Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

C. Wolverton (PI), H. Kung
Northwestern University

V. Ozolins
UCLA

A. Sudik, J. Yang, D. Siegel*
Ford Motor Company
current address: Univ. of Michigan

ST028

Overview

Timeline

- Project Start Date: 9/1/08 (Funding started Feb. 09)
- Project End Date: 8/31/13
- ~30% complete

Budget

- Total Budget: $2714K
  - DOE Share: $2160K
  - Contractors Share: $554K
- Funding for FY08: $75K
- Funding for FY09: $450K
- Funding for FY10: $450K (anticipated)

Barriers

- Barriers addressed
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

Partners

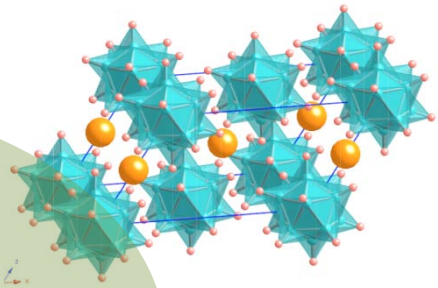
- Northwestern University
- UCLA
- Ford Motor Company
- Project lead: Northwestern University

Relevance - Project Objectives

- 3 Materials Classes (chemical, metal/complex, physisorptive) divided into DOE Centers of Excellence
- **Our project: <u>Combine</u> materials from <u>distinct categories</u> to form novel multicomponent reactions**
- Systems to be studied include mixtures of complex hydrides and chemical hydrides [e.g. $LiNH_2$+NH_3BH_3] and nitrogen-hydrogen based borohydrides [e.g. $Al(BH_4)_3(NH_3)_3$].
- These types of combinations have only recently begun to be explored – initial results look very promising!

Approach

Our approach involves a powerful blend of:
1) H2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective



Hydrogen Storage Measurements and Auto Perspective (Sudik and Yang, Ford)

Computational Prediction of Novel Reactions (Wolverton, Ozolins)

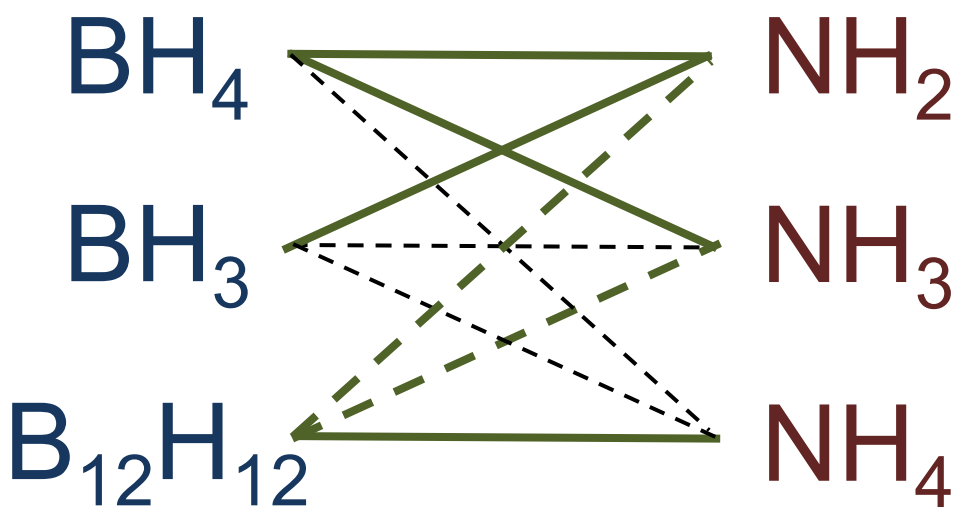
Kinetics/Catalysis Experiments (Kung, NU)

NORTHWESTERN UNIVERSITY

UCLA

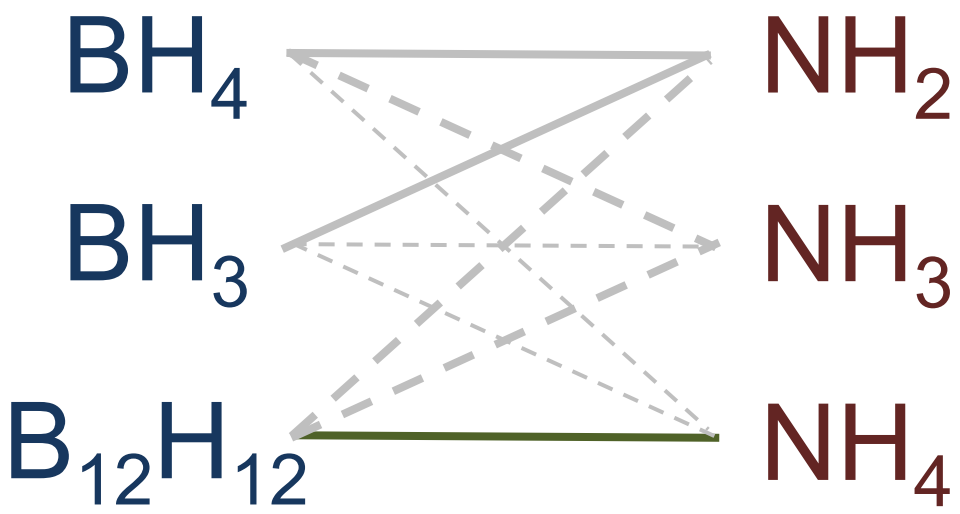
Ford

Technical Accomplishments: Searching for Combinations of B- and N-containing Materials



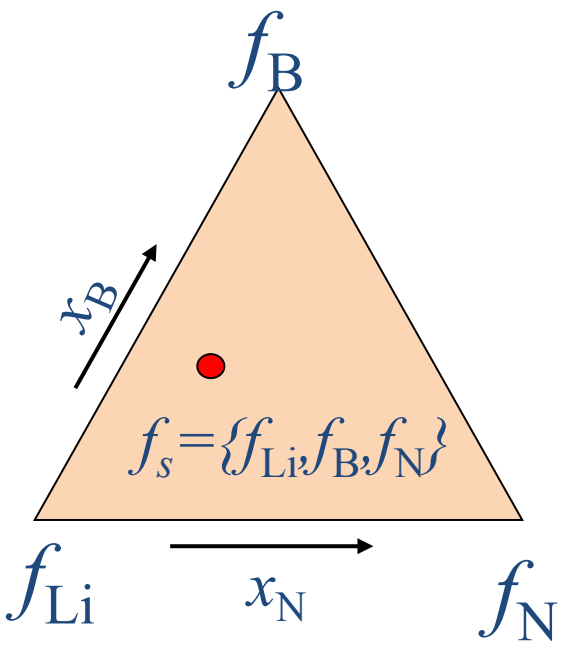
Solid Green Lines: Will show examples today
Dashed Green Lines: Will explore computationally as part of this project
(promising materials/reactions will be investigated experimentally)

High-Throughput Computational Survey for Novel Reactions involving Light-Weight Elements



