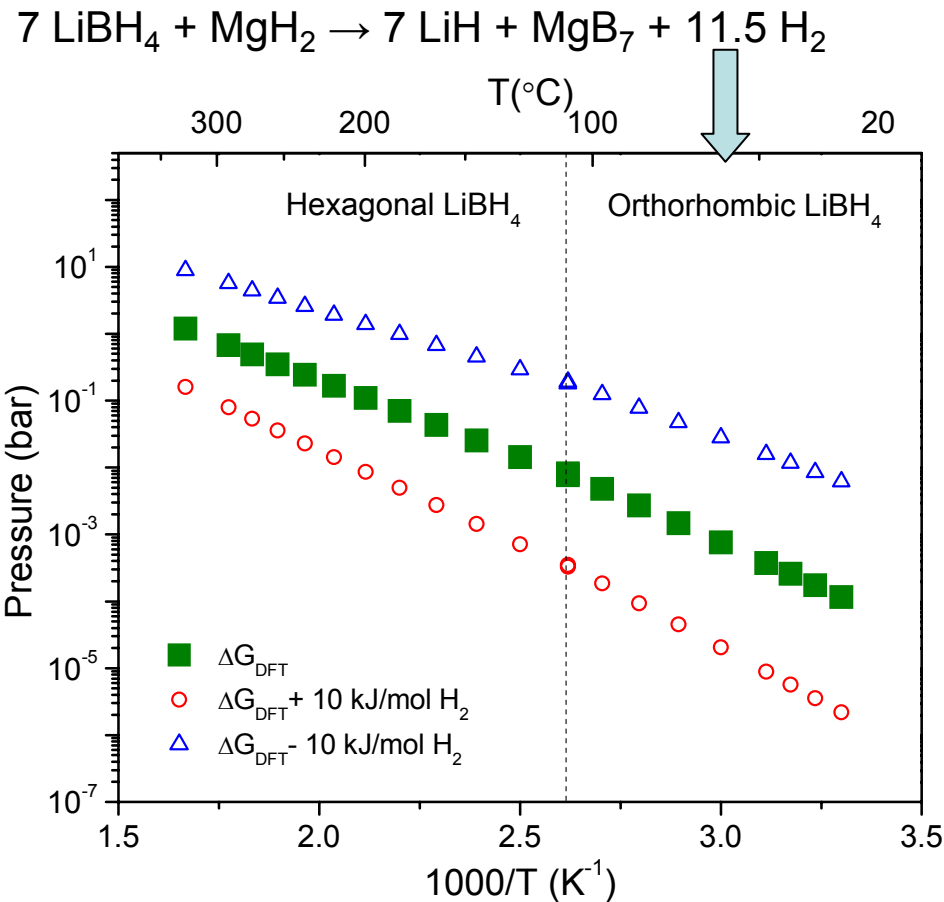
$\Delta H \sim 20 \text{ kJ/mol H}_2$ in 20 – 300 °C
 $\Delta U_0 = 32 \text{ kJ/mol H}_2$



