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

J. Karl Johnson

David S. Sholl

University of Pittsburgh & Georgia Institute of Technology

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# Overview

## Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 100%

## 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
- FY09 $225K (DOE)
- FY10 $64K (DOE)

## 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
- Conclude study of 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

We have added 147 new compounds in FY09-FY10 containing Al-B-C-Ca-K-Li-Mg-N-Na-Sc-Si-Ti-V-H

Structures taken from ICSD and recent literature

$(K(NH_2))(NH_3)_2$, $(Li(NH_3)_4)_2(B_6H_6)(NH_3)_2$, $(NH_2)CN$, $(NH4)_2B_{12}H_{12}$, $(NH_4)B(CN)_4$, $Al(BH_4)_3$, $Al_{14}Mg_{13}$, $Al_{18}Mg_3Ti_2$, $Al_{23}V_4$, $Al_2MgC_2$, $Al_{30}Mg_{23}$, $Al_{45}V_7$, $Al_4C_3$, $Al_4Ca$, $AlB_{12}$, $AlNC_3H_{10}$, $B_{10}C_6H_{30}N_2$, $B_{13}C_2$, $B_{13}N_2$, $B_{20}C_3H_{30}N_2$, $B_4C$, $BC_2N$, $BC_4KN_4$, $BCH_5N_2$, $C_{12}N_6$, $C_2Ca$, $C_2H_{18}N_{18}$, $C_2H_4N_4$, $C_2N_2$, $C_2N_2(NH)$, $C_3N_4$, $C_5N_4$, $Ca(BH_4)_2$, $Ca(NH_2BH_3)_2$, $Ca_{11}N_6(CN_2)_2$, $Ca_2Si$, $Ca_2Si_5N_8$, $Ca_4Al_3Mg$, $Ca_4N_2(CN_2)$, $Ca_4TiN_4$, $Ca_5(Si_2N_6)$, $CaAlSi$, $CaB_{12}H_{12}$, $CaB_4$, $CaC_4N_6$, $CaSiN_2$, $CH_3NH_2BH_3$, $H_9CN_9$, $K(HCN_2)$, $K_2(B_{10}H_{10})$, $K_2B_{12}H_{12}$, $K_2B_6H_6$, $K_2Li(NH_2)_3$, $K_2LiAlH_6$, $K_2Mg(NH_2)_4$, $K_2Na(NH_2)_3$, $K_2NaAlH_6$, $K_3Si_6N_{11}H_6$, $K_5C_2HN_4$, $K_8Si_{46}$, $KAl(NH_2)_4$, $KB_{21}H_{18}$, $KBH_4$, $KC_4N_3$, $KC_8$, $KCaN_3H_6$, $KLi_3(NH_2)_4$, $KLi_7N_8H_{16}$, $KNH_2$, $KSi$, $Li(B(CN)_4)$, $Li(NH_2BH_3)$, $Li_{12}Si_7$, $Li_{13}Si_4$, $Li_{15}Si_4$, $Li_2B_{12}C_2$, $Li_2B_{12}H_{12}$, $Li_2B_{12}Si_2$, $Li_2Ca(NH)_2$, $Li_2MgSi$, $Li_2Na_4N_2$, $Li_2NaN$, $Li_3(BH_6)$, $Li_3Na_3N_2$, $Li_3NaSi_6$, $Li_4Na_2N_2$, $Li_5NaN_2$, $LiAlB_{14}$, $LiAlC_4H_{16}N_4$, $LiAlMg_{10}H_{24}$, $LiB$, $LiB_{13}C_2$, $LiBH$, $LiBH_2$, $LiK(BH_4)_2$, $LiMg$, $LiMgH_3$, $LiN_3Si_2$, $LiNa_2(NH_2)_3$, $LiNa_2AlH_6$, $LiNa_2N$, $LiNa_5N_2$, $LiSc(BH_4)_4$, $LiSi_3C_9H_{27}N_2$, $Mg(BH_4)_2(NH_3)_2$, $Mg_2B_{24}C$, $Mg_7TiH_{16}$, MgAl2Si$_2$, $MgB_{12}C_2$, $MgB_{12}H_{12}$, $MgB_{12}Si_2$, $MgC_4N_6$, $N_2B_{10}H_{18}$, $N_2BH_7$, $N_3B_3H_{12}$, $N_3B_3H_6$, $N_4B_{10}H_{22}$, $N_4B_{10}H_8$, $N_4B_9H_{11}$, $Na_2(B_{10}H_{10})$, $Na_2B_{29}$, $Na_3(BN_2)$, $Na_3B_{20}$, $Na_3C_6N_9$, $Na_4Si_4$, $Na_5Al_3H_{14}$, $Na_8Si_{46}$, $NaAl(NH_2)_4$, $NaB(CN)_4$, $NaB_{15}$, $NaBH_4$, $NH_3BH_3$, $NH_4HCN_2$, $Sc_{15}C_{19}$, $Sc_2AlC$, $Si_2B_2C_{12}H_{37}N_5$, $Si_2C_7H_{18}N_2$, $SiB_3$, $SiC$, $Ti_2AlC$, $Ti_6Si_2B$, $TiV$, $V_{12}Al_3C_8$, $V_2N$, $V_5Si_3$, $V_5SiB_2$, $VC_8H_{24}N_4$

