First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Overview

Timeline

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

Barriers

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

Budget

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

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

Objectives-Relevance

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 $MgB_{12}H_{12}$ 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 ✓	**Identify single-step reactions having acceptable hydrogen gravimetric densities and thermodynamics using the automated free energy search procedure.** Paper has now been published: *J. Phys. Chem. C*, **112**, 5258-5262 (2008).
Jun-08 ✓	**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.
Sept-08 ✓	**Investigate dehydrogenation/hydrogenation pathways for $Mg(BH_4H)_2$ in concert with experimental efforts.** Experiments have identified $Mg(B_{12}H_{12})$ as a possible amorphous phase intermediate.

Approach

- 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

Technical Accomplishments: New Database Entries

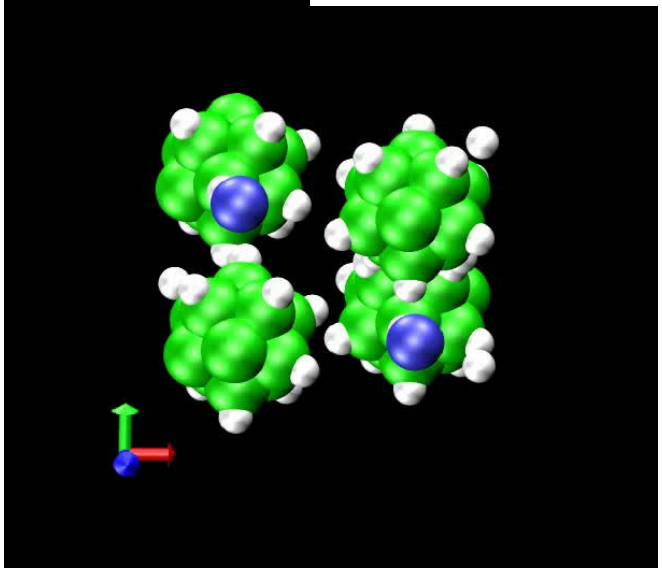
MH Database: Library of compounds used to predict thermodynamics for new reactions

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

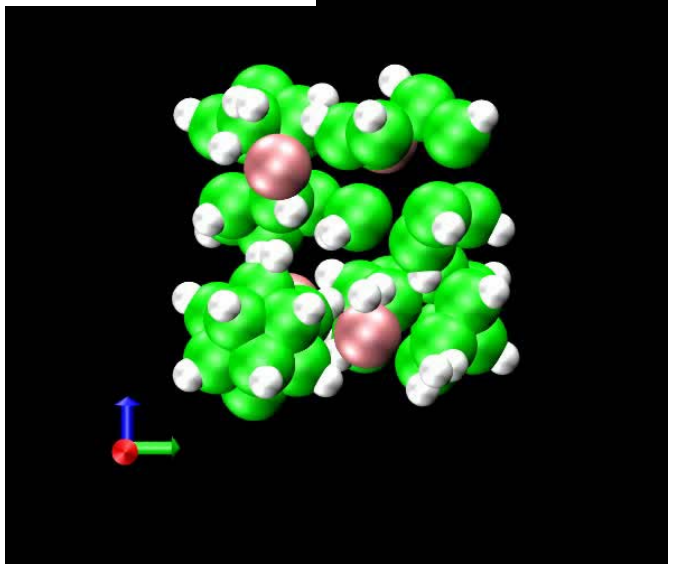
Ti_2AlC, SiC, $MgAl_2Si_2$, $K_7B_7Si_{39}$, $C_2N_2(NH)$, $Li_2Ca(NH)_2$, $Ca(BH_4)_2$, $Al(BH_4)_3$, Ca_2Si, $NaBH_4$, $KB_{21}H_{18}$, Ca_4TiN_4, $Li_4(BH_4)(NH_2)_3$, K_2LiAlH_6, Mg_2B_{25}, $Mg_2B_{24}C$, $CaAlSi$, $CaB_{12}H_{12}$, CaB_4, $MgB_{12}H_{12}$, $Mg(NH_3)_2(N_3)_2$, NH_4HCN_2, $(B_{10}H_{13})_2$, $MgB_{12}Si_2$, $Ca_4N_2(CN_2)$, Si_3N_4, $LiMgH_3$, $MgB_{12}C_2$, $B_{13}N_2$, $Li_{15}Si_4$, $LiSc(BH_4)_4$, $LiK(BH_4)_2$, $LiB_{13}C_2$, $Li_2B_{12}C_2$, $(K(NH_2))(NH_3)_2$, $Ca_5(Si_2N_6)$, $Li(B(CN)_4)$, $NaB(CN)_4$, $(NH_4)B(CN)_4$, $Ca_3(BN_2)_2$, K_2NaAlH_6, Mg_7TiH_{16}, $LiNa_2AlH_6$, $LiAlMg_{10}H_{24}$, LiB, $Li_3(BH_6)$, $LiBH$, $Li(BH_2)$, $Na_2(B_{10}H_{10})$, $K_2(B_{10}H_{10})$, $K_2Na(NH_2)_3$, $K_2Li(NH_2)_3$, Ca_4Al_3Mg, $Ca_{11}N_6(CN_2)_2$, Sc_2AlC, $V_{12}Al_3C_8$, B_7SiH_4, NH_3BH_3

