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

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ST028

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Overview

Timeline

- Project Start Date: 9/1/08 (Funding started Feb. 09)
- Project End Date: 8/31/13
- ~60% complete

Budget

- Total Budget: $2714K
  - DOE Share: $2160K
  - Contractors Share: $554K
- Funding for FY11: $200K
- Planned FY12: $400K

Barriers

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

Partners

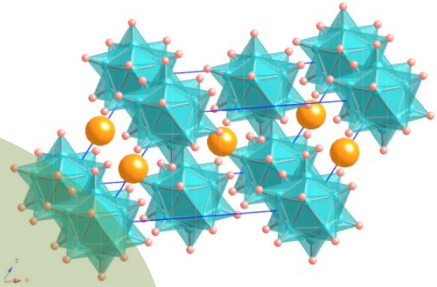
- Northwestern University
- UCLA
- Ford Motor Company
- Project lead: Northwestern University

Relevance - Project Objectives

- **Our project: <u>Combine</u> materials from <u>distinct categories</u> to form novel multicomponent reactions**
- Examples of systems to be studied include mixtures of complex hydrides and chemical hydrides and novel multicomponent complex hydride materials and reactions

Approach

Our approach involves a 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



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

Computational Prediction of Novel Reactions (Wolverton, Ozolins)

Kinetics/Catalysis Experiments
(Kung, NU)

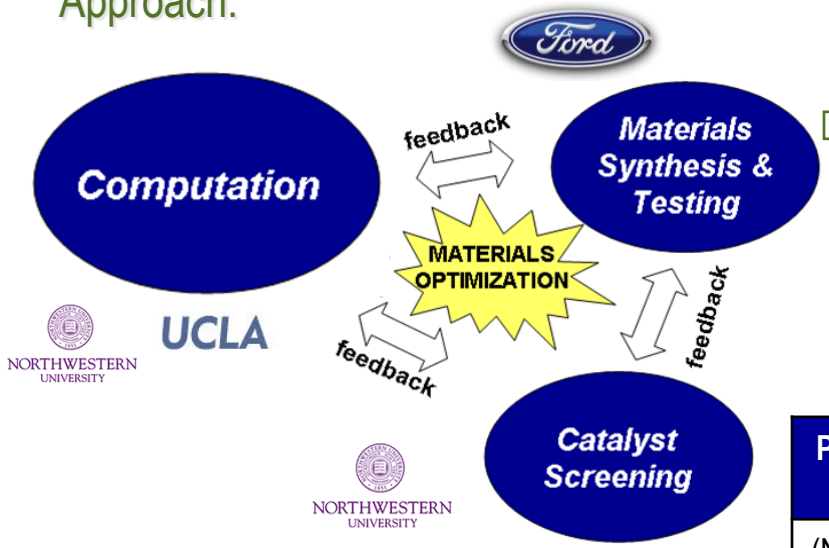
NORTHWESTERN UNIVERSITY

UCLA

Ford

Technical Accomplishments: Experimental Screening & Testing of Theoretical Predictions

Approach:



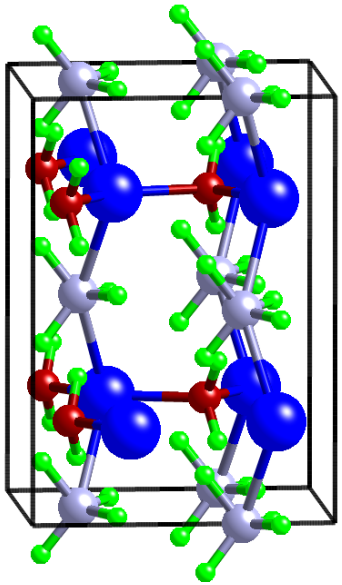
Experimental Objectives:

- Synthesize, characterize, and test promising storage reactions predicted by computation
- Interface with kinetics-focused work to provide materials of interest for catalysis studies and assist in detailed testing of catalyzed reactions.

Predicted Compositions of Interest	Experimental Status
$(NH_4)_2B_{12}H_{12}$	Material received from OSU (Zhao)
$5Mg(BH_4)_2 + 2LiBH_4$	Material prepared & experiments initiated
$Mg(BH_4)_2$	Deferred given existing literature data
$Mg(BH_4)_2 + Mg(NH_2)_2$	Material prepared & experiments initiated
$5MgH_2 + MgB_{12}H_{12}$	Deferred given existing literature data

= current experimental focus

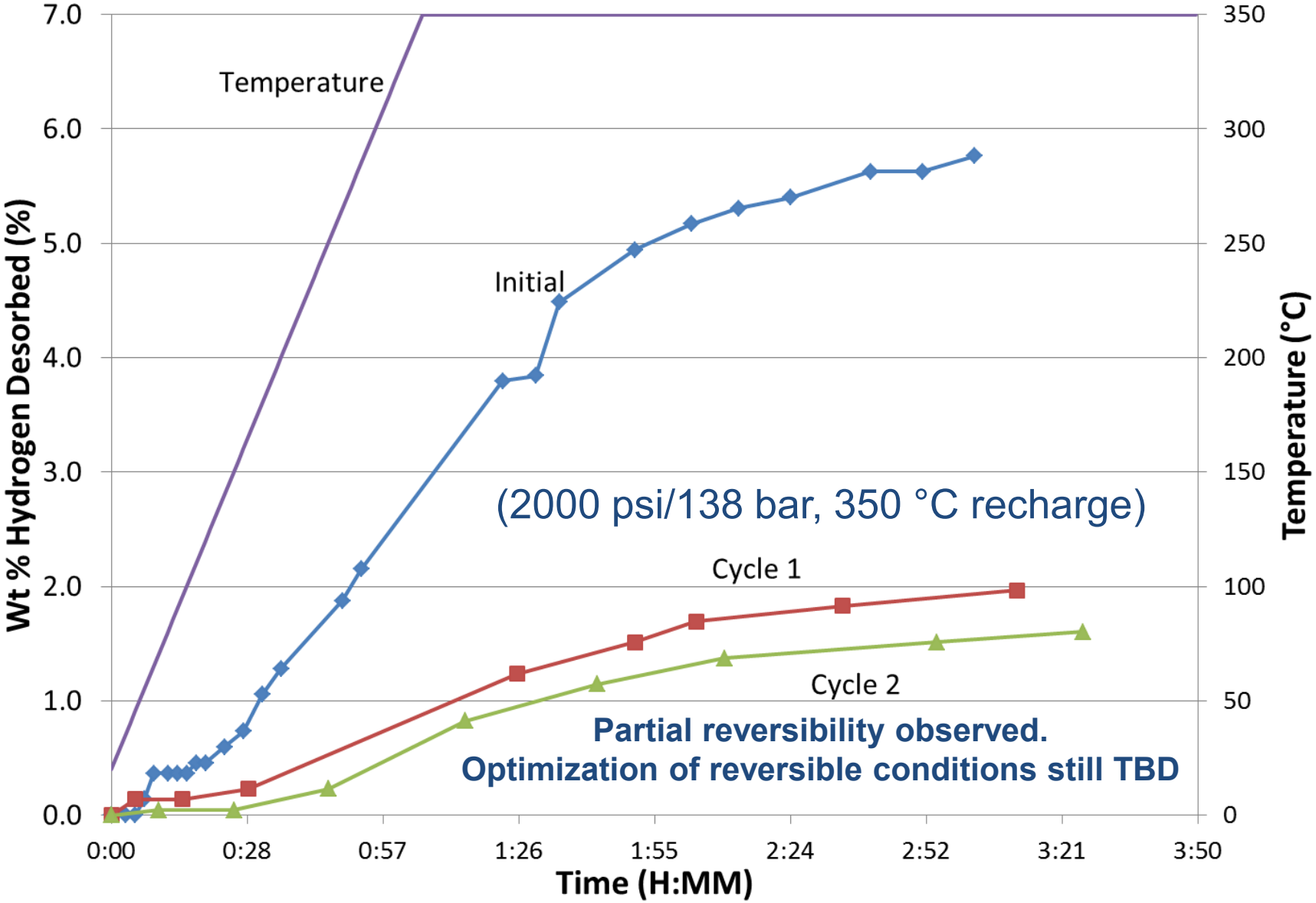
PEGS Predicted Mg-B-N-H Structure



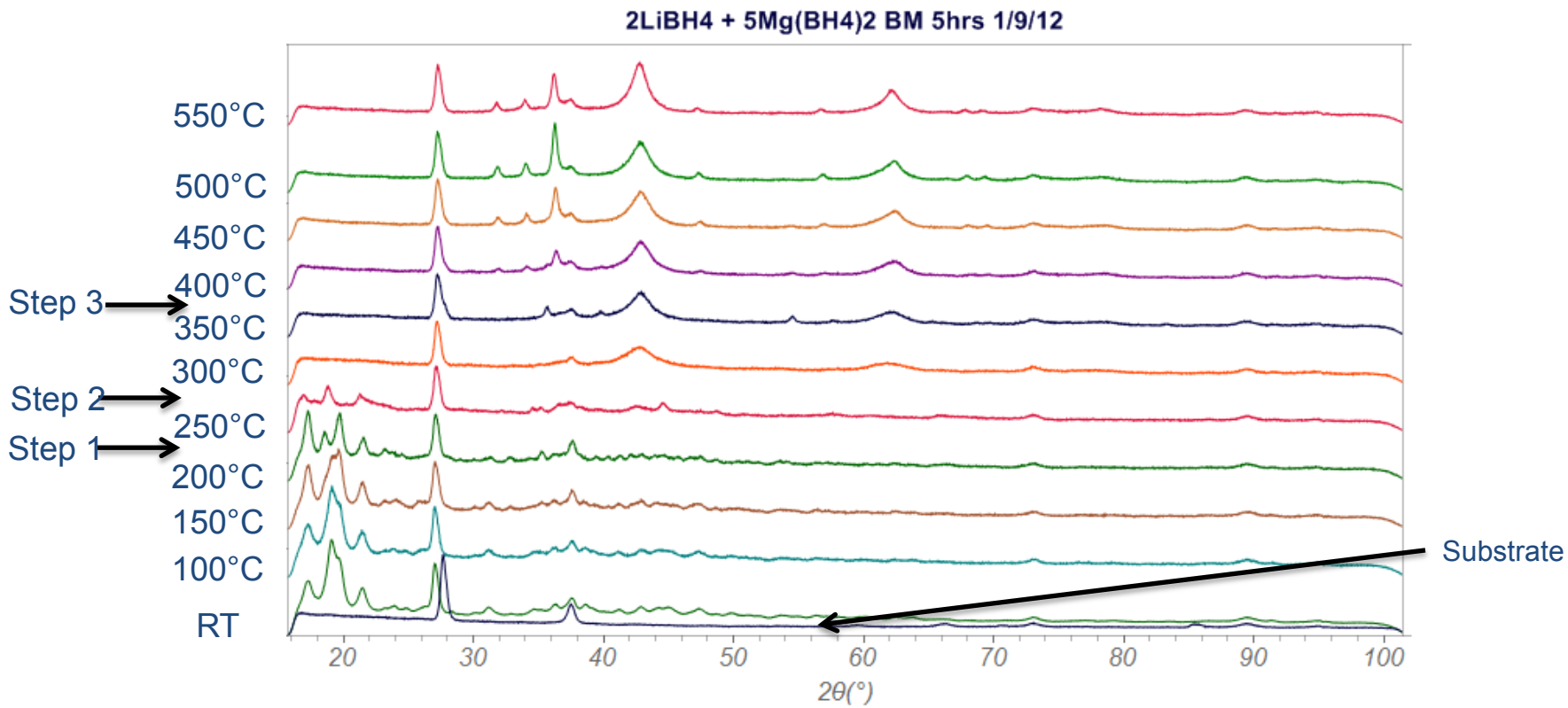
Guiding Questions:

- Is there experimental evidence of a new reactant structure (e.g., Mg-B-N-H)?
- What is the experimentally observed desorption pathway?
- How do these results compare with predictions?