Technical Accomplishments
Computational Methodology: DFT+GCLP
(Developed under previous work)

- Density Functional Theory
  - VASP Package
  - Static Energies, Zero-point energies, Vibrational Thermodynamics
- Grand Canonical Linear Programming*
  - *Given the list of possible compounds, ALL thermodynamically reversible reactions are predicted automatically*
- Survey compounds in ICSD involving first-row elements



*Akbarzadeh, A.; Ozolins, V.; Wolverton, C. ***Adv. Mater.*** 2007, *19,* 3233–3239

Technical Accomplishments: Computational Screening of the Li-Mg-B-N-H system

- The Li-Mg-B-N-H system includes most of the known high-capacity hydrides
- Constructed a database of 1st principles free energies (including vibrations) of all (~50) known Li-Mg-B-N-H compounds:
  - Borohydrides [$LiBH_4$, $MgBH_4$, $Li_2B_{12}H_{12}$, $MgB_{12}H_{12}$]
  - Amides/imides [$LiNH_2$, $Mg(NH_2)_2$, Li_2NH, MgNH, $Li_2Mg(NH)_2$, etc.]
  - Borohydride-based compounds [Li_2BNH_6, $Li_4BN_3H_{10}$,$Mg(BH_4)_2 \cdot 2NH_3$]
  - Ammonia borane and derivatives (BH_3NH_3, BH_2NH_2, $LiBH_2NH_3$, etc.)
  - B-N-H and B-H compounds [B_2H_6, B_4H_{10}, $B_{16}H_{20}$, $B_{20}H_{16}$, $(NH_4)_2B_{12}H_{12}$, etc.]
  - Reaction products: elements (Li, Mg, B, N_2), hydrides (LiH, MgH2), borides (MgB_2, MgB_4, MgB_7), nitrides (Mg_2N_3, Li_3N, LiMgN), boronitrides (BN, Li_3BN_2, $LiMgBN_2$), etc.
- Predicted new compounds using PEGS:
  - Ammoniated borohydrides
  - Metal-substituted ammonia borane derivatives

Technical Accomplishments: Novel, High-Capacity Predicted Reactions

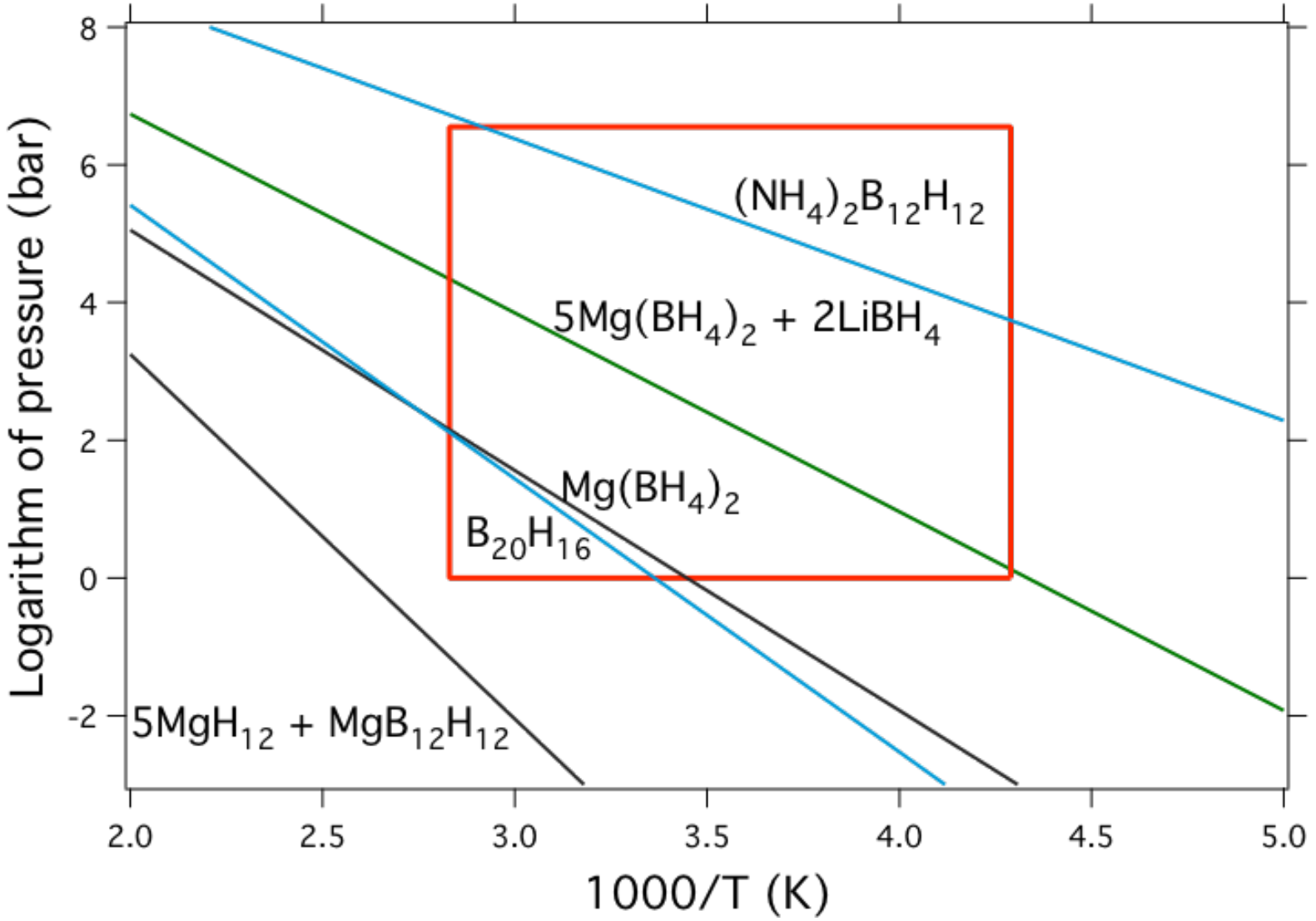
- Grand-Canonical Linear Programming (GCLP) predicted reversible high-capacity reactions:

Reactions	Wt.% H_2	ΔH^{300K} (kJ/mol H_2)	ΔS^{300K} (J/mol-K)
$2(NH_4)_2B_{12}H_{12} \rightarrow 4BN + B_{20}H_{16} + 12H_2$	6.81	17	104
$5Mg(BH_4)_2 + 2LiBH_4 \rightarrow 5MgH_2 + Li_2B_{12}H_{12} + 13H_2$	8.37	24	104
$6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$	8.10	29	100
$B_{20}H_{16} \rightarrow 20B + 8H_2$	6.95	33	111
$5MgH_2 + MgB_{12}H_{12} \rightarrow 6MgB_2 + 11H_2$	7.46	44	115