$\Delta H \sim 5 \text{ kJ/mol H}_2$ in 20 – 300 °C

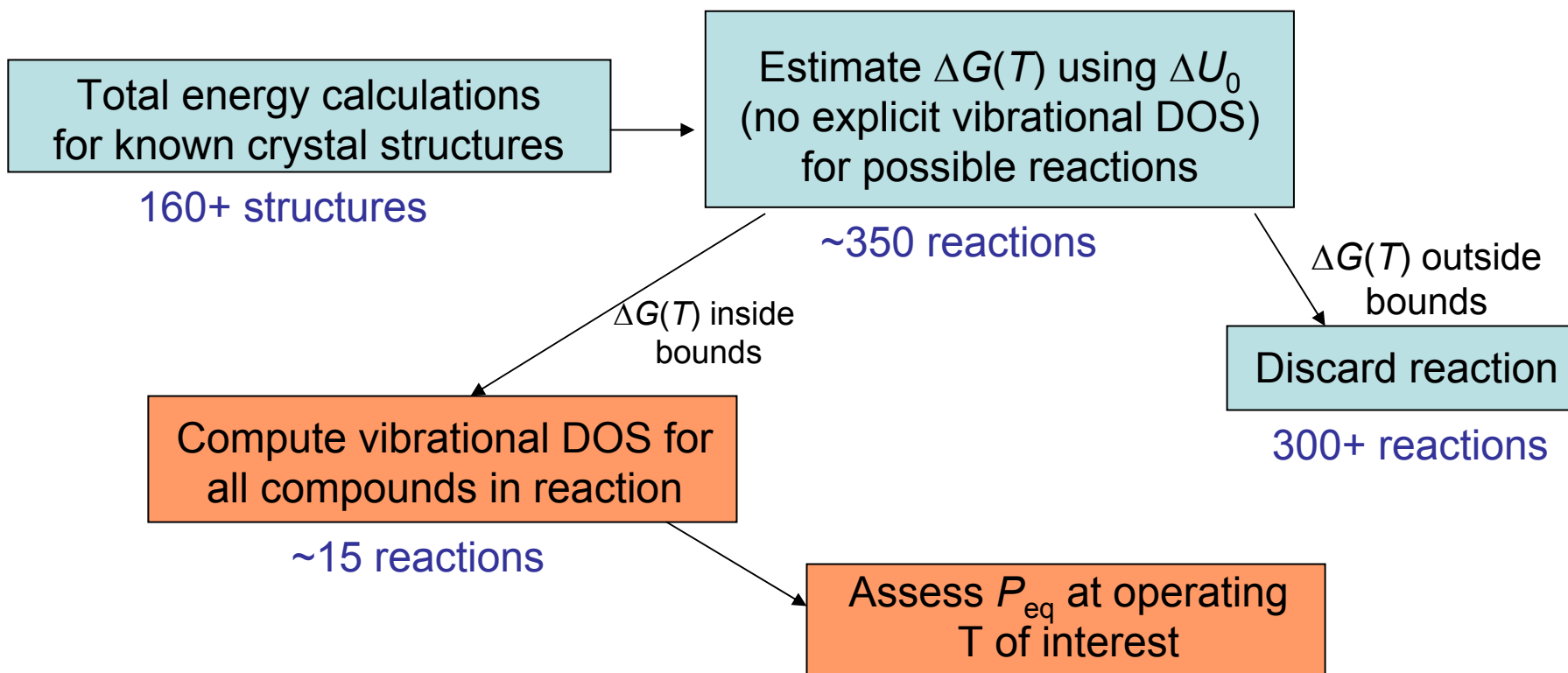
Low enthalpies lead to very high equilibrium pressures—possible reversibility issues

Free Energies of New Hydrides



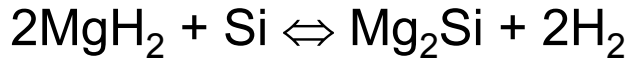
- $\Delta H_{300\text{K}} = 34.1 \text{ kJ/mol H}_2$
- $P_{\text{eq}} = 1 \text{ bar at } 330 \text{ K}$
- Currently being investigated by MHCoe experimentalists
- Unfortunately, Sc is very expensive

