

# 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  
Ford Motor Company



NORTHWESTERN  
UNIVERSITY

**UCLA**



**ST028**

# 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: Combine materials from distinct categories 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

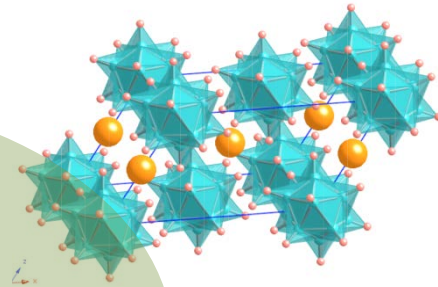
Our approach involves a powerful blend of:

- 1) H<sub>2</sub> 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)



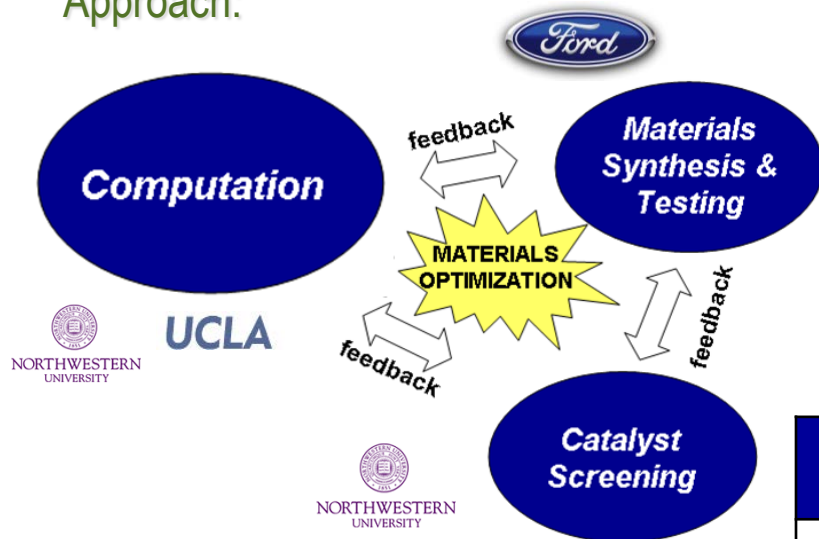
**NORTHWESTERN  
UNIVERSITY**

**UCLA**



# 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.

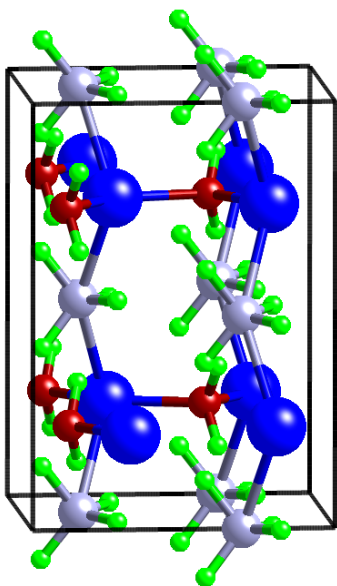
Predicted Compositions of Interest	Experimental Status
$(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$	Material received from OSU (Zhao)
$5\text{Mg}(\text{BH}_4)_2 + 2\text{LiBH}_4$	Material prepared & experiments initiated
$\text{Mg}(\text{BH}_4)_2$	Deferred given existing literature data
$\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$	Material prepared & experiments initiated
$5\text{MgH}_2 + \text{MgB}_{12}\text{H}_{12}$	Deferred given existing literature data

= current experimental focus

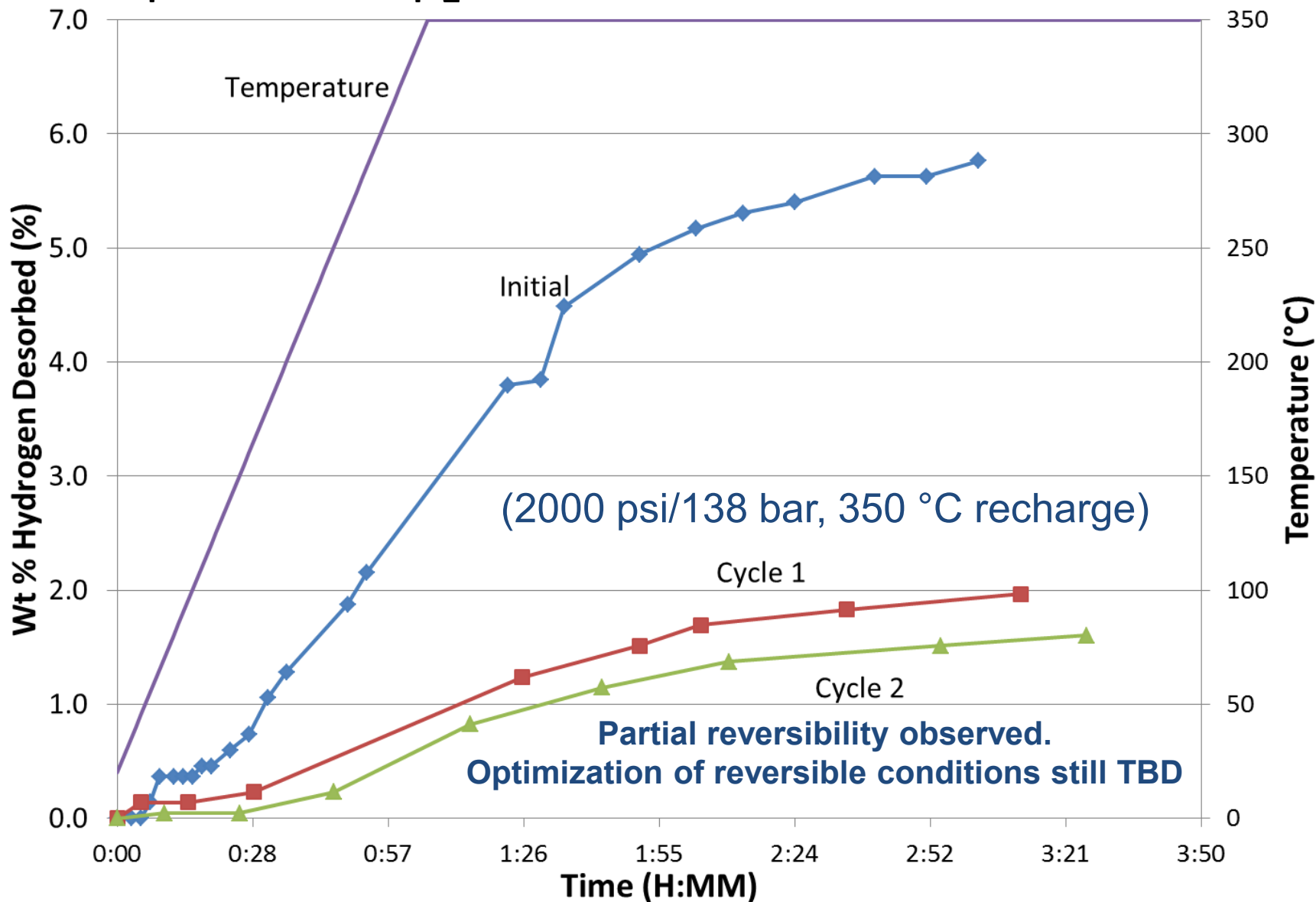
Guiding Questions:

- 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?

