



First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Project ID#
ST_08_Johnson



Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 80%

Budget

- Requested total: \$1.05M (DOE)
- Cost sharing: \$0.33M
- FY08 \$218K (DOE)
- FY09 \$225K (DOE) planned

Barriers

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

Partners

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




Overall Objectives

- Predict new metal hydrides with favorable thermodynamics
- Compute interfacial properties of hydrides
- Address fundamental processes in hydrogenation

Specific Objectives for FY09-FY10

- Complete reaction screening including multistep and metastable reactions and new additions to the database
- Finalize work on thermodynamics of multiple gas-phase species
- Include thermodynamics of amorphous and crystalline closo-borane structures such as $\text{MgB}_{12}\text{H}_{12}$ and related materials in the screening of candidate reactions
- Finish work on mixed metal hydrides

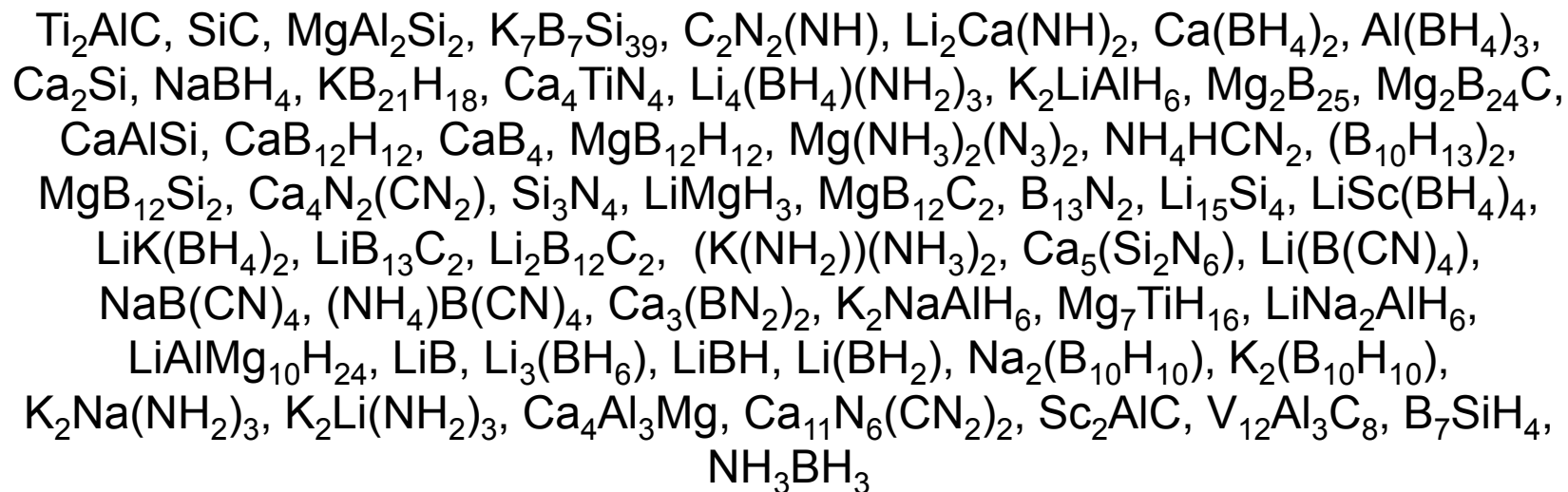
Milestones

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 $\text{Mg}(\text{BH}_4\text{H})_2$ in concert with experimental efforts. Experiments have identified $\text{Mg}(\text{B}_{12}\text{H}_{12})$ as a possible amorphous phase intermediate.</p>

- We use first principles density functional theory to compute structures and energies of solids and gas phase species
- Phonon density of states calculations are performed for finite temperature thermodynamics
- A free energy minimization linear program is used for screening mixtures for promising reactions
- Surface energy calculations are used to assess nanoparticle effects on the thermodynamics
- First principles molecular dynamics is used to generate amorphous phases
- Transition state theory employed for studying surface reactions and diffusion mechanisms

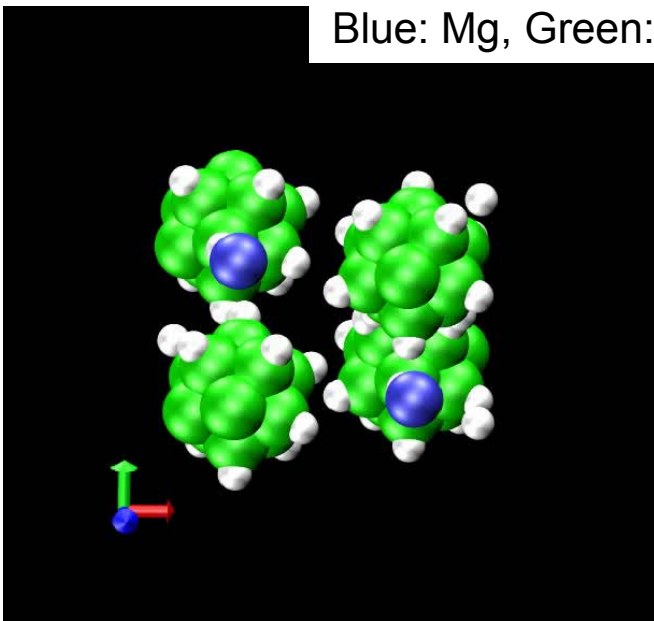
MH Database: Library of compounds used to predict thermodynamics for new reactions

We are adding new structures from the ICSD and from recent literature (experiments & modeling):

