First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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DOE Metal Hydride Center of Excellence

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Project ID #STP25

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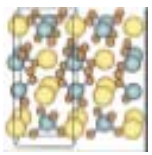
Project Overview

- Overall Goals:
  - Provide modeling support for experimental MHCoE group members
  - Predict thermodynamic and materials properties prior to experimental work—guide experimental efforts in new materials development
- Modeling Capabilities:
  - We use *ab initio* and classical methods to compute structural, electronic, thermophysical and chemical properties of materials
  - We can calculate:
    - Enthalpies and free energies of formation
    - Interfacial energies
    - Diffusion pathways and kinetics (transition states)
    - Reaction pathways and kinetics



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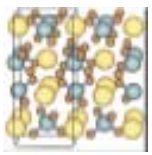
Project Overview

- Specific Research Areas:
  - Thermodynamic properties of alloys
    - Destabilization alloys such as MgH_2/Si
    - Goal is to compute thermodynamics to aid experimental work and to identify mechanisms to find better materials
  - Calculation of interfacial energies
    - Thin films and nanoparticles potentially have different thermodynamic properties
    - Goal is to compute energetics and thermodynamics to aid in the search for promising nanostructured materials
  - Understanding the role of Ti in catalyzing Na_3AlH_6
    - Mechanisms of Ti in catalyzing hydrogenation and dehydrogenation processes in alanates is still not completely understood
    - Goal is to identify the fundamental mechanisms with the aim of applying them to other, more promising materials
  - Fundamental Processes in Hydrogenation of Al/NaH
    - Hydrogenation of sodium alanate is a model system that is well-studied experimentally
    - We aim to apply what we learn about hydrogenation to other more promising materials



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Administrative Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: New Start

Budget

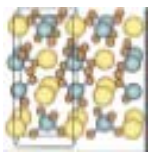
- Requested total: $1.38M
- Cost sharing: 20%
- FY05 $150k (DOE), $37.5k (cost share)

Barriers

- Access to adequate computing resources
- Efficient and accurate electronic structure algorithms
- Thermodynamic properties from first principles

Partners

- Collaborations with all experimental groups are sought
- Current collaborators:
  - HRL
  - GE
  - U. Hawaii
  - Stanford



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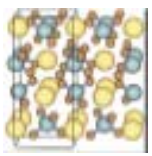
Objectives

- Compute thermodynamic properties of metal hydride alloys, e.g., ΔH for:
  - $2MgH_2 + Si \leftrightarrow Mg_2Si + 2H_2$
  - $LiBH_4 + 1/2MgH_2 \leftrightarrow LiH + 1/2MgB_2 + 2H_2$
  - $4LiH + Si \leftrightarrow Li_4Si + 2H_2$
  - Many others
- Compute interfacial properties of hydrides
  - Metal-hydride interfaces, e.g., Al/NaH
  - Surface energies of metal hydrides for nanoscopic hydrides
  - Apply principles learned on model systems, e.g., alanates, to more promising novel materials.



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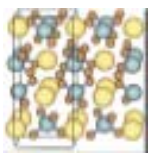
Objectives

- Catalysis processes in hydrides
  - Role of Ti in the decomposition of Na_3AlH_6
  - Inducing reversibility through catalysis of alloy destablized hydrides
- Fundamental processes in hydrogenation Al/NaH and other materials
  - Look for common pathways that might be applicable to other materials
  - What is the role of interfacial transport?



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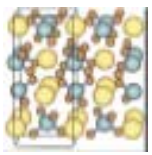
Approach

- First principles density functional theory (DFT) for periodic systems (plane wave)
- Generalized gradient approximation (GGA) for the exchange-correlation functional
- Cluster expansion methods for both ground state and finite-temperature properties
- Transition state finding methods for reaction and diffusion problems
  - Nudged elastic band method
  - Dimer method



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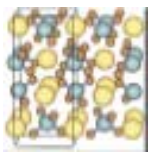
Results

Hydride Alloy Structure & Energetics

- We have computed structural (lattice parameters) and energetic (total energies) for a number of different alloys using GGA DFT
- The energies were used to compute enthalpy of reaction for four different destabilization reactions
- Calculations were compared with experiments to assess the accuracy of GGA DFT for these systems
- This is a validation of our technique!