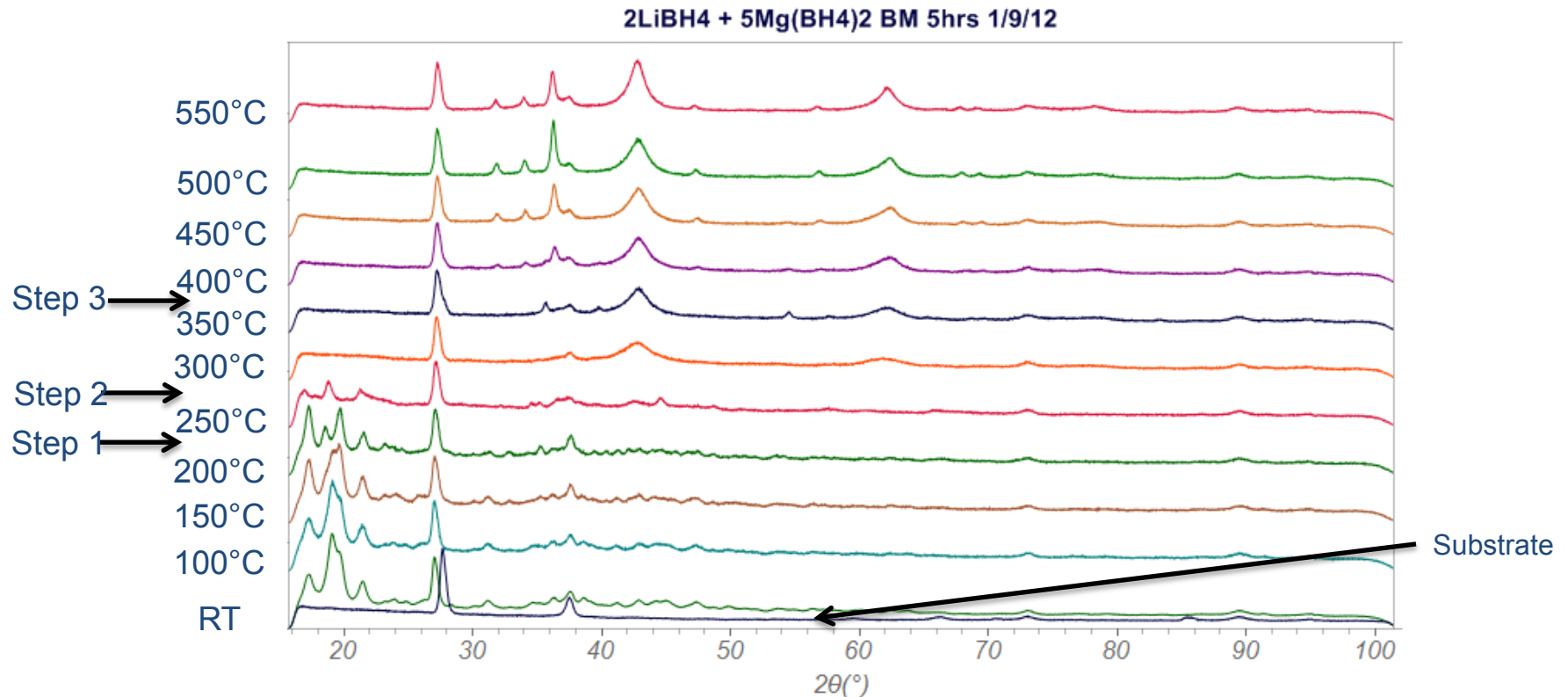
PEGS Predicted Mg-B-N-H Structure



# $2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$ : Desorption and Partial Reversibility

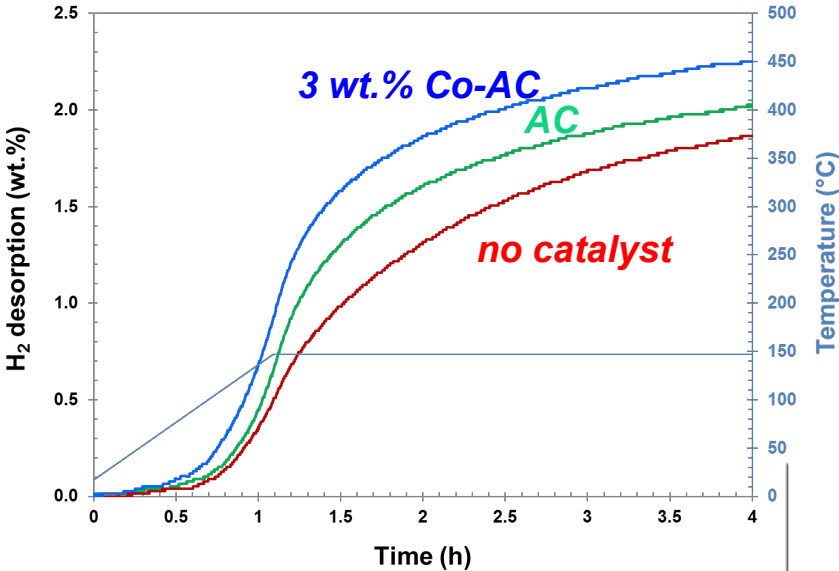


# $2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$ : Phase Evolution



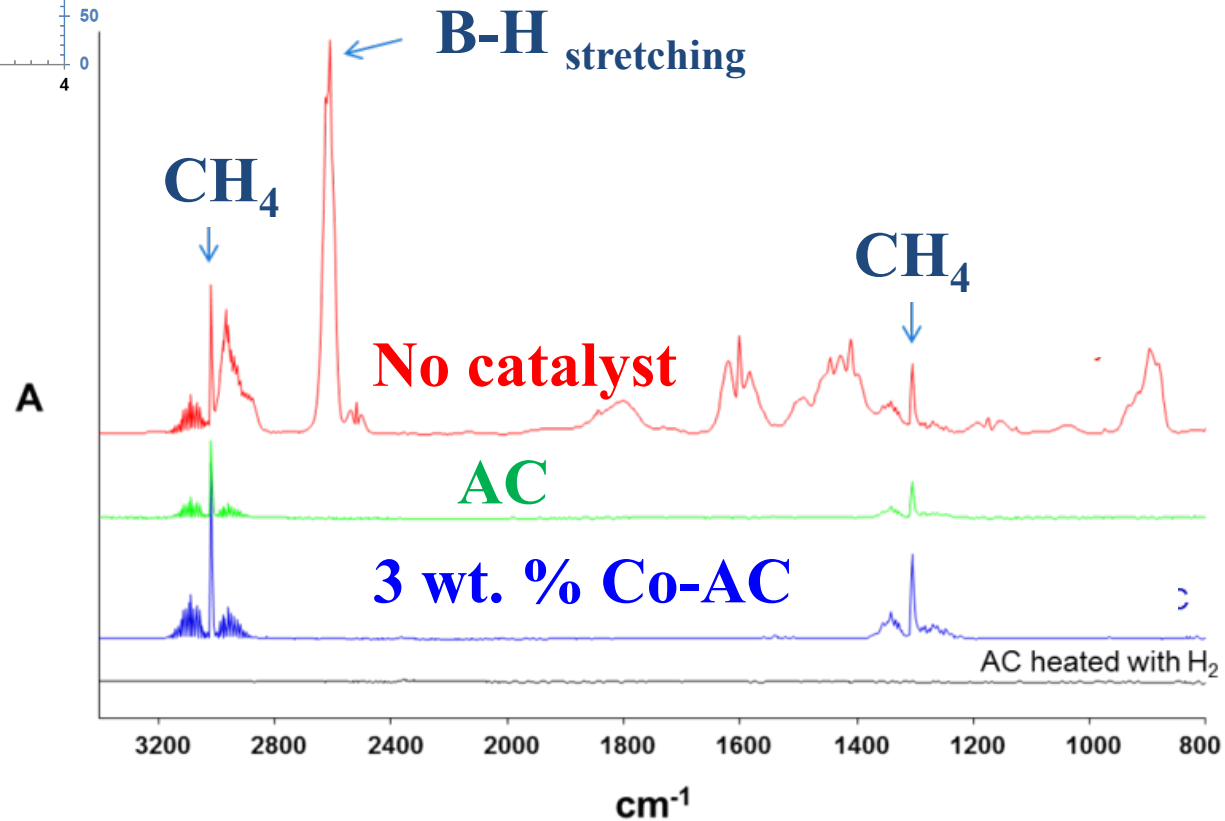
- XRD indicates initially similar to physical mixture, evolution in 2-3 steps:
  - ~200-250 °C :  $\text{Mg}(\text{BH}_4)_2$  & (possibly)  $\text{LiBH}_4$  consumption
  - ~250-300 °C : Continued  $\text{Mg}(\text{BH}_4)_2$  consumption, formation of  $\text{MgB}_2$  or possibly  $\text{MgH}_2$
  - Possible 3<sup>rd</sup> step over 350 °C : continued  $\text{MgB}_2$  formation, other unidentified phase?

# Effect of 3 wt. % Co-activated carbon on the dehydrogenation of $2\text{LiBH}_4\text{-}5\text{Mg}(\text{BH}_4)_2$



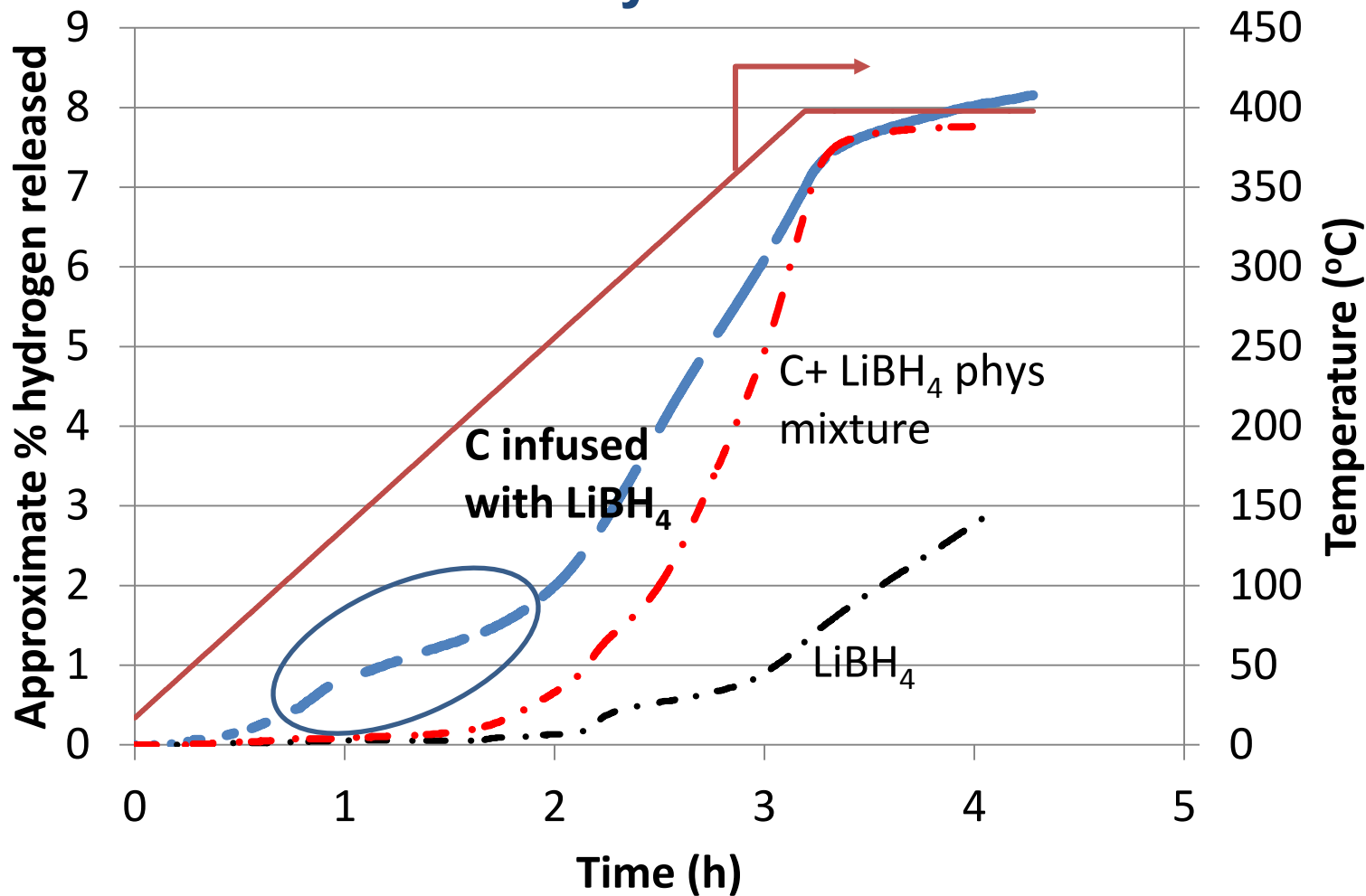
3 wt % Co-AC catalyst ( 70 wt.% catalyst) accelerated the rate of dehydrogenation

