

# First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Project ID # STP3

This presentation does not contain any proprietary or confidential information



Carnegie Mellon

# Overview

## Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 20%

## Budget

- Requested total: \$1.38M
- Cost sharing: 20%
- FY06 \$175k (DOE), \$44k (cost share)

## Barriers

- Access to adequate computing resources
- Efficient and accurate electronic structure algorithms

## Partners

- Collaborations with all experimental groups are sought
- Current collaborators:
  - HRL, GE, U. Hawaii, Stanford, UIUC, U. Utah, NIST, JPL, Cal Tech

# Objectives

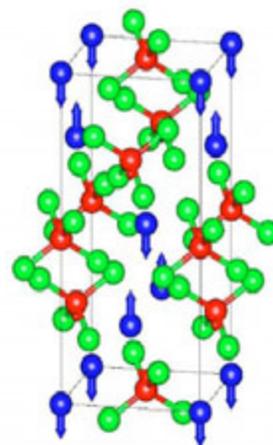
- Compute thermodynamic properties of metal hydride alloys—Heat of reaction,  $\Delta H$ 
  - Compute  $\Delta H$  for known reactions to test accuracy of our approach
  - Compute  $\Delta H$  for new reactions to identify promising destabilized compounds
  - This work complements experimental work on identifying destabilized metal hydrides (Focus area A—Destabilized Hydrides)
- Compute interfacial properties of hydrides
  - Metal-hydride interfaces
  - Surface energies of metal hydrides for nanoscopic hydrides
  - Apply principles learned on model systems to more promising novel materials.
  - Complements experimental work on improving kinetics for destabilized hydrides and other materials

# Objectives

- Fundamental processes in hydrogenation
  - Study hydrogenation in destabilized hydrides and other systems to assess reversibility
  - Look for common hydrogenation pathways that might be applicable to other materials
  - Assess the role of interfacial transport
  - Some destabilized hydrides are not easily hydrogenated—this work supports experimental efforts to design a practical destabilized hydride system

# Approach

- First principles density functional theory (DFT) for periodic systems (plane wave)
- Generalized gradient approximation (GGA) for the exchange-correlation functional
- Finite temperature and entropic properties computed from a phonon density of states approach with the PHONON software package
- Transition state finding methods for reaction and diffusion problems



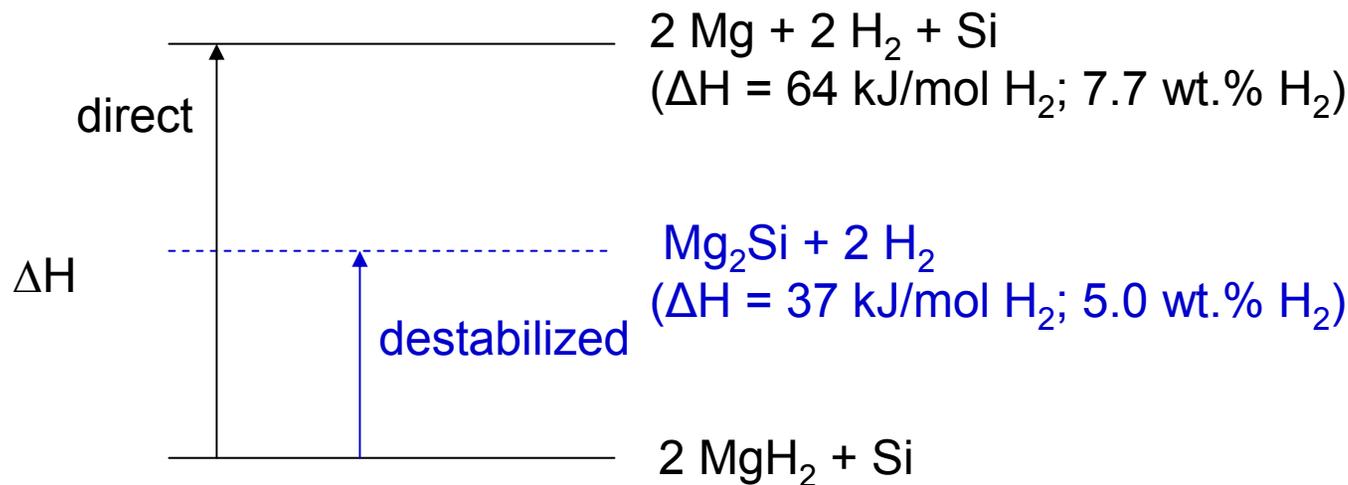
# Destabilization of Metal Hydrides

Original concept introduced by Reilly and Wiswall<sup>1</sup> in late 1960's for Ni hydrides

Modification of dehydrogenation thermodynamics using additives

- Stabilized dehydrogenated state reduces enthalpy of dehydrogenation

Recent application of this concept to light metal hydrides by Vajo et al.<sup>2,3</sup>



1. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.* **1967**, 6, 2220
2. J. J. Vajo et al., *J. Phys. Chem. B* **2005**, 109, 3719
3. J. J. Vajo et al., *J. Phys. Chem. B* **2004**, 108, 13977

# Technical Accomplishments

## A DFT-based Database of Reaction Enthalpies

We have optimized the crystal structures of 52 solid materials listed in Wyckoff<sup>1</sup>, Pearson<sup>2</sup> and ICSD<sup>3</sup> comprised of Al, B, Ca, Li, Mg, Si, C, N, or H

Using this DFT-based database, we have considered 130 reactions that could not previously be evaluated as potential H<sub>2</sub> storage schemes.

1. R. W. G. Wyckoff, *The Structure of Crystals*, The Chemical Catalog Company Inc., New York, 1931.
2. P. Villars, *Pearson's handbook : crystallographic data for intermetallic phases*; Desk ed. ed.; ASM International
3. The Inorganic Crystal Structure Database (ICSD), <http://www.fiz-informationsdienste.de/en/DB/icsd/>.