Summary: Free Energies of New Hydrides

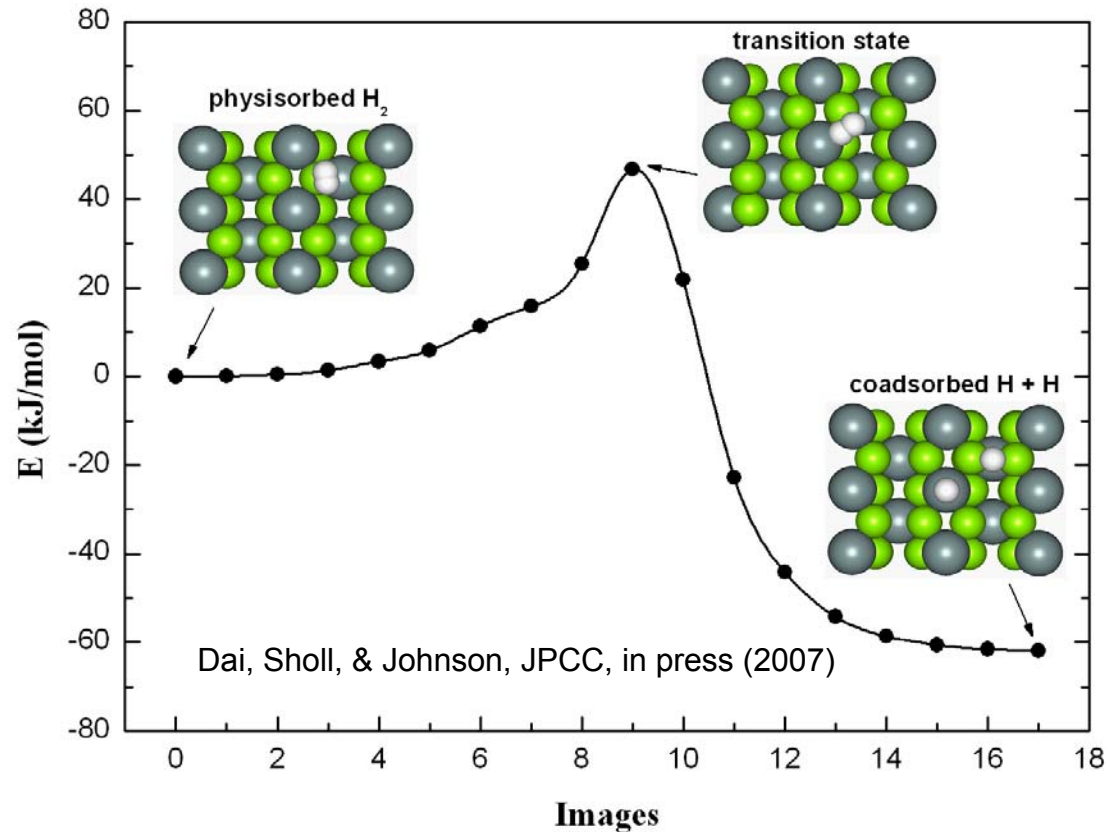


Kinetics of Reversibility: H₂ Dissociation on Clean Mg₂Si

- Experiments indicate that the following reaction is not easily reversible:

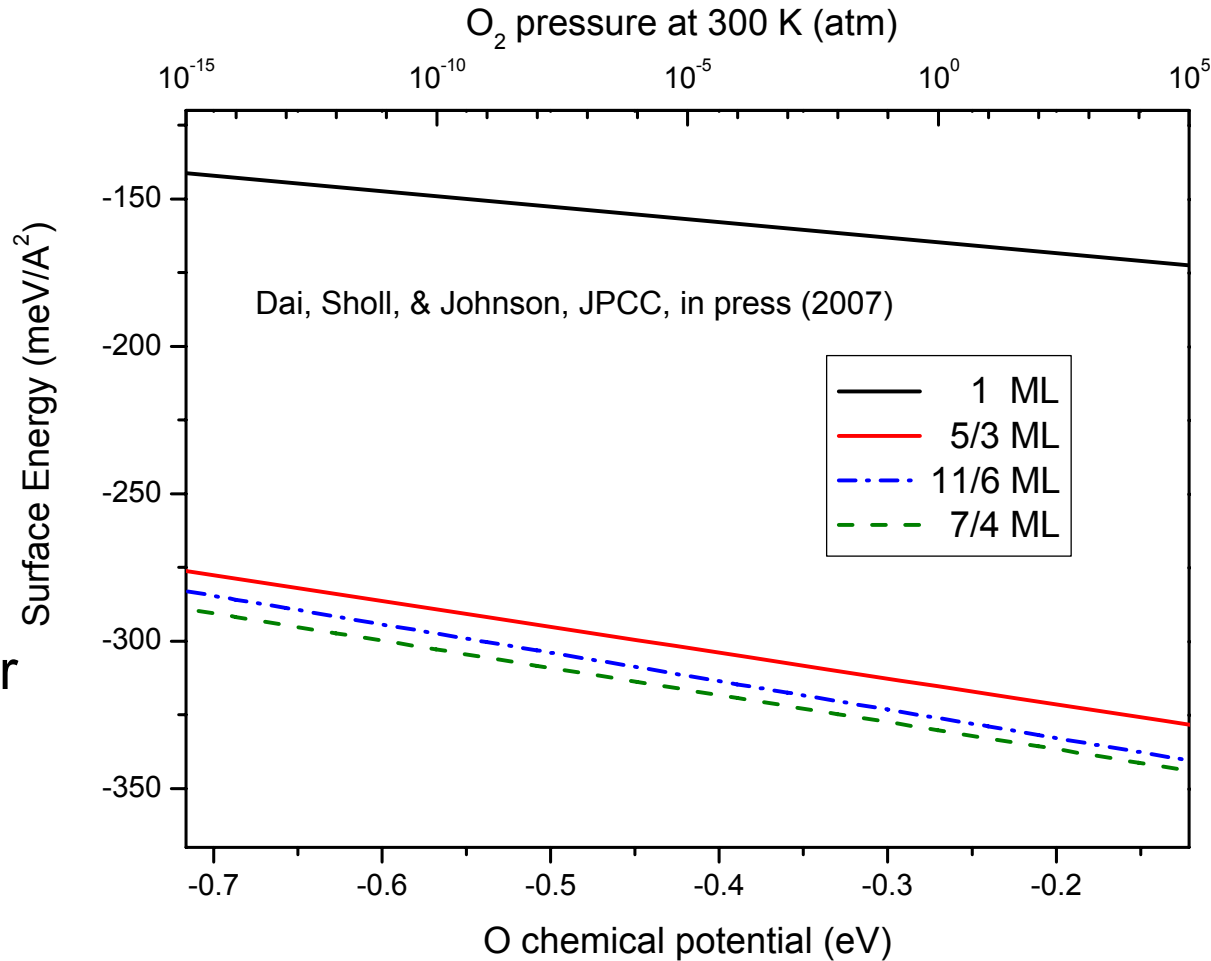


- DFT calculations indicate that H₂ dissociation on the clean Mg₂Si surface is facile
- Possible reasons for the lack of reversibility include
 - Oxide formation on surface
 - Formation of Si-H bonds passivate the surface
 - Mass transfer limitations in forming bulk MgH₂ from bulk Mg₂Si
- We use DFT to study oxide formation on Mg₂Si and its effect on H₂ dissociation



Kinetics of Reversibility: High Oxide Coverage on Mg₂Si

- Surface energy calculations indicate that the Mg₂Si surface is extremely susceptible to oxidation
- The equilibrium coverage at room temperature is at least 1.75 monolayer
- Does this level of oxide formation inhibit H₂ dissociation?



$$\gamma = \frac{1}{2A} \left[E^{slab} - \frac{1}{2} N_O E_{O_2} - N_{Mg_2Si} E_{Mg_2Si}^{bulk} - N_O \mu_O(p, T) \right]$$