Gas-phase IR indicated no borane release from catalyzed hydride

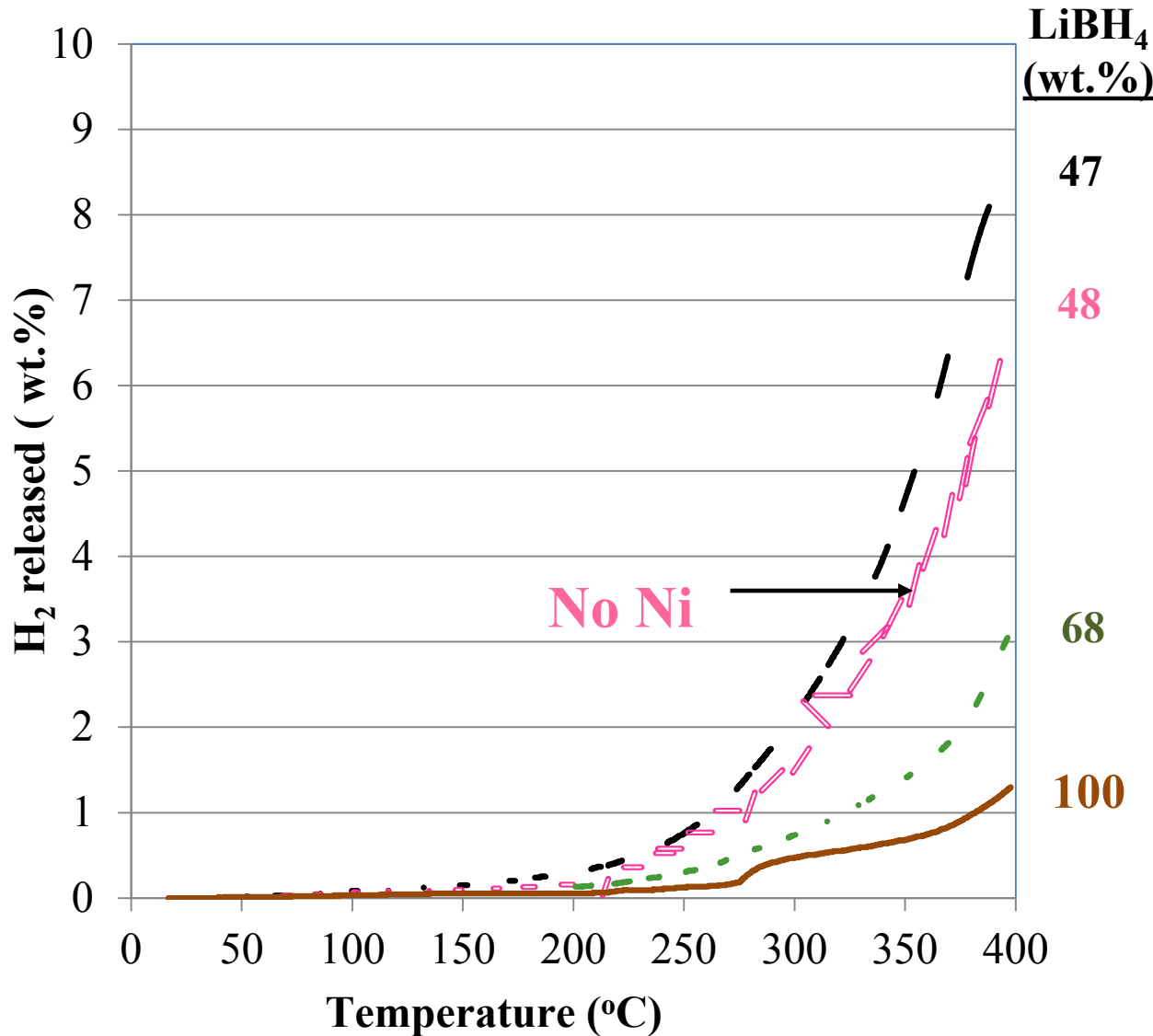




## LiBH<sub>4</sub> decomposition is observed below 250°C when catalyzed with carbon

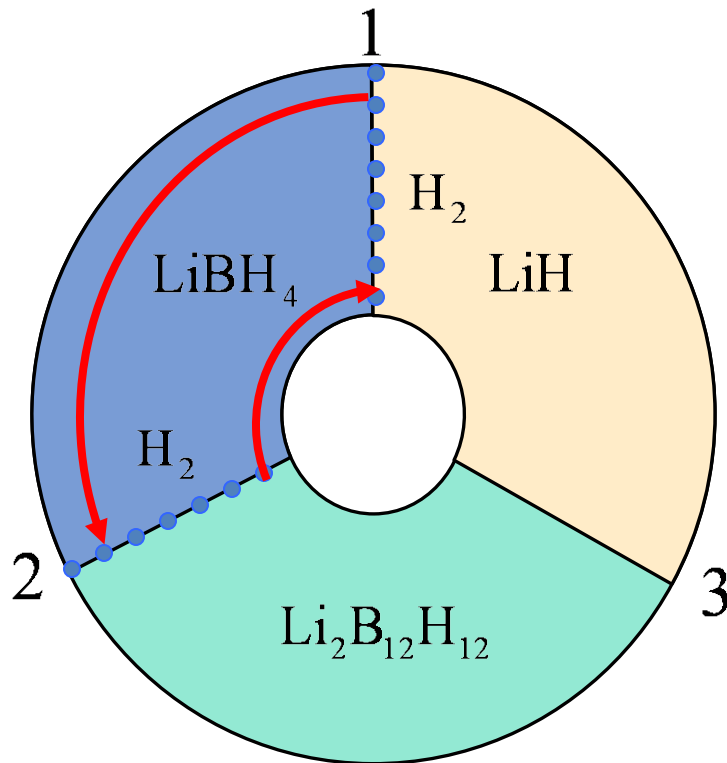
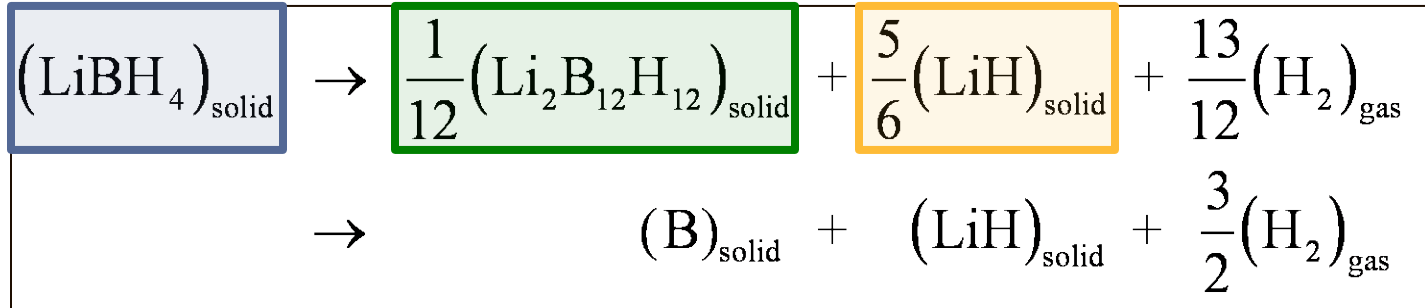


# Phys. Mixture of 2 wt. % Ni-AC catalyst further facilitates dehydrogenation of $\text{LiBH}_4$



- *AC alone greatly enhanced  $\text{LiBH}_4$  dehydrogenation.*
- *The more AC, the faster the rate.*
- *Addition of Ni further improved dehydrogenation kinetics.*
- *Future work includes using infusion technique.*

# LiBH<sub>4</sub> dehydrogenation Model for Mass Transport



1 LiBH<sub>4</sub> : H<sub>2</sub> : LiH → equilibrium  
→ C<sup>1</sup>[defects]

2 LiBH<sub>4</sub> : H<sub>2</sub> : Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> → equilibrium  
→ C<sup>2</sup>[defects]

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

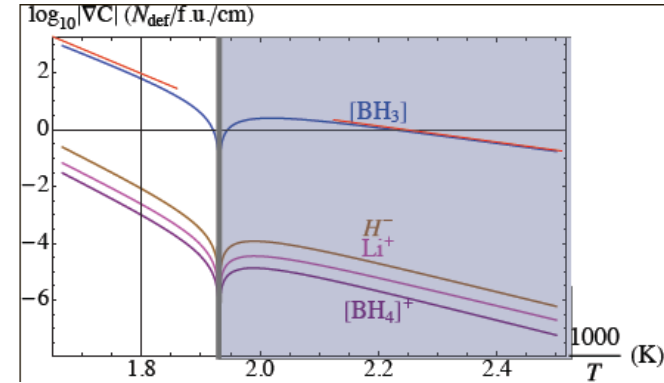
$$\mathbf{J} = -D\vec{\nabla}C$$

# Native defect concentration gradient

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

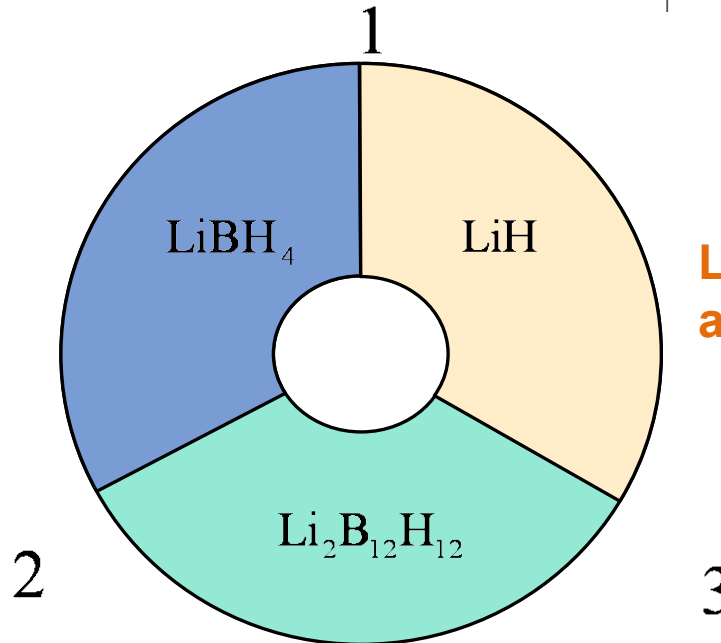
$[BH_x]$	$[LiH_x]$
$[B]^{3-}$	$[Li]^-$
$[BH]^{2-}$	$[LiH]$
$[BH_2]^-$	$[H]^+$
$[BH_3]$	$[H]^-$
$[BH_4]^+$	$[H]^0$

iH	
iLi <sup>+</sup>	iH <sup>+</sup>
iB <sup>3+</sup>	iH <sup>-</sup>
	iH <sup>0</sup>



The  $BH_3$  vacancy has the largest concentration gradient.

But how about  $D$ ?

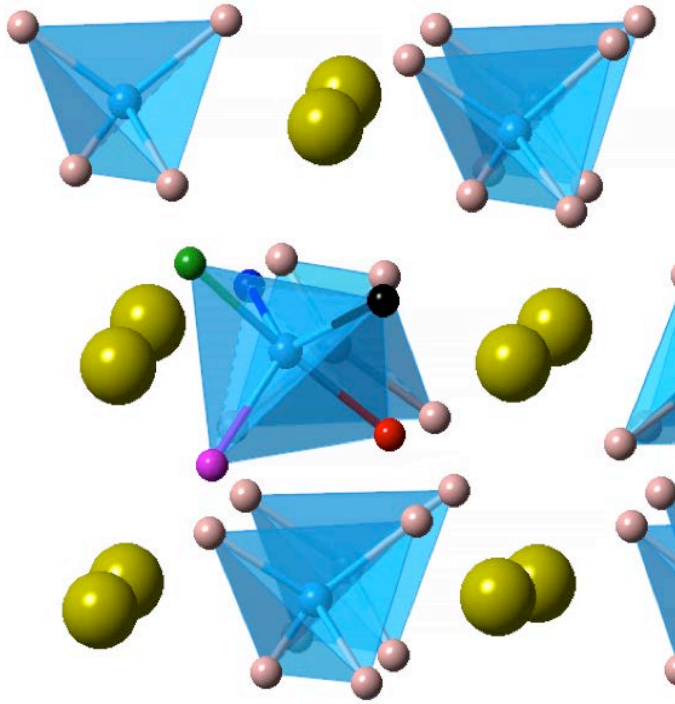


Low-energy defects: H and Li vacancy pair

Low-energy defects: Li vacancy and interstitial pair

# Can $[\text{BH}_3]$ diffuse through $\text{LiBH}_4$ ?

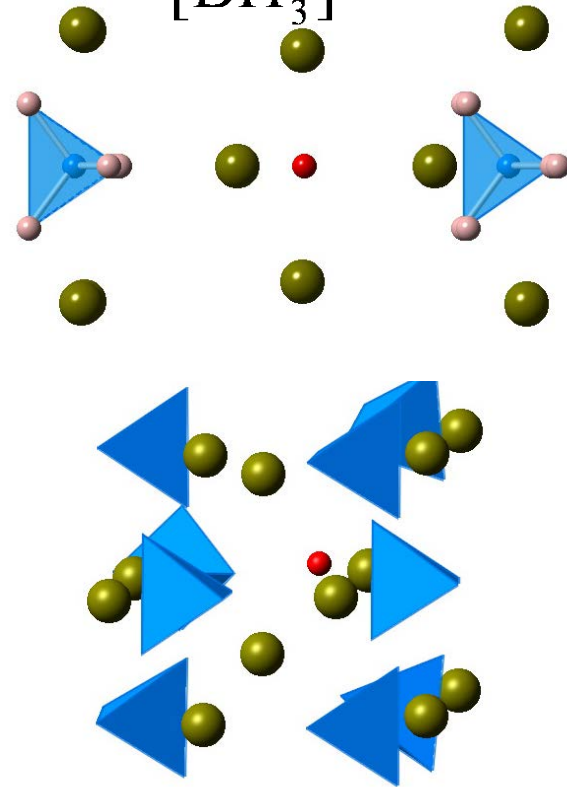
$[\text{AlH}_3]$  diffusion in  $\text{NaAlH}_4$



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

$\text{AlH}_3$  vacancy diffusion in sodium alanate:  $\text{AlH}_3$  vacancy leaves a negative H. The H then combines with the neighboring  $\text{AlH}_4$  unit, thus leaving space for the vacancy to diffusion.

$[\text{BH}_3]$



${}^i\text{H}^-$

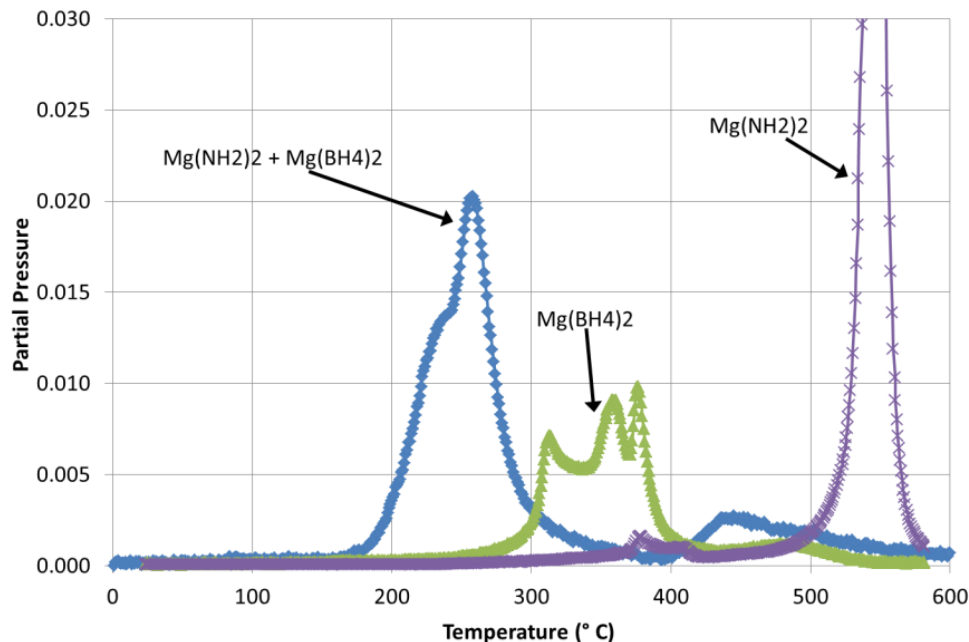
After taking  $\text{BH}_3$  from the original  $\text{BH}_4$  negative unit, a negative H forms, which lies exactly at the original  $\text{BH}_4$  position. The negative H does not combine to the neighboring  $\text{BH}_4$  unit.