# Technical Accomplishments

## A DFT-based Database of Reaction Enthalpies Crystal Structure Issues:

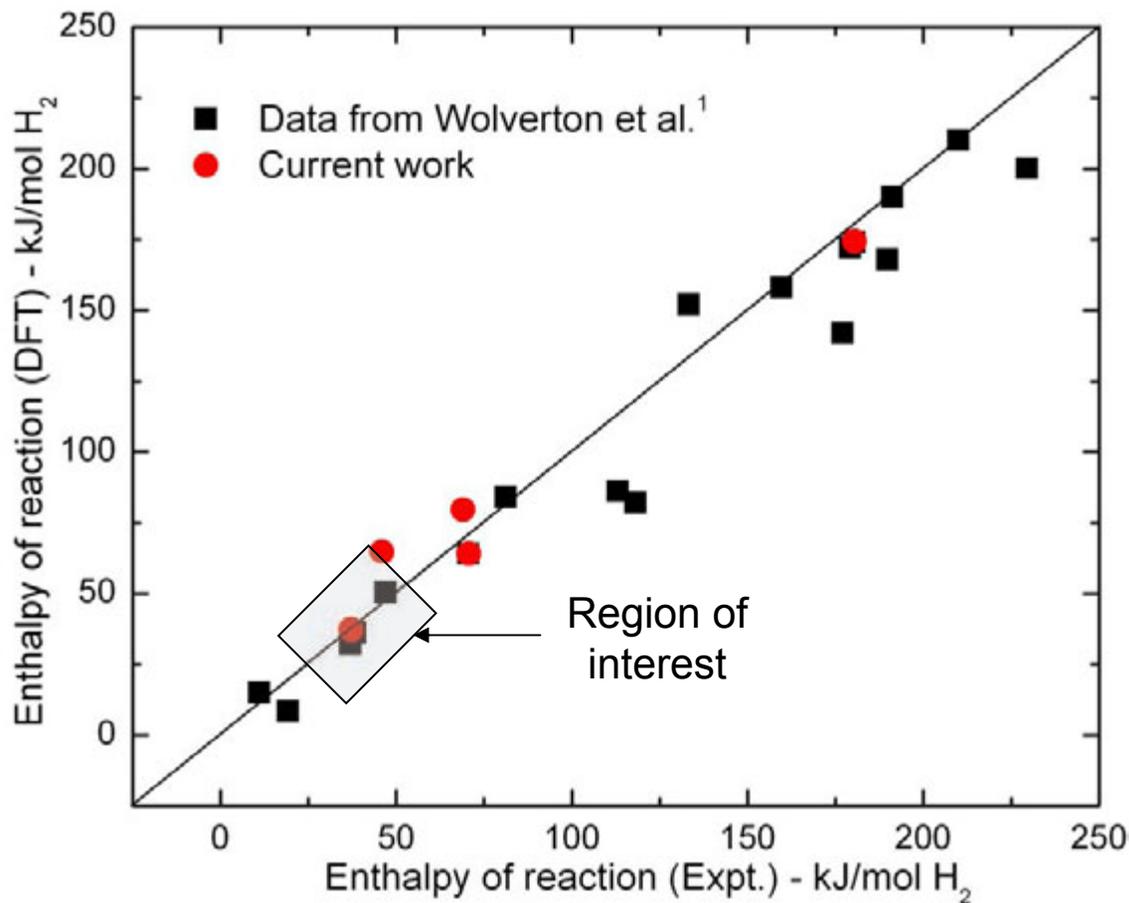
Full crystal structure of  $\text{Ca}(\text{AlH}_4)_2$  is not known experimentally.  
We used *ab initio* prediction of Løvvik<sup>1</sup>

$\text{Li}_5\text{N}_3\text{Si}$  has very large unit cell with partial atomic occupancies.  
DFT calculations performed with two materials with compositions  
 $\text{Li}_{54}\text{N}_{32}\text{Si}_{10}$  and  $\text{Li}_{53}\text{N}_{32}\text{Si}_{11}$  with Si distributed randomly.

1. O. M. Løvvik, *Phys. Rev. B* **2005**, 71, 144111

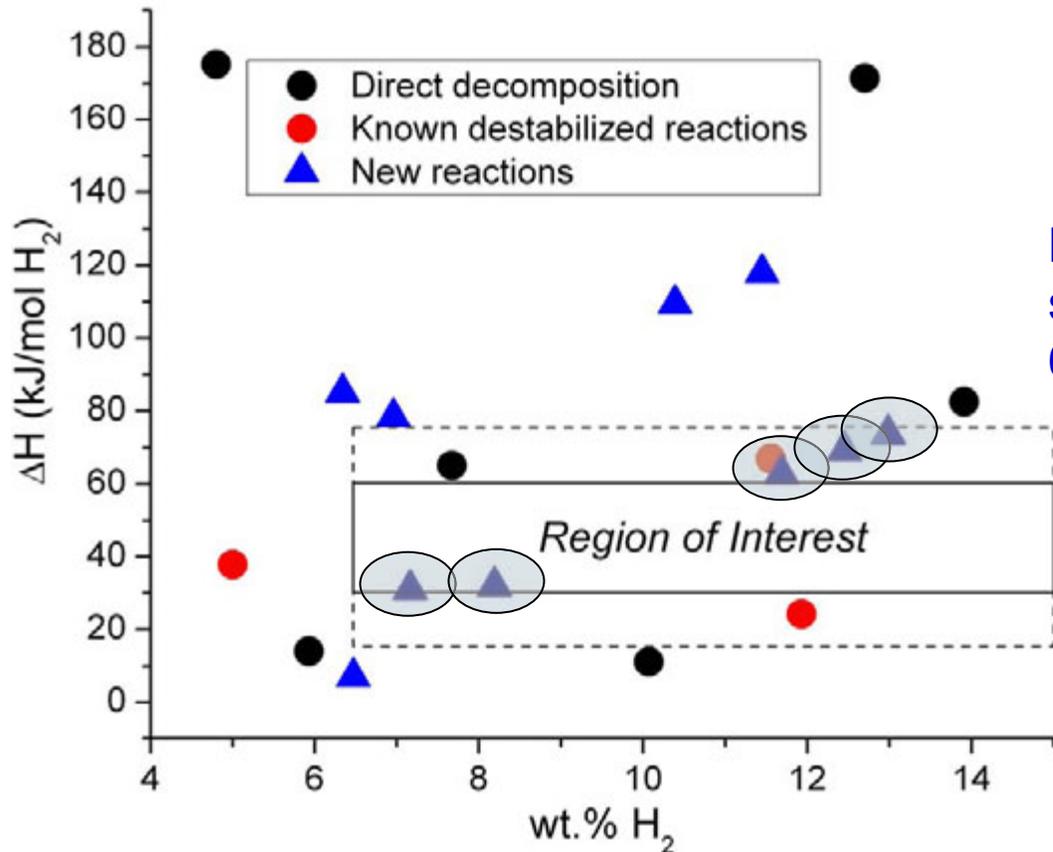
# Accuracy of DFT - based Values of $\Delta H$

Experimental data available for many high Z metal hydrides (e.g. Sc, Pd, Ni, etc.)