- Novel two-step reaction involving complex hydride with *ammonium cation*:

$$2(NH_4)_2B_{12}H_{12} \xrightarrow{-120\ ^oC} 4BN + B_{20}H_{16} + 12H_2 \xrightarrow{+20\ ^oC} 4BN + 20B + 20\ H_2 \qquad \textbf{11.3 wt.\% } H_2$$

Technical Accomplishments: Predicted van't Hoff diagram



Experimental Characterization of $(NH_4)_2B_{12}H_{12}$

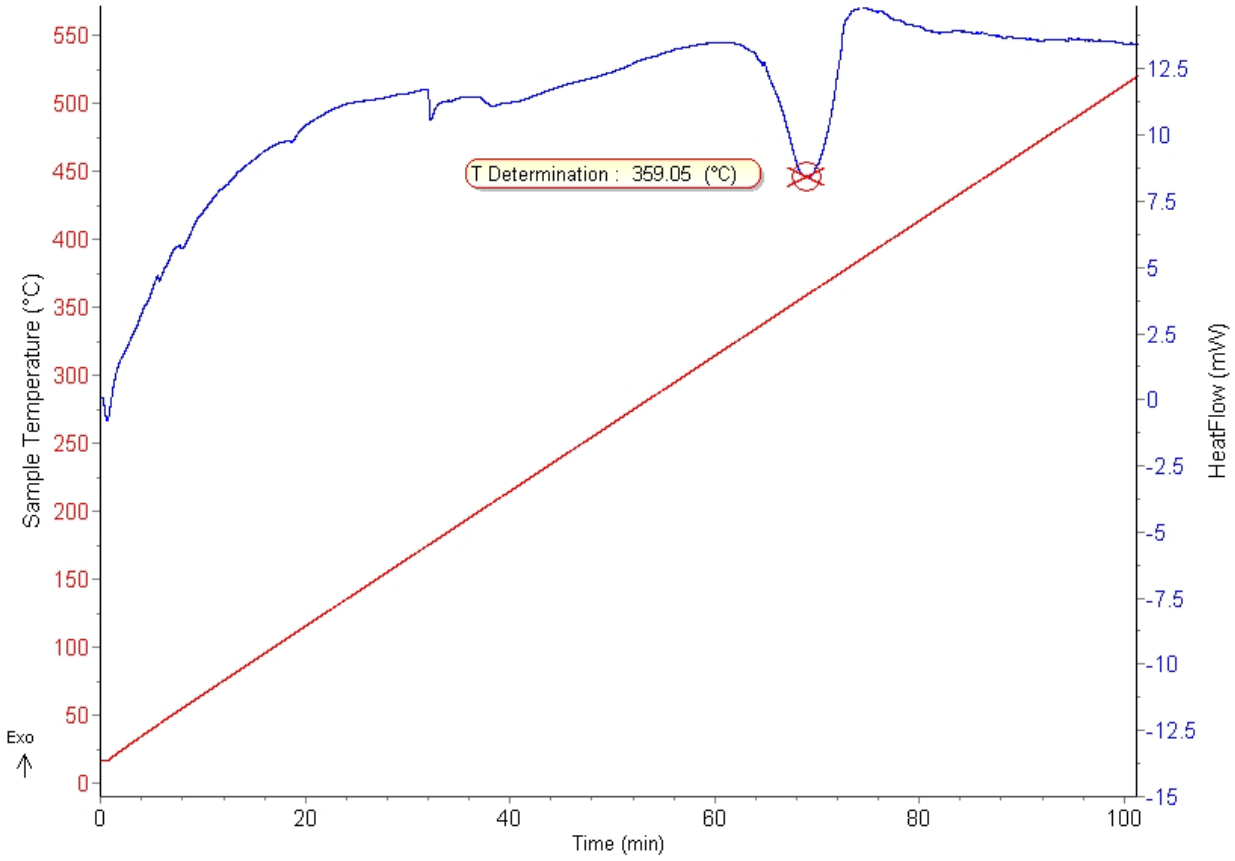
Preliminary Results:

DSC reveals endothermic step at ~ 360ºC based on 5º/min ramp

Next Steps:

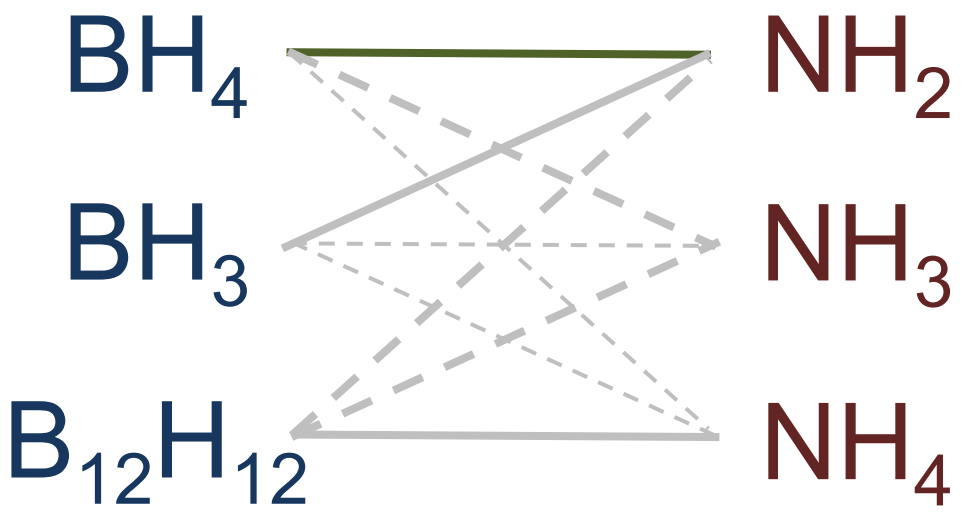
Complete characterization of starting material and desorption pathway (i.e. via XRD & IR) for comparison with computation

DSC of $(NH_4)_2B_{12}H_{12}$



Material acquired from J. C. Zhao (OSU)

Discovery of Novel Compounds in Borohydride-Amide Systems



Technical Accomplishments: Discovery of Novel Compounds in Borohydride-Amide Systems