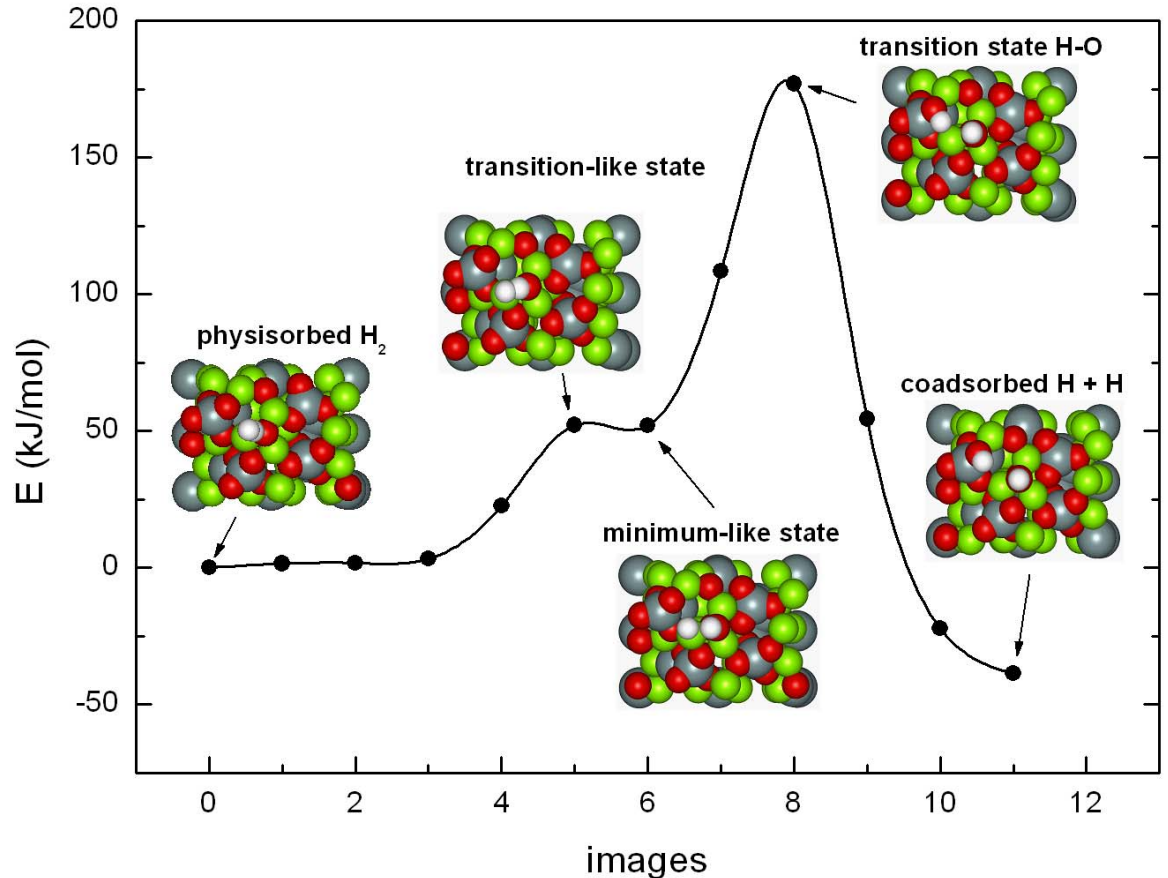
Kinetics of Reversibility:

H₂ Dissociation on Oxide-covered Mg₂Si

Carnegie Mellon

Our calculations indicate that H₂ dissociation is suppressed on the Mg₂Si oxide surface

Dai, Sholl, & Johnson, JPCC, in press (2007)

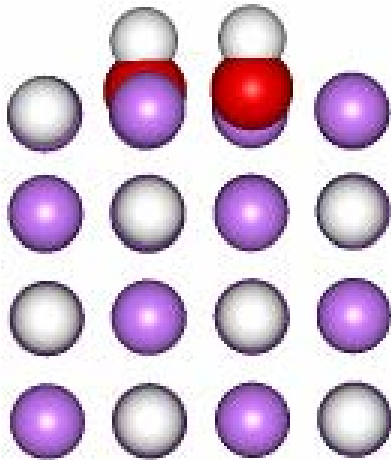


- R. Janot et al. (*Intermetallics* **2006**, 14, 163) have observed reversibility by ball milling in H₂
- Ball milling may create fresh surfaces that overcome oxidation (and transport) issues
- Other kinetic issues, not readily addressable with DFT modeling, may also inhibit reversibility

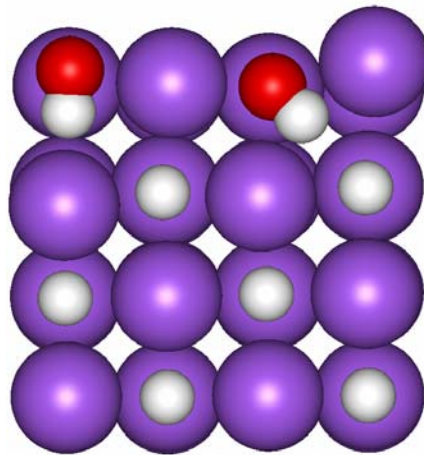
Kinetics of Reversibility: Poisoning of Metal Hydride Surfaces