$2LiBH_4 + 5Mg(BH_4)_2$: Desorption and Partial Reversibility

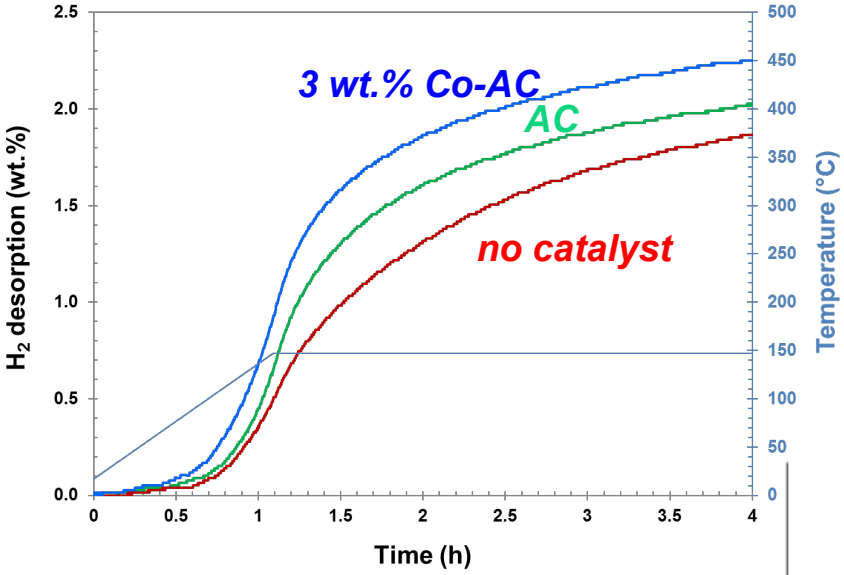


$2LiBH_4 + 5Mg(BH_4)_2$: Phase Evolution



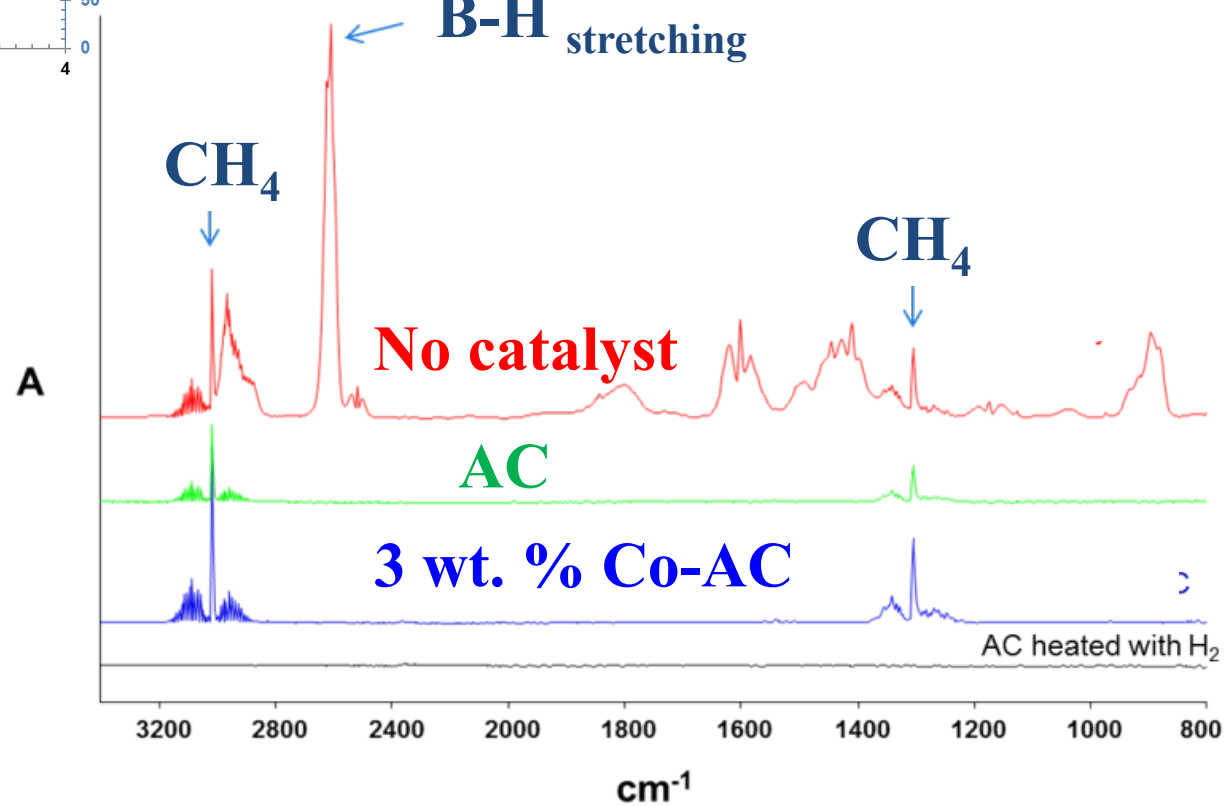
- XRD indicates initially similar to physical mixture, evolution in 2-3 steps:
  - ~200-250 °C : $Mg(BH_4)_2$ & (possibly) $LiBH_4$ consumption
  - ~250-300 °C : Continued $Mg(BH_4)_2$ consumption, formation of MgB_2 or possibly MgH_2
  - Possible 3rd step over 350 °C : continued MgB_2 formation, other unidentified phase?

Effect of 3 wt. % Co-activated carbon on the dehydrogenation of $2LiBH_4$-$5Mg(BH_4)_2$

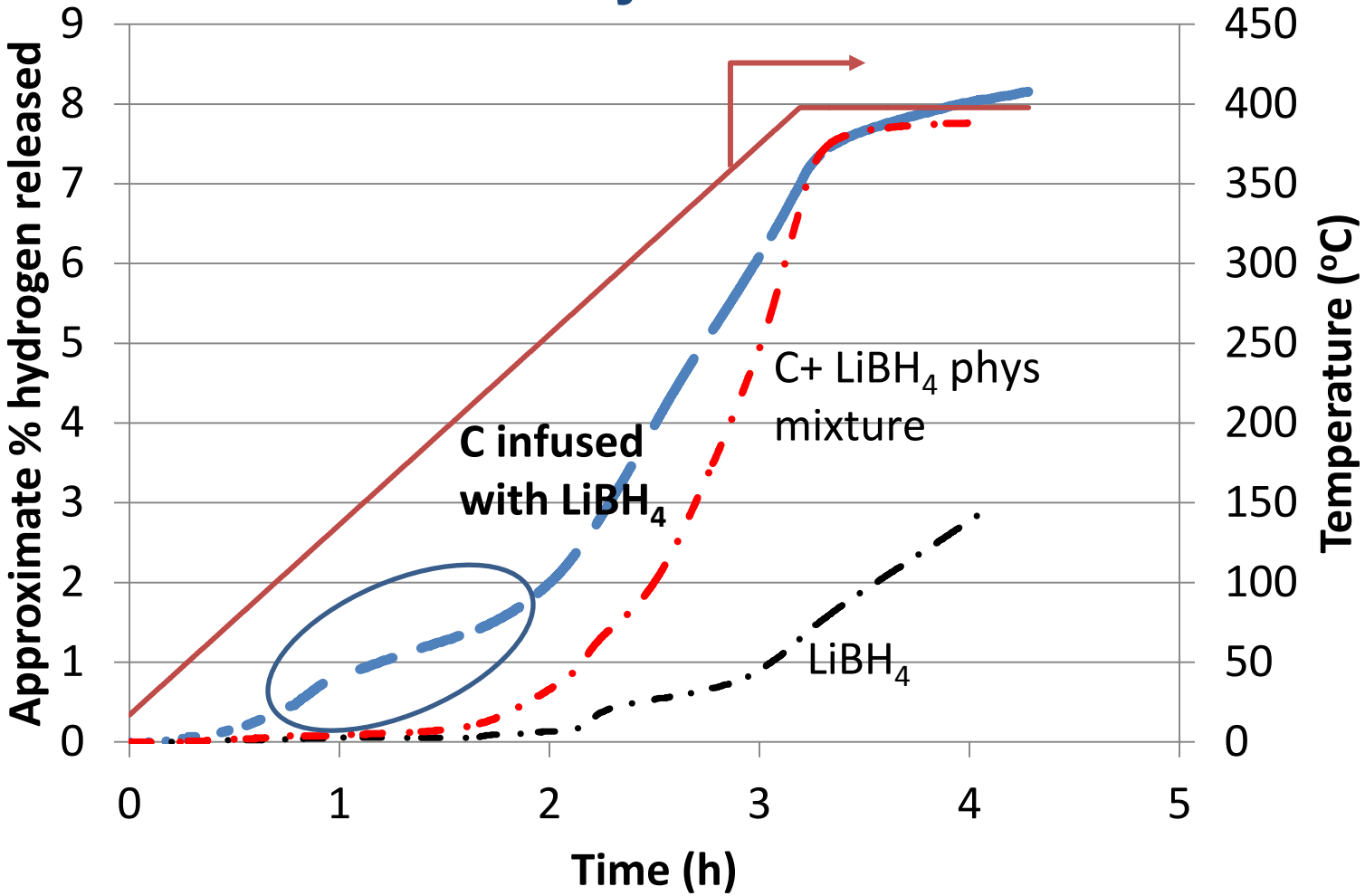


3 wt % Co-AC catalyst (70 wt.% catalyst) accelerated the rate of dehydrogenation

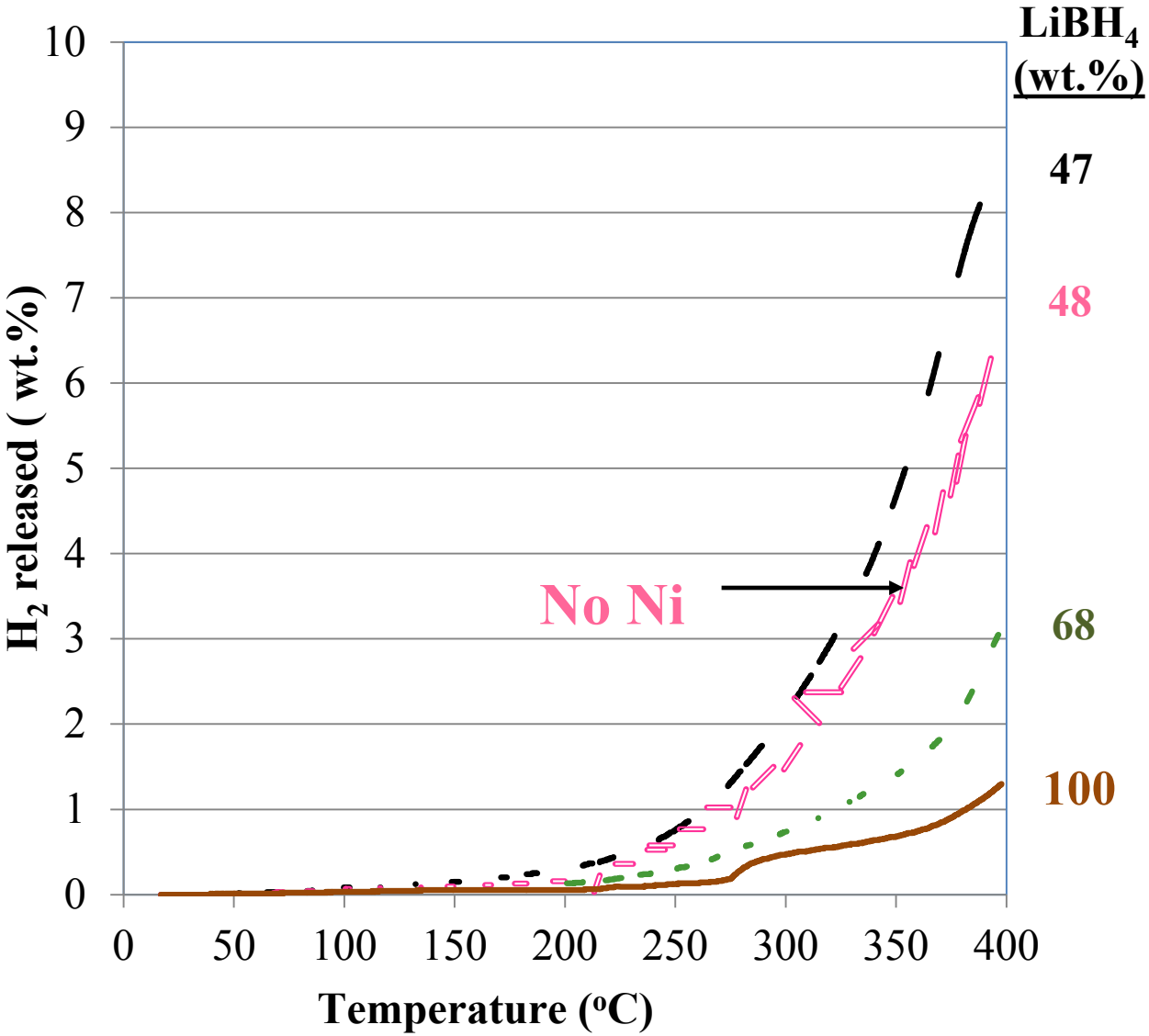
Gas-phase IR indicated <u>no borane release</u> from catalyzed hydride