**${}^i\text{H}^-$  left by  $[\text{BH}_3]$  blocks  $[\text{BH}_3]$  diffusion.**

**Very different diffusion in borohydrides vs. alanates:  
Mass transport in  $\text{LiBH}_4$  is very low.**

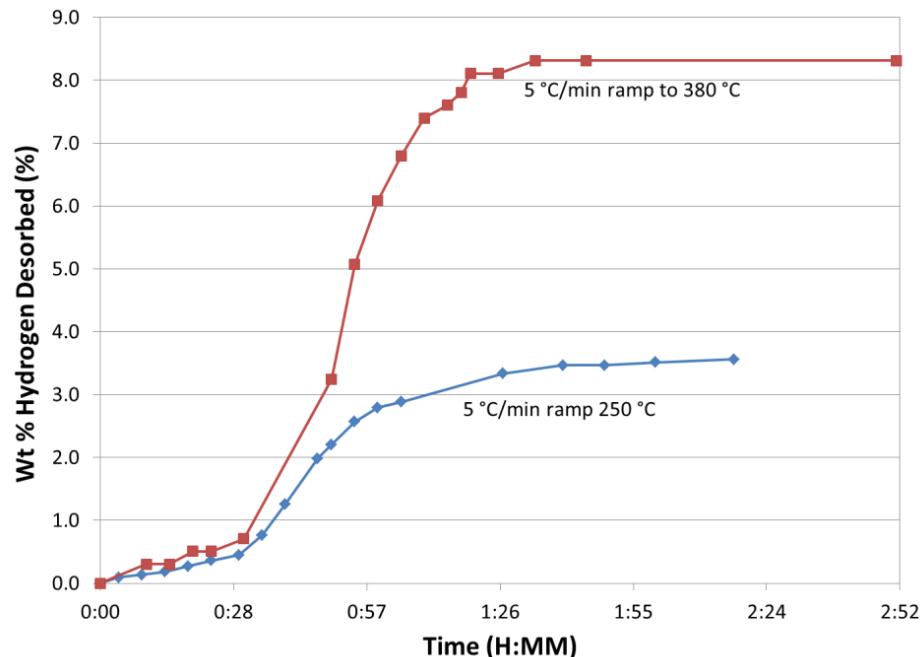
# Mg(NH<sub>2</sub>)<sub>2</sub>+Mg(BH<sub>4</sub>)<sub>2</sub>: Desorption Quantification and Reversibility

H<sub>2</sub> Desorption for Mg(NH<sub>2</sub>)<sub>2</sub> + Mg(BH<sub>4</sub>)<sub>2</sub>  
(5 °C/min ramp from RT to 550 °C)



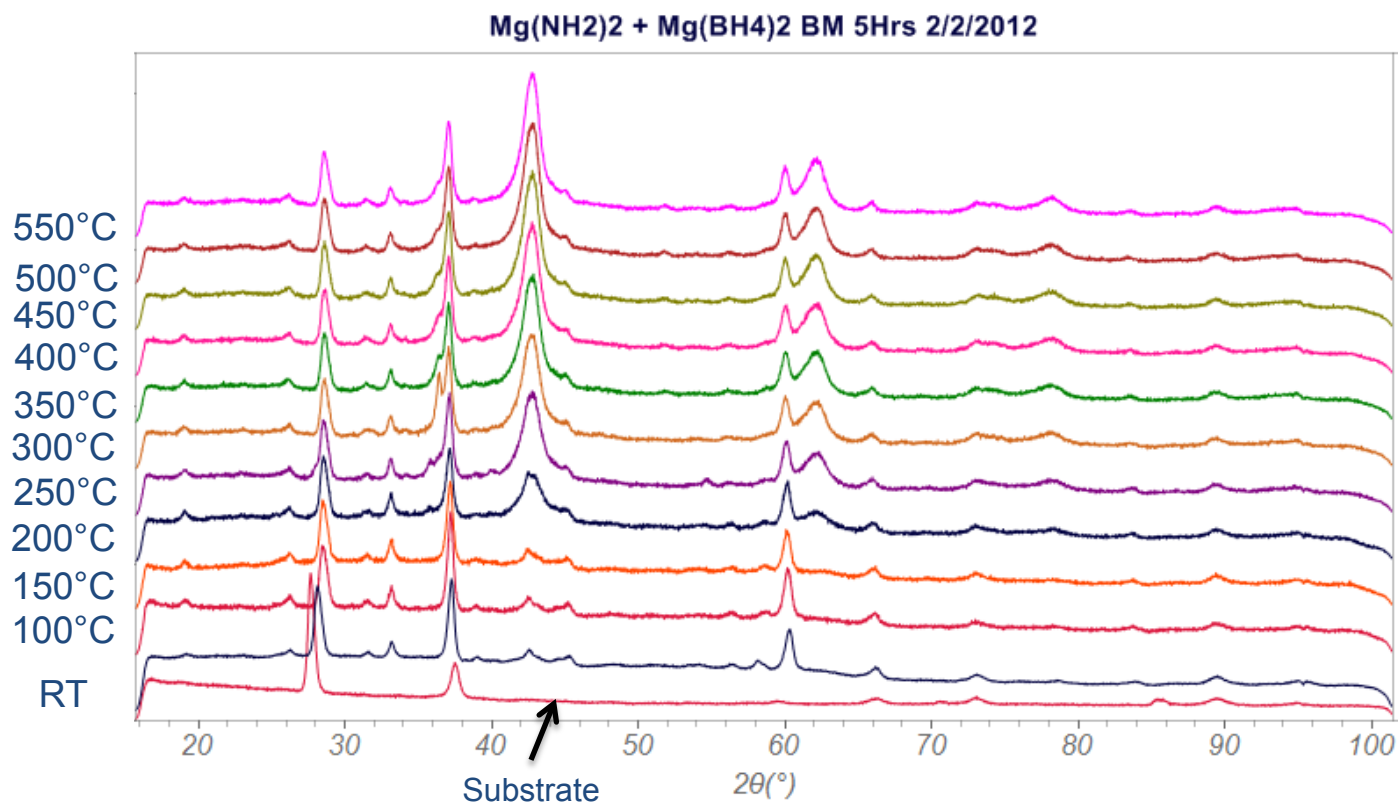
- Ammonia release nearly undetectable
- The dangerous compounds diborane and borazine are not detected
- Mg(NH<sub>2</sub>)<sub>2</sub> + Mg(BH<sub>4</sub>)<sub>2</sub> exhibits a comparatively very low desorption onset (~180°C)

## Mg(NH<sub>2</sub>)<sub>2</sub> + Mg(BH<sub>4</sub>)<sub>2</sub>



- Mg(NH<sub>2</sub>)<sub>2</sub> + Mg(BH<sub>4</sub>)<sub>2</sub> desorbed ~8.3 wt. % at 380 °C
  - No reversibility at 250°C or 380°C (computation also supports lack of reversibility)

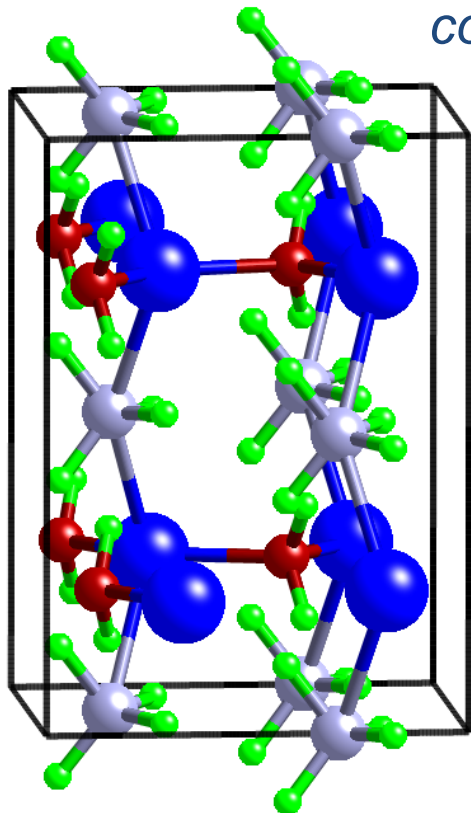
# Mg(NH<sub>2</sub>)<sub>2</sub> + Mg(BH<sub>4</sub>)<sub>2</sub> : Phase Evolution



- 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<sub>4</sub>)(NH<sub>2</sub>)-PEGS (4 fu)  
Space group: Ima2 (46)



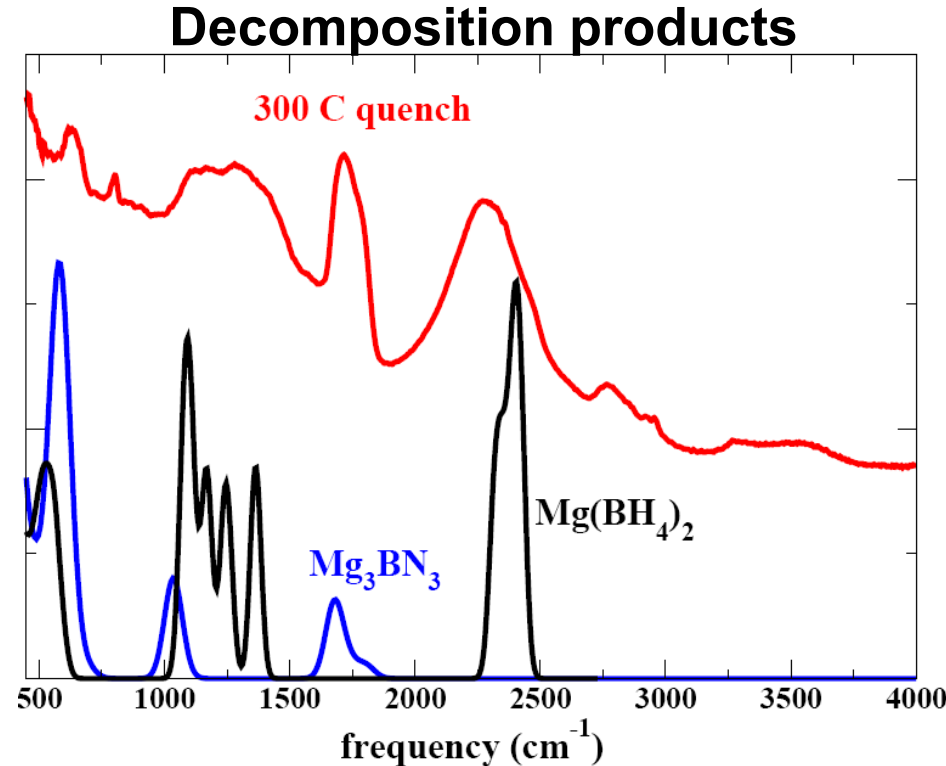
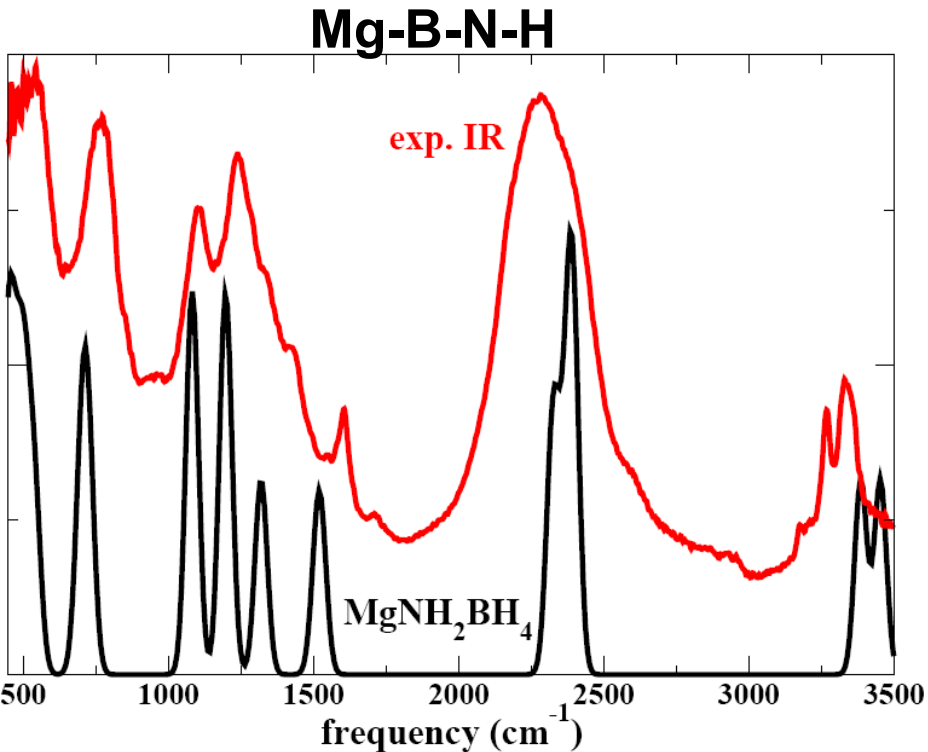
<b>kJ/(mol Mg)</b>	$\Delta E_{\text{Static}}$	$\Delta H_{\text{ZPE}}^{T=0\text{K}}$	$\Delta H^{T=300\text{K}}$
<b>Mg(BH<sub>4</sub>)(NH<sub>2</sub>)</b>	<b>-9.75</b>	<b>-8.18</b>	<b>-8.63</b>