Carnegie Mellon

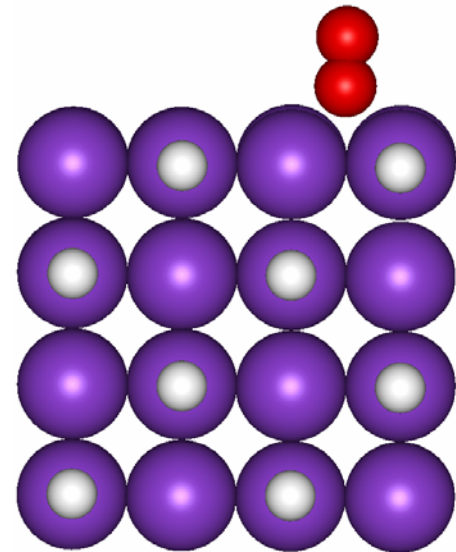
- We are studying reactions of the form $3MH + Al + 3/2H_2 \Leftrightarrow M_3AlH_6$, where $M = (Li, Na, \text{ or } K)$
- This reaction is reversible for $M=K$, reversibly with a catalyst for $M=Na$, and not reversible for $M=Li$. This is a clearly defined kinetic problem
- We are working with the MHCoe TheoryGroup to investigate poisoning of the MH surfaces with O_2 and H_2O
- We have so far found that O_2 dissociates on the LiH and NaH surfaces without a barrier (dissociative adsorption), but we have not yet found a barrierless dissociation pathway for O_2 on KH.



LiH + O₂



NaH + O₂

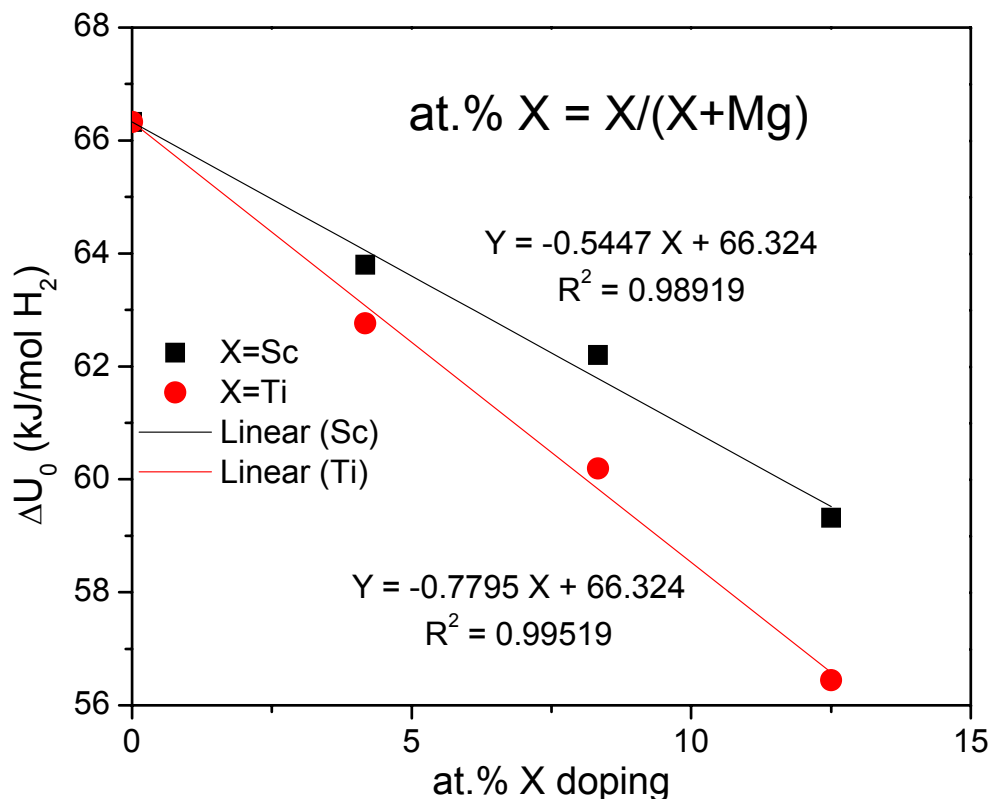
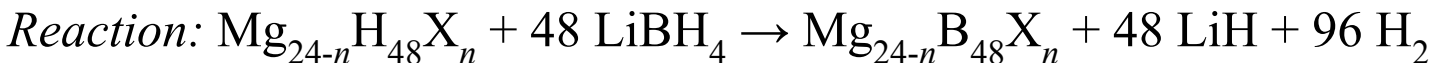