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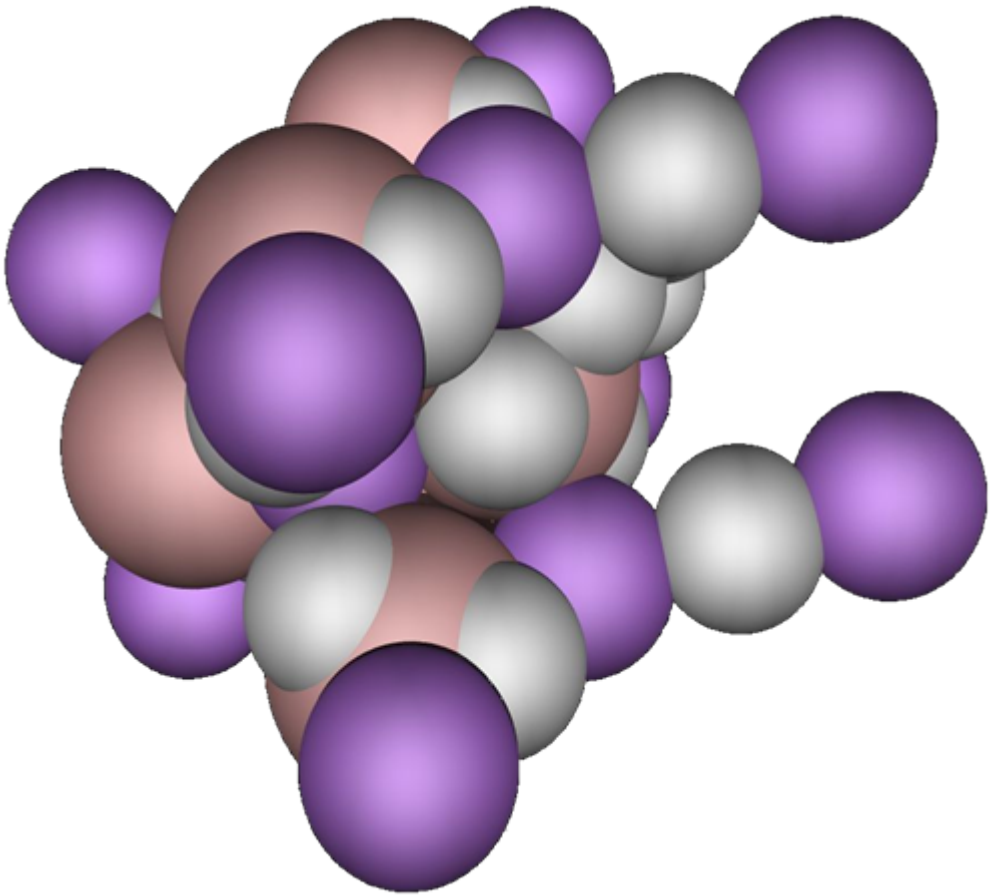
$LiBH_4$



Calculations are in good agreement with experiments!

Orthorhombic Lattice

Lattice Parameter	**a (Å)**	**b (Å)**	**c (Å)**
*Experimental**	7.173	4.434	6.798
DFT-GGA	7.209	4.324	6.422

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* L. Schlapach and A. Zùttel, Nature (London) **414**, 353 (2001)