*New, predicted compound stable w.r.t.  
Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub>*



# Technical Accomplishments

## product in the decomposition of Mg-B-N-H

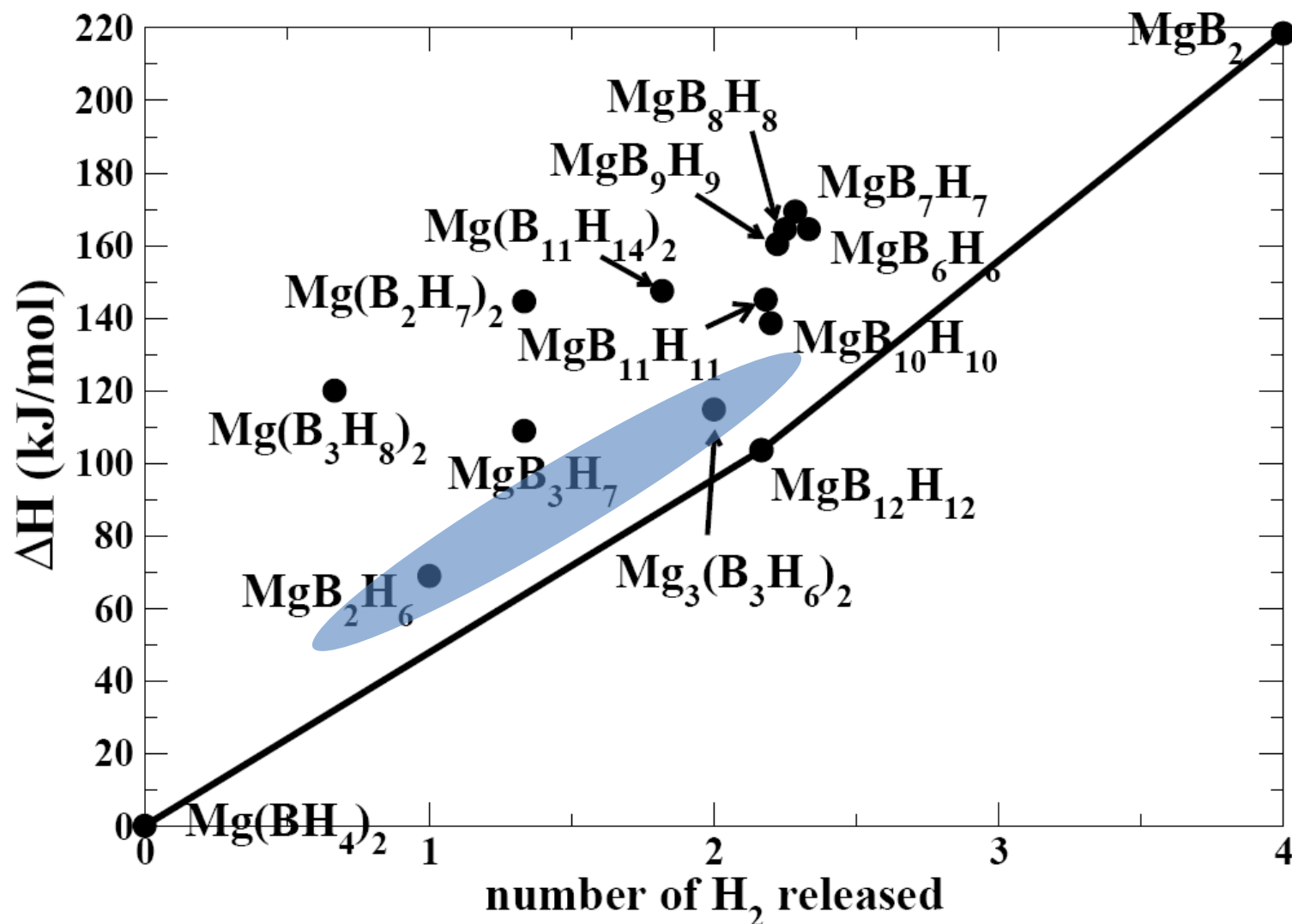


The pDOS of the theoretically predicted  $\text{MgBH}_4\text{NH}_2$  is in a good agreement with the experimental IR measurements.

The decomposition products contain part of  $\text{Mg}(\text{BH}_4)_2$  and compounds including N-B-N linear cluster, such as  $\text{Mg}_3\text{BN}_3$ .

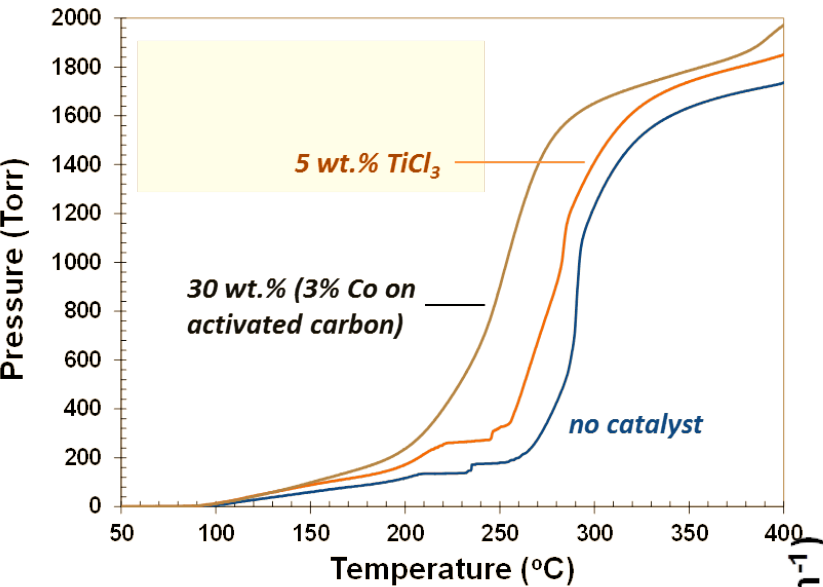
**DOWNSELECT: End work on borohydride/amide combination (due to lack of reversibility and formation of B-N bonds in product).**

# All possible $\text{Mg}(\text{BH}_4)_2$ decomposition pathways



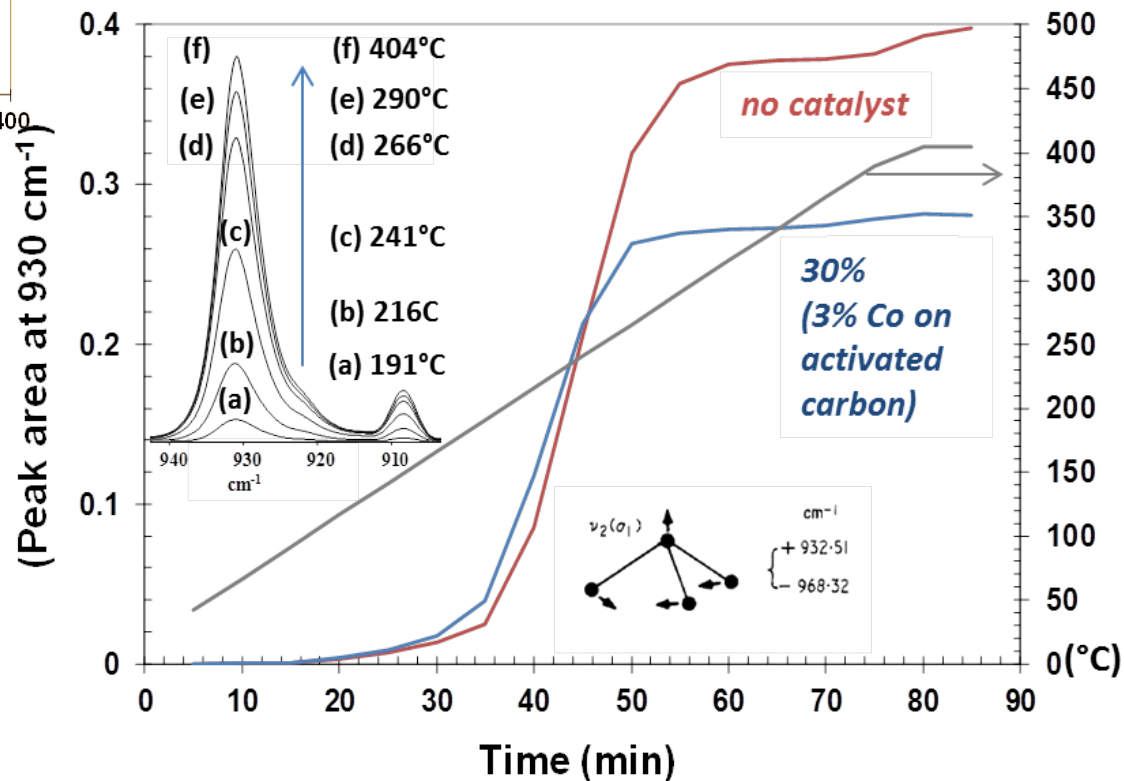
All  $[\text{B}_n\text{H}_m]$  intermediates have higher reaction energies than  $\text{MgB}_{12}\text{H}_{12}$ .  
Only the reactions to  $\text{MgB}_2\text{H}_6$  and  $\text{Mg}_3(\text{B}_3\text{H}_6)_2$  are close to the  $\text{MgB}_{12}\text{H}_{12}$  convex hull.  
 $\text{Mg}_3(\text{B}_3\text{H}_6)_2$  is a metastable intermediate in the decomposition of  $\text{Mg}(\text{BH}_4)_2$ .