RMS deviation in DFT results is 15 kJ/mol H<sub>2</sub> ;  
this is sufficiently accurate for screening purposes

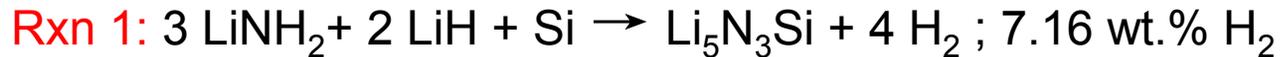
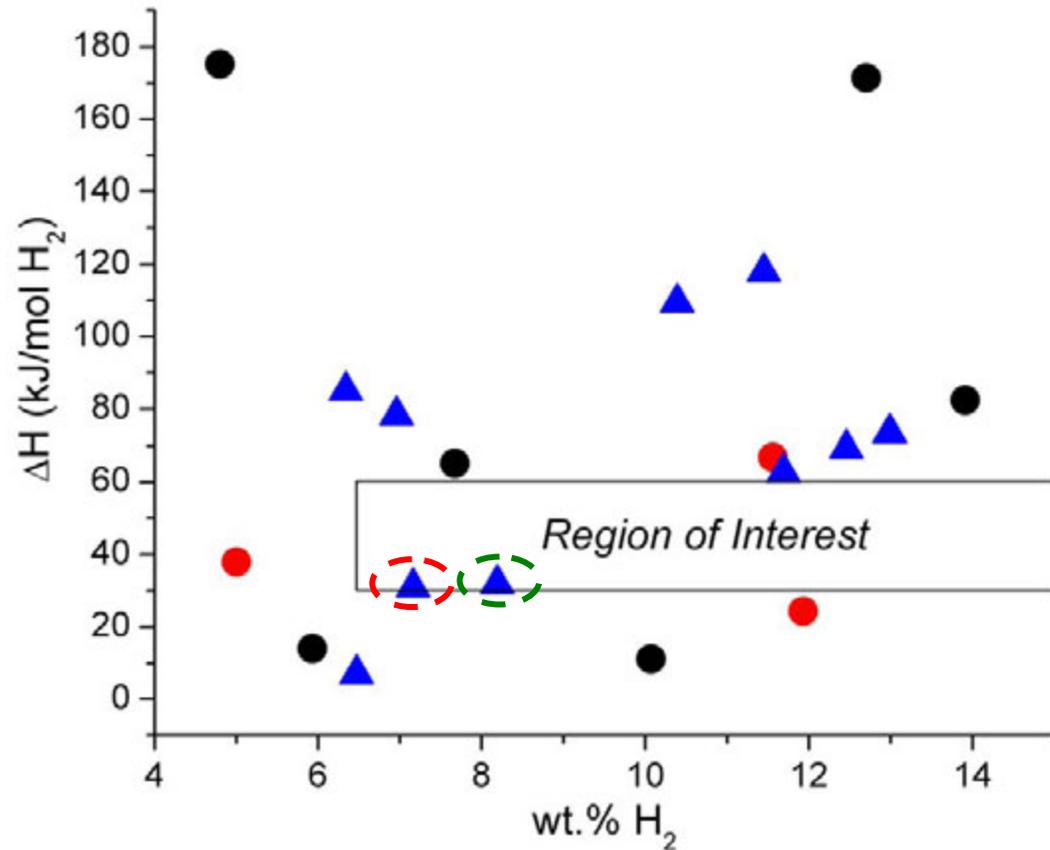
# Reactions of Interest



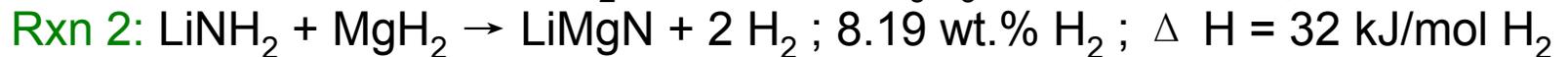
Multiple interesting reaction schemes identified which have  $> 6.5$  wt% H<sub>2</sub>

- Five new promising destabilization schemes identified – all have high storage densities and have promising thermodynamics.
- A large number of schemes (not shown) are less promising for either storage density or thermodynamic reasons (or both).

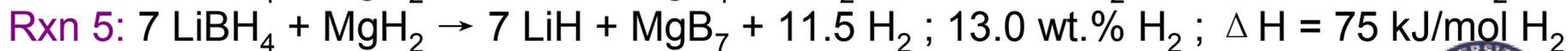
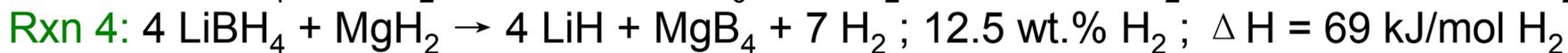
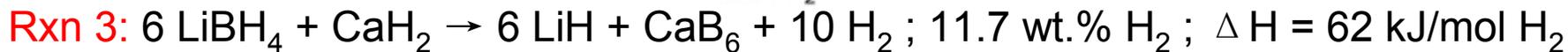
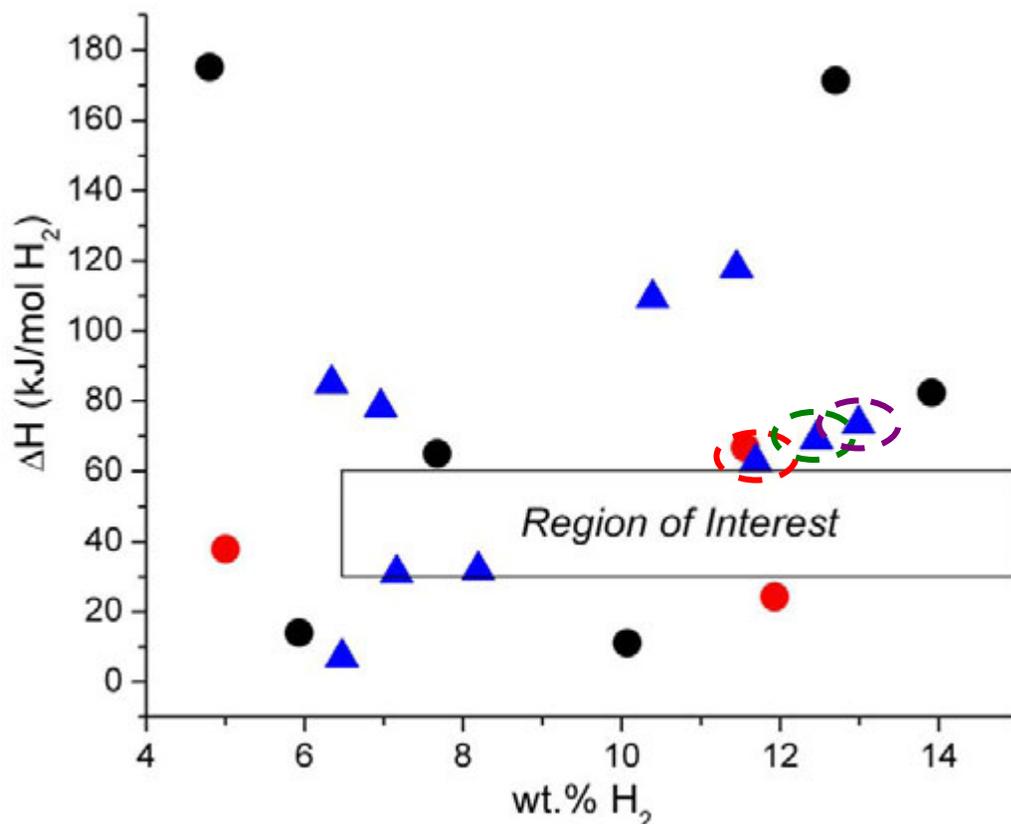
# Reactions of Interest (cont.)