$LiBH_4$ decomposition is observed below 250°C when catalyzed with carbon



Phys. Mixture of 2 wt. % Ni-AC catalyst further facilitates dehydrogenation of $LiBH_4$

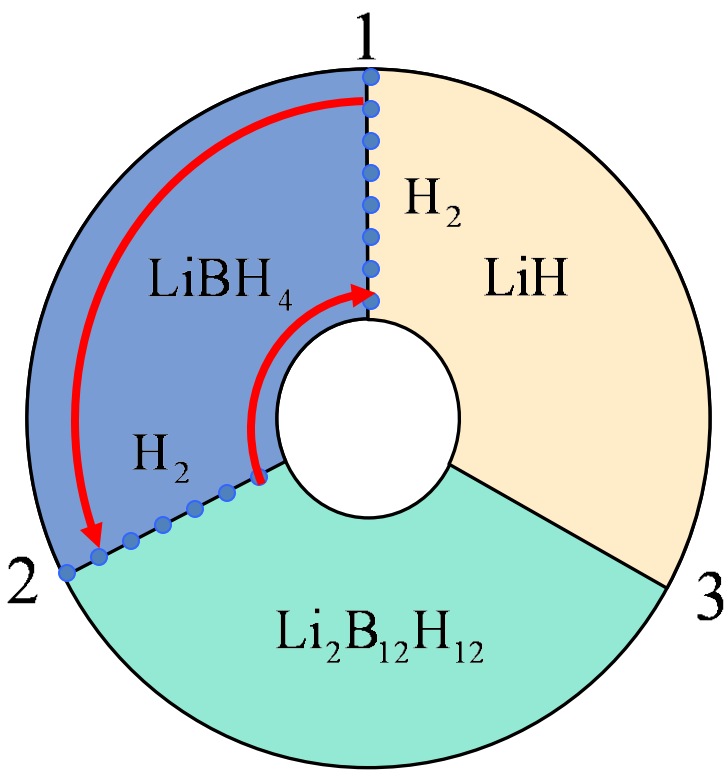


- *AC alone greatly enhanced $LiBH_4$ dehydrogenation.*
- *The more AC, the faster the rate.*
- *Addition of Ni further improved dehydrogenation kinetics.*
- *Future work includes using infusion technique.*

$LiBH_4$ dehydrogenation Model for Mass Transport

$$\boxed{(LiBH_4)_{solid}} \rightarrow \boxed{\frac{1}{12}(Li_2B_{12}H_{12})_{solid}} + \boxed{\frac{5}{6}(LiH)_{solid}} + \frac{13}{12}(H_2)_{gas}$$

$$\rightarrow (B)_{solid} + (LiH)_{solid} + \frac{3}{2}(H_2)_{gas}$$



1 $LiBH_4 : H_2 : LiH \rightarrow$ equilibrium

$\rightarrow C^1[\text{defects}]$

2 $LiBH_4 : H_2 : Li_2B_{12}H_{12} \rightarrow$ equilibrium

$\rightarrow C^2[\text{defects}]$

$$\nabla C = \frac{C^1[\text{defects}] - C^2[\text{defects}]}{d}$$

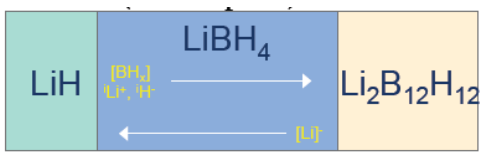
$$\boldsymbol{J = -D\vec{\nabla}C}$$

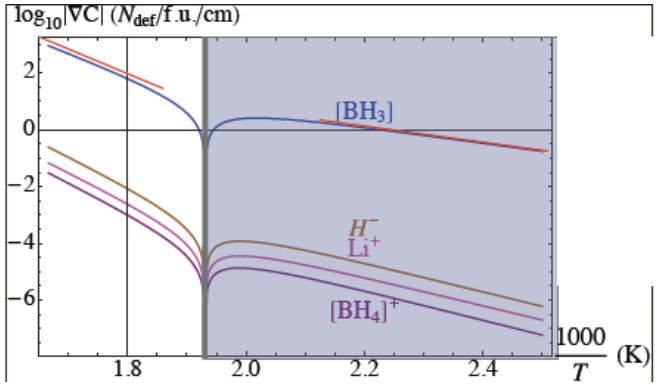
Native defect concentration gradient

$$J = -D\vec{\nabla}C$$

$[BH_x]$	$[LiH_x]$
$[B]^{3-}$	$[Li]^-$
$[BH]^{2-}$	$[LiH]$
$[BH_2]^-$	$[H]^+$
$[BH_3]$	$[H]^-$
$[BH_4]^+$	$[H]^0$

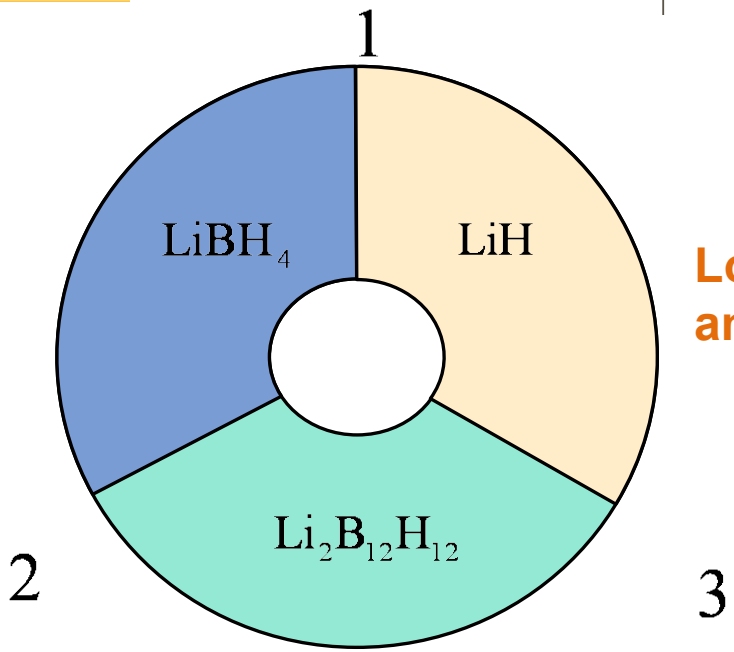
	^iH
$^iLi^+$	$^iH^+$
$^iB^{3+}$	$^iH^-$
	$^iH^0$





The BH_3 vacancy has the largest concentration gradient.

But how about D?

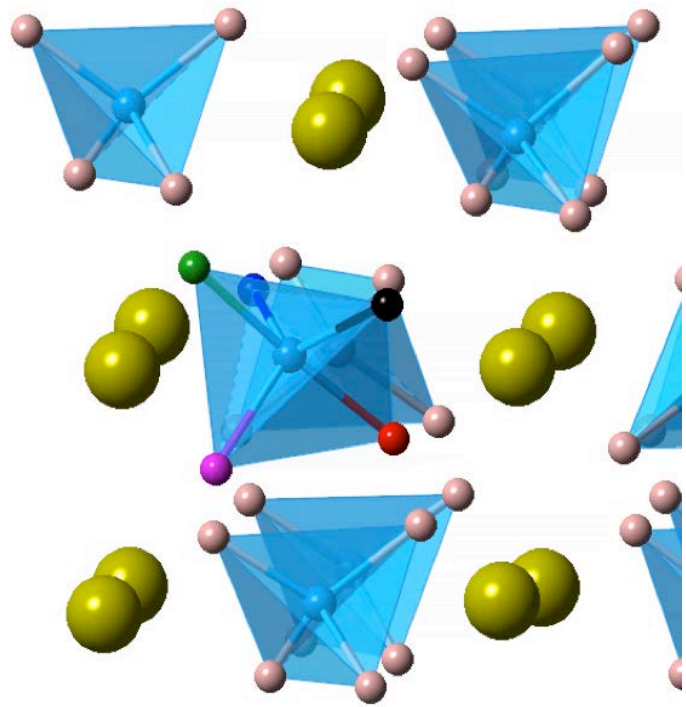


Low-energy defects: H and Li vacancy pair

Low-energy defects:
Li vacancy and interstitial pair

Can $[BH_3]$ diffuse through $LiBH_4$?

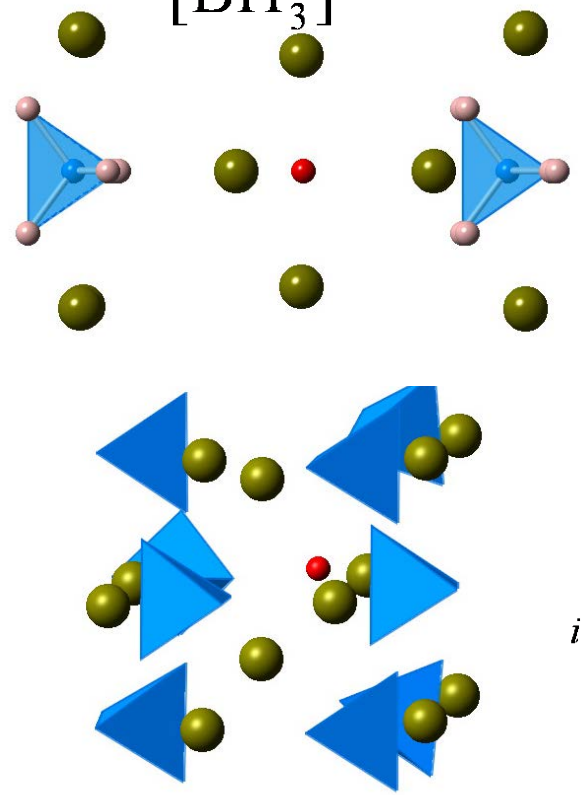
$[AlH_3]$ diffusion in $NaAlH_4$



K. J. Michel and V. Ozolins, J Phys Chem C **115** (43), 21443 (2011).

AlH_3 vacancy diffusion in sodium alanate: AlH_3 vacancy leaves a negative H. The H then combines with the neighboring AlH_4 unit, thus leaving space for the vacancy to diffusion.