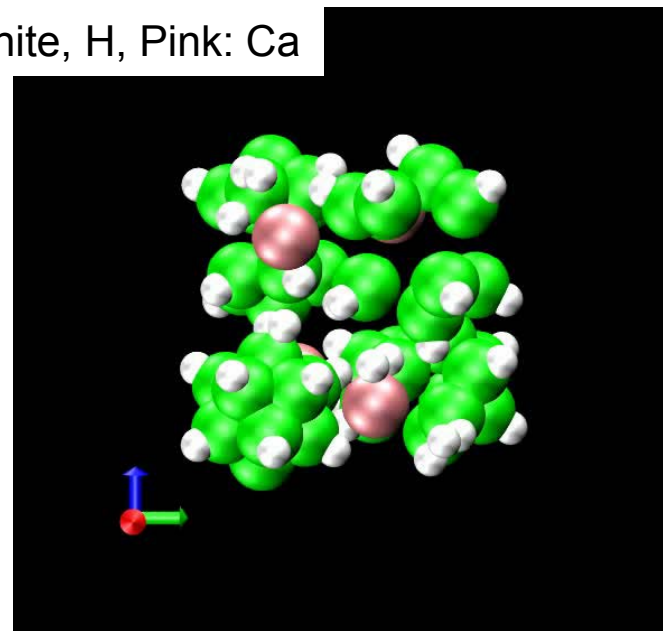


Technical Accomplishments Generating Amorphous Structures

Blue: Mg, Green: B, White, H, Pink: Ca



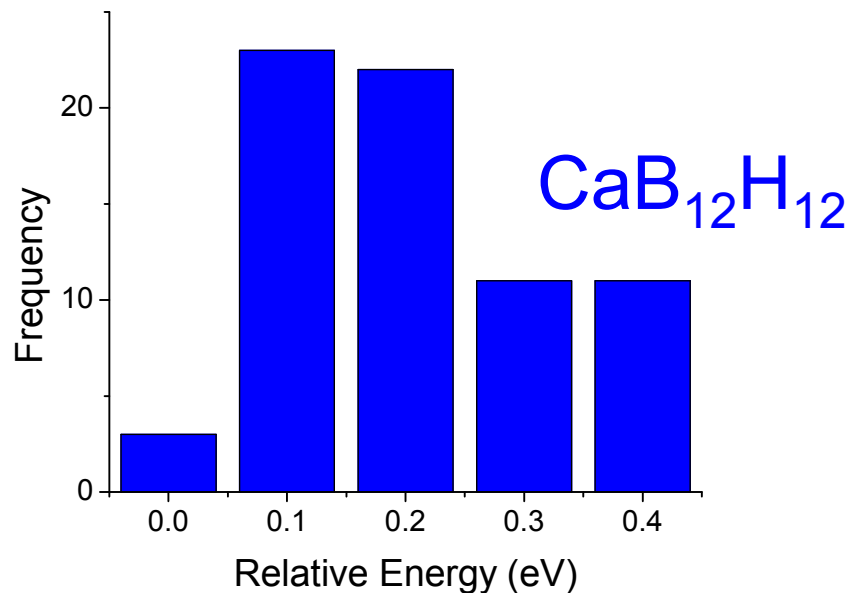
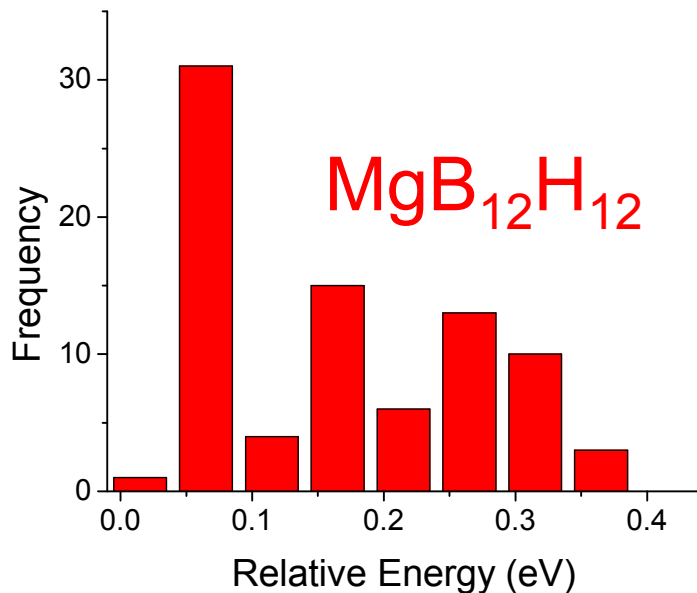
$\text{MgB}_{12}\text{H}_{12}$