Technical Accomplishments
Generating Amorphous Structures

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



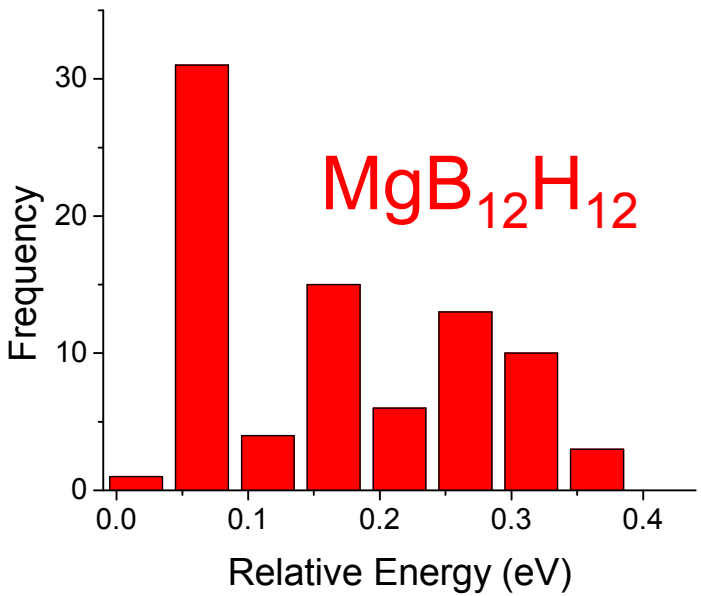
$MgB_{12}H_{12}$

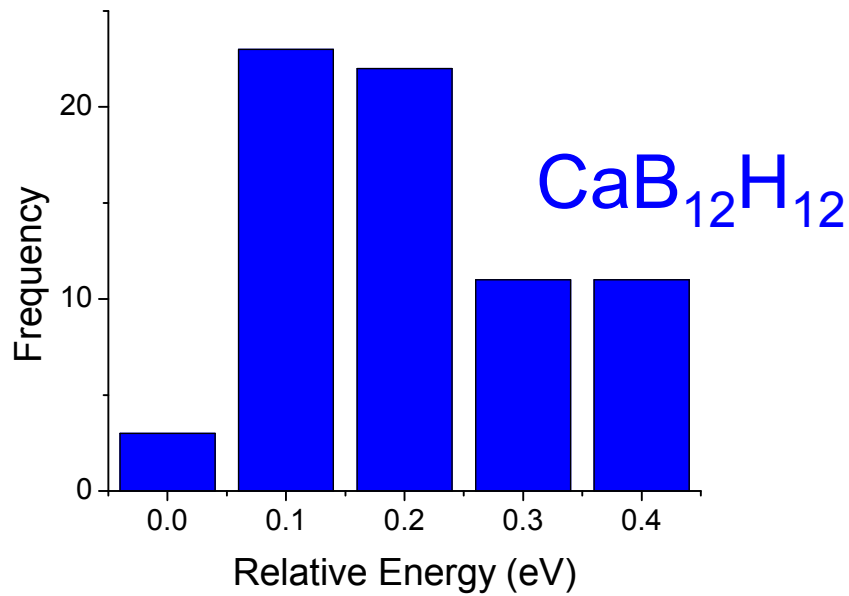


$CaB_{12}H_{12}$

- Experiments: Dehydrogenation of $M(BH_4)_2$ can give amorphous $MB_{12}H_{12}$ 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 $B_{12}H_{12}$ units.
- Collaboration with D. Johnson, D. Graham, I. Robertson (Illinois), paper in progress.