- $Li_4(NH_2)_3(BH_4)$ phase discovered by GM, Toyota, & Oxford:

$$3\ LiNH_2 + 1\ LiBH_4 \Rightarrow Li_4(NH_2)_3(BH_4) \quad (11\ wt\%)$$

  - *Benefits:*

    High capacity & crystalline reaction species

  - *Limitations:*

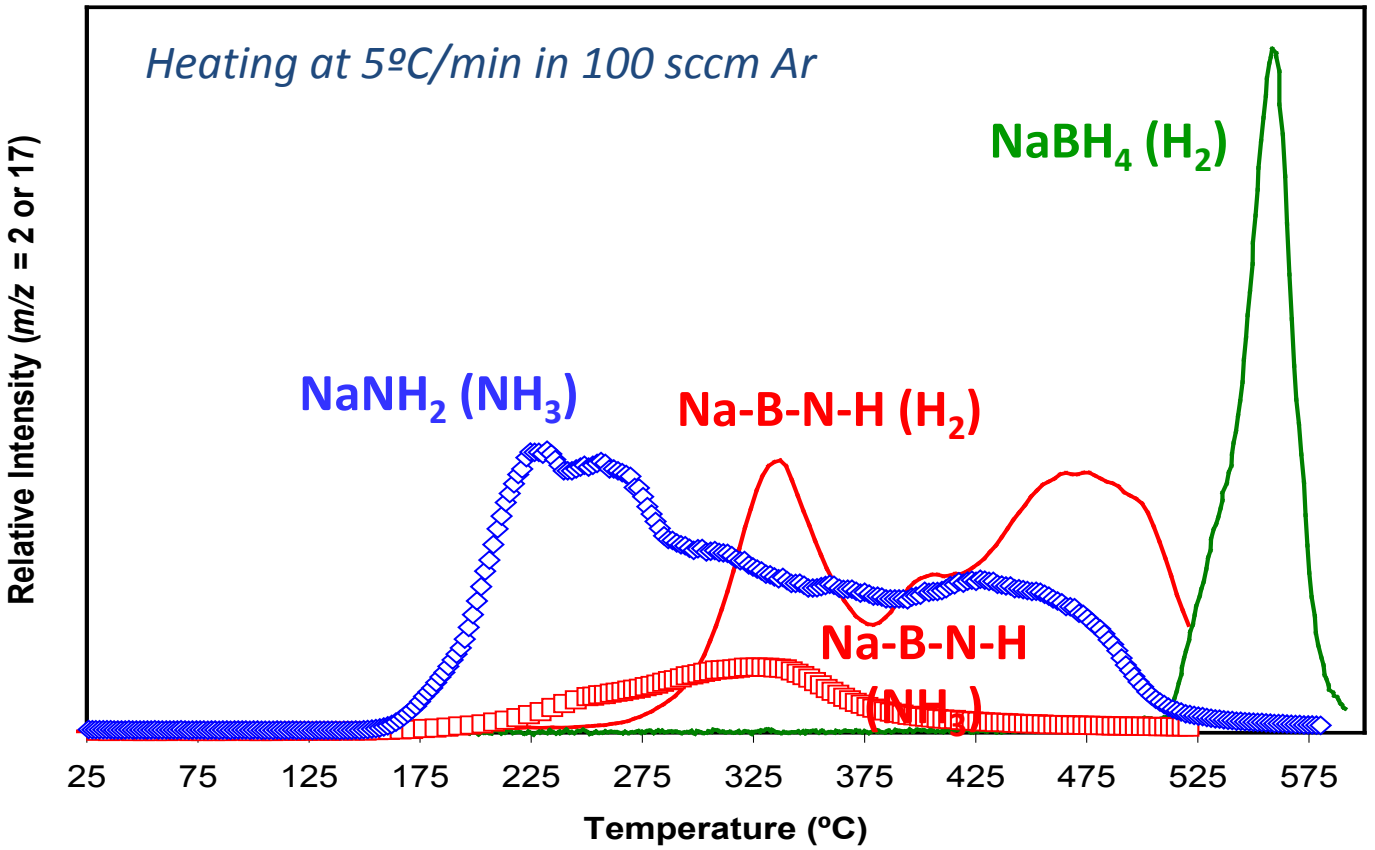
    Poor kinetics, NH_3 release, irreversible: DFT calculated $\Delta H = 12$ kJ/mol

- Potential for improvement in properties by replacing Li:

$$M_1(NH_2) + M_2(BH_4) \rightarrow M_1M_2(NH_2)(BH_4) \leftrightarrow [products] + H_2$$

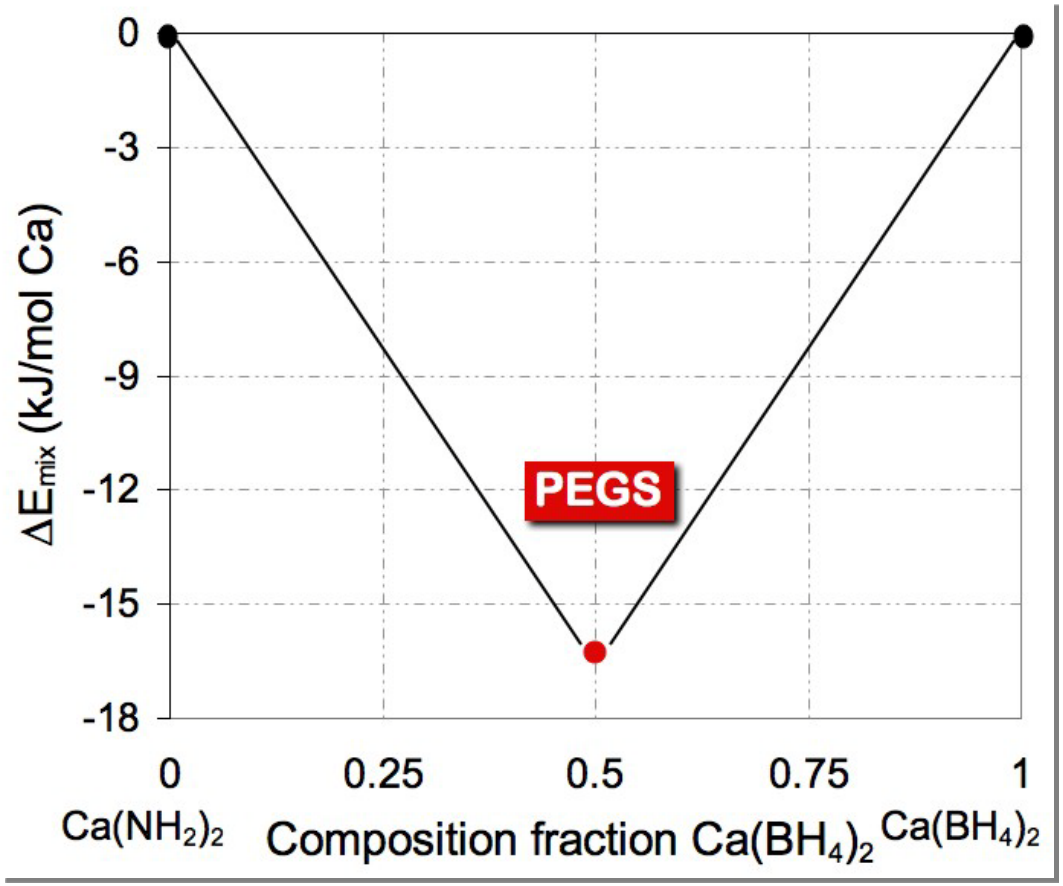
Amides			Borohydrides	
$NaNH_2$	[purchase]	+	$NaBH_4$	[purchase]
$LiNH_2$	[purchase]		$LiBH_4$	[purchase]
$Mg(NH_2)_2$	[synthesize]		$Mg(BH_4)_2$	[synthesize]
$Ca(NH_2)_2$	[synthesize]		$Ca(BH_4)_2$	[synthesize]