$\text{CaB}_{12}\text{H}_{12}$

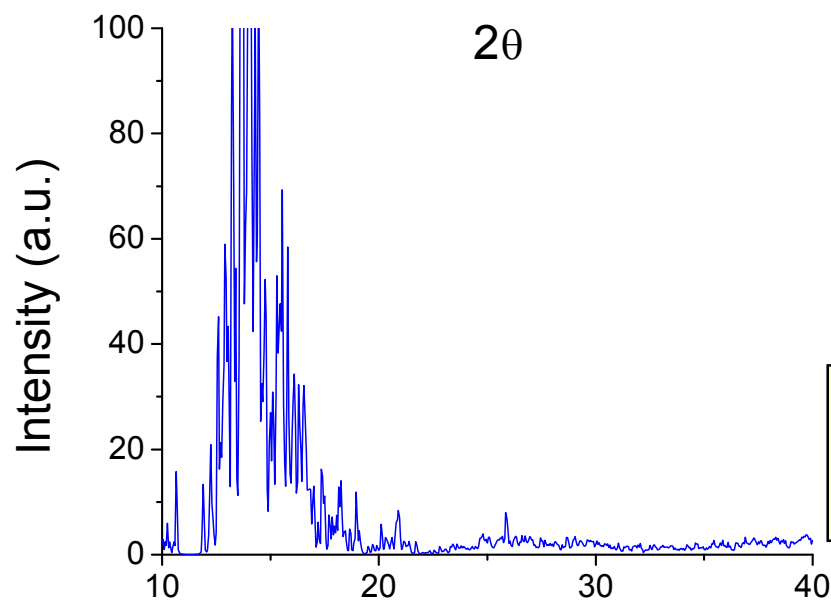
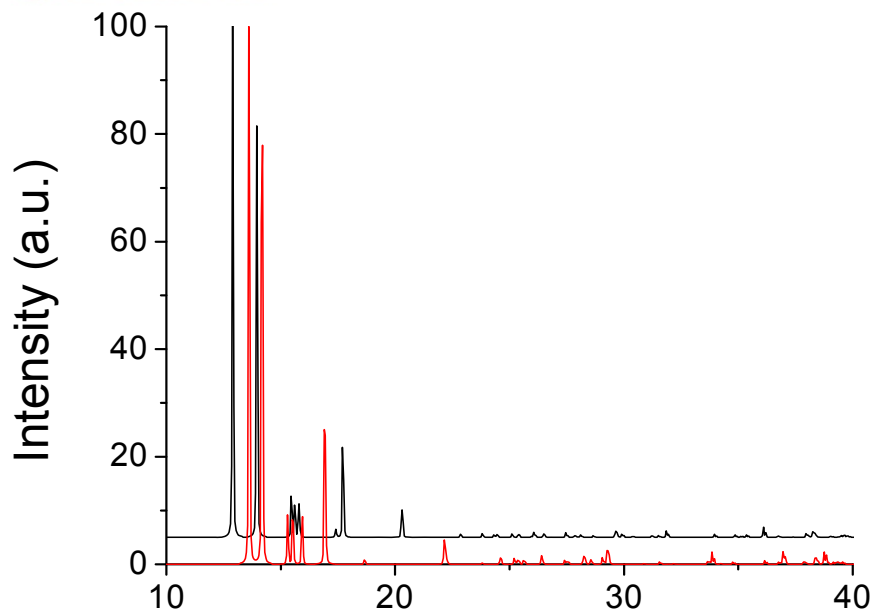
- Experiments: Dehydrogenation of $\text{M}(\text{BH}_4)_2$ can give amorphous $\text{MB}_{12}\text{H}_{12}$ intermediate products: Ahn et al., *J. Phys. Chem. C* **2008**, 112, 3164-3169; D. Graham, I. Robertson, in preparation
- Tech Team suggested simulations with amorphous structures
- Ab initio MD with a 100 atom supercell, $T=1000$ K, used to generate candidate amorphous structures
- Snapshots picked out and relaxed to ground state low energy structures
- We find many structures that are nearly isoenergetic, differing in the location of the cations and the rotation of the $\text{B}_{12}\text{H}_{12}$ units.
- Collaboration with D. Johnson, D. Graham, I. Robertson (Illinois), paper in progress.

Amorphous Materials: Many Low Energy Structures



- Energy histograms of structures optimized from MD melt snapshots
- Many structures have energies that are within tens of meV of the ground state—some within a few meV (NB $kT=0.03$ eV)
- The ground states are the PEGS structures generated by Majzoub et al. *J. Am. Chem. Soc.*, **2009**, 131, 230-237

Many structures are populated at room temperature



- Top graph: simulated XRD of two low-energy crystal structures
- Bottom graph: Boltzmann average of simulated XRD of all structures at 300 K
- The cation positional disorder and $B_{12}H_{12}$ orientational disorder leads to amorphous-like XRD patterns

Simulated Boltzmann averaged XRD is amorphous-like

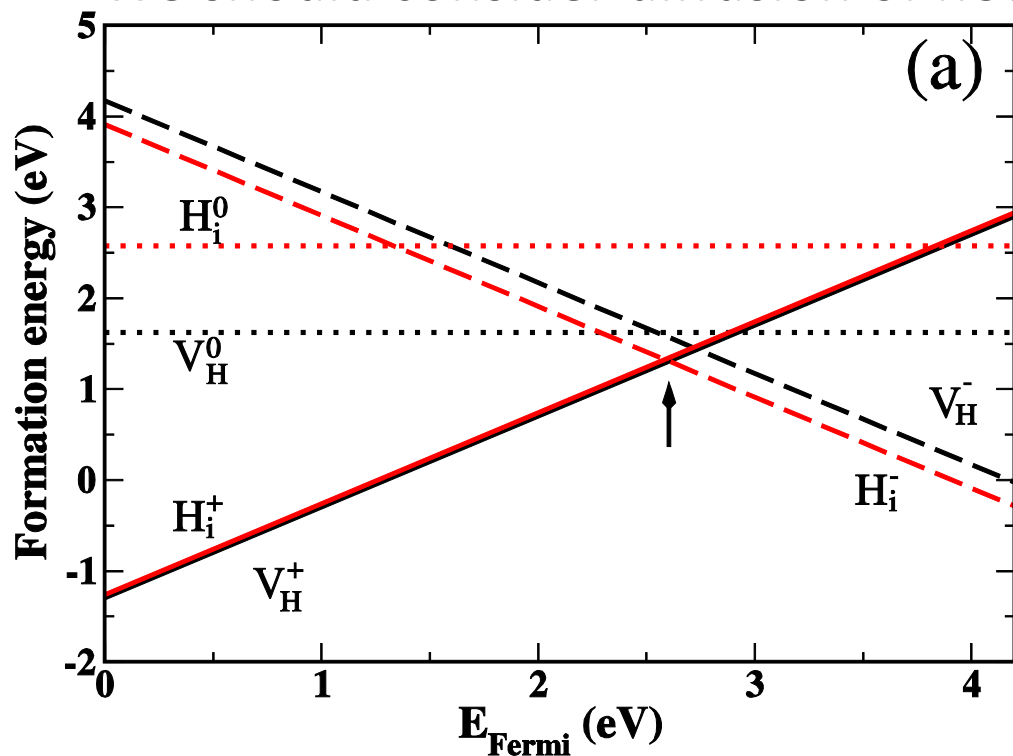
Mechanism of H Diffusion in MgH_2 and NaMgH_3