Amorphous Materials: Many Low Energy Structures

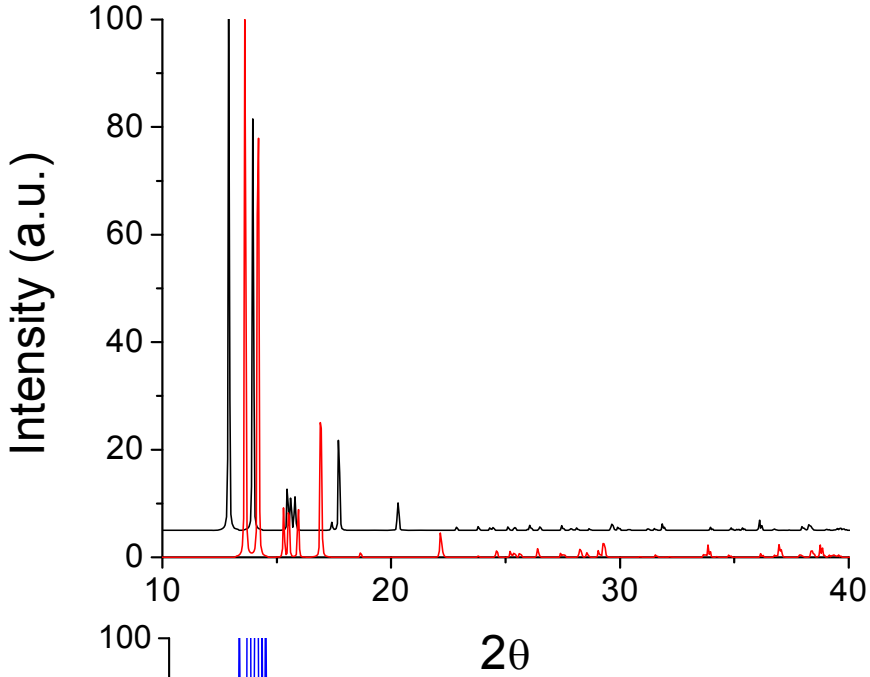


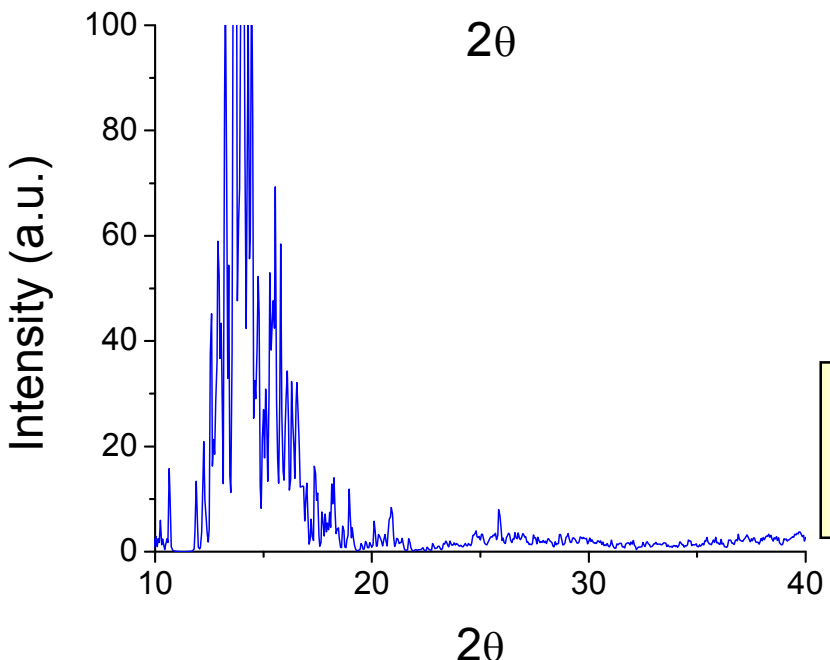


- Energy histograms of structures optimized from MD melt snapshots
- Many structures have energies that are within tens of meV of the ground state—some within a few meV (NB kT=0.03 eV)
- The ground states are the PEGS structures generated by Majzoub et al. *J. Am. Chem. Soc.*, ***2009,*** *131*, 230-237