$\Delta H = 24\text{-}30 \text{ kJ/mol H}_2$  (variants of  $\text{Li}_5\text{N}_3\text{Si}$  stoichiometry)



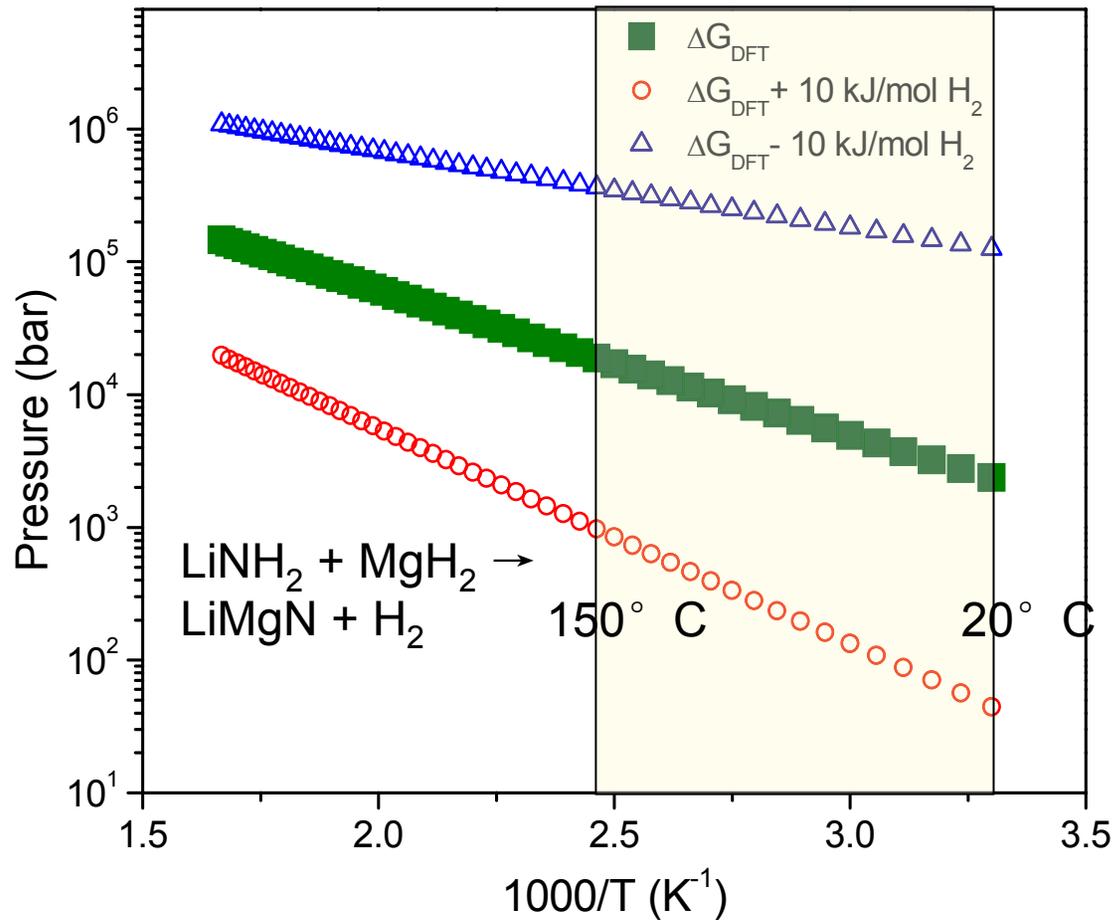
# Reactions of Interest (cont.)