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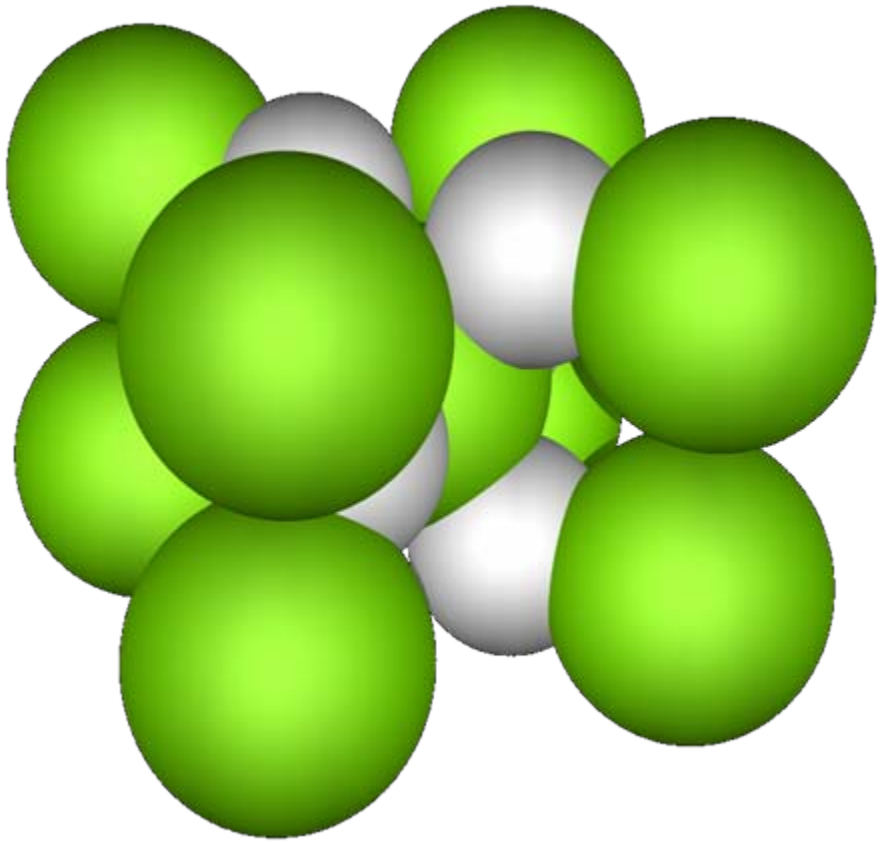
MgH_2



Calculations are in good agreement with experiments!

Body centered Tetragonal Lattice

Lattice Parameter	**a (Å)**	**b (Å)**	**c (Å)**
*Experimental**	4.517	4.517	3.021
DFT-GGA	4.466	4.466	2.992

* W.M. Mueller, J.P. Blackledge and G.G. Libowitz, *Metal Hydrides* (Academic Press, New York 1968)

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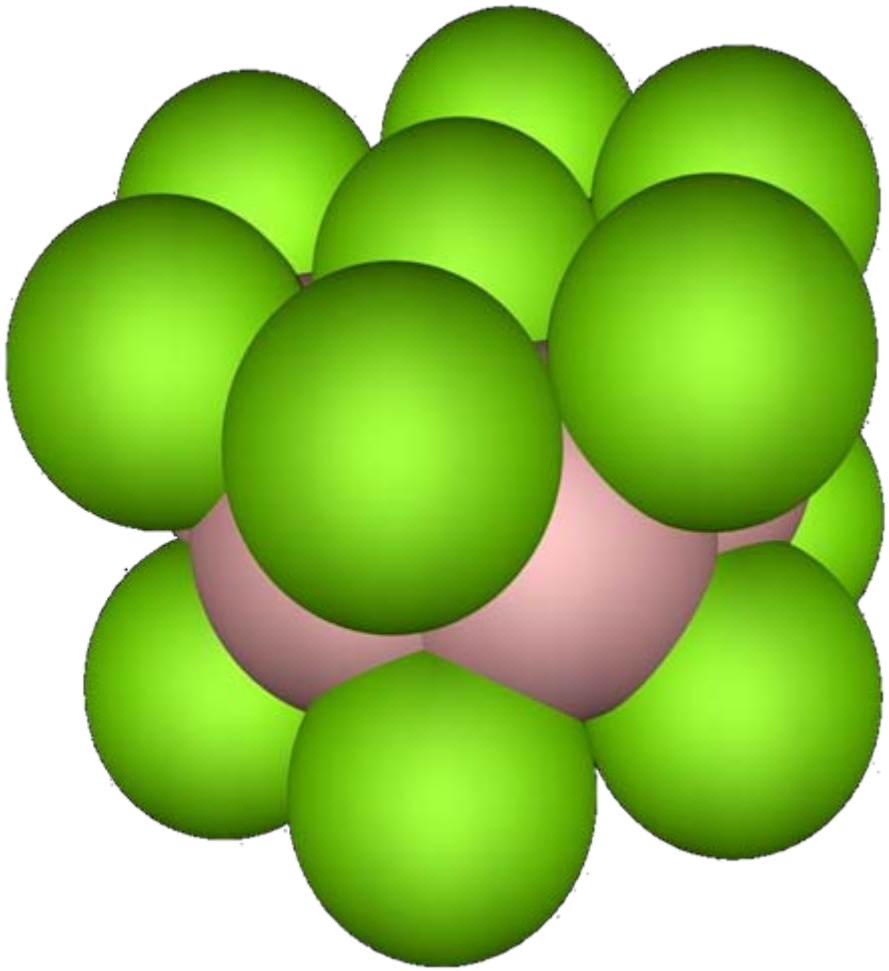
MgB_2



Calculations are in good agreement with experiments!