# Technical Accomplishments: Promising New Single Step Reactions

| **Interesting reactions (2 reactions)** | **wt.%** | **$\Delta U_0$ (kJ/mol $H_2$)** |
|---|---|---|
| $2MgH_2+Mg(NH_2)_2 \rightarrow Mg_3N_2+4H_2$ | 7.4 | 26 |
| $LiH+2LiNH_2+KBH_4 \rightarrow Li_3BN_2+KH+4H_2$ | 7.48 | 43.61 |
| **Reactions involving $B_{12}H_{12}$ species (10 reactions)** | **wt.%** | **$\Delta U_0$ (kJ/mol $H_2$)** |
| $5Si+10Mg(BH_4)_2+4KBH_4 \rightarrow 5Mg_2Si+2K_2B_{12}H_{12}+36H_2$ | 8.1 | 37.3 |
| $5Mg(BH_4)_2+2KBH_4 \rightarrow 5MgH_2+K_2B_{12}H_{12}+13H_2$ | 6.94 | 38.04 |
| $4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 5Mg_2Si+2Li_2B_{12}H_{12}+36H_2$ | 9.46 | 40.96 |
| $5Si+10Mg(BH_4)_2+2Ca(BH_4)_2 \rightarrow 5Mg_2Si+2CaB_{12}H_{12}+36H_2$ | 8.85 | 41.18 |
| $5Mg(BH_4)_2+Ca(BH_4)_2 \rightarrow 5MgH_2+CaB_{12}H_{12}+13H_2$ | 7.72 | 43.09 |
| $2LiBH_4+5Mg(BH_4)_2 \rightarrow 5MgH_2+Li_2B_{12}H_{12}+13H_2$ | 8.36 | 43.1 |
| $5Si+12Mg(BH_4)_2 \rightarrow 5Mg_2Si+2MgB_{12}H_{12}+36H_2$ | 9.21 | 43.62 |
| $Mg(BH_4)_2 \rightarrow (5/6)MgH_2+(1/6)MgB_{12}H_{12}+(13/6)H_2$ | 8.09 | 47.06 |
| $LiH+3Ca(BH_4)_2 \rightarrow 3CaH_2+(1/2)Li_2B_{12}H_{12}+(13/2)H_2$ | 6.03 | 56.53 |
| $Ca(BH_4)_2 \rightarrow (5/6)CaH_2+(1/6)CaB_{12}H_{12}+(13/6)H_2$ | 6.26 | 57.41 |

- Many of the single step reactions identified involved refractory materials, e.g., BN, $TiB_2$, etc.
- We have excluded reactions that involve C because of the possibility of forming alkanes in the product stream.

# Technical Accomplishments: Metastable Reactions

- The accuracy of the DFT calculations is estimated to be about $\pm$10 kJ/mol $H_2$
- It is therefore possible that reactions with DFT free energies ~10 kJ/mol $H_2$ higher than the reaction identified in the linear program may actually be lower in energy experimentally
- It is also possible that kinetic pathways will favor reactions with slightly larger free energies
- To account for these possibilities we have developed a method of identifying metastable reactions:
  - The linear program identifies the equilibrium reaction
  - Each one of the possible solid products is excluded in turn from the database and the linear program is run again
  - If the new run identifies a reaction with a free energy within 10 kJ/mol $H_2$ then the reaction is added to the metastable list
  - The process is repeated for excluding pairs, triples, etc. of compounds

# Technical Accomplishments: Example of Metastable Reaction

| Original reaction | | wt.% | $\Delta U_0$ (kJ/mol $H_2$) | $T_{est}$ (K) |
|---|---|---|---|---|
| $LiH+2LiNH_2+KBH_4 \rightarrow Li_3BN_2+KH+4H_2$ | | 7.48 | 43.61 | 508 |
| Removed materials | Products of metastable paths | wt.% | $\Delta U_0$ (kJ/mol $H_2$) | $T_{est}$ (K) |
| -$Li_3BN_2$ | $2LiH+LiNH_2+BN+KH+2H_2$ | 3.74 | 38.15 | 529 |
| -KH | $LiH+\frac{4}{5}KBH_4+\frac{1}{5}Li_3BN_2+\frac{1}{5}KLi_7N_8H_{16}+\frac{4}{5}H_2$ | 1.5 | 46.64 | 541 |
| -KH & $KLi_7N_8H_{16}$ | $\frac{69}{100}LiH+\frac{23}{100}KBH_4+\frac{31}{100}K+\frac{77}{100}Li_3BN_2+\frac{23}{50}KNH_2+\frac{323}{100}H_2$ | 6.04 | 47.66 | 549 |
| -KH & $KLi_7N_8H_{16}$ & K | $LiH+\frac{1}{3}KBH_4+\frac{2}{3}Li_3BN_2+\frac{2}{3}KNH_2+\frac{8}{3}H_2$ | 4.99 | 47.44 | 550 |
| -KH & $KLi_7N_8H_{16}$ & $KNH_2$ | $K+Li_3BN_2+\frac{9}{2}H_2$ | 8.42 | 48.31 | 550 |
| -KH & $KLi_7N_8H_{16}$ & K & $KNH_2$ | $LiH+\frac{3}{7}KBH_4+\frac{4}{7}Li_3BN_2+\frac{2}{7}K_2Li(NH_2)_3+\frac{16}{7}H_2$ | 4.27 | 48.8 | 565 |
| -$Li_3BN_2$ & KH | $\frac{13}{9}LiH+\frac{7}{9}KBH_4+\frac{2}{9}BN+\frac{2}{9}KLi_7N_8H_{16}+\frac{4}{9}H_2$ | 0.83 | 44.2 | 600 |
| -KH & $Li_3BN_2$ & $KLi_7N_8H_{16}$ & KH & $KLi_7N_8H_{16}$ & $Li_3BN_2KNH_2$ | $2LiH+LiNH_2+K+BN+\frac{5}{2}H_2$ | 4.68 | 47.82 | 606 |

# 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

- **Finish and submit paper on multistep reactions**
- **Finish and submit paper on metastable reactions and additional database entries**
- **Revised and resubmit paper on $B_{12}H_{12}$**