*Rxn 4 and 5 analogous to Vajo et al.<sup>1</sup> reaction:*



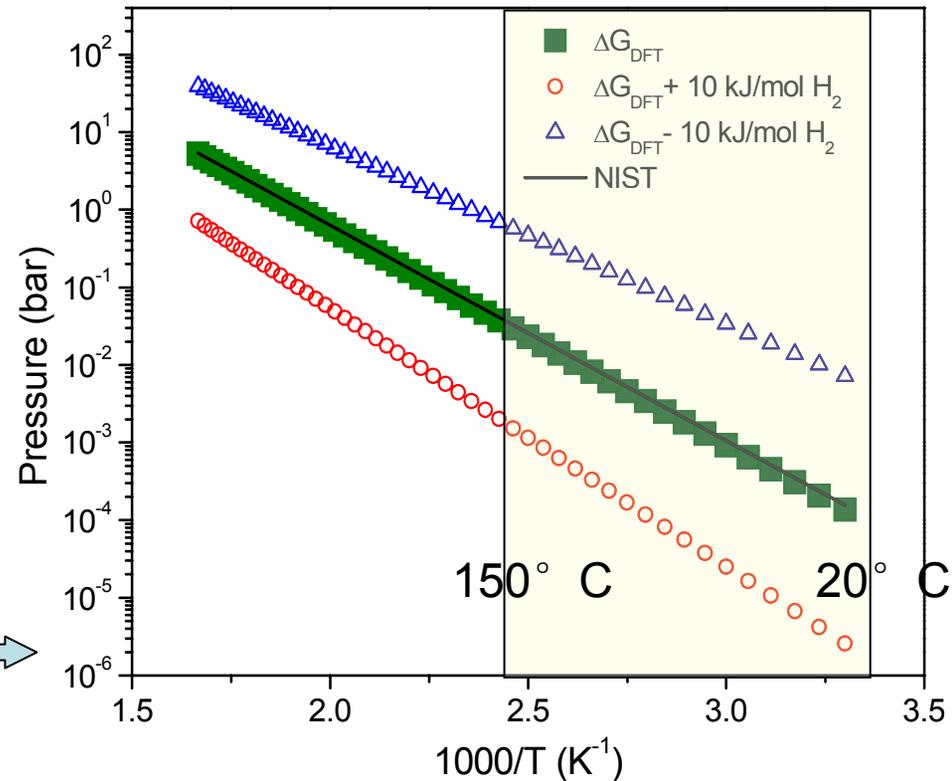
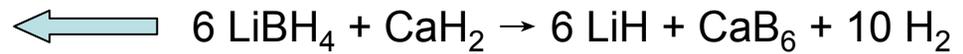
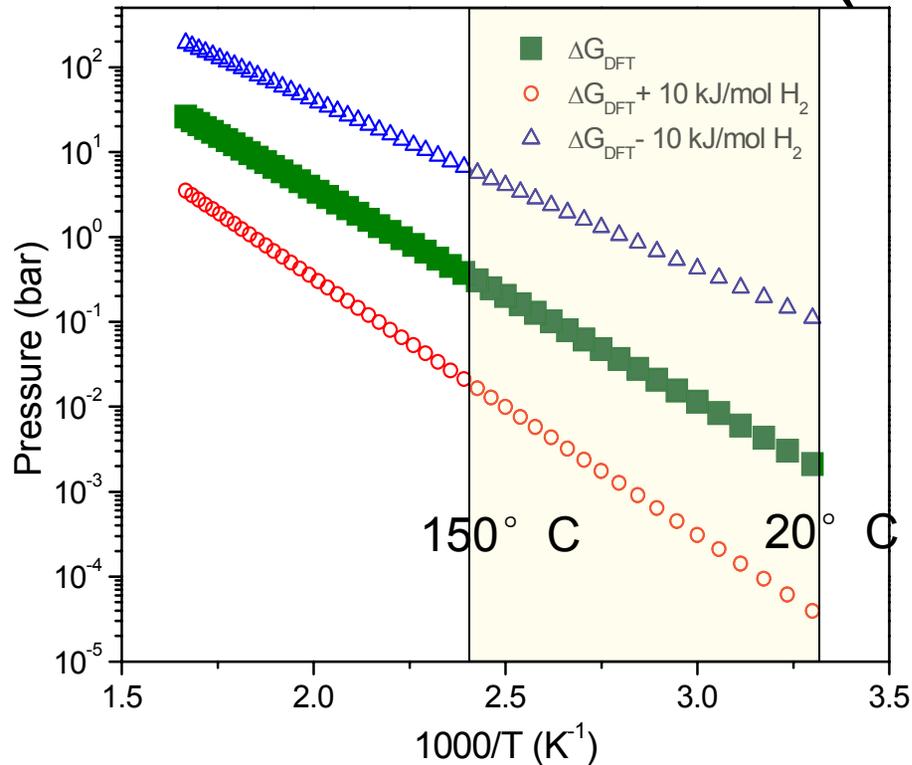
# Van't Hoff Plots for New Reactions



- The equilibrium pressure is very high over the temperature range of interest
- May be a useful material at lower temperatures
- $\Delta H \sim 20 \text{ kJ/mol H}_2$  over the temperature range

**Caveat:** Reversibility might be an issue as  $\Delta H$  is low

# Van't Hoff Plots for New Reactions (cont.)



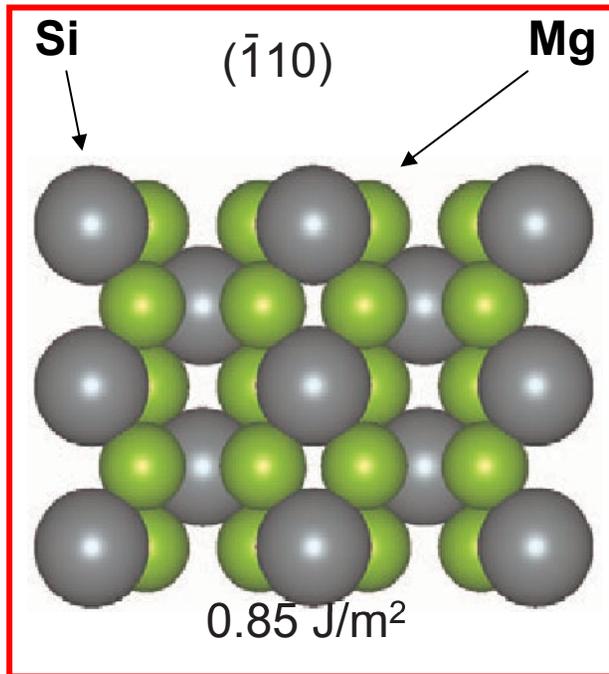
- Both these reactions have  $P_{\text{eq}} < 1$  bar at room temperature
- The equilibrium pressure would need to be increased for these reactions to be useful

# Computational Study of Dissociation of Hydrogen on Mg<sub>2</sub>Si Surface

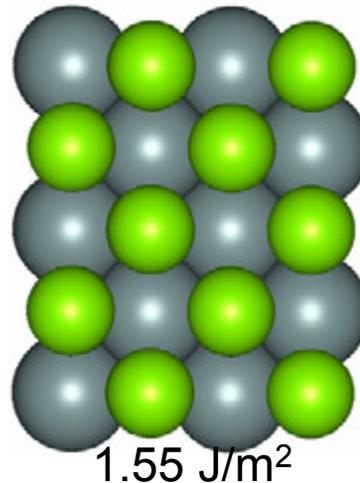
- One possible kinetic barrier to  $\text{Mg}_2\text{Si} + \text{H}_2 \rightarrow \text{MgH}_2 + \text{Si}$  is the dissociation of  $\text{H}_2$  on surfaces of  $\text{Mg}_2\text{Si}$ .  
[Large barriers to  $\text{H}_2$  dissociation are known to exist on  $\text{Mg}(0001)$ <sup>1</sup> ]
- This hypothesis can be disproved if facile pathways for  $\text{H}_2$  dissociation are identified
- Many other atomic-scale processes must still be considered before a complete description of the overall hydrogenation reaction is available, i.e. oxide overlayer formation