KH + O₂

Accomplishments: Computational Screening of Dopants



$\text{XH}_2 + \text{LiBH}_4 \rightarrow \text{XB}_2 + \text{LiH} + 2 \text{H}_2$ for $\text{X} = \text{Mg}, \text{Ti}, \text{Sc}$
 Sc is miscible in Mg (up to ~15 at.%), but Ti is essentially immiscible in Mg



- Sc and Ti doping reduces ΔU_0
- Results similar to those reported experimentally for NaAlH_4 with Ti doping¹
- ΔU_0 reduction per 1% of X doping
 - Sc -0.54 kJ/mol H_2
 - Ti -0.78 kJ/mol H_2

DFT calculations of this sort should be useful to predicting useful dopants 19

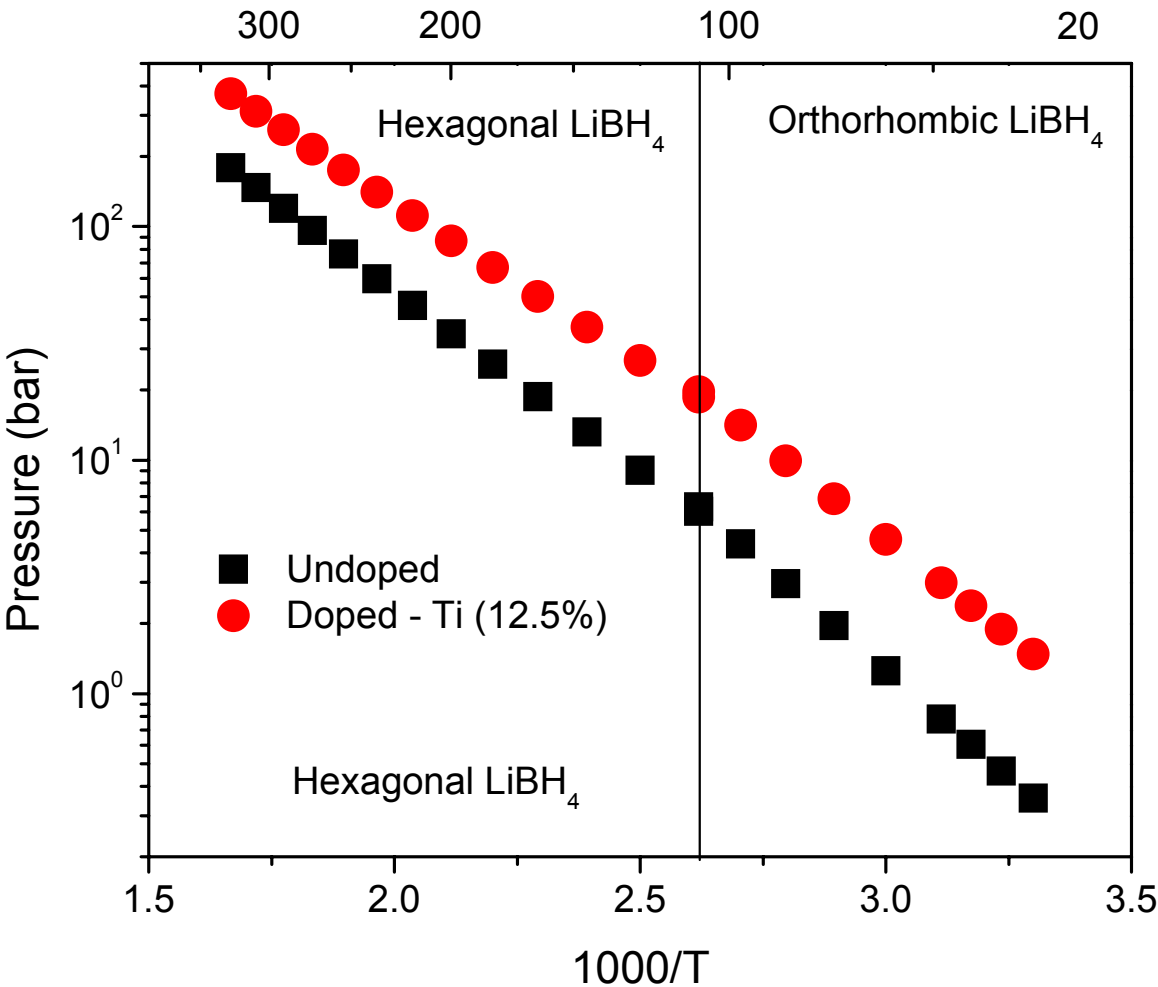
1. G. Streukens et al., *Phys. Chem. Chem. Phys.* **2006**, 8, 2889