Motivation: Accurate description of diffusion allows identification of dopants to improve diffusion kinetics

Chemistry point of view: MgH_2 an ionic solid $(\text{Mg})^+ 2(\text{H})^-$

Physics point of view: MgH_2 an insulator, DFT band gap > 4 eV

We should consider diffusion of neutral and charged defects



Use methods introduced by
Chris van de Walle
(*Phys. Rev. B* **76** (2007) 214101)

Position of Fermi level is fixed
by charge neutrality

Hao and Sholl, *Appl. Phys. Lett.*, 93 (2008) 251901

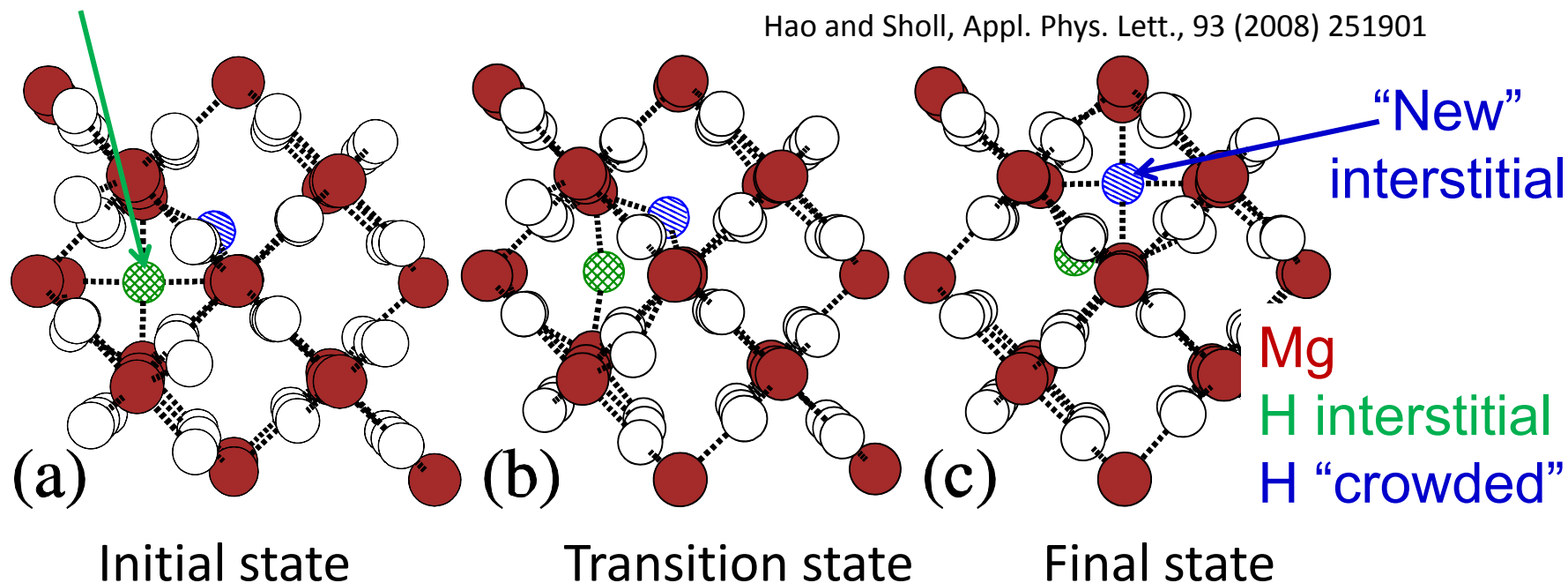
Key result: Dominant defect is (vacancy)⁺ and (H interstitial)⁻

Diffusion Mechanisms for Charged Defects in MgH_2

- Hopping of (vacancy)⁺ has energy barrier 0.30 eV (compared to 0.60 eV for neutral vacancy)
- Diffusion of (interstitial H)⁻ in MgH_2