Hexagonal Lattice

Lattice Parameter	**a (Å)**	**c (Å)**
*Experimental**	3.084	3.522
DFT-GGA	3.068	3.520

* R.W.G. Wycoff, *The Structure of Crystals* (The Chemical Catalog Company Inc., New York 1931)

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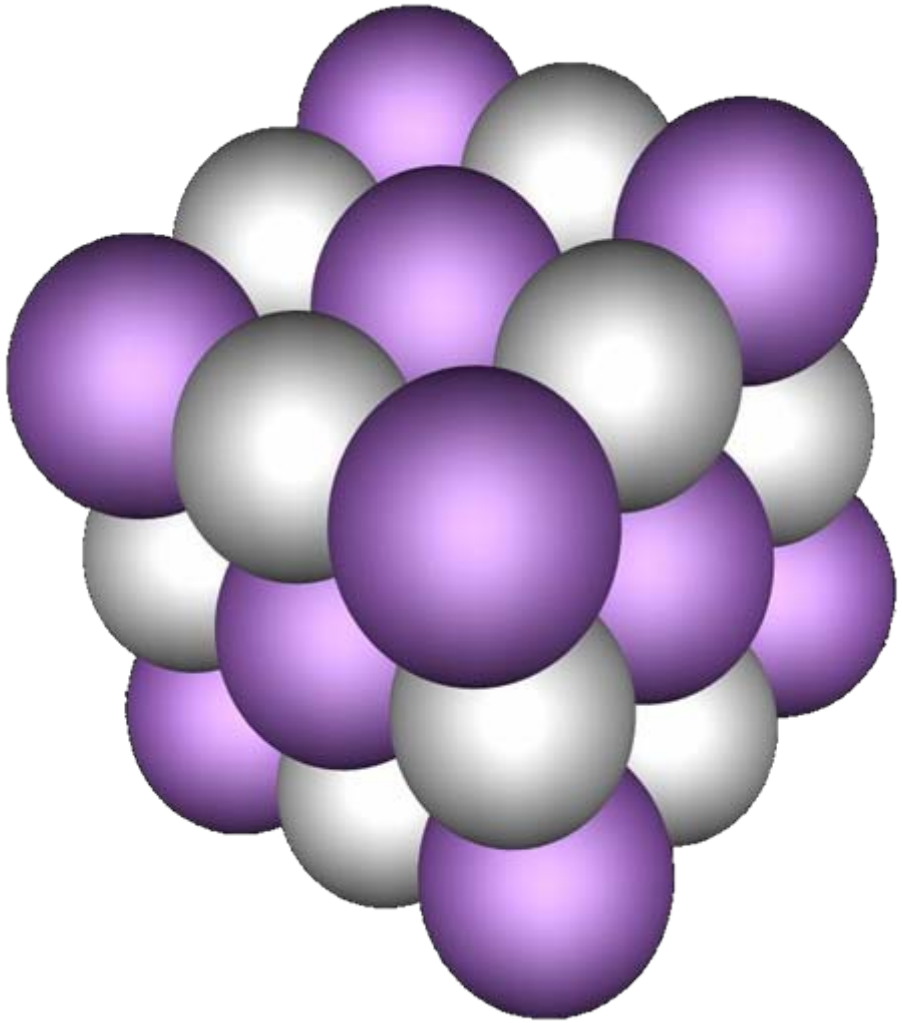
LiH



Calculations are in good agreement with experiments!