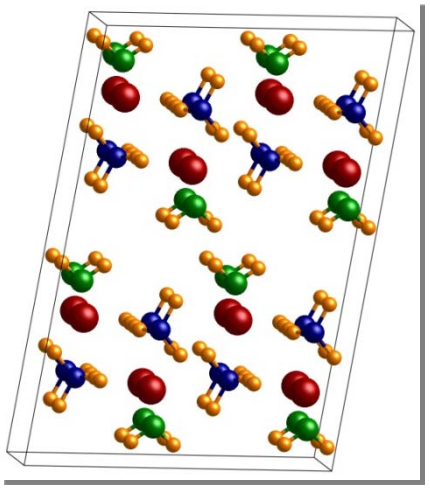
Technical Accomplishments: Example TPD-MS Results from Na-B-N-H Mixture (*i.e.*, 1 $NaBH_4$ + 1 $NaNH_2$)



- XRD and IR data consistent with new quaternary phase
  - *New low temperature hydrogen release events*
- *NH_3 liberation could be reduced by optimization of composition*

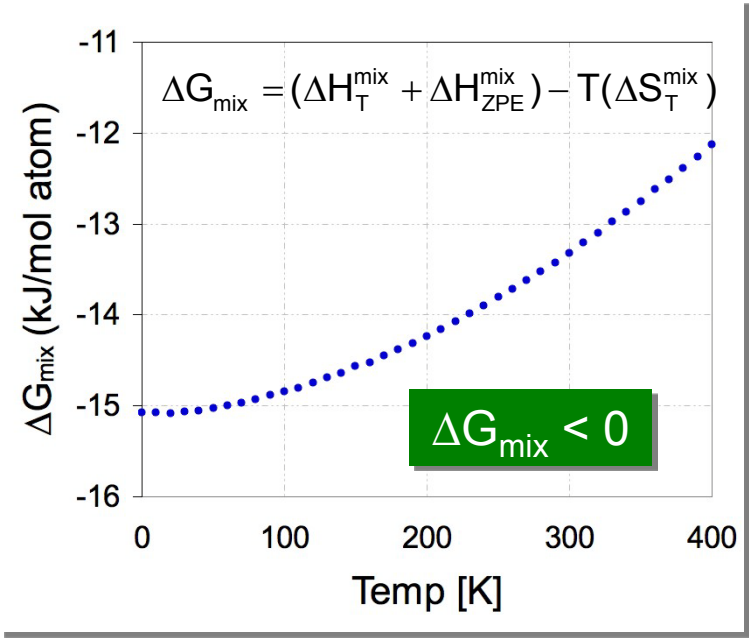
Technical Accomplishments: PEGS+DFT Computational Prediction of a New $Ca(BH_4)(NH_2)$ Compound





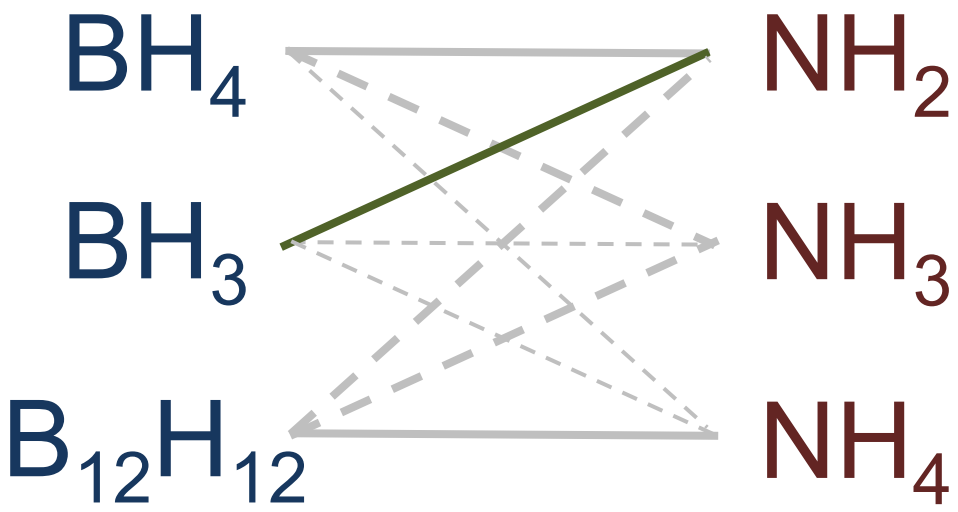
2x2x2 supercell

Space Group: # 2



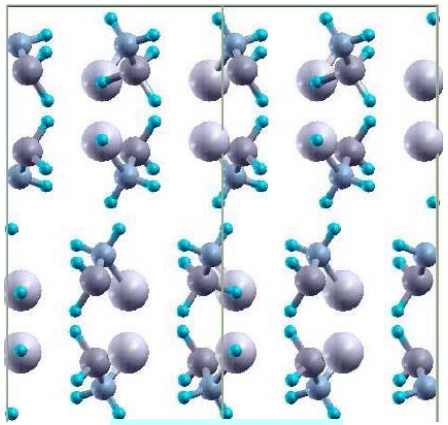
A new Ca-B-N-H quaternary compound is predicted to be stable with respect to $Ca(BH_4)_2 + Ca(NH_2)_2$

Discovery of Novel Metal Amidoborane $(NH_2BH_3)^-$ Systems

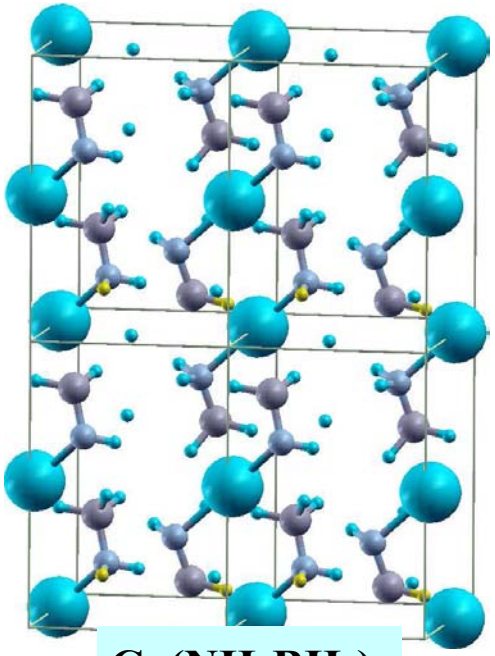


Technical Accomplishments: Metal amidoboranes (MNH_2BH_3)

- High H_2 capacity
  - $LiNH_2BH_3$: 13.70 wt%
  - $Ca(NH_2BH_3)_2$: 10.10 wt%
- Low H_2 release *T*
  - NH_3BH_3: 110~200°
  - $LiNH_2BH_3$: 90°
  - $Ca(NH_2BH_3)_2$: 100°
- Pure H_2 release without $[N_3B_3H_6]$