# Mg<sub>2</sub>Si Surface Energies

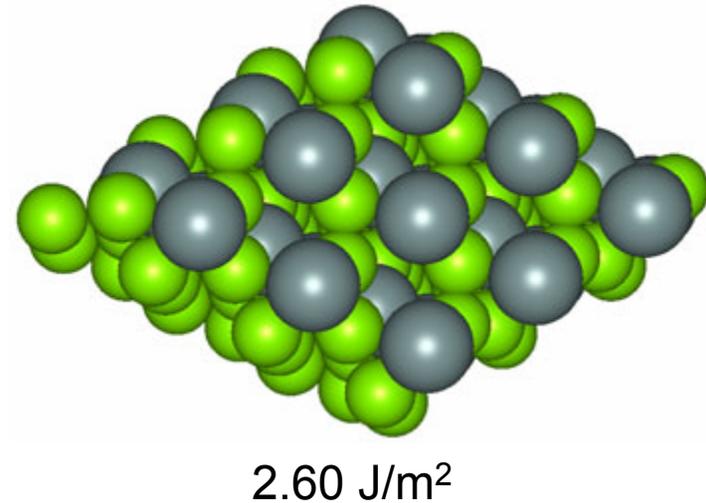
Surface energy is defined as:  $E_{\text{surface}} = (E_{\text{total}} - N \times E_{\text{bulk}}) / 2A$



(110)  $\leftrightarrow$  (101)



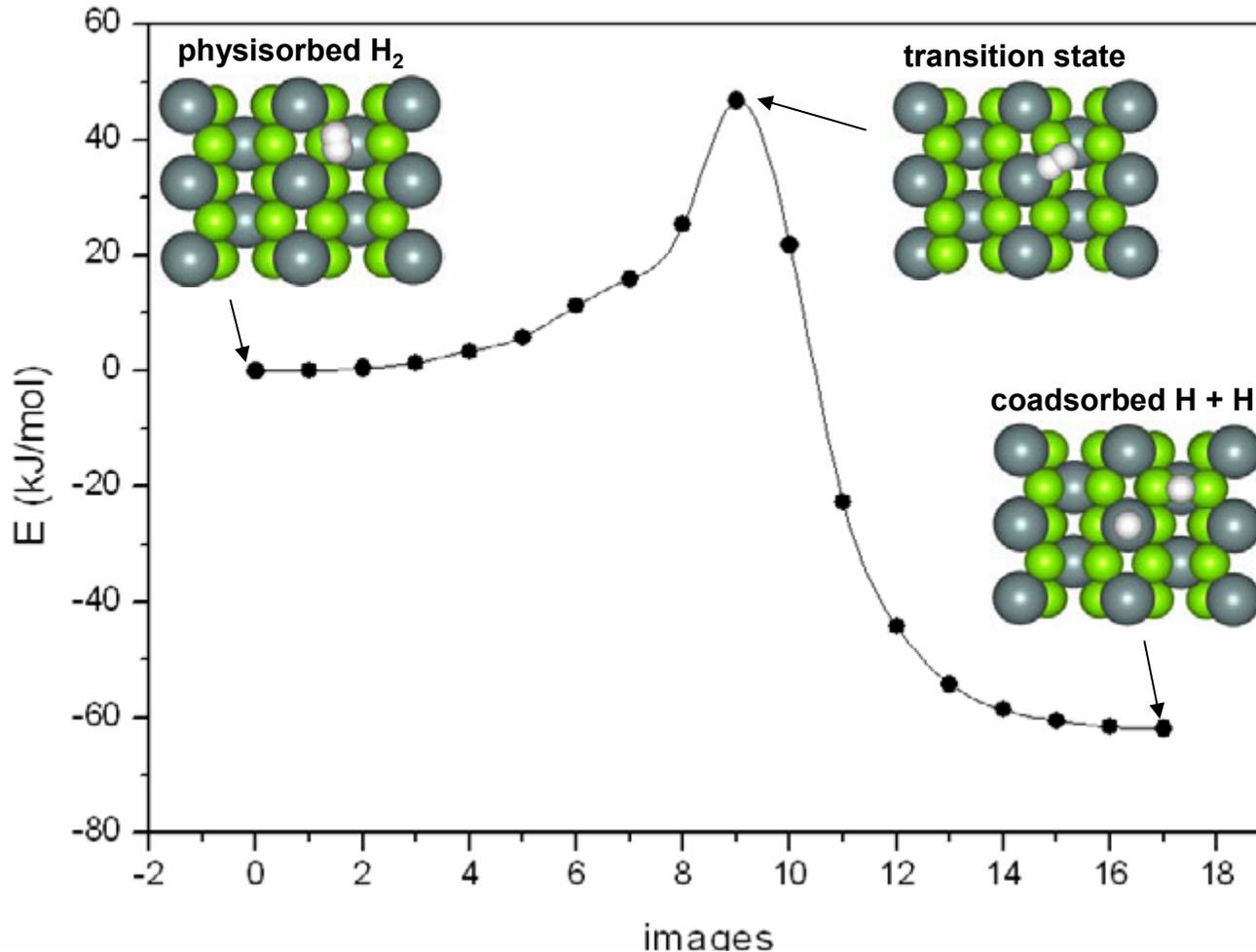
(111)  $\leftrightarrow$  (100)  $\leftrightarrow$  (010)  $\leftrightarrow$  (001)