NaCl Structure

Lattice Parameter	**a (Å)**
*Experimental**	4.083
DFT-GGA	3.93

* R.W.G. Wycoff, *The Structure of Crystals* (The Chemical Catalog Company Inc., New York 1931)

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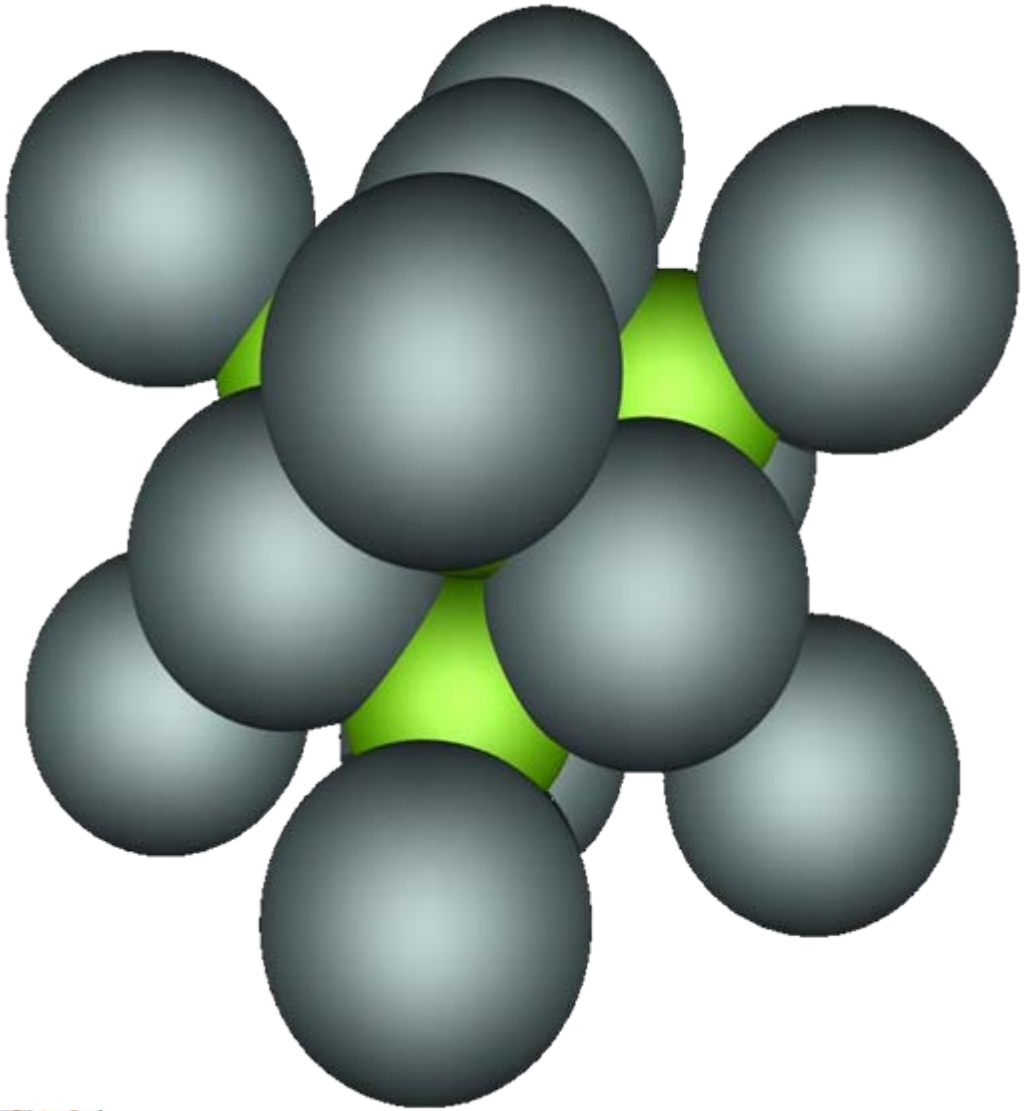
Mg_2Si



Calculations are in good agreement with experiments!