$LiNH_2BH_3$



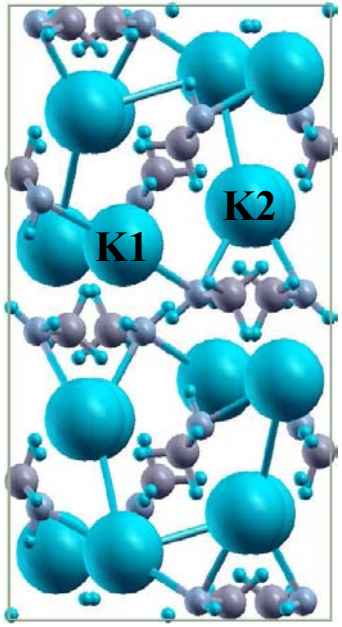
$Ca(NH_2BH_3)_2$

Can we find new metal amidoboranes?
Can we use PEGS for the NH_2BH_3 anion?
What are the thermodynamics of these reactions?
What are the trends as the metal cation is varied?

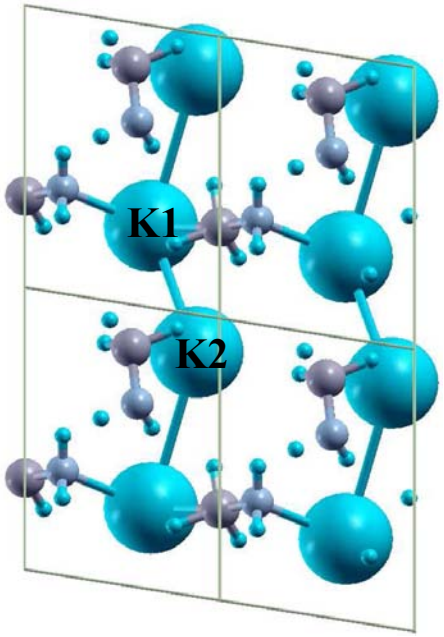
Z. Xiong, etc., Nature 7, 138 (2008)
H. Wu, W. Zhou and T. Yildirim, J. Am. Chem. Soc. 130, 14834 (2008)
Y. Chua, G. Wu, Z. Xiong, T. He and P. Chen, (2009)

Technical Accomplishments: Example: KNH_2BH_3 structure

Experimental Structure
(Burrell et al.)
16 f.u.



Predicted Structure (PEGS+DFT)
2 f.u.



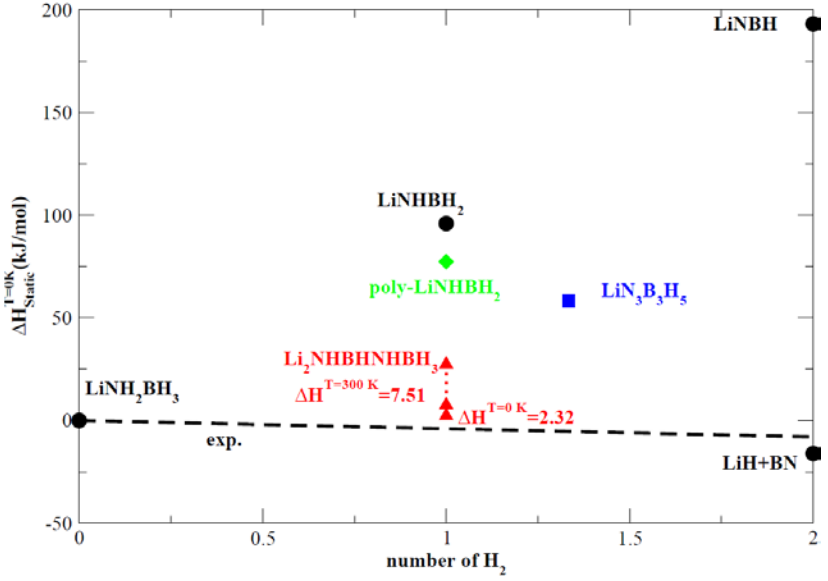
Predicted structure nearly degenerate with experimental structure (within 11 meV/f.u.)
Predicted structure also has two symmetrically distinct K positions, in agreement with expt.

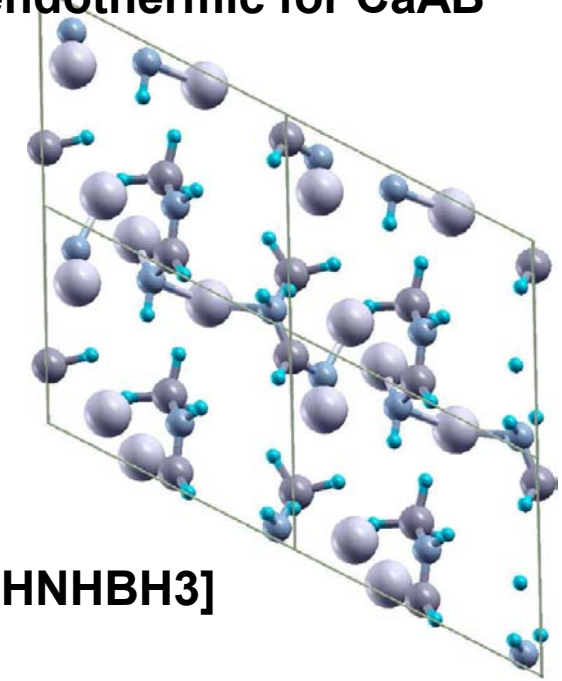
PEGS+DFT gives excellent predictions for the energies of amidoboranes! (PEGS+DFT energy very close to experimental structure, where known)

We have performed similar calculations for: Li, Na, K, Mg, Ca, Sc amidoboranes, finding good predictions in each case.

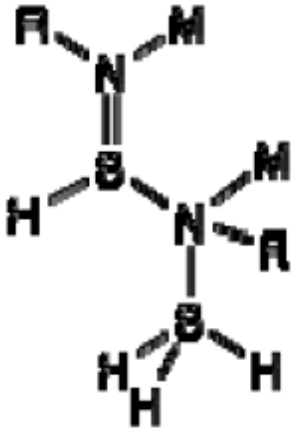
Technical Accomplishments
Amidoborane Decomposition Products: Dianion $[NHBHNHBH_3]^{2-}$

- B-N-B-N bridge proposed AB decomposition product.
- DFT calculations support this proposal: $NHBHNHBH_3$ is lowest energy decomposition intermediate (out of many possibilities calculated).
- Near thermoneutral for LiAB, slightly endothermic for CaAB