Many structures are populated at room temperature

Amorphous Materials: Structural Analysis





- 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

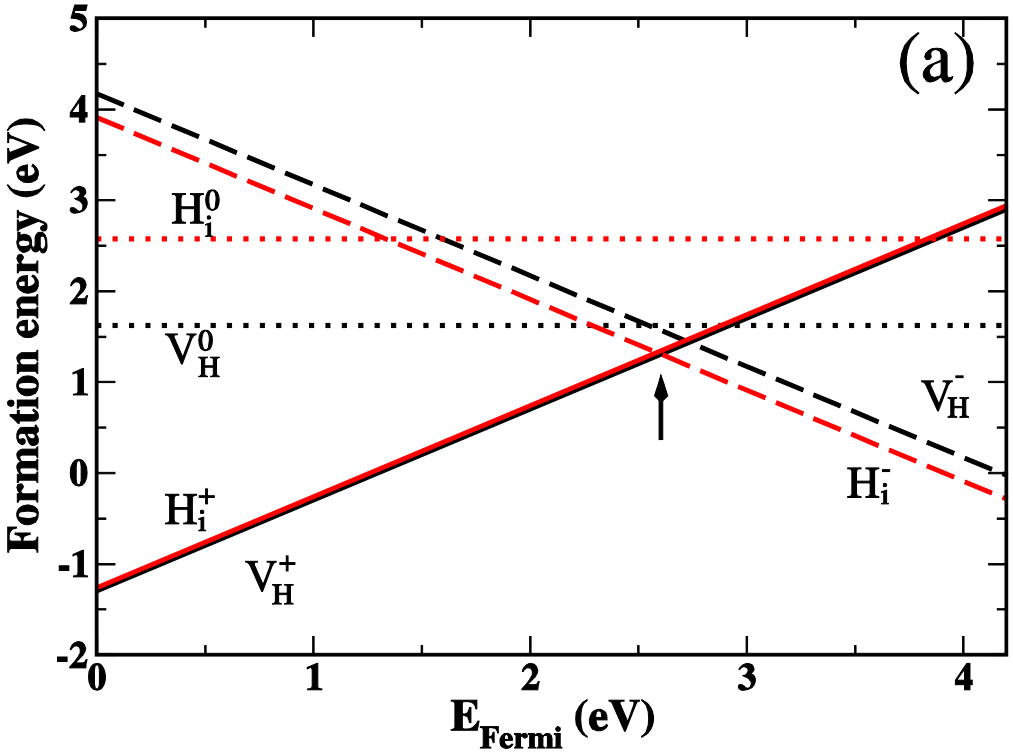
Mechanism of H Diffusion in MgH_2 and $NaMgH_3$

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

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

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

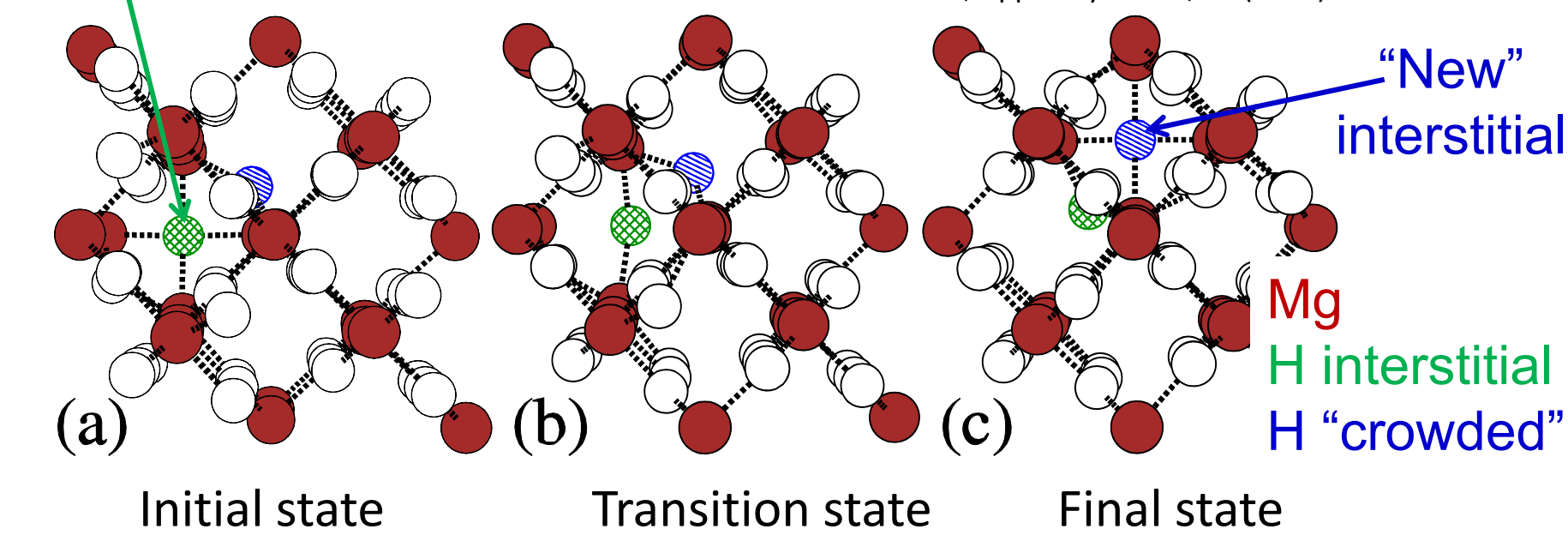
Hao and Sholl, Appl. Phys. Lett., 93 (2008) 251901