Interstitial

Hao and Sholl, Appl. Phys. Lett., 93 (2008) 251901

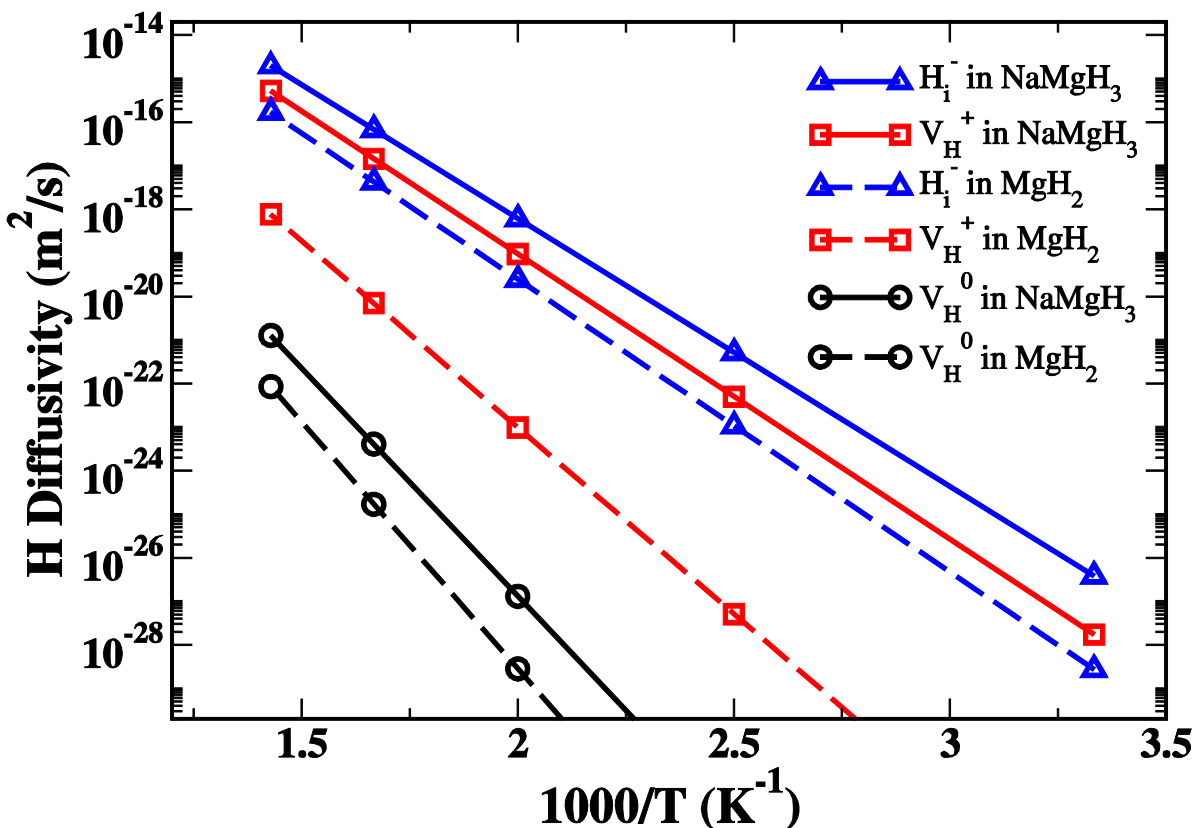


This is an “interstitialcy” mechanism
Energy barrier for this process is 0.003 eV

H Diffusion Rates Mediated by Charged Defects in MgH_2 and NaMgH_3



Hao and Sholl, Appl. Phys. Lett., 93 (2008) 251901



- Diffusion dominated by charged defects in MgH_2 and NaMgH_3 , qualitatively confirmed by experiments in samples with applied voltage by Griessen and co-workers (Appl. Phys. Lett. 90 (2007) 071912)
- Results based on neutral defects are wrong by many orders of magnitude

Dopants Enhance H Diffusion in MgH_2 and NaMgH_3

Presence of charged dopants can greatly enhance H diffusion rates.

This idea advanced by Peles & van de Walle for NaAlH_4 (Phys. Rev. B. 76 (2007) 214101)

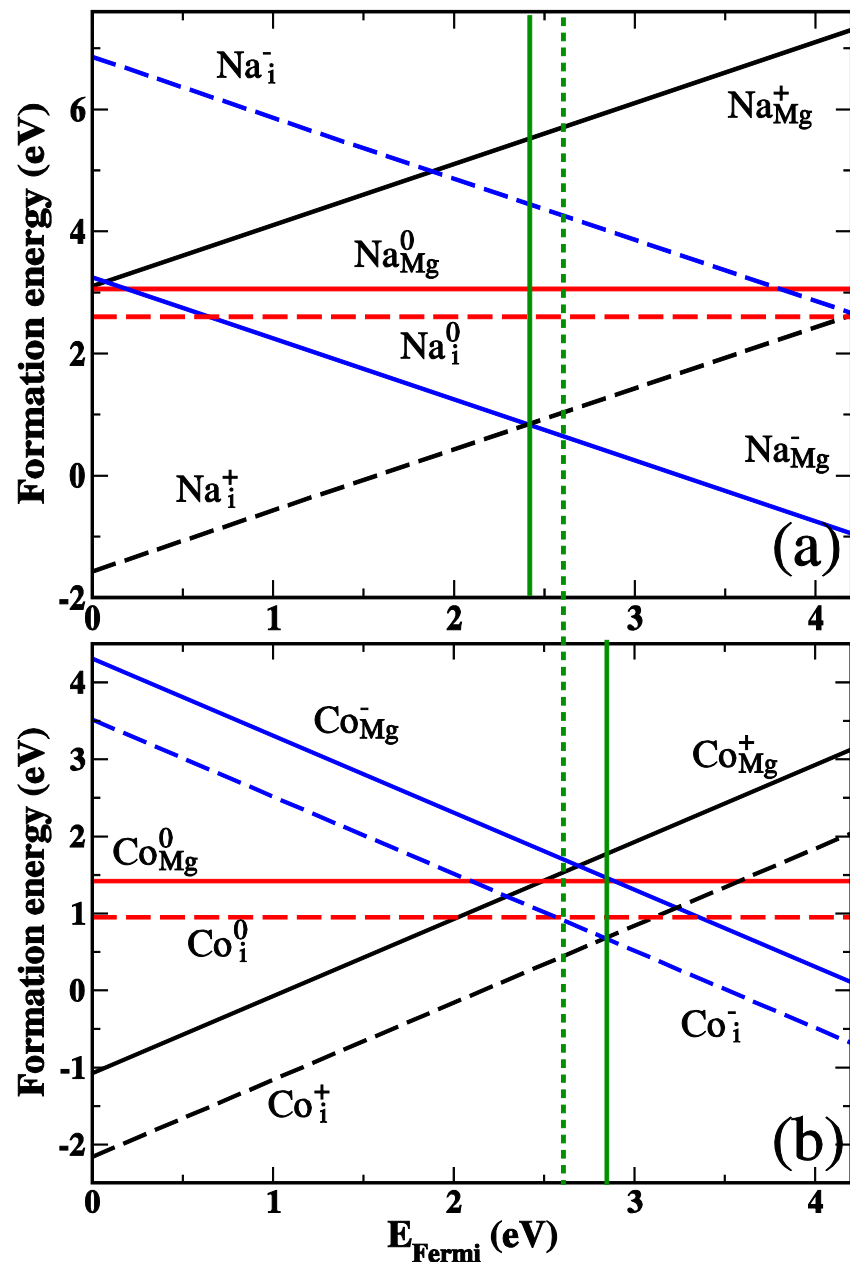
DFT calculations used to assess dopants in MgH_2 and NaMgH_3