$[BH_3]$



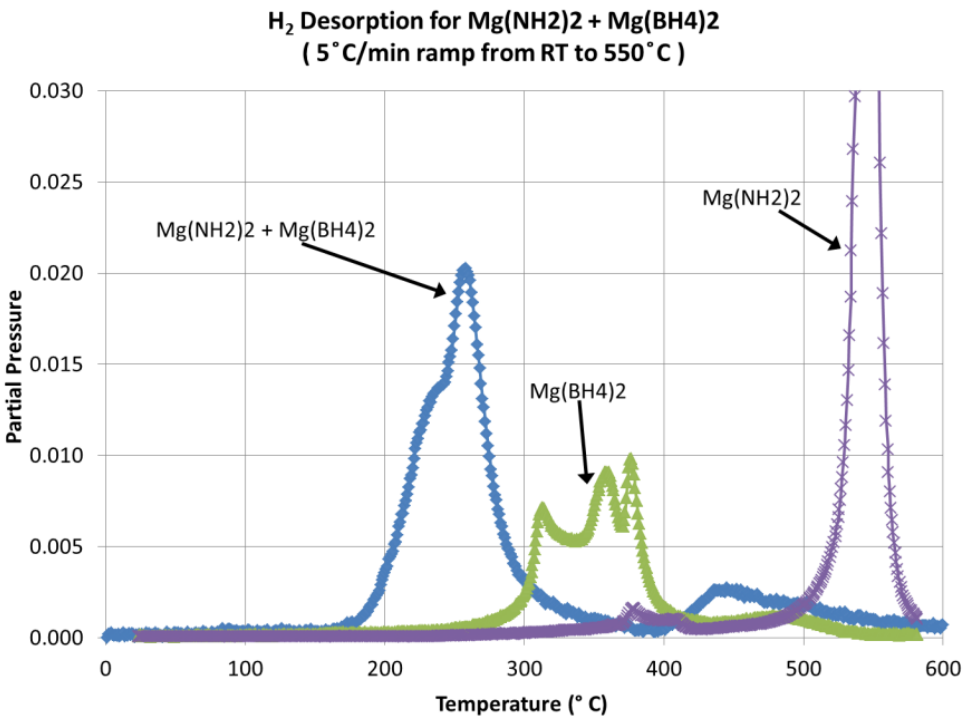
$^{i}H^{-}$

After taking BH_3 from the original BH_4 negative unit, a negative H forms, which lies exactly at the original BH_4 position. The negative H does not combine to the neighboring BH_4 unit.

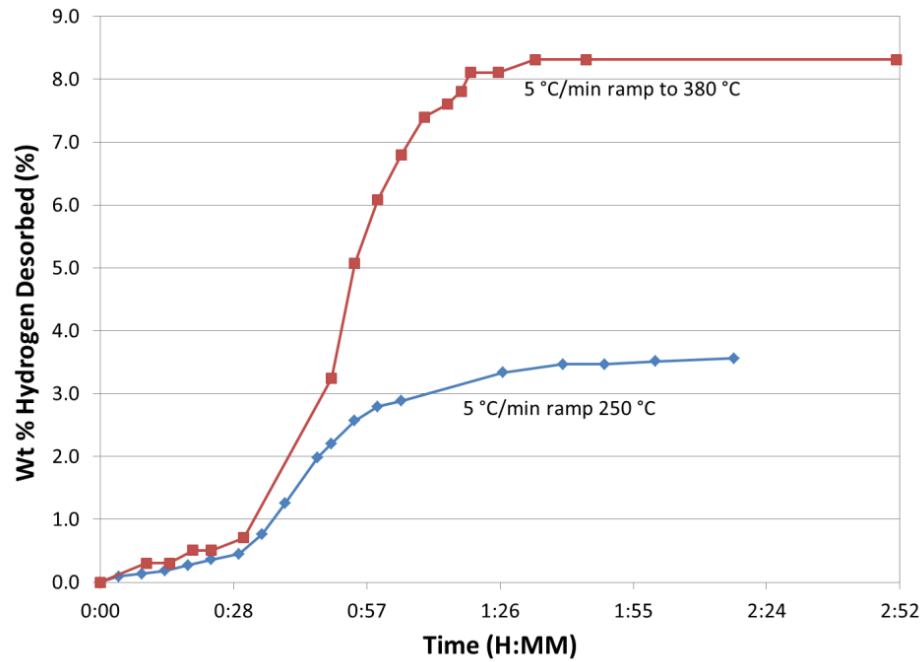
$^{i}H^{-}$ left by $[BH_3]$ blocks $[BH_3]$ diffusion.

Very different diffusion in borohydrides vs. alanates: Mass transport in $LiBH_4$ is very low.

$Mg(NH_2)_2$+$Mg(BH_4)_2$: Desorption Quantification and Reversibility



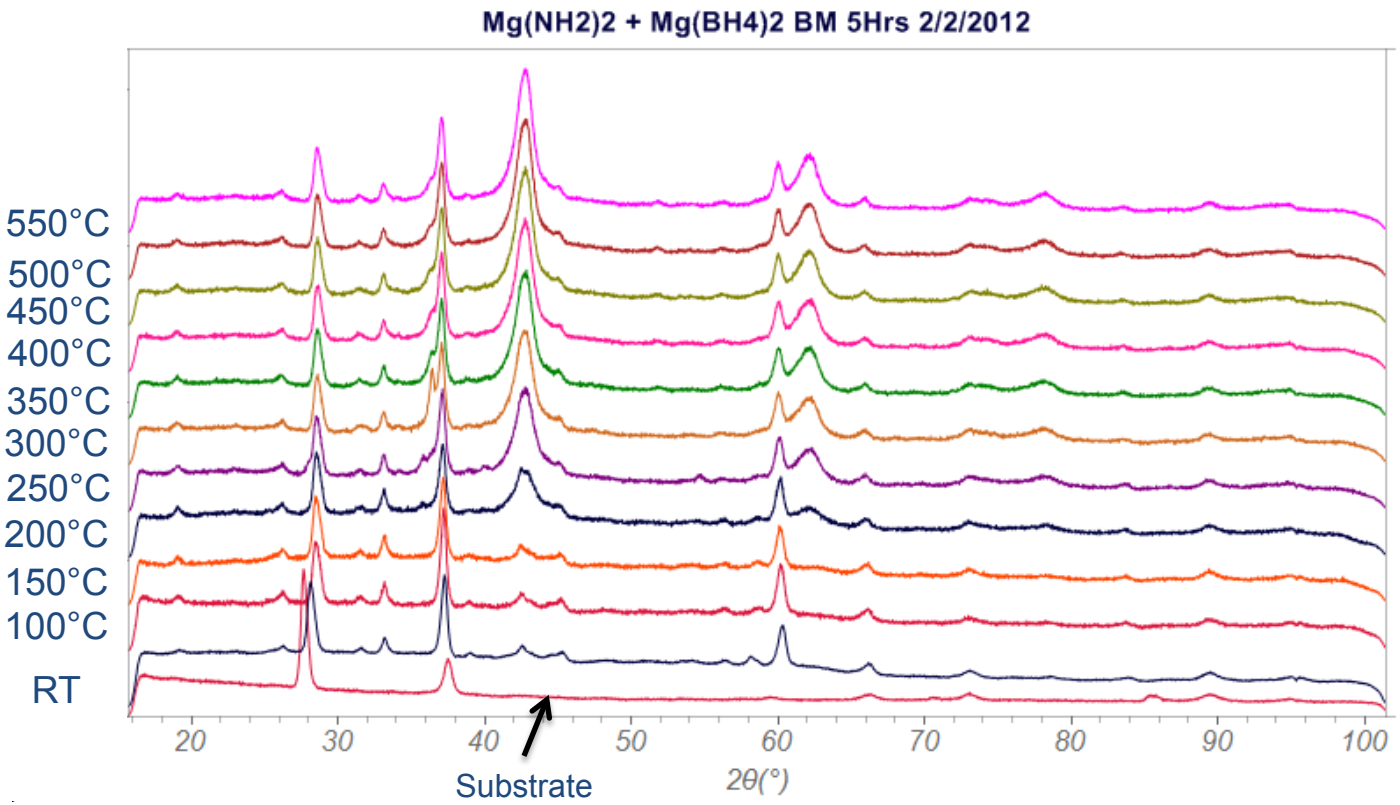
$Mg(NH_2)_2$ + $Mg(BH_4)_2$



- Ammonia release nearly undetectable
- The dangerous compounds diborane and borazine are not detected
- $Mg(NH_2)_2$ + $Mg(BH_4)_2$ exhibits a comparatively very low desorption onset (~180°C)

- $Mg(NH_2)_2$ + $Mg(BH_4)_2$ desorbed ~8.3 wt. % at 380 °C
  - **No reversibility at 250°C or 380°C (computation also supports lack of reversibility)**

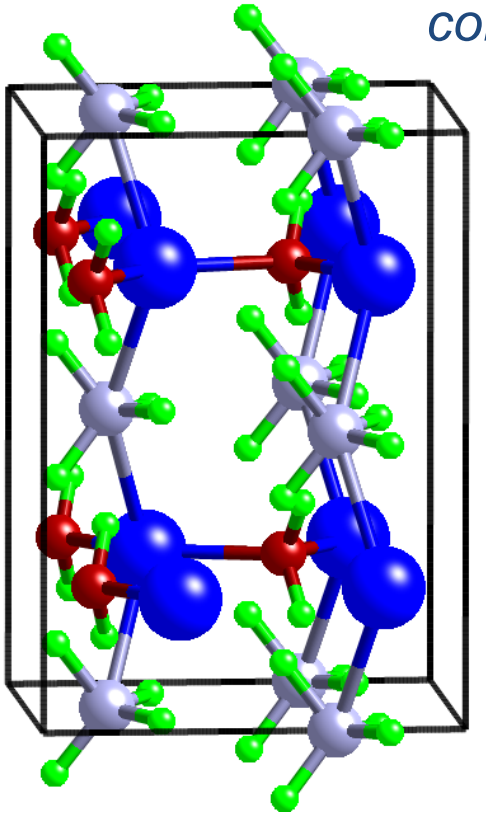
$Mg(NH_2)_2 + Mg(BH_4)_2$: Phase Evolution



- XRD: Possible new RT phase, only 1 step observed at ~150 °C
  - Low temperature signal improved vs. prior work
  - Strongest peaks overlap with substrate, baseline is high – possibly some amorphous character?

Technical Accomplishments: Experimental Testing of Predicted Compounds

Previously, no known quarternary borohydride/amide compounds in Mg-B-N-H system



$Mg(BH_4)(NH_2)$-PEGS (4 fu)
Space group: Ima2 (46)

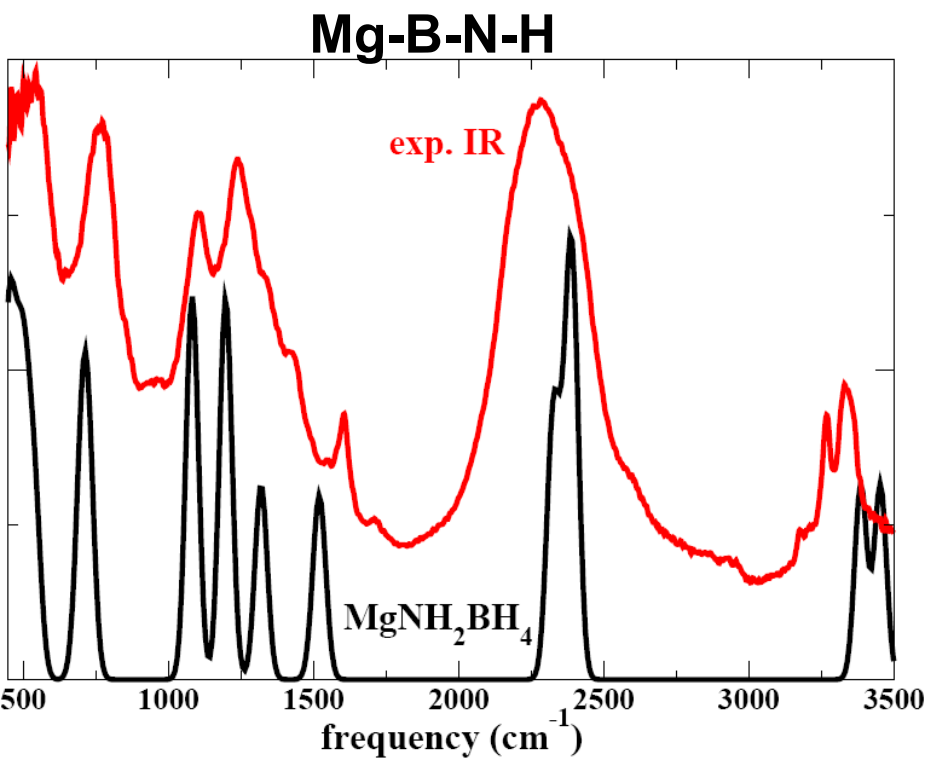
$Mg(BH_4)_2 + Mg(NH_2)_2 \rightarrow MgBNH_6$