Cubic Anti-fluorite Structure

Lattice Parameter	**a (Å)**
*Experimental**	6.39
DFT-GGA	6.361

* R.W.G. Wycoff, *The Structure of Crystals* (The Chemical Catalog Company Inc., New York 1931)

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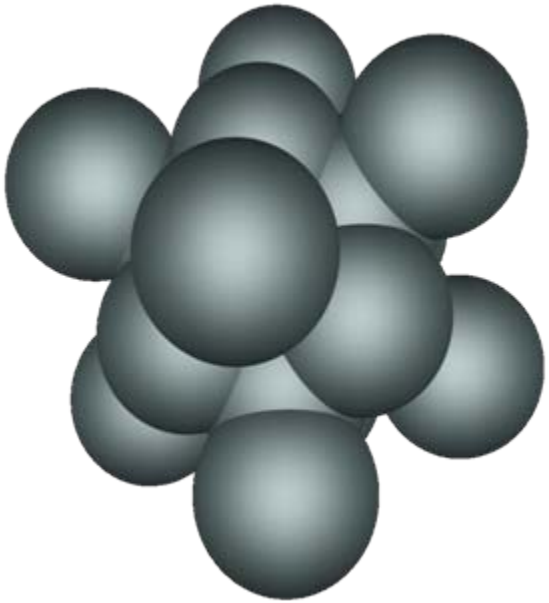
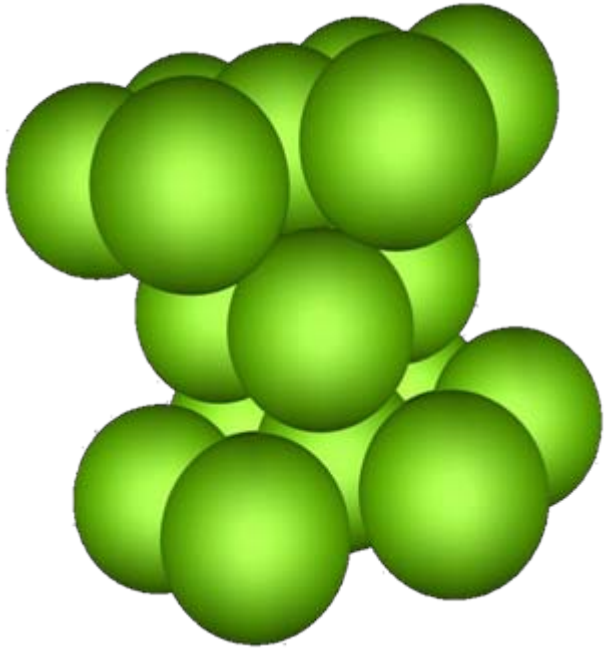
Si, Mg, Li



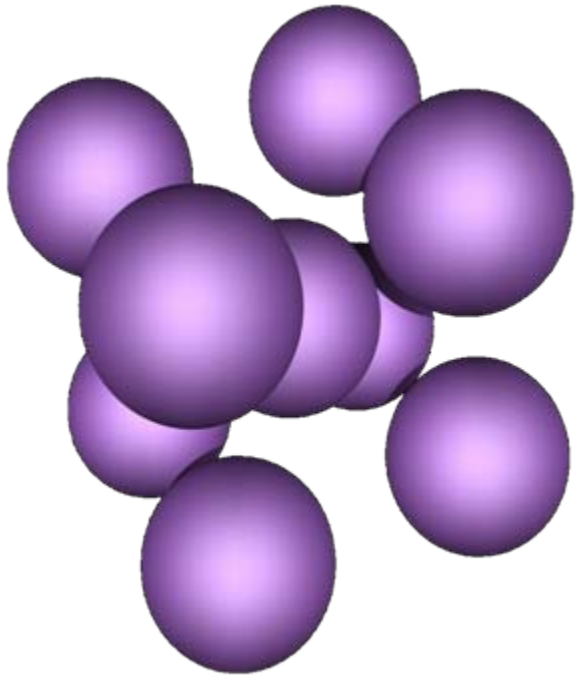
Diamond Structure

Lattice Parameter	a (Å)
*Exp**	5.43
DFT-GGA	5.46



Hexagonal Lattice

Lattice Parameter	a (Å)	c (Å)
*Exp**	3.209	5.210
DFT-GGA	3.228	5.083



BCC Lattice

Lattice Parameter	a (Å)
*Exp**	3.51
DFT-GGA	3.401

* R.W.G. Wycoff, *The Structure of Crystals* (The Chemical Catalog Company Inc., New York 1931)