Na in MgH_2 acts as a *p*-type dopant, increasing population of H^+ vacancies but not enhancing overall H diffusion.

Co in MgH_2 acts as an *n*-type dopant, increasing population of H^- interstitials and enhancing overall H diffusion.

At 400 K, H diffusion is predicted to be enhanced by a factor of ~ 1000 .

Potential to identify dopants
for other systems



Extension of Screening Formalism: Thermodynamic Calculations With Multiple Gas-phase Species

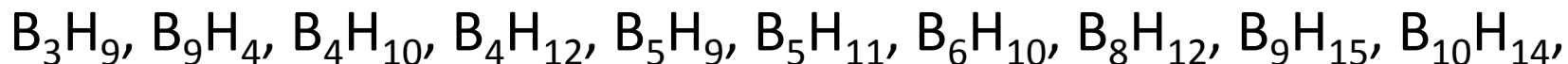
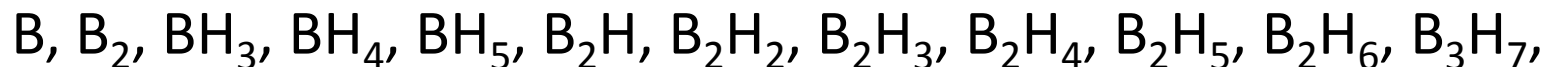
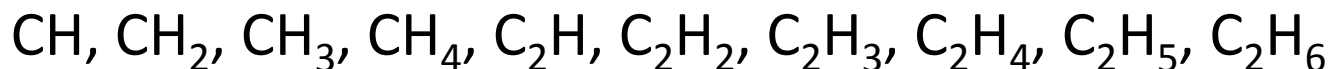
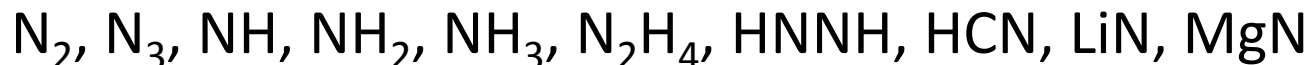


—*In collaboration with Mark Allendorf, Sandia*



Sandia
National
Laboratories

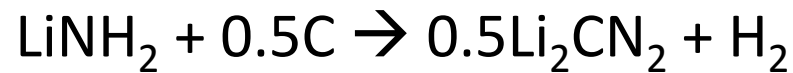
- Previous grand potential method was limited to a single gas phase product: Pure H₂.
- FactSage used to perform thermodynamic calculations with free energies for solid phases computed using DFT (including zero point energies and vibrational contributions)
- Gas phase species included in calculations:



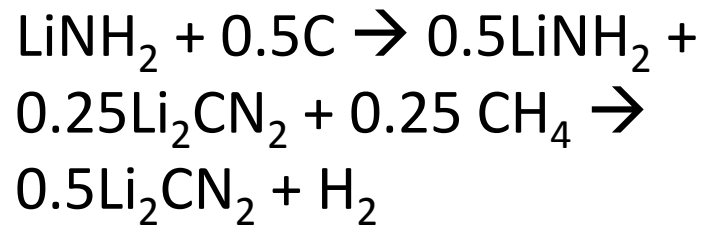
- All calculations performed in closed systems

Example: $\text{LiNH}_2 + \text{C}$

Nominal reaction (only H_2 gas phase):