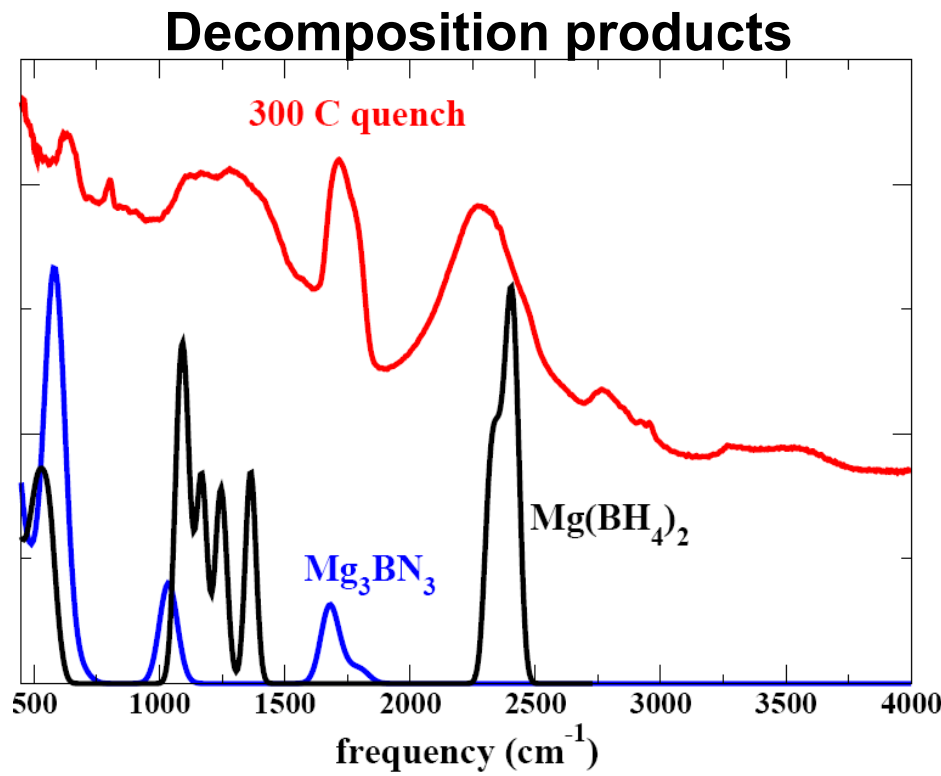
kJ/(mol Mg)	ΔE_{Static}	$\Delta H_{ZPE}^{T=0K}$	$\Delta H^{T=300K}$
$Mg(BH_4)(NH_2)$	-9.75	-8.18	-8.63

New, predicted compound stable w.r.t. $Mg(BH_4)_2 + Mg(NH_2)_2$

Y.-S. Zhang and C. Wolverton, unpublished (2011).

Technical Accomplishments
product in the decomposition of Mg-B-N-H



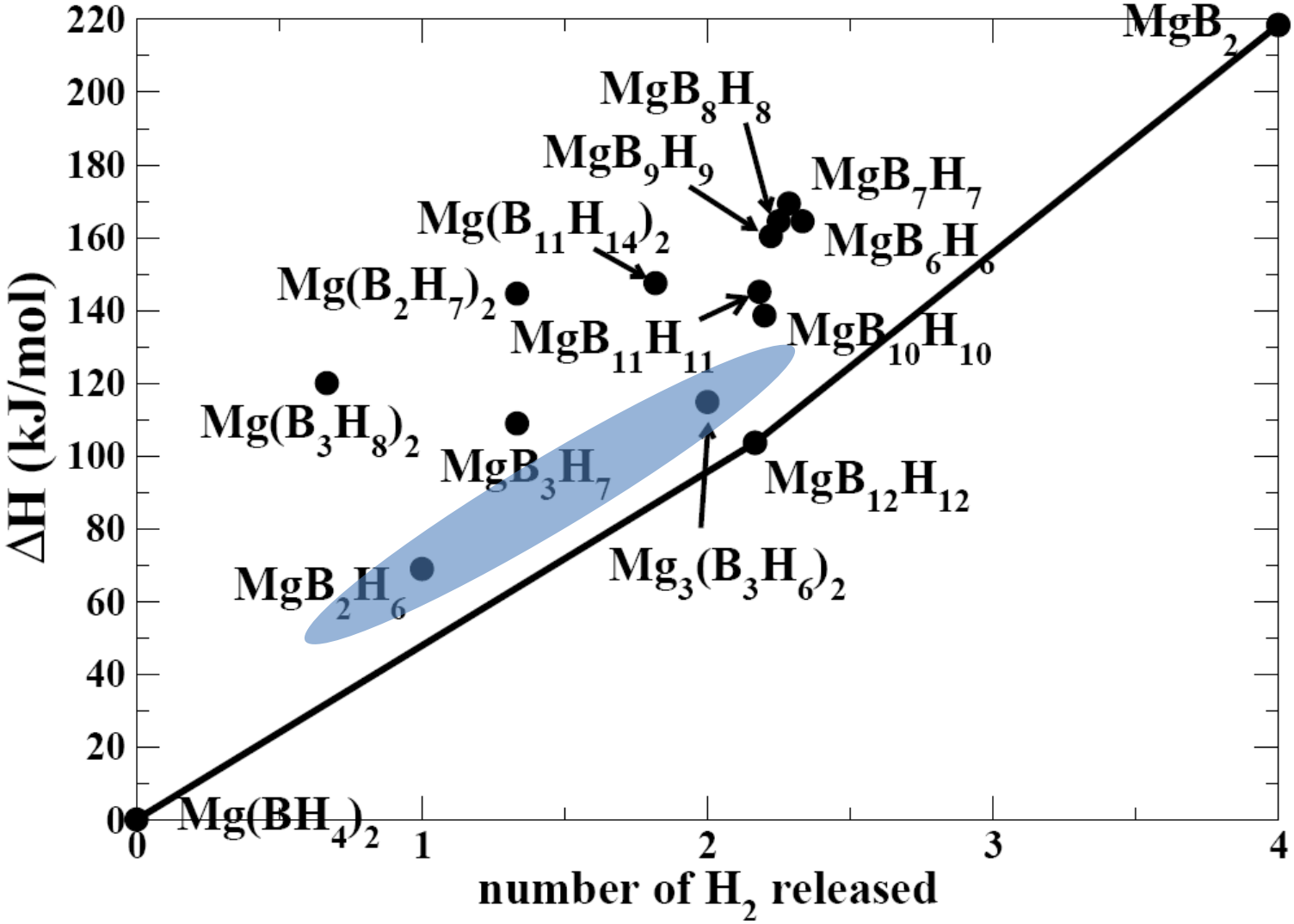


The pDOS of the theoretically predicted $MgBH_4NH_2$ is in a good agreement with the experimental IR measurements.

The decomposition products contain part of $Mg(BH_4)_2$ and compounds including N-B-N linear cluster, such as Mg_3BN_3.

DOWNSELECT: End work on borohydride/amide combination (due to lack of reversibility and formation of B-N bonds in product).

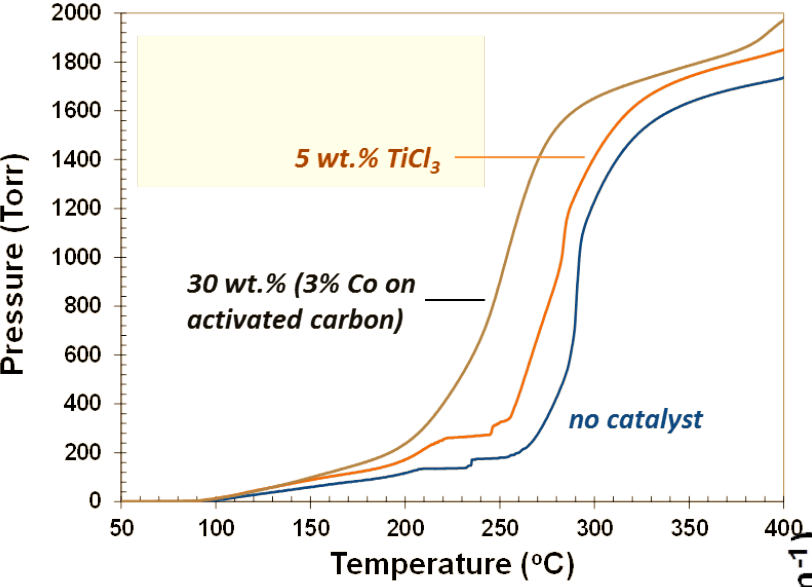
All possible $Mg(BH_4)_2$ decomposition pathways



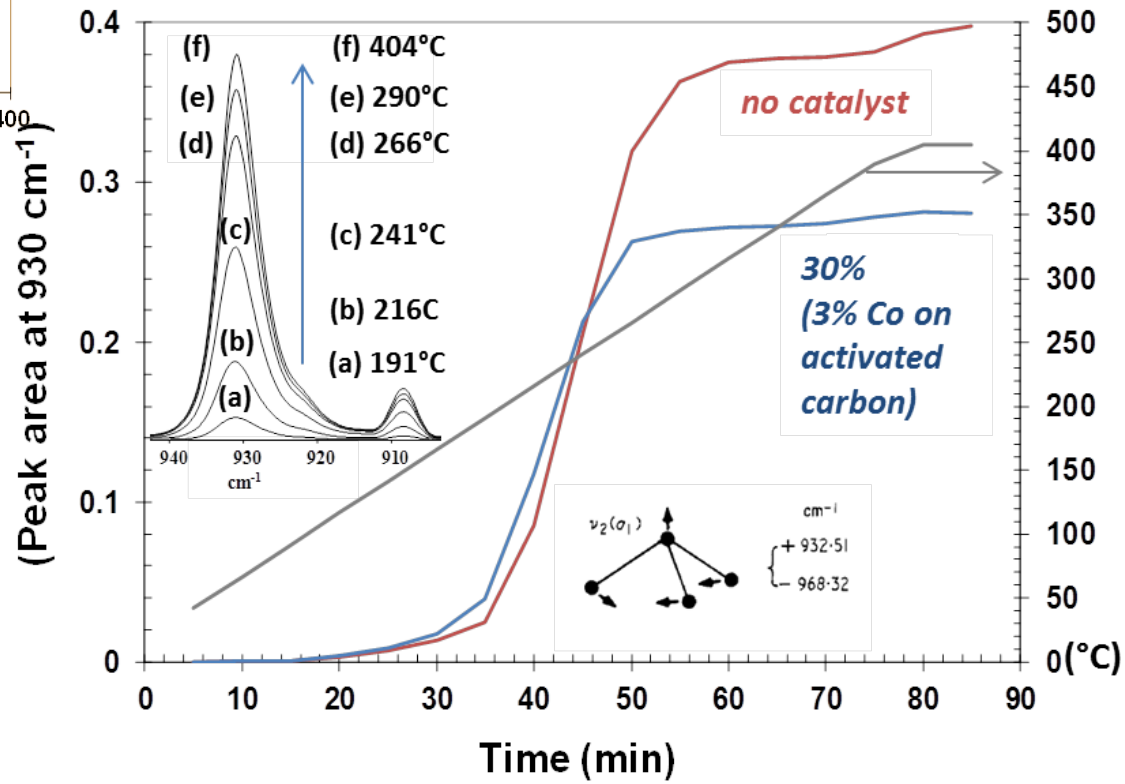
All $[B_nH_m]$ intermediates have higher reaction energies than $MgB_{12}H_{12}$.
Only the reactions to MgB_2H_6 and $Mg_3(B_3H_6)_2$ are close to the $MgB_{12}H_{12}$ convex hull.
$Mg_3(B_3H_6)_2$ is a metastable intermediate in the decomposition of $Mg(BH_4)_2$.