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

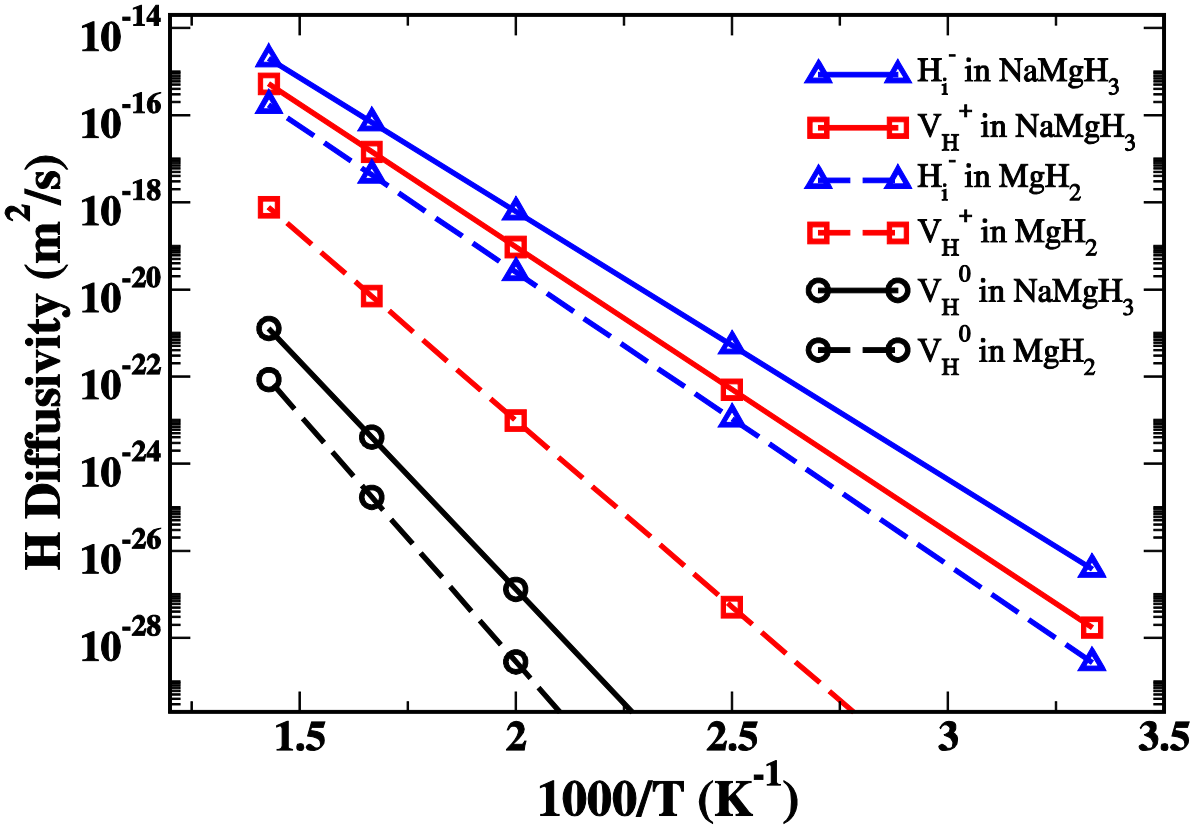
Hao and Sholl, Appl. Phys. Lett., 93 (2008) 251901



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)