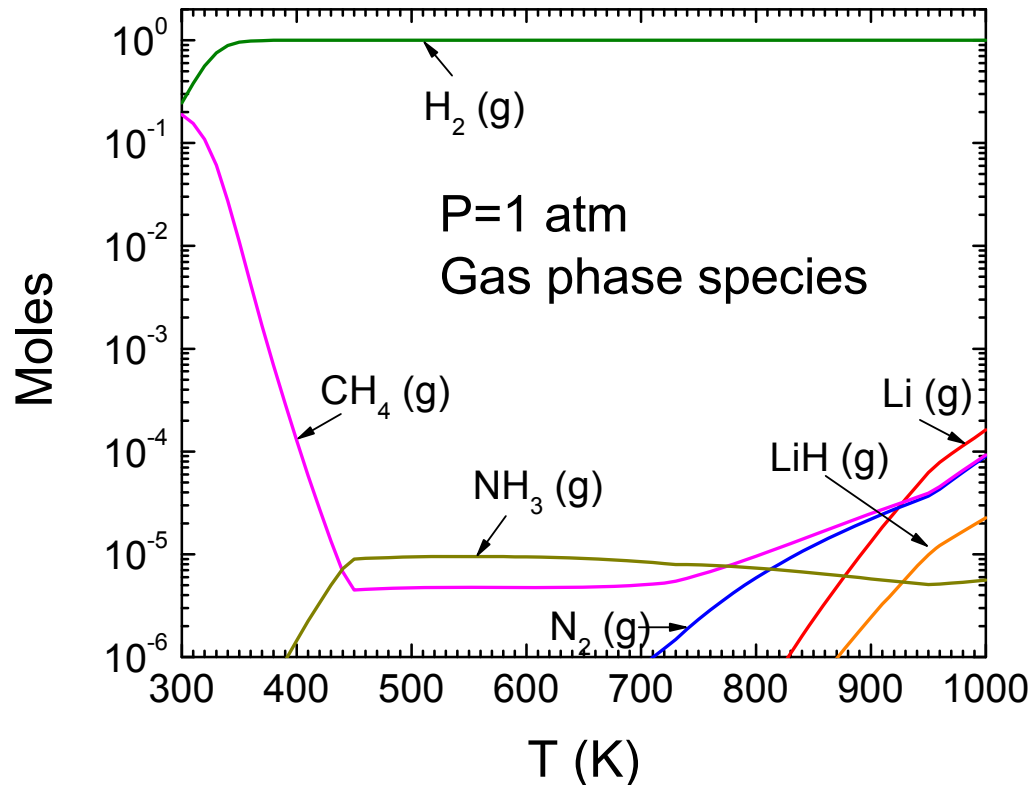


Adding other gas phase species:



Side reactions: Formation of NH_3 , N_2 are low

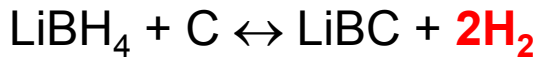
At higher T: LiH , Li appear in the gas phase



Screening now identifies generation of CH_4 —Desired products are metastable

Example: $\text{LiBH}_4 + \text{C}$

Nominal reaction



Also possible:

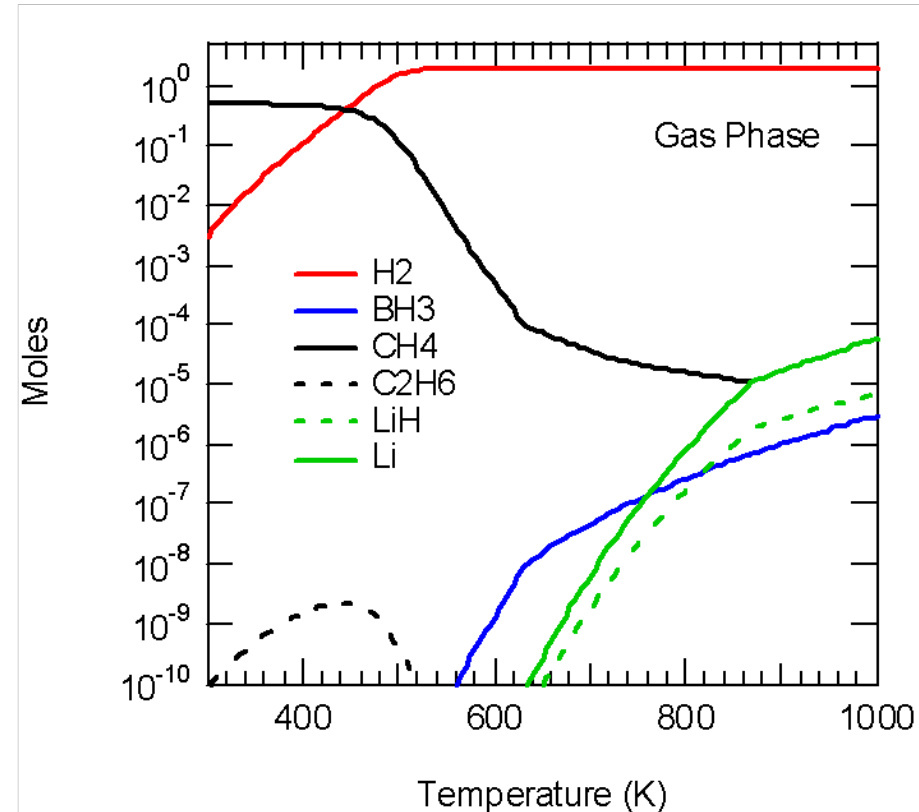
- $\text{LiBH}_4 + 2\text{C} \leftrightarrow \text{LiBC} + \text{CH}_4$
- $\text{LiBH}_4 + 0.75\text{C} \leftrightarrow \text{LiH} + \text{B} + 0.75\text{CH}_4$