Y. Zhang, et. al. submitted to J. Phys. Chem. C

3 wt.% Co-AC catalyst promotes dehydrogenation of $Mg(NH_2)_2$–$Mg(BH_4)_2$ and reduces NH_3 formation



- *Co–AC catalyst showed a better kinetic improvement than $TiCl_3$*

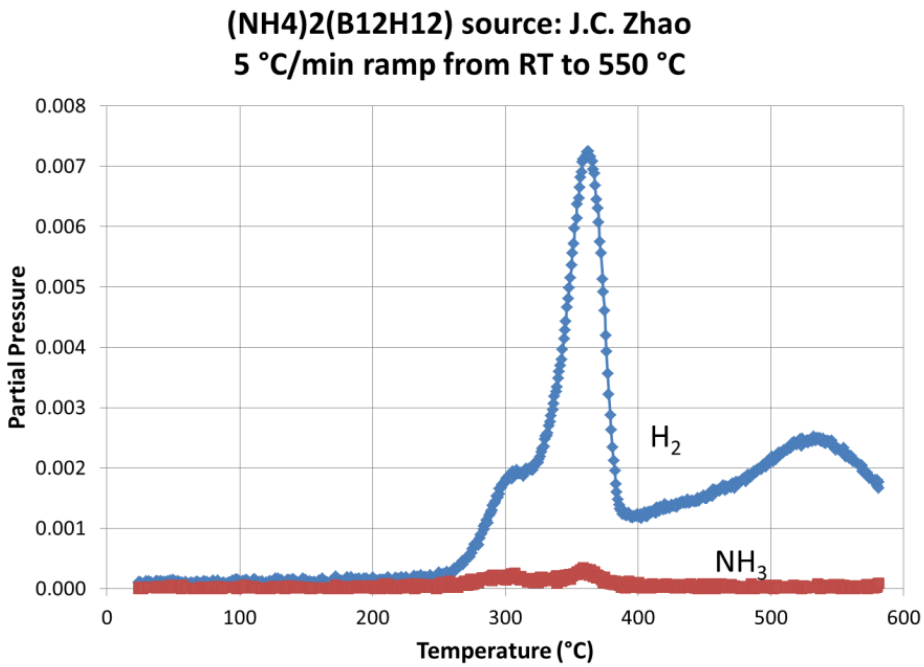


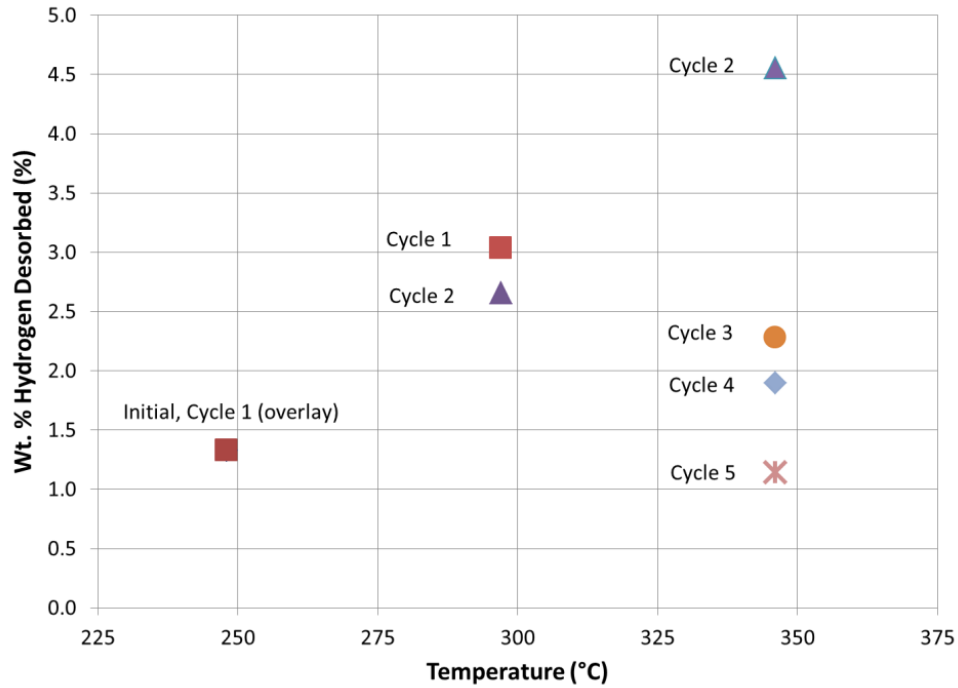
- *Gas-phase IR indicated <u>smaller NH_3 release</u> from catalyzed hydride*

$(NH_4)_2B_{12}H_{12}$: Desorption and Reversibility

$2(NH_4)_2B_{12}H_{12} \leftrightarrow 4BN + B_{20}H_{16} + 12H_2 \leftrightarrow 4BN + 20B + 8H_2$ **11.3 H_2 wt%**

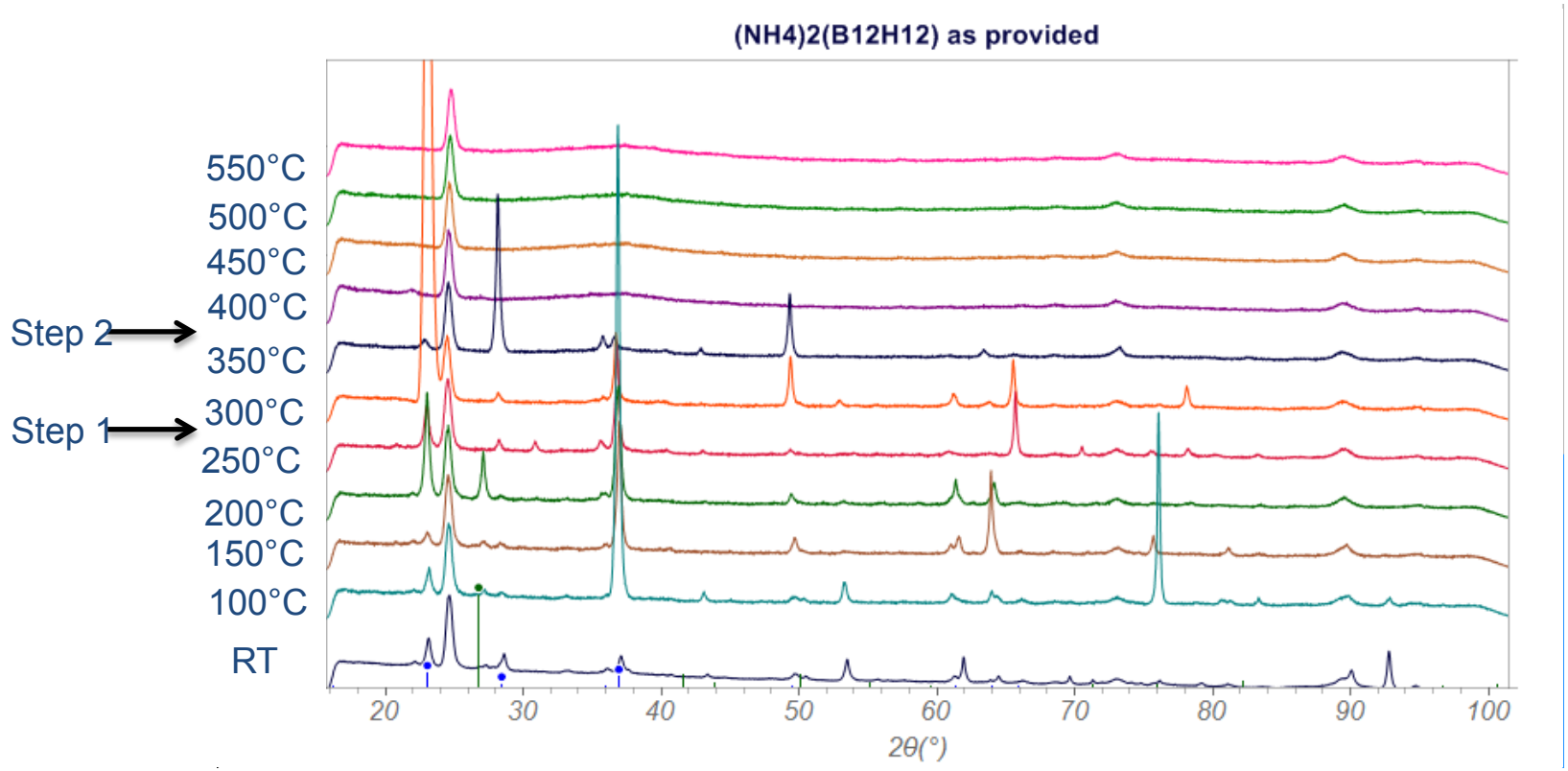
W. Q. Sun, et. al. Phys. Rev. B **83** 064112 (2011)





- Ammonia release nearly undetectable, and diborane and borazine are not detected
- Partial reversibility (but degrading performance) under cycling at 350°C (2000 psi H_2 recharge at 350°C)
  - Small sample size for $(NH_4)_2(B_{12}H_{12})$ due to limited quantity may exacerbate response

$(NH_4)_2(B_{12}H_{12})$: Phase Evolution



- XRD indicates some unidentified phases appearing
  - Initial signal matches pretty well with ICSD $(NH_4)_2(B_{12}H_{12})$ structure
  - Some BN possibly formed, see peaks disappearing – at end amorphous w/substrate
- In Situ IR indicates B-N stretch above ~300 °C

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)
F.-C. Chuang (Nat'l Sun Yat-Sen U)
J. C. Zhao (OSU)

Future Plans

- Experimentally characterized storage properties/reactions of $(NH_4)_2B_{12}H_{12}$ and other predicted reactions; Optimize reversibility conditions for $5Mg(BH_4)_2+2LiBH_4$ mixture
- Extend experimental catalyst studies to other predicted promising materials; explore optimal morphology of carbon/metal catalysts;
- Focus experimental efforts on rehydriding reactions/reversibility (subject to pressure limitations of experimental equipment)
- Focus computational efforts on kinetics, defects, diffusion/mass transport/hydrogen dissociation in promising predicted reactions
- Downselect decision: End work on borohydride/amide combinations (No reversibility from computational or experimental work; B-N bonds in product).