Enthalpy Change for Reactions

$$MgH_2(s) + 2LiBH_4(s) \rightarrow 2LiH(s) + MgB_2(s) + H_2(g)$$

	Tabulated*	DFT-GGA
ΔH/mol H_2(KJ/mol)	45.96	46.2

$$2MgH_2(s) + Si \rightarrow Mg_2Si(s) + H_2(g)$$

	Tabulated*	DFT-GGA
ΔH/mol H_2(KJ/mol)	37.24	37.1

Enthalpies can be calculated with good accuracy from DFT

$$LiH(s) \rightarrow Li(s) + H_2(g)$$

	Tabulated*	DFT-GGA
ΔH/mol H_2(KJ/mol)	181.26	183.3

$$MgH_2(s) \rightarrow Mg(s) + H_2(g)$$

	Tabulated*	DFT-GGA
ΔH/mol H_2(KJ/mol)	76.15	64.1

*J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (HPC., New York, 1989)

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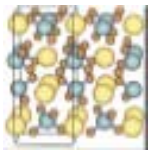
Conclusions

- DFT is a very effective tool for predicting the enthalpy of reactions
- DFT can be used to compute enthalpies for which no tabulated or experimental data are available, provided the lattice structure is known
- Calculations can be used to screen reactions with high enthalpy without actually conducting any experiments
- We can predict which materials may be suitable as hydrogen storage devices based on calculated enthalpy changes



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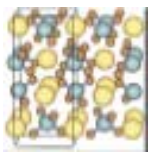
Results

Reversibility of Destablized Hydrides

- Vajo and coworkers at HRL have found that alloying very stable metal hydrides can substantially increase the release of hydrogen
  - $2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$
- However, the reverse reaction, while thermodynamically favorable, is not observed
  - $Mg_2Si + 2H_2 \rightarrow 2MgH_2 + Si$
- We are studying the adsorption and dissociation on Mg_2Si to identify the kinetic barriers



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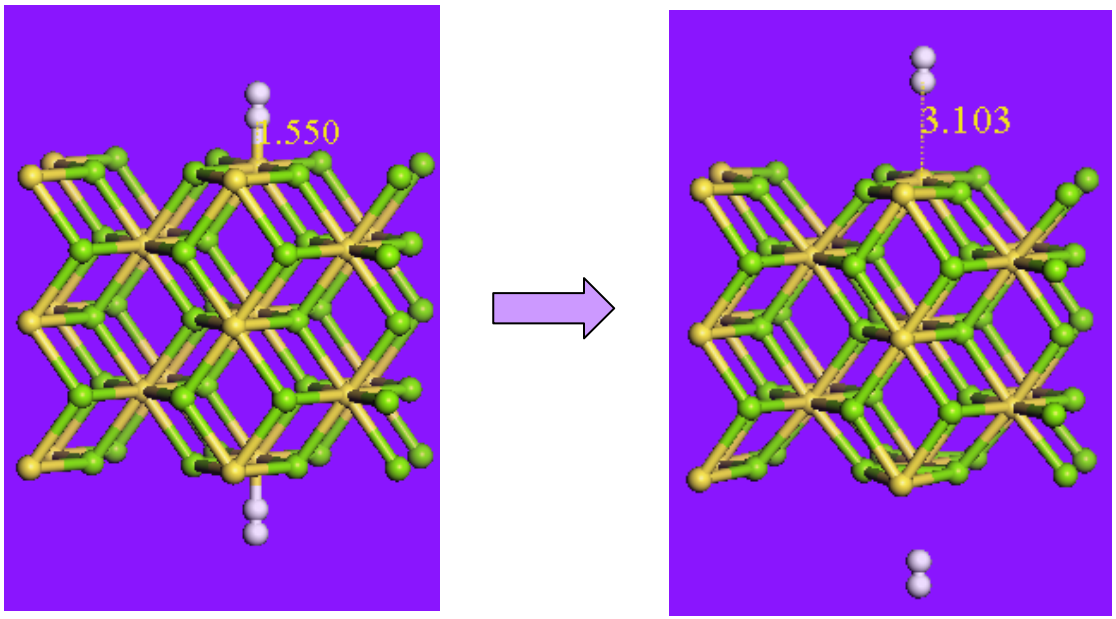
Results

Reversibility of Destablized Hydrides

Initial calculations using plane wave DFT to find adsorption geometries and energetics

