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

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Ford Motor Company

S. Hwang

Caltech

S. Shore

Ohio St. Univ.

NORTHWESTERN
UNIVERSITY

UCLA

Ford

ST028

# Overview

## Timeline

- Project Start Date:  9/1/08 (Funding started Feb. 09)
- Project End Date: 8/31/13
- ~80% complete

## Budget

- Total Budget:  $2714K
  - DOE Share:  $2160K
  - Contractors Share:  $554K
- Funding for FY12: $600K
- Funding for FY13: $100K (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 – Objectives and Approach
## Our project: Combinations of materials to form novel multicomponent reactions
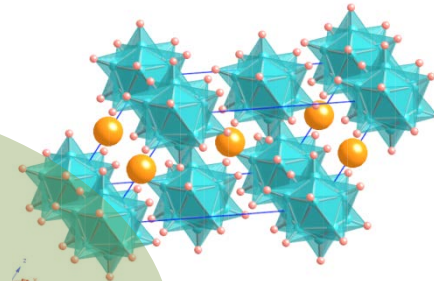


**Hydrogen Storage Measurements and Auto Perspective**
Yang and Veenstra, Ford;
Hwang (NMR), Caltech

**Computational Prediction of Novel Reactions** Wolverton,
NU; Ozolins, UCLA

**Kinetics/Catalysis/ Synthesis Experiments**
Kung, NU
Shore, Ohio St.

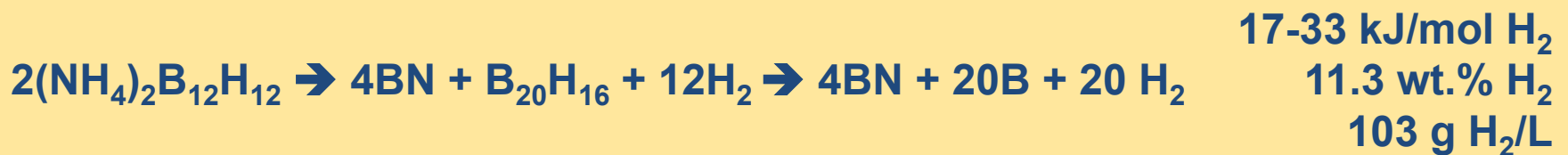NORTHWESTERN UNIVERSITY

UCLA

Ford

# Technical Accomplishments (previous): Novel, High-Capacity Predicted Reactions

- High-throughput computational screen through all possible high capacity reactions with suitable thermodynamics in Li-Mg-B-N-H quinary.
- We focus on the reactions in bold (grayed out reactions were known previously and have been studied experimentally)

| Reactions | Wt.% $H_2$ | Vol. $H_2$ (g $H_2$/L) | $\Delta H^{300K}$ (kJ/mol $H_2$) | $\Delta S^{300K}$ (J/mol-K) |
|---|---|---|---|---|
| $2(NH_4)_2B_{12}H_{12} \rightarrow 4BN + B_{20}H_{16} + 12H_2$ | 6.81 | 62 | 17 | 104 |
| $5Mg(BH_4)_2 + 2LiBH_4 \rightarrow 5MgH_2 + Li_2B_{12}H_{12} + 13H_2$ | 8.37 | 66 | 24 | 104 |
| $6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$ | 8.10 | 65 | 29 | 100 |
| $B_{20}H_{16} \rightarrow 20B + 8H_2$ | 6.95 | 77 | 33 | 111 |
| $5MgH_2 + MgB_{12}H_{12} \rightarrow 6MgB_2 + 11H_2$ | 7.46 | 81 | 44 | 115 |

- Combination of 1st and 4th reactions above gives a very high capacity reaction:

$$2(NH_4)_2B_{12}H_{12} \rightarrow 4BN + B_{20}H_{16} + 12H_2 \rightarrow 4BN + 20B + 20 H_2$$