Lower surface energies correspond to more energetically stable surfaces

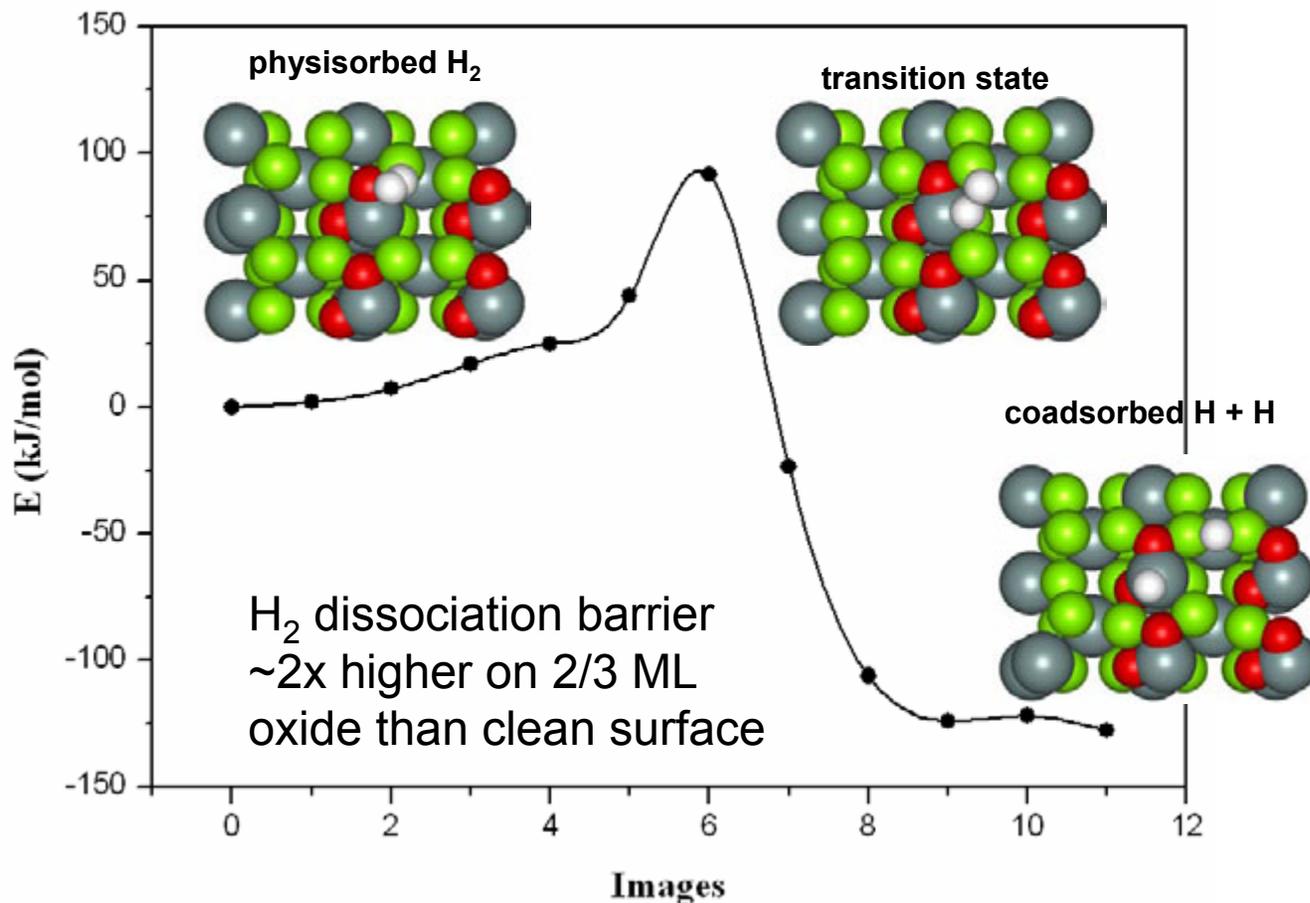
# H<sub>2</sub> Dissociation on Mg<sub>2</sub>Si( $\bar{1}10$ )

Pathway for H<sub>2</sub> dissociation determined using Nudged Elastic Band method



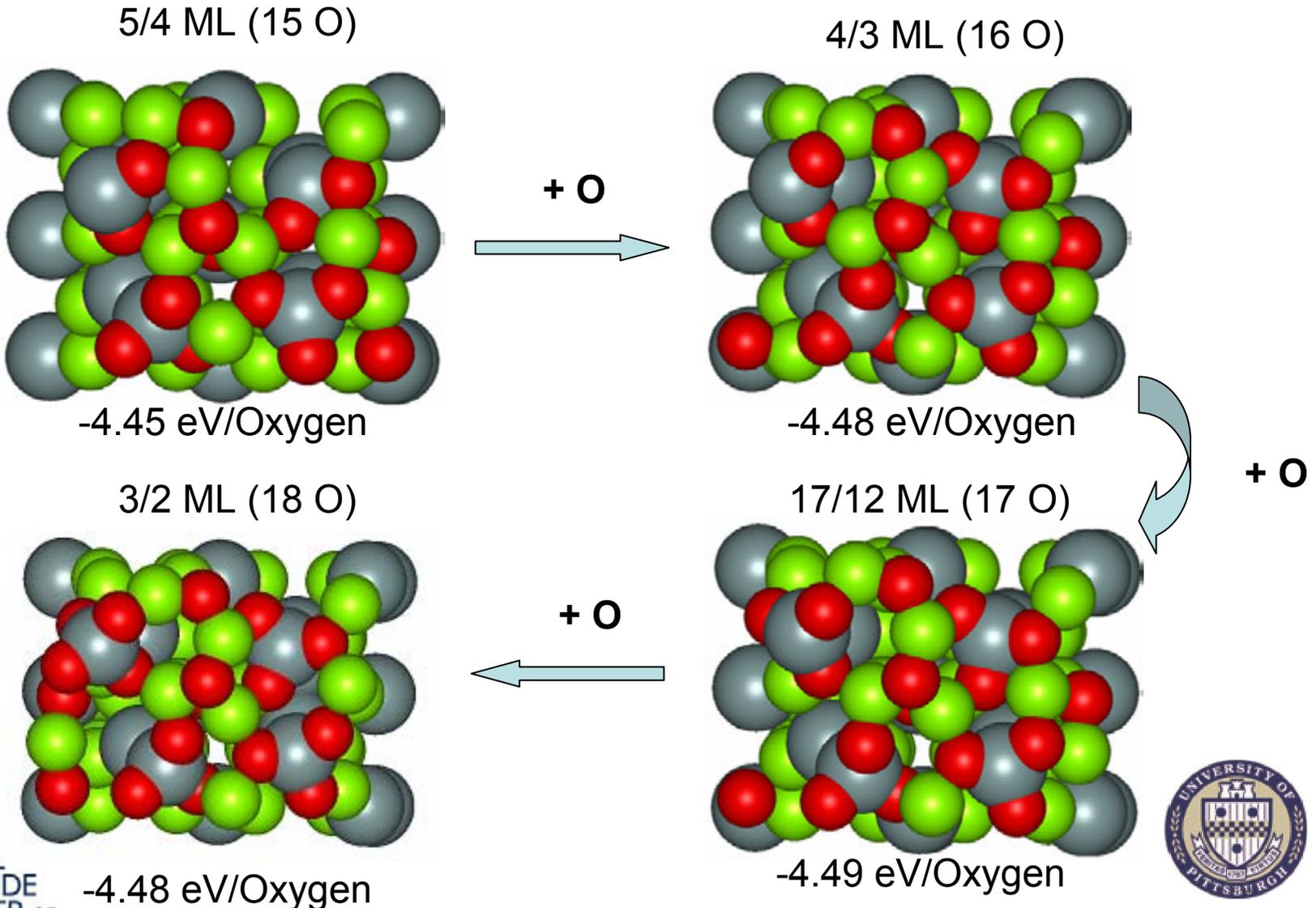
**Energy barrier to H<sub>2</sub> dissociation is 47 kJ/mol  
(39 kJ/mol after zero point vibrational energy corrections)**