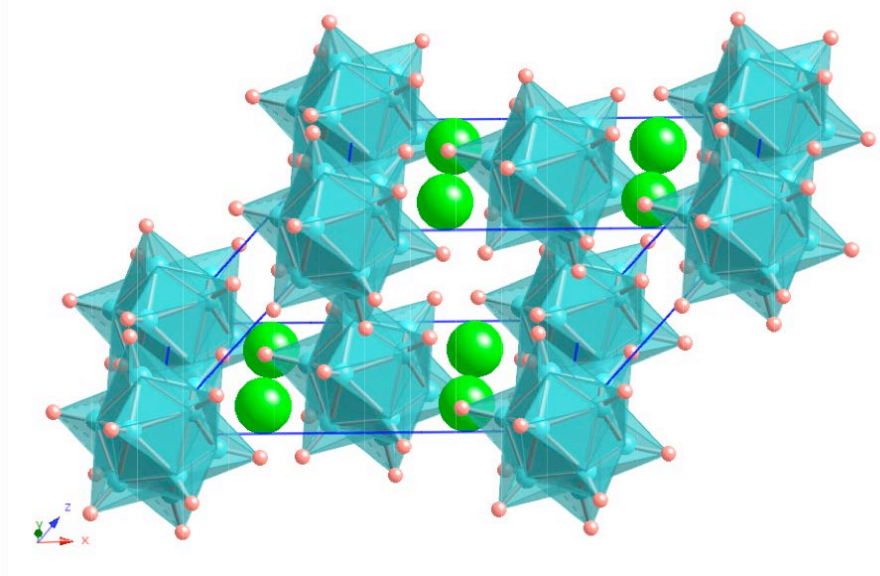
Summary – Technical Accomplishments

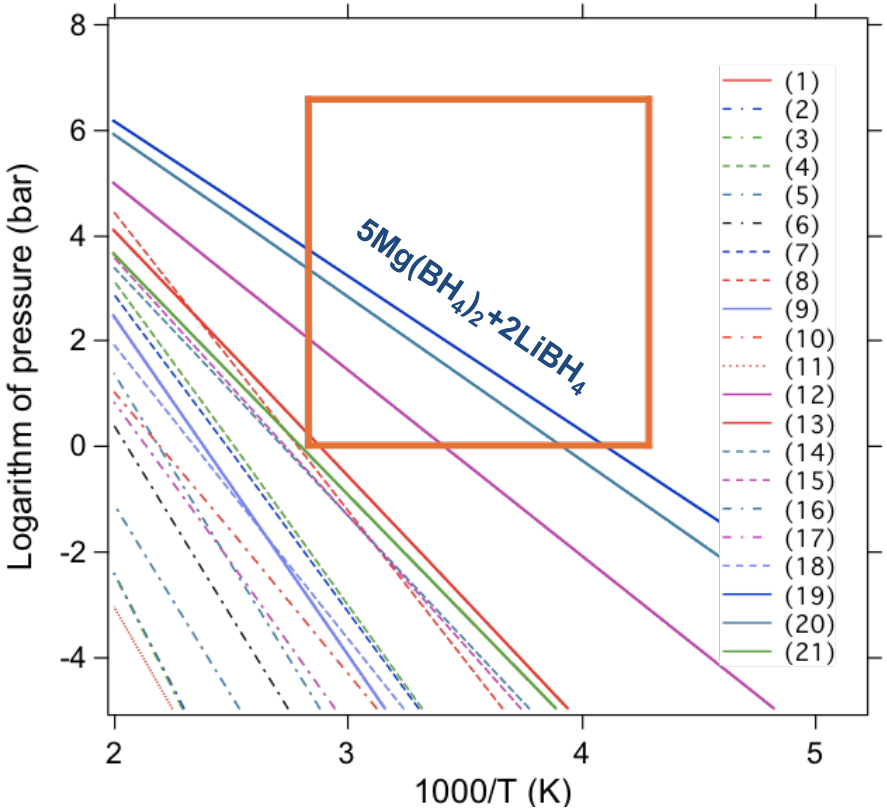
- H_2 desorption and decomposition pathways have been studied in
  - $5LiBH_4 + 2Mg(BH_4)_2$ (~5.8 wt.% desorbed)
  - $Mg(BH_4)_2 + Mg(NH_2)_2$ (~8.3 wt.% desorbed)
  - $(NH_4)_2B_{12}H_{12}$. (~4.5 wt.% desorbed)
- Partial reversibility (~1-2.5 wt.%) found in $5LiBH_4 + 2Mg(BH_4)_2$ and $(NH_4)_2B_{12}H_{12}$
- Proposed new metal-carbon catalyst: Tested on $NaAlH_4$, and applied to $Mg(BH_4)_2 + Mg(NH_2)_2$, $2LiBH_4+5Mg(BH_4)_2$ and $LiBH_4$; Effective catalyst - lowers desorption temperature, improves dehydrogenation rate, and suppresses formation of borane and NH_3
- Downselect the mixed borohydride/amide systems as promising hydrogen storage material (lack of reversibility and B-N bonds in products)
- Predicted a new metastable $Mg_3(B_3H_6)_2$ intermediate in decomposition of $Mg(BH_4)_2$, but showed that recently-proposed $Mg(B_3H_8)_2$ is not stable.
- PEGS+DFT combined of experimental measurements is used in unique way to solve amorphous AlB_4H_{11} polymeric structure (w/ JC Zhao)
- Using the predictive models of defects, kinetics of mass transport: mass transport in $LiBH_4$ is very low (much lower than that in $NaAlH_4$)

Technical Accomplishments: Experimental Testing of Predicted Reactions

$$5Mg(BH_4)_2 + 2LiBH_4 \xrightarrow{-29\ ^oC} Li_2B_{12}H_{12} + 5MgH_2 + 13\ H_2 \qquad 8.4\ wt.\%\ H_2$$

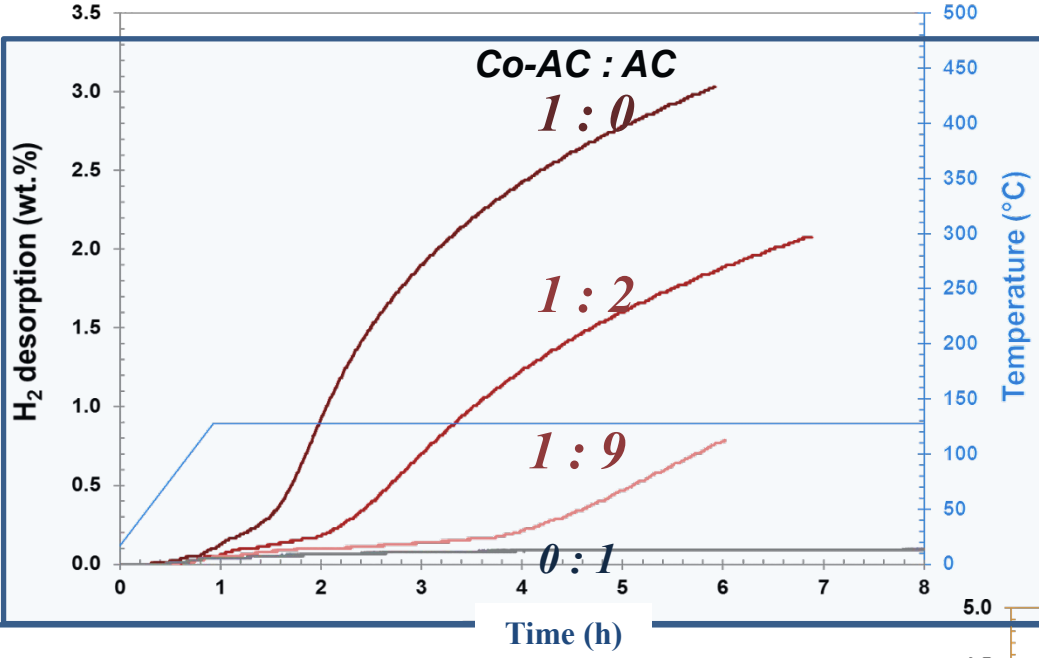
$Li_2B_{12}H_{12}$





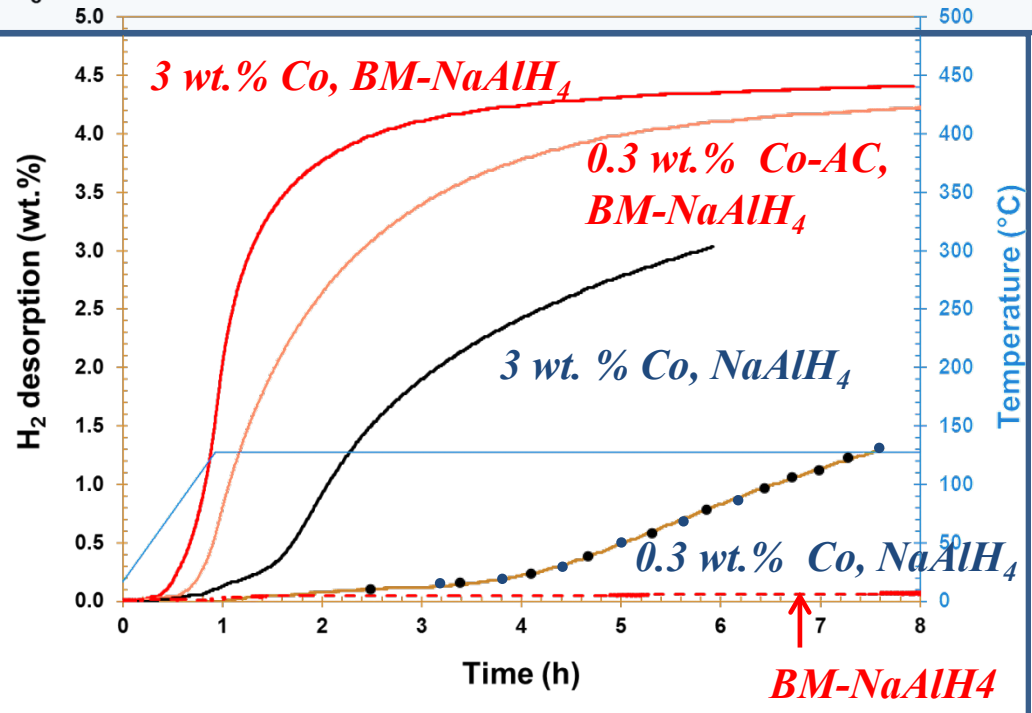
V. Ozolins, E. H. Majzoub, and C. Wolverton, JACS **131** (1), 230-237 (2009).

Metal NPs supported on activated carbon (AC) and good catalyst-hydride contact facilitate hydride dehydrogenation

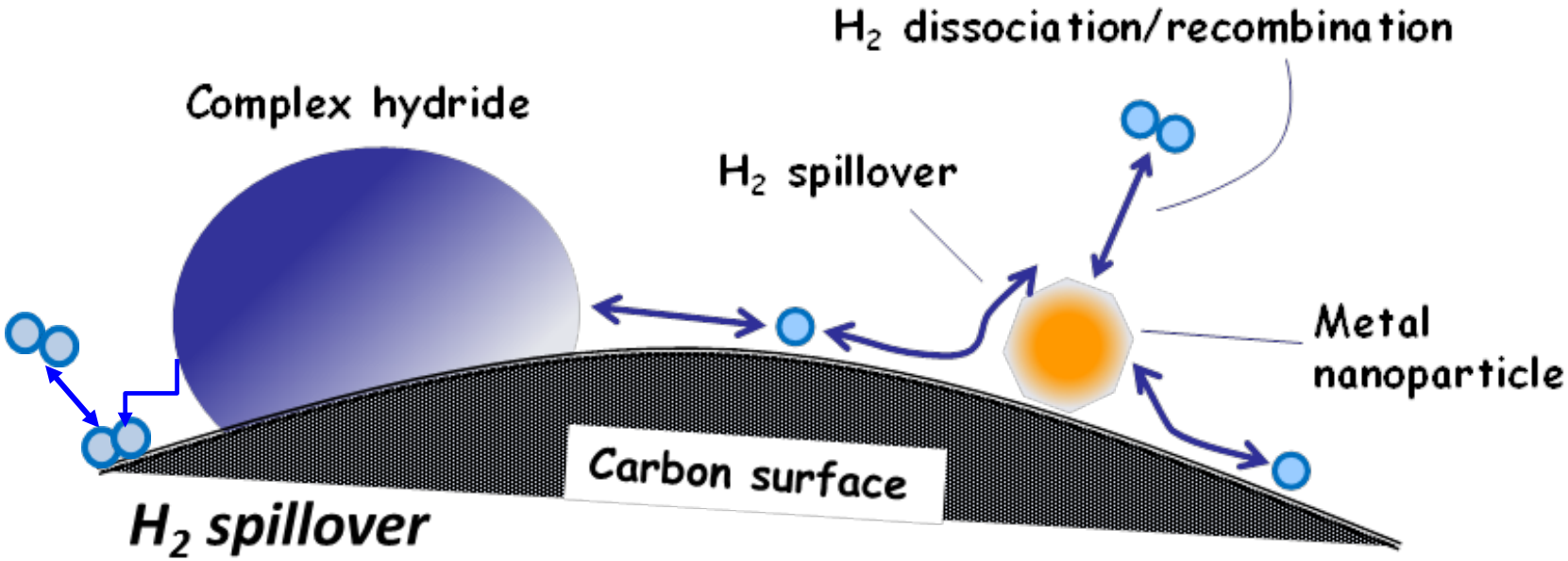


- Catalyst to hydride ratio maintained at 0.7 while varying Co-AC and AC ratio in the catalyst.
- The more Co-AC , i. e. The more Co, the faster the dehydrogenation kinetics

- 70 wt.% Co-AC catalyst but vary Co loading on the carbon support.
- Ball-milled hydride is in much closer contact with carbon catalyst and shows accelerated dehydrogenation kinetics