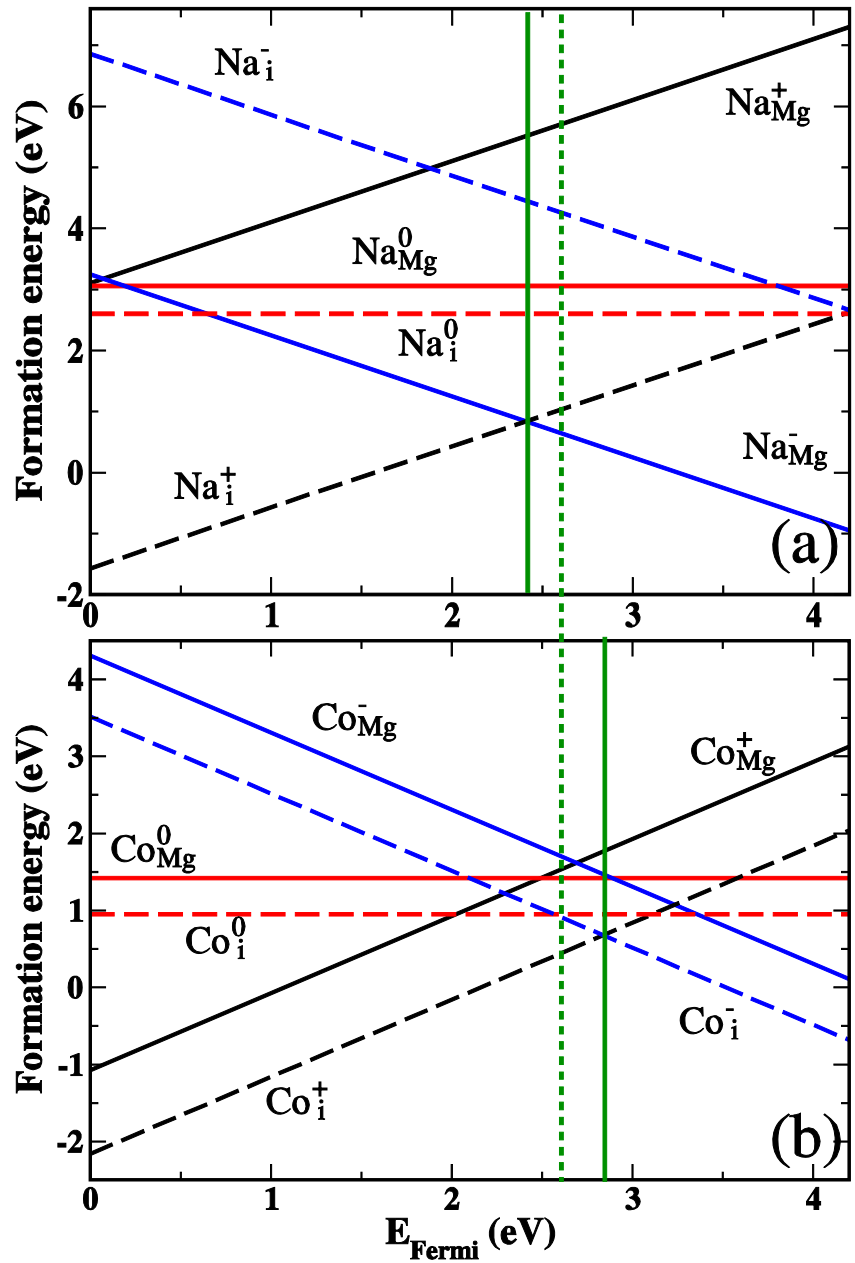
DFT calculations used to assess dopants in MgH_2 and $NaMgH_3$

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



Hao and Sholl, Appl. Phys. Lett., submitted

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

—In collaboration with Mark Allendorf, Sandia

- Previous grand potential method was limited to a single gas phase product: Pure H_2.
- 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:

H_2, Li, Li_2, Mg, Mg_2, LiH, MgH, Ar,
N_2, N_3, NH, NH_2, NH_3, N_2H_4, HNNH, HCN, LiN, MgN
CH, CH_2, CH_3, CH_4, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6
B, B_2, BH_3, BH_4, BH_5, B_2H, B_2H_2, B_2H_3, B_2H_4, B_2H_5, B_2H_6, B_3H_7,
B_3H_9, B_9H_4, B_4H_{10}, B_4H_{12}, B_5H_9, B_5H_{11}, B_6H_{10}, B_8H_{12}, B_9H_{15}, $B_{10}H_{14}$,
BN, BC, $B_3H_6N_3$

- All calculations performed in closed systems

Example: $LiNH_2$ + C

Nominal reaction (only H_2 gas phase):