H_2 is on the Si site



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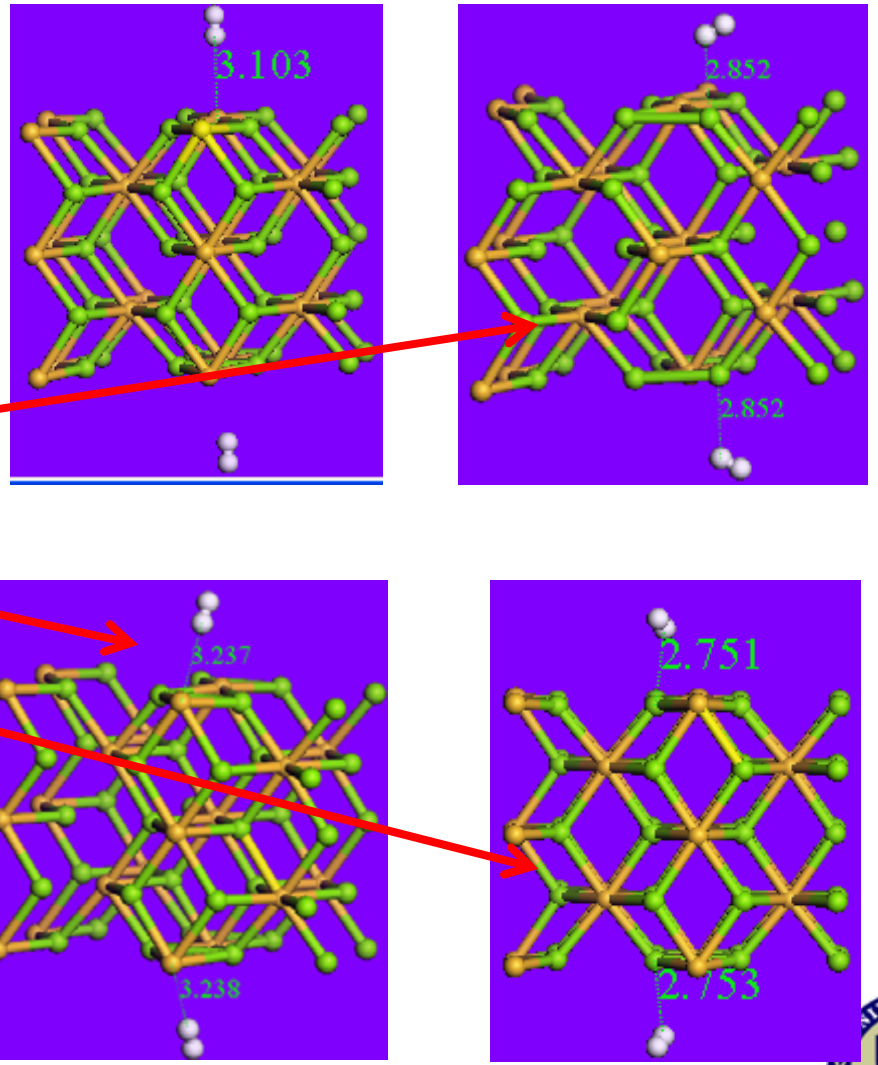
Results

Reversibility of Destablized Hydrides

- Four different adsorption sites have been identified
  - Si top
  - Mg top
  - Mg-Si bridge site
  - Hollow site
- All sites lead to a weakly adsorbed (physisorbed) state for H_2



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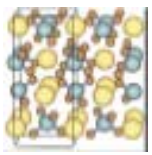
Conclusions

- Molecular hydrogen adsorbs very weakly through physisorption (van der Waals interactions) on the Mg_2Si surface
- The binding energies are on the order of 0.1 eV
- Dissociation of H_2 on the Mg_2Si surface must have a substantial energy barrier



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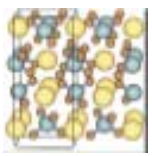
Future Work

- Calculate dissociation pathways for H_2 on Mg_2Si
- Calculate binding energies and adsorption barriers for atomic H on Mg_2Si
- Consider catalytic pathways to facilitate the reversibility of $Mg_2Si + 2H_2 \rightarrow 2MgH_2 + Si$



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