Effect of doping on P_{eq}

Carnegie Mellon



T(°C)



- We have computed stabilities for 18 systems containing Li, B, Si, Ti, Mg, and H
- Most doped systems are unstable with respect to phase segregation except at high temperatures
- This system is estimated to be stable close to 300 K
- 12.5% Ti doping leads to ~ 3 kJ/mol H_2 reduction in ΔH
- P_{eq} at 300 K
 - Undoped \rightarrow 0.3 bar
 - Doped \rightarrow 1.3 bar

Future Work

FY07-FY08

- Conclude development of an automated approach for identifying all possible compounds from a given set of reactants and products
- Compute surface reactions related to poisoning and initial kinetics of hydrogenation & dehydrogenation
- Complete calculations for ΔH of substituted (doped) complex hydrides, including collaborative work on $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$
- Screen doped hydrides for phase stability
- Conclude calculations for CALPHAD databases for metal hydrides
- Explore new collaborations with BNL and Hawaii on the alanes project

Project Summary

- Density functional theory has been useful in identifying potentially interesting reactions and experiments are being performed on several of the predicted reactions:
 - Utah: $\text{LiNH}_2 + \text{MgH}_2$ This reaction appears to form $\text{Mg}(\text{NH}_2)_2$ (Fang et al., Ozoliņš et al.)
 - CalTech: $\text{ScH}_2 + 2\text{LiBH}_4$ & $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$
 - JPL: $\text{ScH}_2 + 2(\text{LiBH}_4)$
- Free energies can be computed with accuracy within ± 10 kJ/mol H_2
- One of our papers, “Using First Principles Calculations To Identify New Destabilized Metal Hydride Reactions for Reversible Hydrogen Storage”, *Phys. Chem. Chem. Phys.* **9**, 1438-1452 (2007), was selected by the editors of *Science* as an “Editors’ Choice” article (*Science*, **315**, 1638, 2007) and was one of the top ten downloaded *PCCP* articles in March, 2007.
- We have contributed DFT data to the UIUC cluster expansion toolkit (collaboration with D. Johnson)
- DFT calculations have been used to augment CALPHAD for phase diagram calculations of the LiB system (collaboration with U. Kattner, NIST)
- Doping calculations have been performed on a number of systems and calculations are continuing on systems of specific interest to experimentalists— $\text{Mg}(\text{BH}_4)_2$ for GE and $\text{Ca}(\text{BH}_4)_2$ for Sandia
- We have begun work on examining kinetic issues related to rehydrogenation of various systems (collaboration with MHCoe Theory Group members: M. Allendorf, E. Ronnebro, E. Majzoub @ Sandia, D. Johnson & N. Zarkevich @ UIUC)
- Interfacial energy calculations were performed in collaboration with B. Clemens @ Stanford
- Predictions to be experimentally tested:
 - $\text{MgH}_2 + 2 \text{LiBH}_4 + 2 \text{C} \rightarrow \text{MgB}_2\text{C}_2 + 2 \text{LiH} + 4 \text{H}_2$
 - $\text{LiBH}_4 + \text{C} \rightarrow \text{LiBC} + 2 \text{H}_2$
 - Doping of $\text{ScH}_2 + \text{LiBH}_4$ with Ti