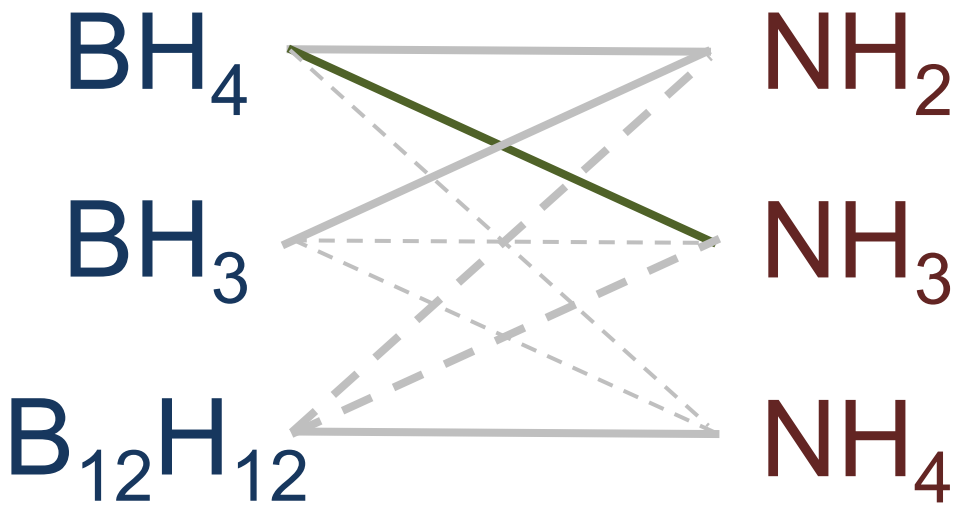
$Li_2[NHBHNHBH3]$



J. Spielmann. etc.,
Angew. Chem. Int. Ed. 47, 6290 (2008)

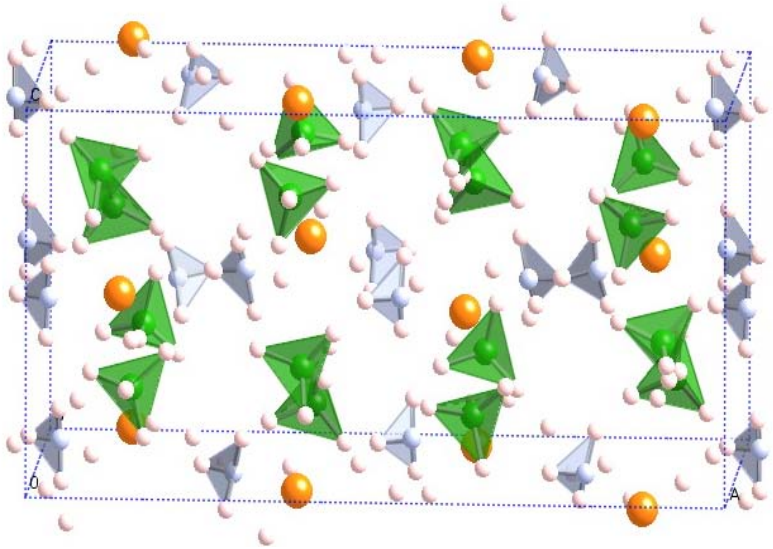
T. Autrey (private communication)

Borohydride-Ammonia Systems

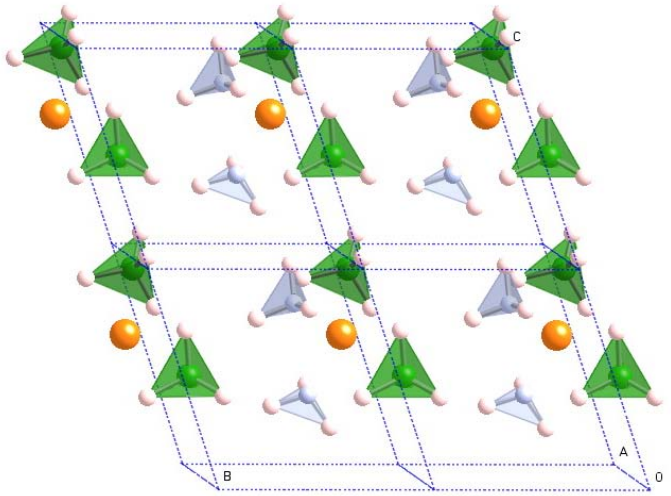


Technical Accomplishments:
PEGS Predictions for $Mg(BH_4)_2$-$m$$NH_3$

Prototype electrostatic ground state search (PEGS) successfully predicts energetics:



Orthorhombic *Pcab* structure obtained by Soloveichik et al. Inorg Chem **47** (10), 4290-4298 (2008).



PEGS-DFT predicts monoclinic *Cm* structure, which is 2 kJ/mol lower than *Pcab*.

GCLP predicts that $Mg(BH_4)_2(NH_3)_2$ has an exothermic decomposition pathway:

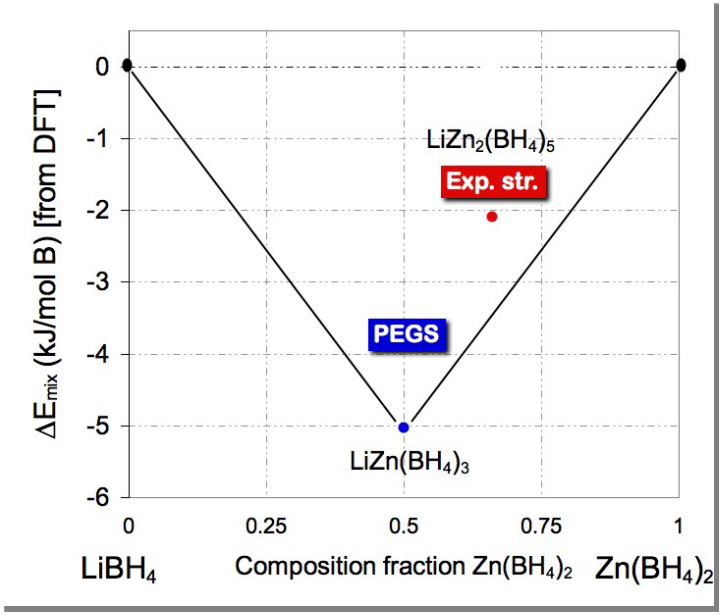
$Mg(BH_4)_2(NH_3)_2 \rightarrow 2BN + MgH_2 + 7\ H_2$ 13.6 wt. % H_2, ΔH=-21 kJ/mol-H_2