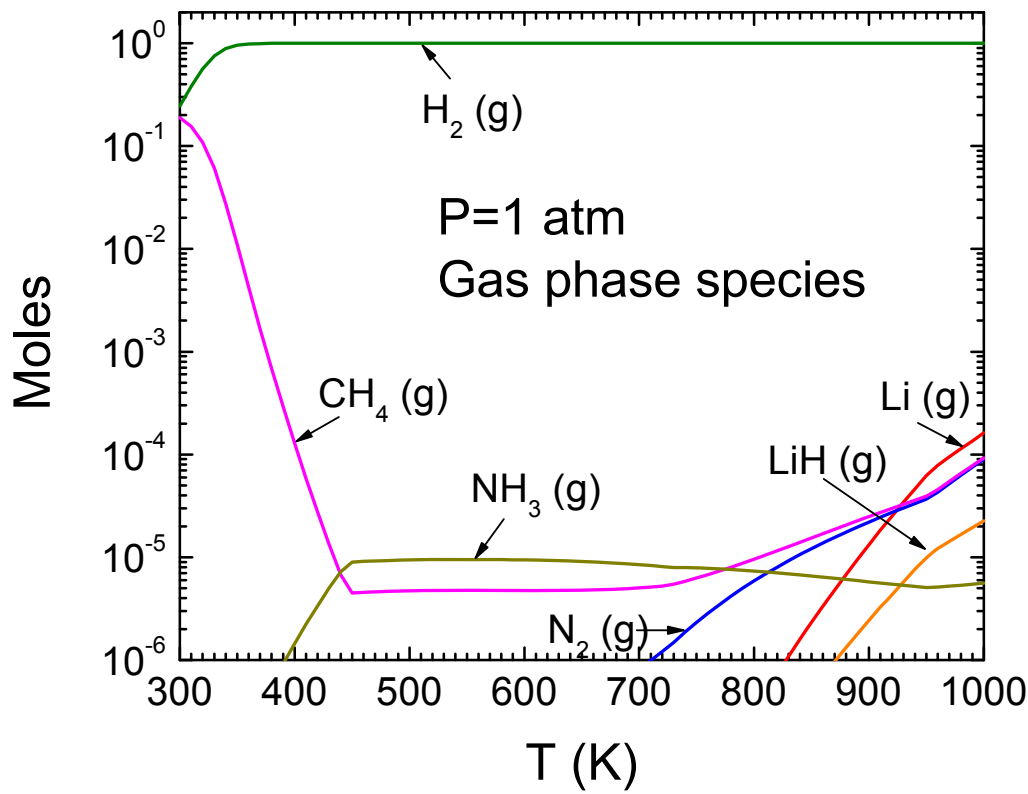
$LiNH_2 + 0.5C \rightarrow 0.5Li_2CN_2 + H_2$

Adding other gas phase species:

$LiNH_2 + 0.5C \rightarrow 0.5LiNH_2 + 0.25Li_2CN_2 + 0.25\ CH_4 \rightarrow 0.5Li_2CN_2 + H_2$

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: $LiBH_4$ + C

Nominal reaction

$LiBH_4 + C \leftrightarrow LiBC + \mathbf{2H_2}$

Also possible:

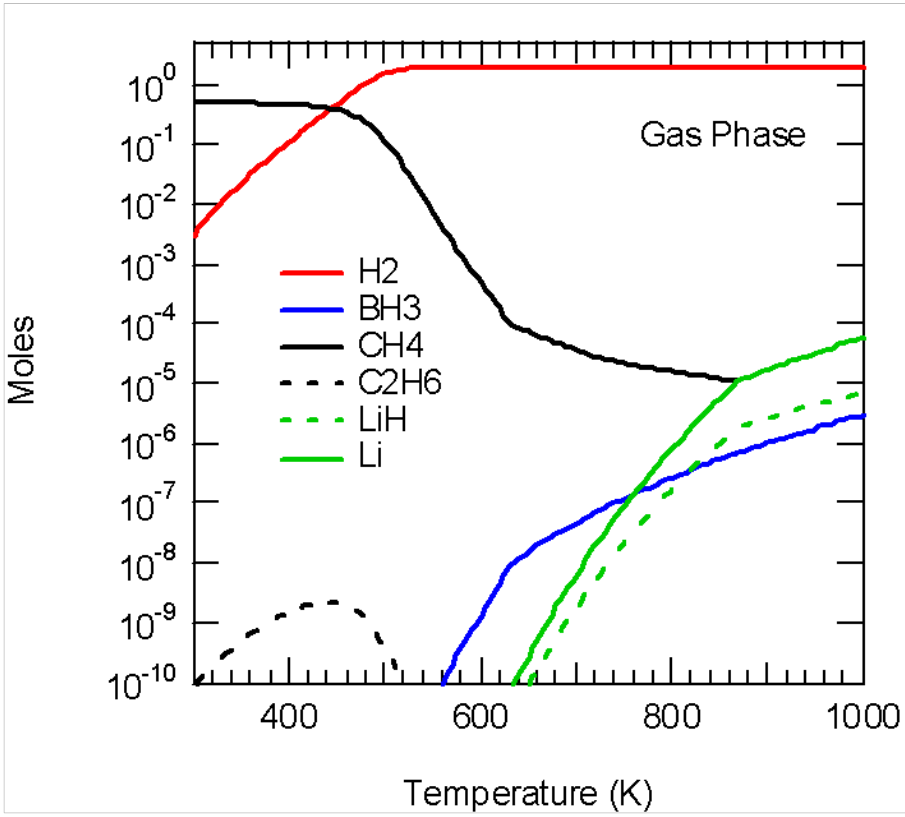
- $LiBH_4 + 2C \leftrightarrow LiBC + \mathbf{CH_4}$
- $LiBH_4 + 0.75C \leftrightarrow LiH + B + \mathbf{0.75\ CH_4}$