Conditions for each calculation

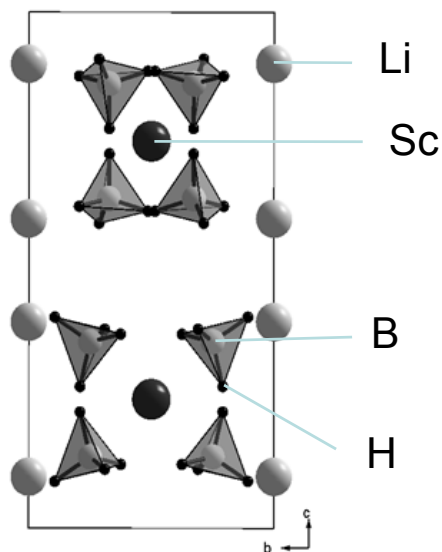
- 1 mole LiBH_4 + 1 mole C as graphite
- Constant P (1 atm), constant T

Results

- LiH and C(s) not stable 300-640 K
 - Converted to CH_4 and LiBC
- Complete conversion to $\text{LiBC} + \text{H}_2$ only at $T > 540\text{ K}$
- BH_3 is only significant B-containing gas-phase species

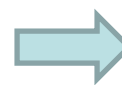


New Borohydrides: LiSc(BH₄)₄ and LiK(BH₄)₂



Experimental observation

Li : Half occupancy (4k position)



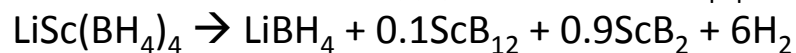
Our DFT calculation

Li : Full occupancy (2a position)

H. Hagemann *et al.* J. Phys. Chem. A 112 (2008) 7551

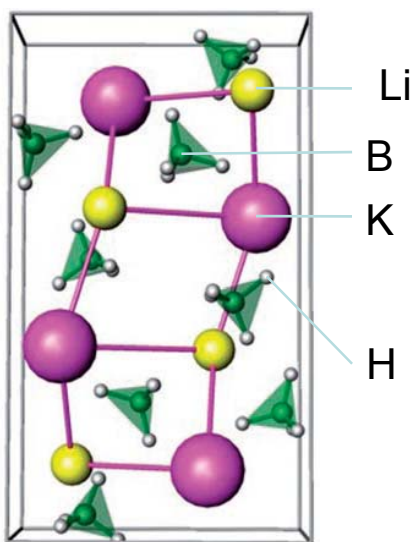
-We identified reaction thermodynamics of LiSc(BH₄)₄ using thermodynamic calculations:

1. Minimum free energy path of LiSc(BH₄)₄ decomposition reaction



2. Destabilization reactions of LiSc(BH₄)₄

Also investigated by Eric Majzoub & others in MHCoe



- Experimental observation

LiK(BH₄)₂ is synthesized by the mixture of LiBH₄ and KBH₄

E. A. Nickels *et al.* Angew. Chem. Int. Ed. 47 (2008) 2817

-Our calculations:

1. Bulk optimizations for LiK(BH₄)₂, KBH₄, and NaBH₄

2. Thermodynamic examination of LiK(BH₄)₂

LiK(BH₄)₂ is not the stable compound compared with the mixture of LiBH₄ and KBH₄

Collaborations: Experimental



- Rebecca Newhouse, Sandia and Ewa Ronnebro (formerly Sandia)
 - We are computing the thermodynamics of the doped materials: $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ and $\text{Mg}(\text{B}_{(1-x)}\text{C}_x)_2$
- Y. Filinchuk, R. Černý, Grenoble, Geneva
 - Experimental powder XRD gave $\text{Mg}(\text{BH}_4)_2$ structure of $P6_1$, Our DFT calculations gave $P6_122$ as the ground state, which prompted Filinchuk et al. to obtain single crystal XRD, which confirmed our predicted $P6_122$ structure as the correct ground state. *Chem. Mater.*, **2009**, *21*, 925.
- Channing Ahn, CalTech
 - Testing several systems we predicted to have favorable thermodynamics, including $\text{LiBH}_4/\text{TiH}_2$ and $\text{LiBH}_4/\text{CaH}_2$
- Zak Fang, Utah
 - We are providing calculations for the LiMgN system
- Andrew Goudy, DSU / Fred Pinkerton, GM
 - Independently both working on $\text{CaH}_2 + 6 \text{LiBH}_4$
- John Vajo, HRL
 - Testing several systems for which we have made predictions, including LiBC and $\text{Mg}(\text{BC})_2$

Collaborations: Theory



We are working closely with many other computational people within the MHCoE:

- Mark Allendorf (Sandia, leader of Theory Group)
- Bruce Clemens (Stanford)
- Duane Johnson (Illinois)
- Ursula Kattner (NIST)
- Eric Majzoub (Missouri)

Future Work

- **FY 2009**

- Carry out analysis of multi-step reactions, submit paper for publication
- Finish calculations for updated database reactions and carry out screening
- Analyze the thermodynamics and structure of amorphous $MB_{12}H_{12}$ systems for $M=Ca$ and Mg

- **FY 2010**

- Examine diffusion through void spaces in metal hydrides, as prompted by experimental observations
- Implement fast reaction screening with multiple gas phase species in as many cases as possible

- **Relevance:** Theory is a powerful tool for screening candidate materials, predicting thermodynamics, investigating diffusion
- **Technical Accomplishments:**
 - Character of amorphous $\text{MgB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ has been analyzed
 - Diffusion mechanism involving charged species found to be important in metal hydrides—doping produces higher diffusion rates
 - Free energy calculations have been augmented to include multiple gas phase species
 - New mixed metal borohydrides characterized
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- **Personnel:** Ki Chul Kim, Anant Kulkarni