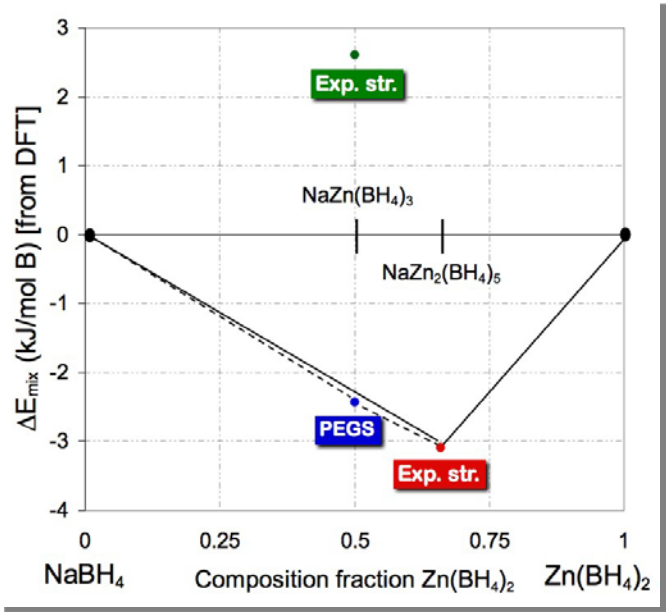
Mixed-Metal Borohydride Systems

Technical Accomplishments: PEGS+DFT Prediction of Novel Mixed-Metal Borohydride Compounds

Li/Zn and Na/Zn systems

*Ravnsbaek et al., Angwe. Chemie., **48**, 6659 (2009)*





PEGS+DFT Calculations show new $LiZn(BH_4)_3$ phase stable; Experimentally-proposed $LiZn_2(BH_4)_5$ is found to be an unstable phase

PEGS+DFT Calculations show new $NaZn(BH_4)_3$ phase stable; Experimentally-proposed $NaZn_2(BH_4)_5$ is found to be an stable phase

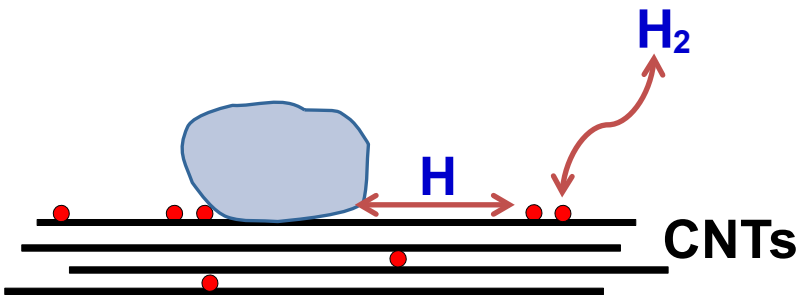
Exploration of Improved Catalysts

Technical Accomplishments:

Facilitating $Ca(BH_4)_2$ decomposition:

Non-precious metal decorated carbon nanotubes (by sonic-assisted impregnation) as catalytic matrix

Proposed catalytic action

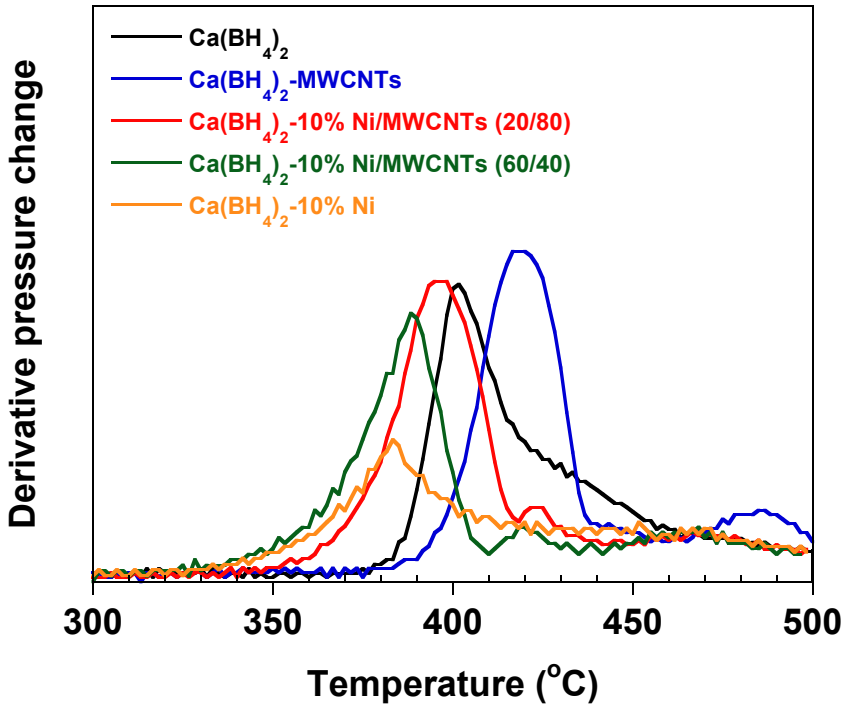


Borohydrides

- **Metal catalyst for H_2 recombination**

Catalyst matrix hypothesized to: (1) increase hydrogen gradients on the high surface/interface area catalytic matrix, and (2) provide nucleation sites for decomposition (by)-products and hydrogen atoms/molecules release.

Ni or Ni-MWCNTs catalysts lowers the decomposition temperature of $Ca(BH_4)_2$



We find Fe, Co, and Ni catalysts all lower the decomposition temperature (only Ni results are shown).

Collaborations

PI's/co-PI's

Chris Wolverton (Northwestern, lead)
Harold Kung (Northwestern)
Vidvuds Ozolins (UCLA, subcontract)
Andrea Sudik (Ford, no-cost collaborator)
Jun Yang (Ford, no-cost collaborator)

Outside Collaborators:

D. Siegel (U. Michigan)
E. Majzoub (UMSL)
G. Ceder, N. Marzari (MIT)
C. Brown (NIST)
T. Burrell (LANL)
T. Autrey (PNNL)

Future Plans

- Extend computational search for all possible promising reversible reactions in Li-Ca-B-N-H system
- Experimentally characterized storage properties/reactions of $(NH_4)_2B_{12}H_{12}$ and other predicted reactions
- Extend experimental catalyst studies to $(NH_4)_2B_{12}H_{12}$ and other predicted promising materials
- Continue computational exploration for: 1) novel BH_4/NH_2 compounds and reversible reactions, 2) mixed metal borohydrides, 3) AB reaction products

Summary – Project Overview

- Project focused on design of novel multi-component mixtures for hydrogen storage
- Focus on mixtures of materials from two distinct classes (e.g., reversible + irreversible)
- Systems being studied include mixtures of complex hydrides and chemical hydrides involving combinations of B- and N-containing materials
- Powerful blend of: 1) H_2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective

Summary – Technical Accomplishments

- Used computational methods (DFT, PEGS, GCLP) to scan through and predict all possible reactions in Li-Mg-B-N-H system with reversible thermodynamics
- New high-capacity reactions predicted, including those involving $(NH_4)_2B_{12}H_{12}$ (preliminary experimental verification underway)
- PEGS prediction of amido-borane structures. Good agreement with experiment where available (e.g., LiAB and KAB) and good prediction of structure for many other cases.
- NHBHNHBH3 dianion as AB intermediate product supported by DFT calculations
- Computational prediction and experimental observation of new mixed BH4/NH2 compounds in Na and Ca systems
- PEGS predictions for ammoniated borohydrides
- PEGS predictions for mixed-metal borohydrides
- Exploration of novel catalyst design - initial results for $Ca(BH_4)_2$