# H<sub>2</sub> dissociation on 2/3 ML Oxidation Mg<sub>2</sub>Si Surface



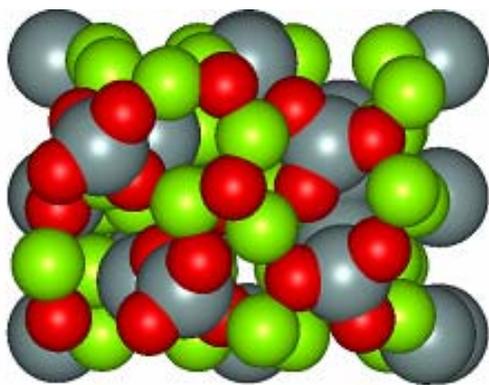
**Energy barrier to H<sub>2</sub> dissociation is 92 kJ/mol  
(80 kJ/mol after zero point energy corrections)**

# Mg<sub>2</sub>Si Surface Oxide Formation (beyond 7/6 ML)



# Mg<sub>2</sub>Si Surface Oxide Formation (beyond 7/6 ML)

19/12 ML (19 O)

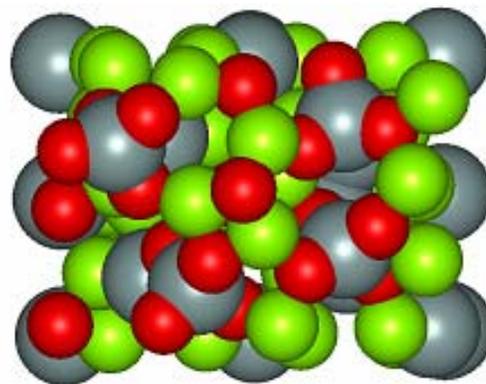


-4.45 eV/Oxygen

+ O

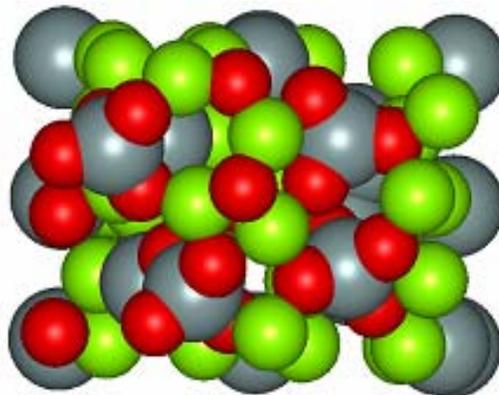


5/3 ML (20 O)



-4.49 eV/Oxygen

7/4 ML (21 O)

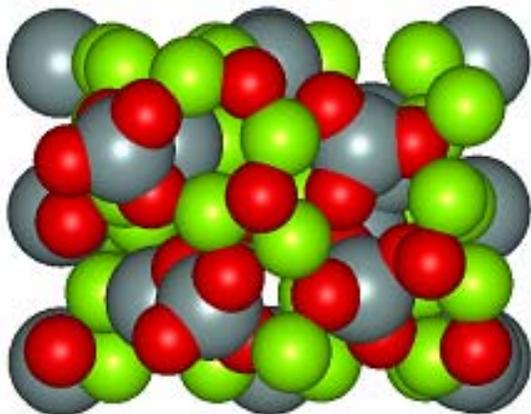


-4.45 eV/Oxygen

+ O



11/6 ML (22 O)



-4.22 eV/Oxygen



+ O

# H<sub>2</sub> Dissociation on Oxide Mg<sub>2</sub>Si Surface

- The adsorption energy per O atom is roughly constant from 1 ML to 7/4 ML, ~-4.5 eV

Coverage (ML)	1/3	2/3	1	13/12	7/6	5/4	4/3	17/12
E <sub>ads/O</sub> (eV)	-3.57	-4.01	-4.44	-4.48	-4.45	-4.45	-4.48	-4.49
E <sub>ads/H</sub> (eV)	----	-0.84	-0.53	-1.21	-0.23	----	----	----
Coverage (ML)	3/2	19/12	5/3	7/4	11/6			
E <sub>ads/O</sub> (eV)	-4.48	-4.45	-4.49	-4.45	-4.22			

# Future Work

- Continue work on destabilized hydride reversibility
- Investigate new reaction schemes for destabilized hydrides including other light elements
- Continue work on computing P-T diagrams for metal hydrides
- Continue work on interfacial energies
- Contribute data to the UIUC toolbox data base
- Collaborate with Ursula Kattner, NIST by computing thermodynamic properties of  $\text{Li}_5\text{B}_4$  and other materials

# Summary

- We have screened over one hundred destabilization reactions based on reaction enthalpy using DFT calculations
- Five promising reaction schemes have been identified
- Equilibrium pressures have been predicted for three of the reactions from first principles
- Facile dissociation of  $H_2$  should be observed on the clean  $Mg_2Si$  surface
- Oxide formation on  $Mg_2Si$  is highly exothermic
- Hydrogen dissociation is inhibited on the oxidized  $Mg_2Si$  surface
- Our calculations are consistent with the experimental observation that ball milling in a hydrogen atmosphere is required for hydrogenation of  $Mg_2Si$

# Publications and Presentations

## ■ Publications:

- Identification of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations, by S.V. Alapati, J.K. Johnson, D.S. Sholl, *J. Chem. Phys. B*, in press

## ■ Presentations:

- Invited talk at the “Hydrogen Storage with Novel Nanomaterials” workshop, 23-28 October, in Ban Honnef, Germany
- “Mechanisms of Hydrogen Adsorption in Metal Organic Frameworks”, AIChE Annual Meeting, Cincinnati, Ohio, 31 October to 4 November, 2005.
- J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, David S. Sholl “Computational Study of Metal Hydride Destabilization” *American Physical Society March Meeting*, Baltimore, MD, 13-17 March, 2006.
- Bing Dai, Sudhakar V. Alapati, David S. Sholl and J. Karl. Johnson “First Principles Investigation of Adsorption and Dissociation of Hydrogen on the Mg<sub>2</sub>Si Surface” 231<sup>st</sup> *American Chemical Society National Meeting*, Atlanta Georgia, 26-30 March 2006.
- Sudhakar V. Alapati, Bing Dai, J. Karl. Johnson and David S. Sholl, “First Principles Calculations of Destabilized Alloys for Hydrogen Storage Applications” *2006 TMS Annual Meeting*, San Antonio, TX, 12-16 March, 2006.
- Organized a session on “Nanotechnology related to the hydrogen economy” as part of the Nanotechnology and the Environment symposium, ACS National Meeting, Atlanta, GA, 26-30 2006