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

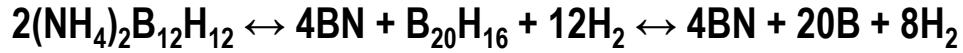


- Gas-phase IR indicated smaller  $NH_3$  release from catalyzed hydride

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



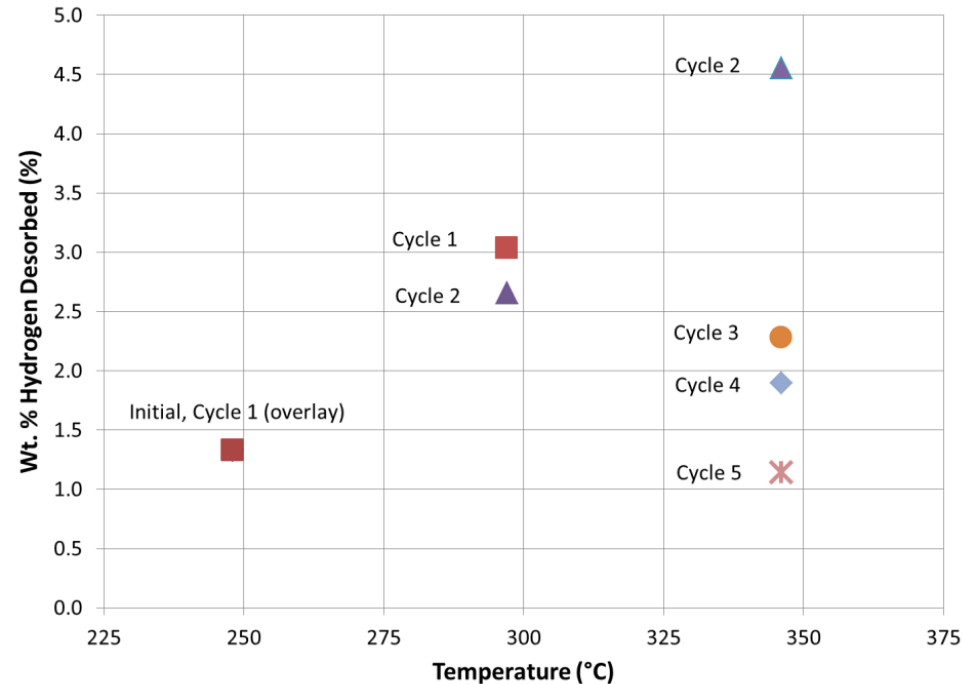
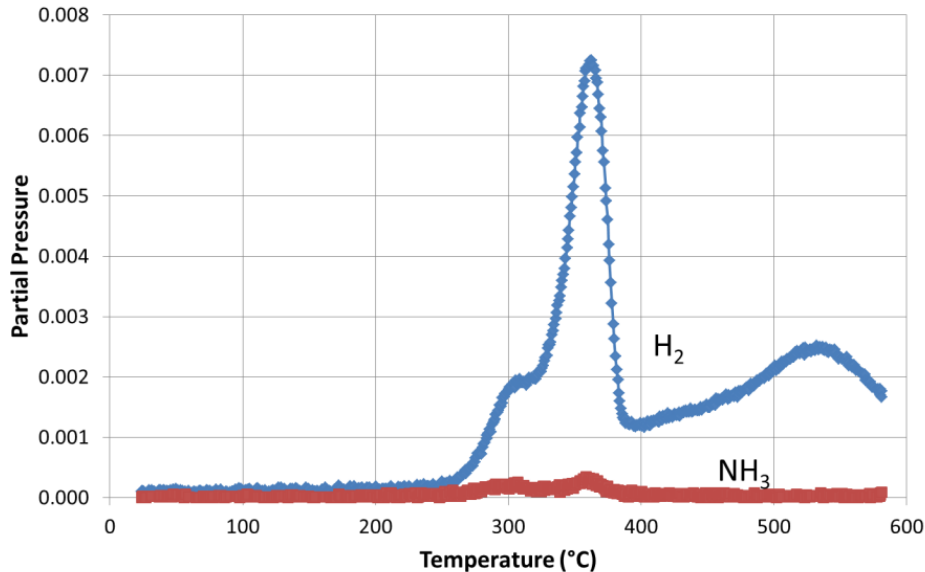
# $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ : Desorption and Reversibility



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

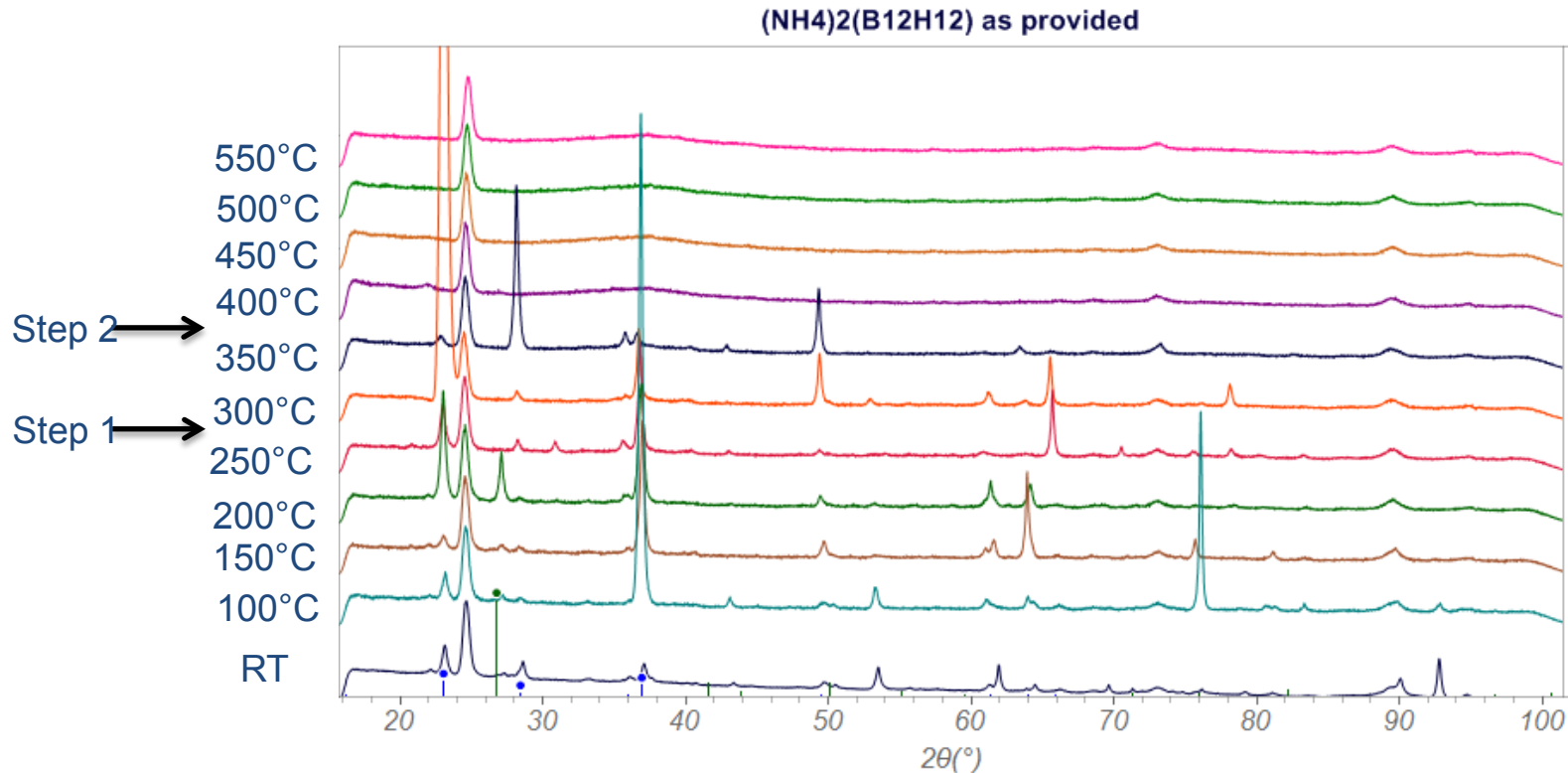
11.3 H<sub>2</sub> wt%

$(\text{NH}_4)_2(\text{B}_{12}\text{H}_{12})$  source: J.C. Zhao  
5 °C/min ramp from RT to 550 °C



- Ammonia release nearly undetectable, and diborane and borazine are not detected
- Partial reversibility (but degrading performance) under cycling at 350°C (2000 psi H<sub>2</sub> recharge at 350°C)
  - Small sample size for  $(\text{NH}_4)_2(\text{B}_{12}\text{H}_{12})$  due to limited quantity may exacerbate response

# $(\text{NH}_4)_2(\text{B}_{12}\text{H}_{12})$ : Phase Evolution



- XRD indicates some unidentified phases appearing
  - Initial signal matches pretty well with ICSD  $(\text{NH}_4)_2(\text{B}_{12}\text{H}_{12})$  structure
  - Some BN possibly formed, see peaks disappearing – at end amorphous w/substrate
- In Situ IR indicates B-N stretch above  $\sim 300^\circ\text{C}$

# 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)



NORTHWESTERN  
UNIVERSITY



## 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

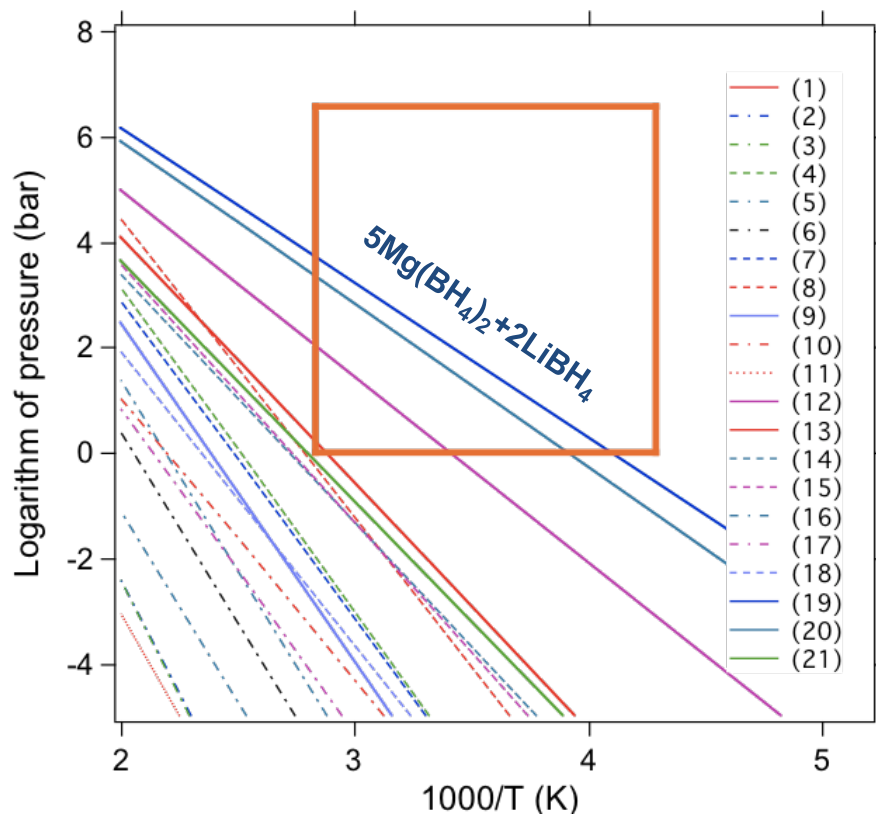
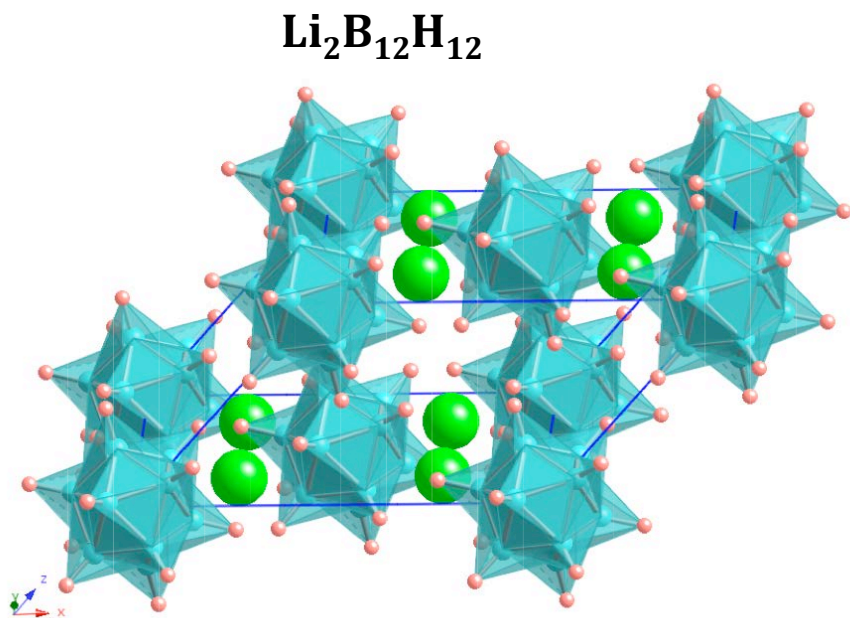
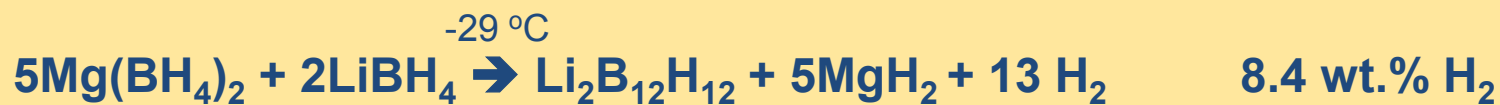
- Experimentally characterized storage properties/reactions of  $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$  and other predicted reactions; Optimize reversibility conditions for  $5\text{Mg}(\text{BH}_4)_2+2\text{LiBH}_4$  mixture
- Extend experimental catalyst studies to other predicted promising materials; 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