Model depicting the metal/carbon catalyst facilitated dehydrogenation of complex hydride



Effect of carbon based catalyst on the dehydrogenation of different hydrides:

- **$Mg(NH_2)_2$–$Mg(BH_4)_2$**
- **$Mg(BH_4)_2$-$LiBH_4$**
- **$LiBH_4$**

Technical Accomplishments: New Theoretical Predictions

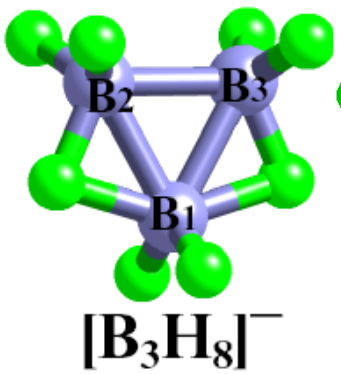
- Decomposition of $Mg(BH_4)(NH_2)$
- New borohydride compounds
  - $Mg_3(B_3H_6)_2$
  - AlB_4H_{11}
- Diffusion & mass transport (required for fast kinetics)

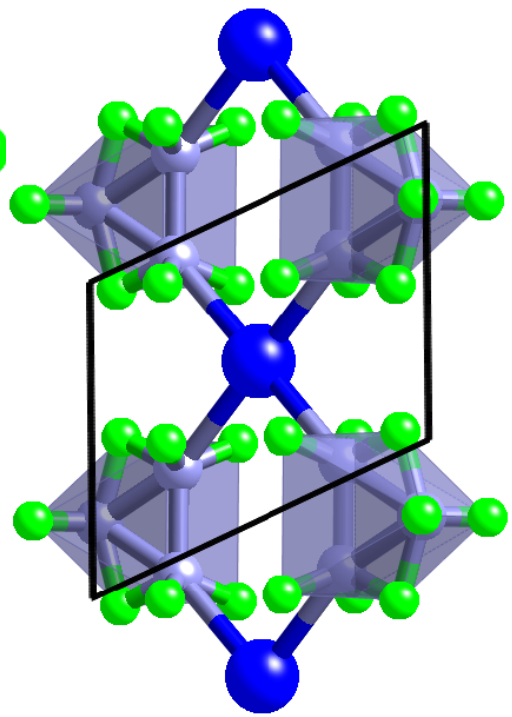
Technical Accomplishments
$Mg(BH_4)_2$ decomposition intermediates search

- **Recent experiments**

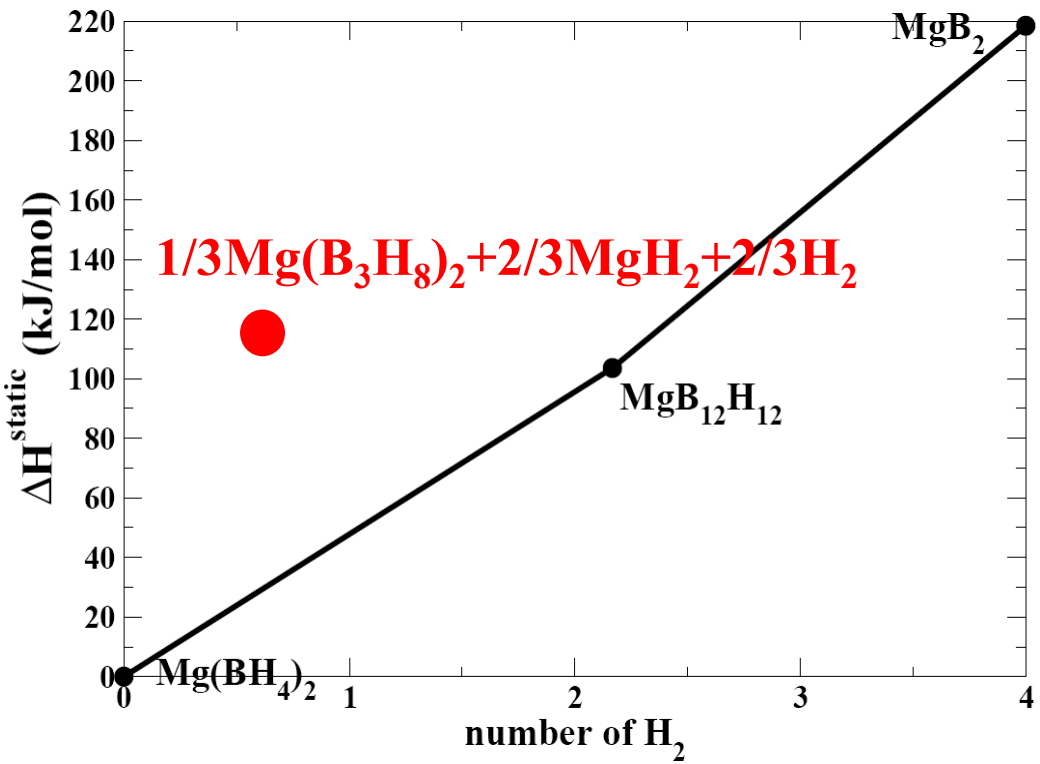
$[B_3H_8]$ intermediate

M. Chong, et. al. Chem. Commun. 47, 1330 (2011).





PEGS-$Mg(B_3H_8)_2$
Space group: P-1 (2)



$Mg(B_3H_8)_2$ is not a stable intermediate in the decomposition of $Mg(BH_4)_2$.

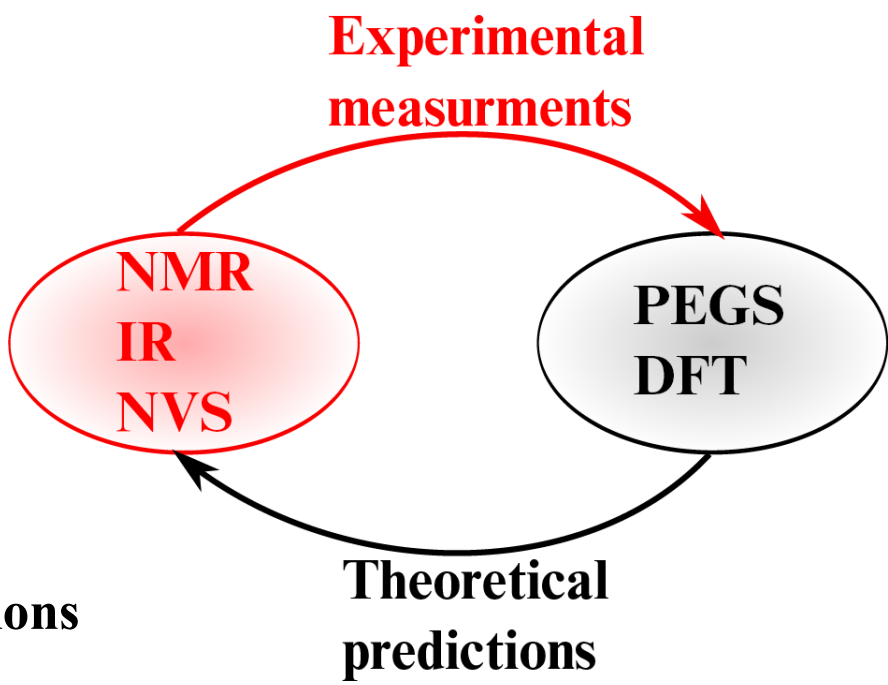
Technical Accomplishments
New metal borohydride: AlB_4H_{11}

In collaboration with Xuenian Chen and JiCheng Zhao (OSU)

- **AlB_4H_{11} synthesis:**

$$2Al(BH_4)_3 + B_2H_6 \rightarrow 2AlB_4H_{11} + 4H_2$$

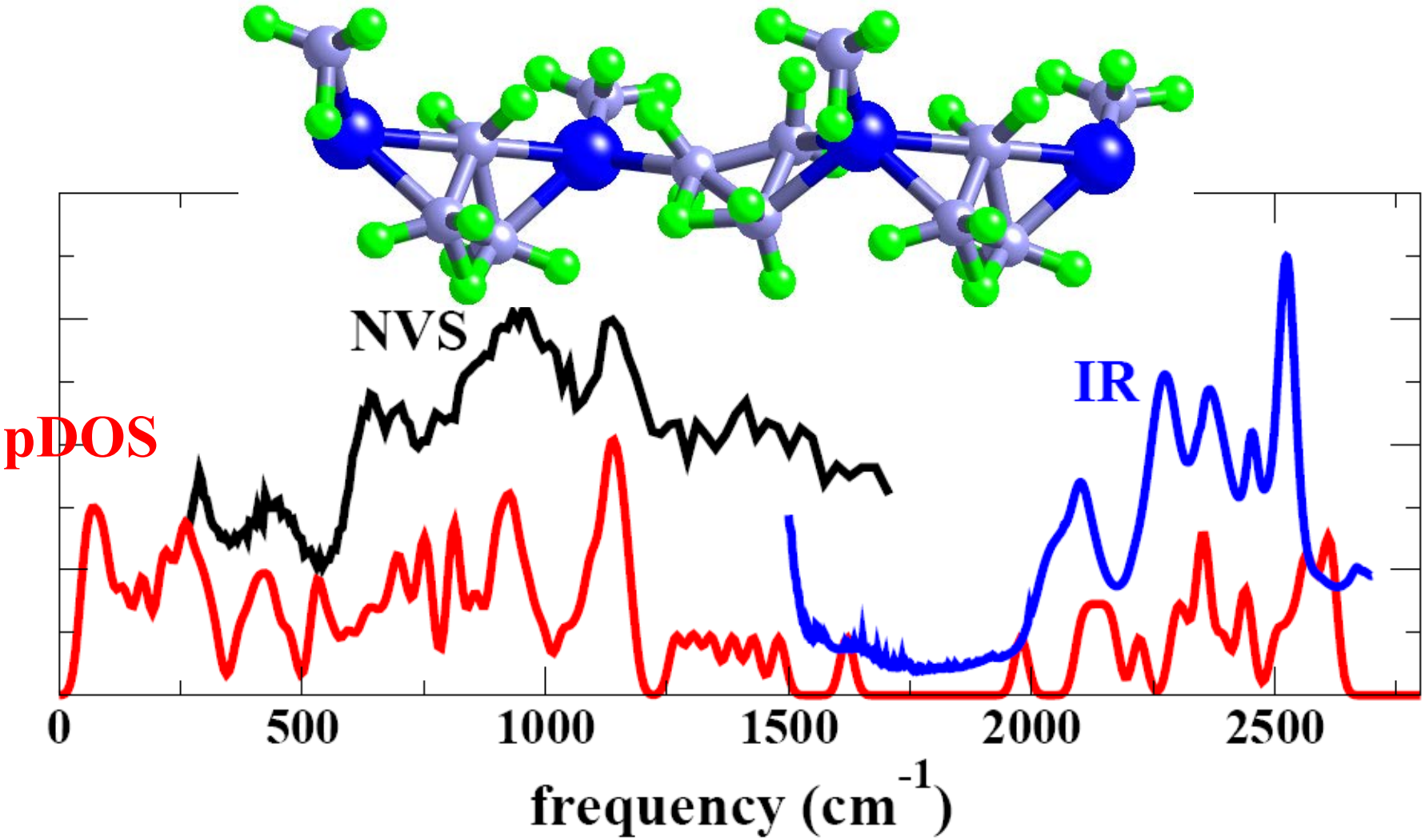
- **AlB_4H_{11} attractive properties**
  - High hydrogen content (13.5% H_2)
  - Moderate stability
  - Decomposition temperature ~125 °C
  - Endothermic dehydrogenation
  - Rehydrogenation at moderate conditions



- **Unknown AlB_4H_{11} structure: amorphous**

Can we use PEGS+DFT to predict the structure?
Or at least help interpret the experimental data?

PEGS+DFT Predicted AlB_4H_{11} low-energy structures



Polymer chain is composed of Al, $[BH_4]$, $[B_3H_7]$ groups, which are confirmed by experimental NMR measurements.

PEGS+DFT, combined of experiment, used in unique way to solve amorphous polymeric structure.