Conditions for each calculation

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

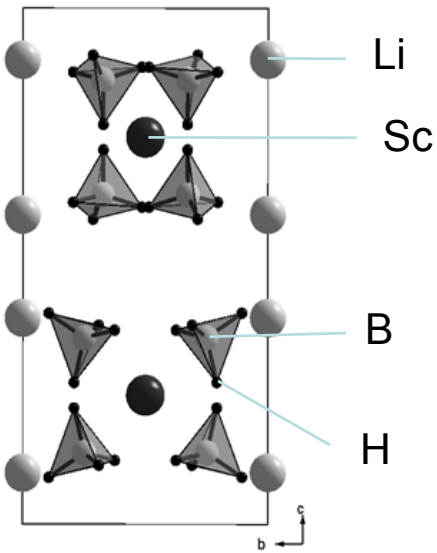
Results

- LiH and C(s) not stable 300-640 K
  - Converted to $\mathbf{CH_4}$ and LiBC
- Complete conversion to $LiBC+H_2$ only at T > 540 K
- BH_3 is only significant B-containing gas-phase species



New Borohydrides: $LiSc(BH_4)_4$ and $LiK(BH_4)_2$

$LiSc(BH_4)_4$



Experimental observation
Li : Half occupancy (4k position)

Our DFT calculation
Li : Full occupancy (2a position)

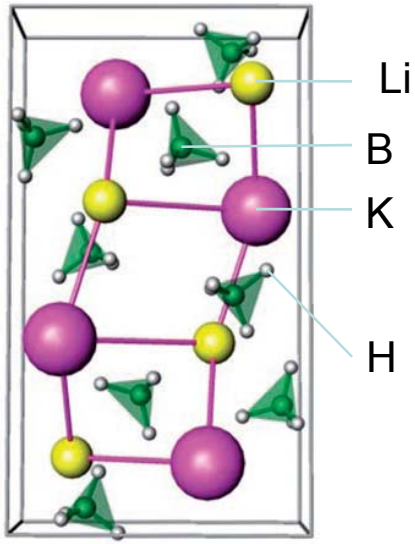
H. Hagemann *et al*. J. Phys. Chem. A 112 (2008) 7551

-We identified reaction thermodynamics of $LiSc(BH_4)_4$ using thermodynamic calculations:

1. Minimum free energy path of $LiSc(BH_4)_4$ decomposition reaction
$LiSc(BH_4)_4 \rightarrow LiBH_4 + 0.1ScB_{12} + 0.9ScB_2 + 6H_2$
2. Destabilization reactions of $LiSc(BH_4)_4$

Also investigated by Eric Majzoub & others in MHCoE

$LiK(BH_4)_2$



- Experimental observation
$LiK(BH_4)_2$ is synthesized by the mixture of $LiBH_4$ and KBH_4

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

-Our calculations:

1. Bulk optimizations for $LiK(BH_4)_2$, KBH_4, and $NaBH_4$
2. Thermodynamic examination of $LiK(BH_4)_2$
$LiK(BH_4)_2$ is not the stable compound compared with the mixture of $LiBH_4$ and KBH_4

Collaborations: Experimental

- Rebecca Newhouse, Sandia and Ewa Ronnebro (formerly Sandia)
  - We are computing the thermodynamics of the doped materials: $Mg_{1-x}Al_xB_2$ and $Mg(B_{(1-x)}C_x)_2$
- Y. Filinchuk, R. Černý, Grenoble, Geneva
  - Experimental powder XRD gave Mg(BH4)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 $LiBH_4/TiH_2$ and $LiBH_4/CaH_2$
- Zak Fang, Utah
  - We are providing calculations for the LiMgN system
- Andrew Goudy, DSU / Fred Pinkerton, GM
  - Independently both working on CaH_2 + 6 $LiBH_4$
- John Vajo, HRL
  - Testing several systems for which we have made predictions, including LiBC and $Mg(BC)_2$

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

Summary

- **Relevance: Theory is a powerful tool for screening candidate materials, predicting thermodynamics, investigating diffusion**
- **Technical Accomplishments:**
  - **Character of amorphous $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ 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**
- **Future work:**
  - 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
  - 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
- **Personnel: Ki Chul Kim, Anant Kulkarni**