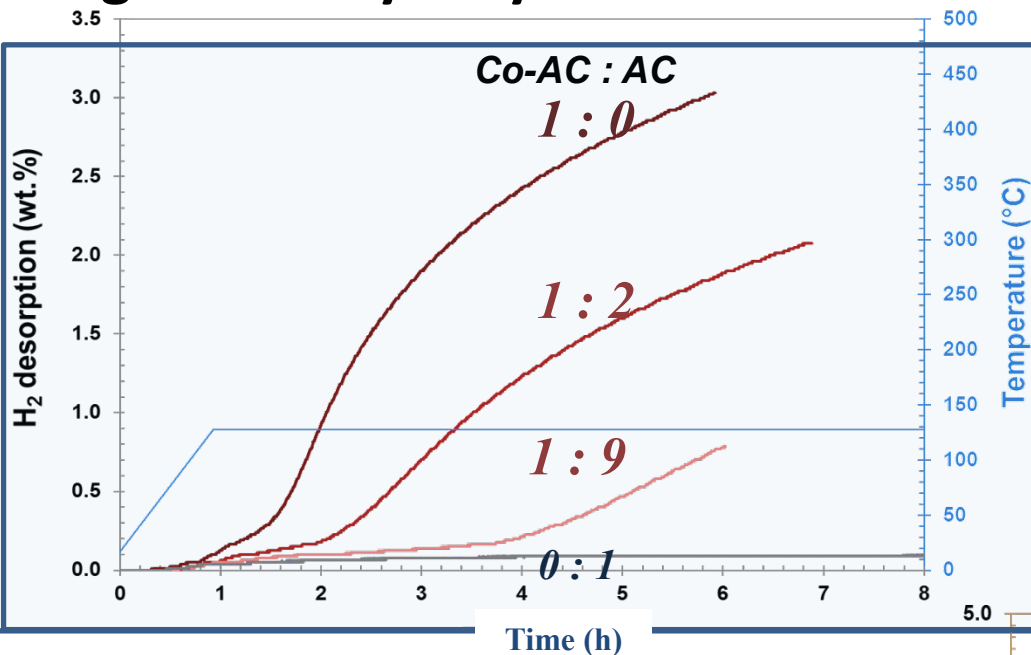
- H<sub>2</sub> desorption and decomposition pathways have been studied in
  - 5LiBH<sub>4</sub> + 2Mg(BH<sub>4</sub>)<sub>2</sub> (~5.8 wt.% desorbed)
  - Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub> (~8.3 wt.% desorbed)
  - (NH<sub>4</sub>)<sub>2</sub>B<sub>12</sub>H<sub>12</sub>. (~4.5 wt.% desorbed)
- Partial reversibility (~1-2.5 wt.%) found in 5LiBH<sub>4</sub> + 2Mg(BH<sub>4</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>B<sub>12</sub>H<sub>12</sub>
- Proposed new metal-carbon catalyst: Tested on NaAlH<sub>4</sub>, and applied to Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub>, 2LiBH<sub>4</sub>+5Mg(BH<sub>4</sub>)<sub>2</sub> and LiBH<sub>4</sub>; Effective catalyst - lowers desorption temperature, improves dehydrogenation rate, and suppresses formation of borane and NH<sub>3</sub>
- 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<sub>3</sub>(B<sub>3</sub>H<sub>6</sub>)<sub>2</sub> intermediate in decomposition of Mg(BH<sub>4</sub>)<sub>2</sub>, but showed that recently-proposed Mg(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub> is not stable.
- PEGS+DFT combined of experimental measurements is used in unique way to solve amorphous AlB<sub>4</sub>H<sub>11</sub> polymeric structure (w/ JC Zhao)
- Using the predictive models of defects, kinetics of mass transport: mass transport in LiBH<sub>4</sub> is very low (much lower than that in NaAlH<sub>4</sub>)



# Technical Accomplishments: Experimental Testing of Predicted Reactions

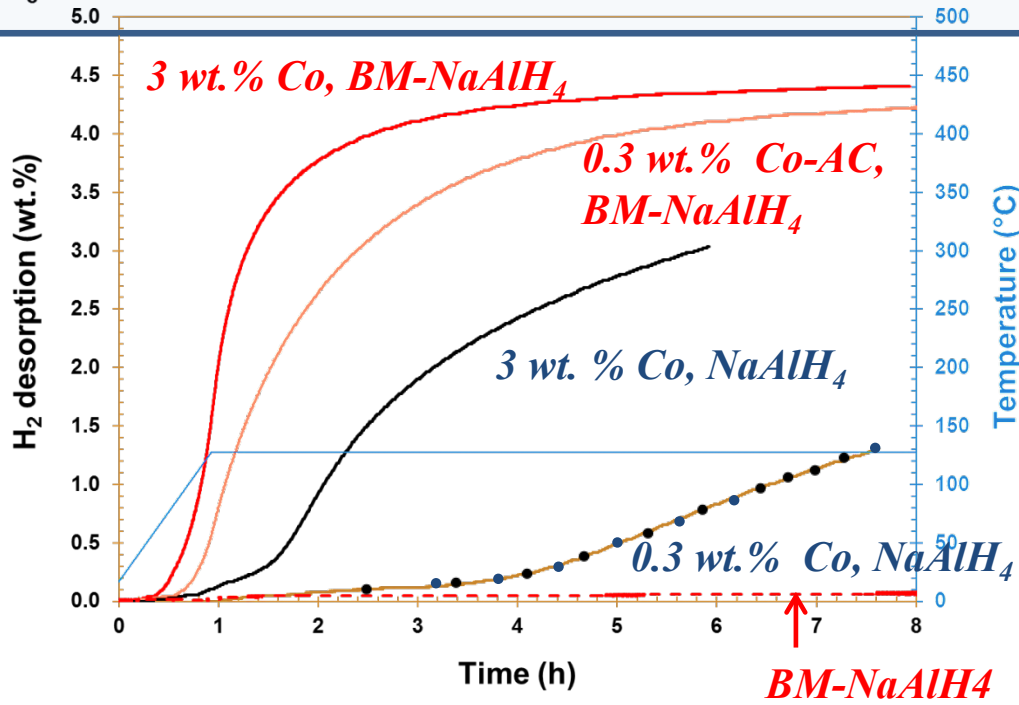


# Metal NPs supported on activated carbon (AC) and good catalyst-hydride contact facilitate hydride dehydrogenation

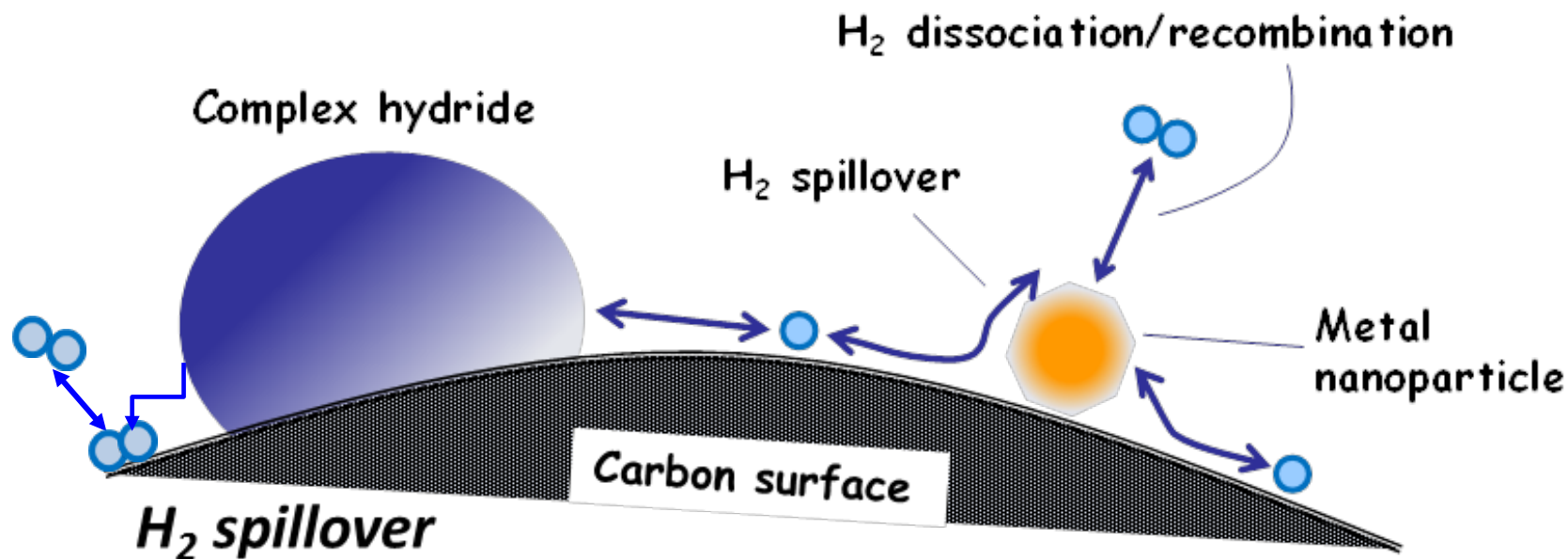


- Catalyst to hydride ratio maintained at 0.7 while varying Co-AC and AC ratio in the catalyst.
- The more Co-AC, i. e. The more Co, the faster the dehydrogenation kinetics

- 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:

- $\text{Mg}(\text{NH}_2)_2\text{-Mg}(\text{BH}_4)_2$
- $\text{Mg}(\text{BH}_4)_2\text{-LiBH}_4$
- $\text{LiBH}_4$

# Technical Accomplishments: New Theoretical Predictions

- Decomposition of  $\text{Mg}(\text{BH}_4)(\text{NH}_2)$
- New borohydride compounds
  - $\text{Mg}_3(\text{B}_3\text{H}_6)_2$
  - $\text{AlB}_4\text{H}_{11}$
- Diffusion & mass transport (required for fast kinetics)

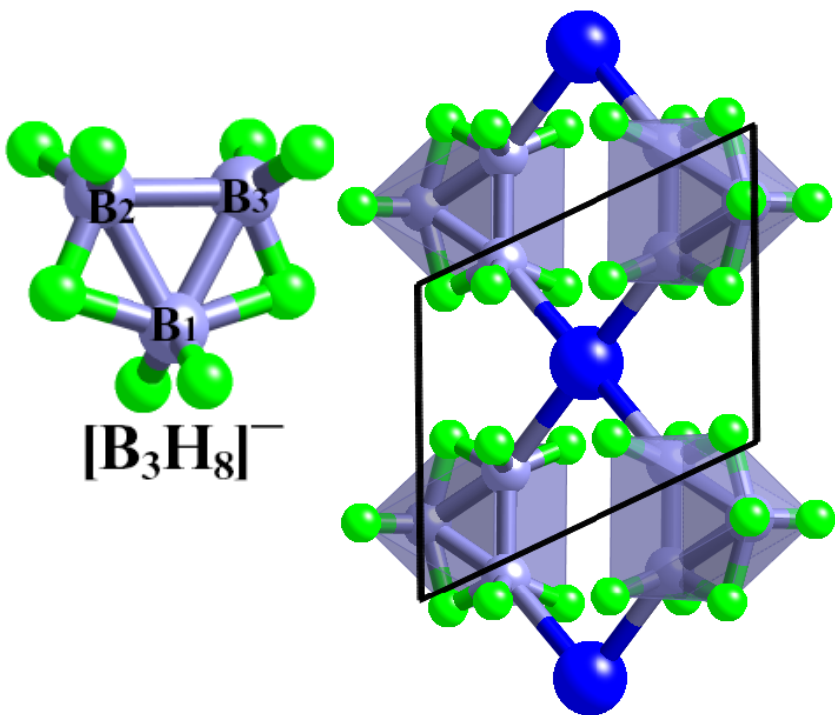
# Technical Accomplishments

## Mg(BH<sub>4</sub>)<sub>2</sub> decomposition intermediates search

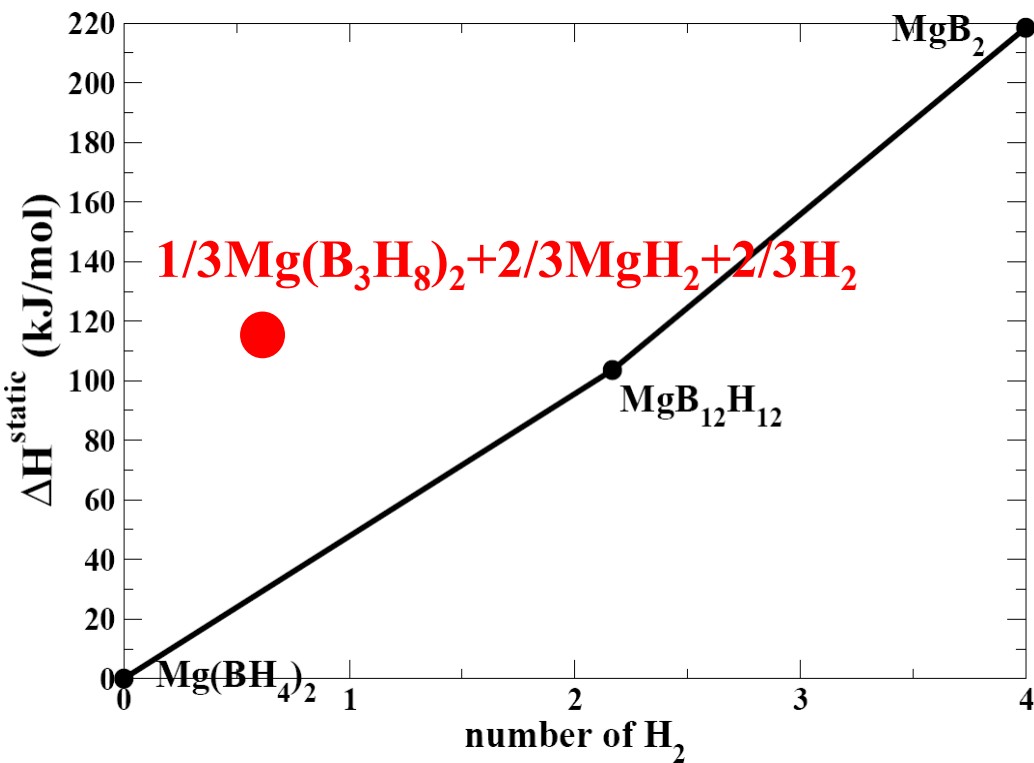
- Recent experiments

  - [B<sub>3</sub>H<sub>8</sub>] intermediate

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



PEGS-Mg(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub>  
Space group: P-1 (2)



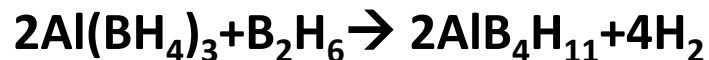
Mg(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub> is not a stable intermediate in the decomposition of Mg(BH<sub>4</sub>)<sub>2</sub>.

# Technical Accomplishments

## New metal borohydride: $\text{AlB}_4\text{H}_{11}$

*In collaboration with Xuenian Chen and JiCheng Zhao (OSU)*

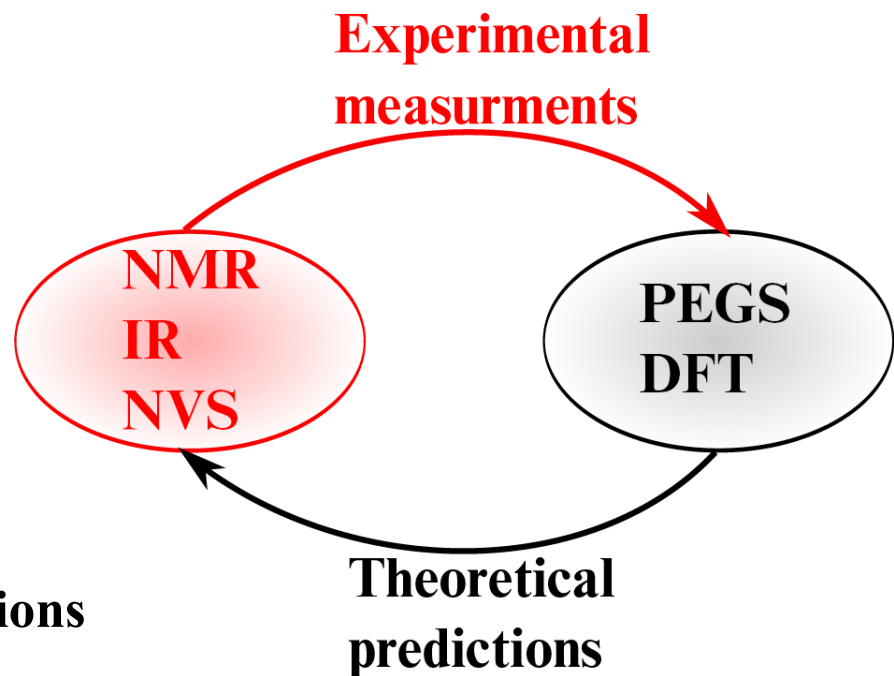
- $\text{AlB}_4\text{H}_{11}$  synthesis:



- $\text{AlB}_4\text{H}_{11}$  attractive properties

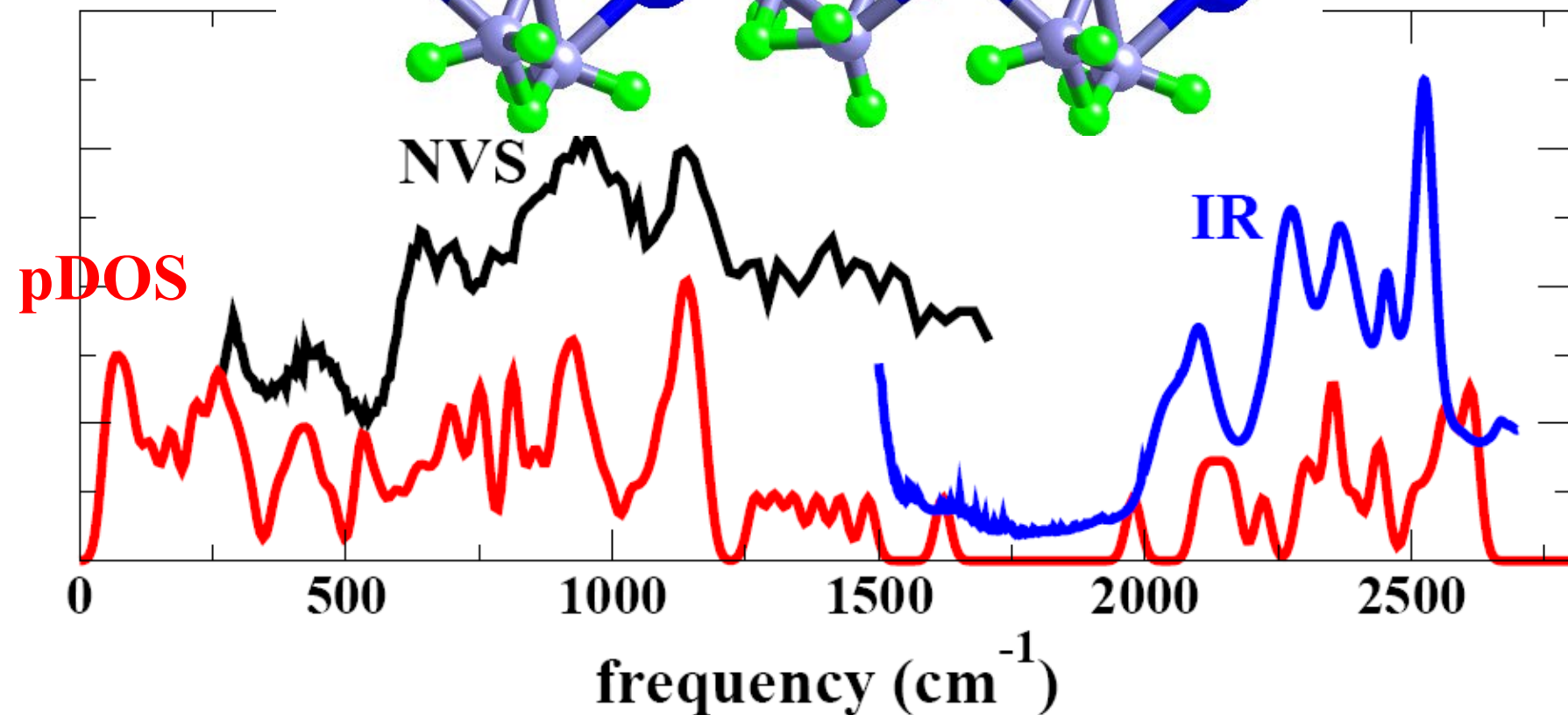
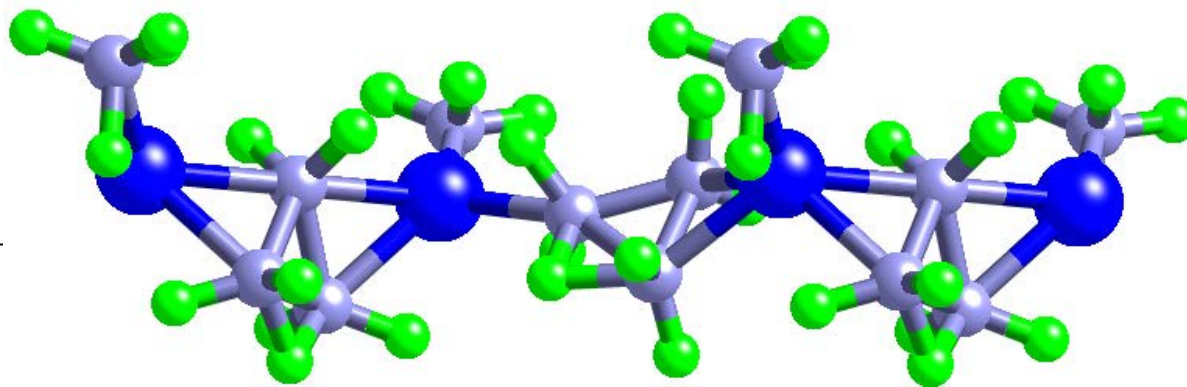
- High hydrogen content (13.5%  $\text{H}_2$ )
- Moderate stability
- Decomposition temperature  $\sim 125^\circ\text{C}$
- Endothermic dehydrogenation
- Rehydrogenation at moderate conditions

- Unknown  $\text{AlB}_4\text{H}_{11}$  structure: amorphous



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

# PEGS+DFT Predicted $\text{AlB}_4\text{H}_{11}$ low-energy structures



Polymer chain is composed of Al,  $[\text{BH}_4]$ ,  $[\text{B}_3\text{H}_7]$  groups, which are confirmed by experimental NMR measurements.

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