17-33 kJ/mol $H_2$
11.3 wt.% $H_2$
103 g $H_2$/L

# Technical Accomplishments:
# Thermodynamics of $B_{20}H_{16}$ to 20B + 8$H_2$

| $(NH_4)_2B_{12}H_{12} \rightarrow 2BN + 0.5B_{20}H_{16} + 6H_2$ | |
|---|---|
| $H_2$ content | 6.76 wt. % |
| $T_{crit}$ | -120°C |
| $\Delta H^{0K}$ | 12 kJ/mol $H_2$ |
| $\Delta H^{300K}$ | 17 kJ/mol $H_2$ |
| $\Delta S^{300K}$ | 104 J/K·mol $H_2$ |

| $B_{20}H_{16} \rightarrow 20B + 8H_2$ | |
|---|---|
| $H_2$ content | 6.90 wt. % |
| $T_{crit}$ | 20°C |
| $\Delta H^{0K}$ | 27 kJ/mol $H_2$ |
| $\Delta H^{300K}$ | 33 kJ/mol $H_2$ |
| $\Delta S^{300K}$ | 111 J/K·mol $H_2$ |

Sun, W.Q.; Wolverton, C.; Akbarzadeh, A.; Ozolins, V.; Phys. Rev. B. 83, 2011, 064112-1

- **Thermodynamics of hydrogen release from $B_{20}H_{16}$ are ideal**

- **Gravimetric storage capacity near 7 wt. % $H_2$**

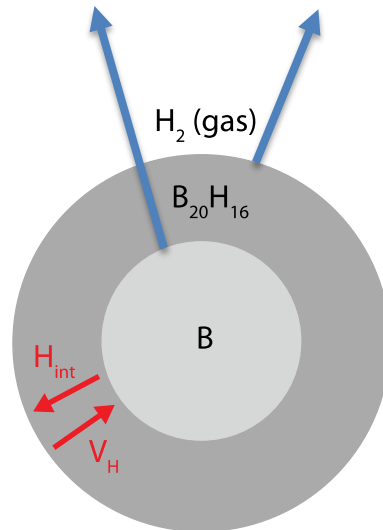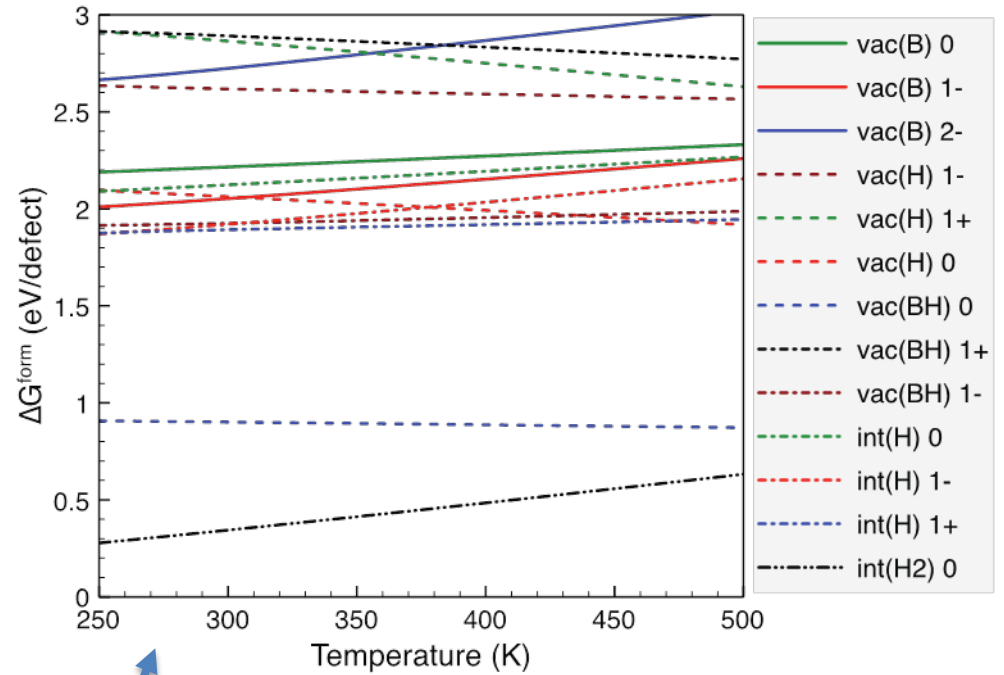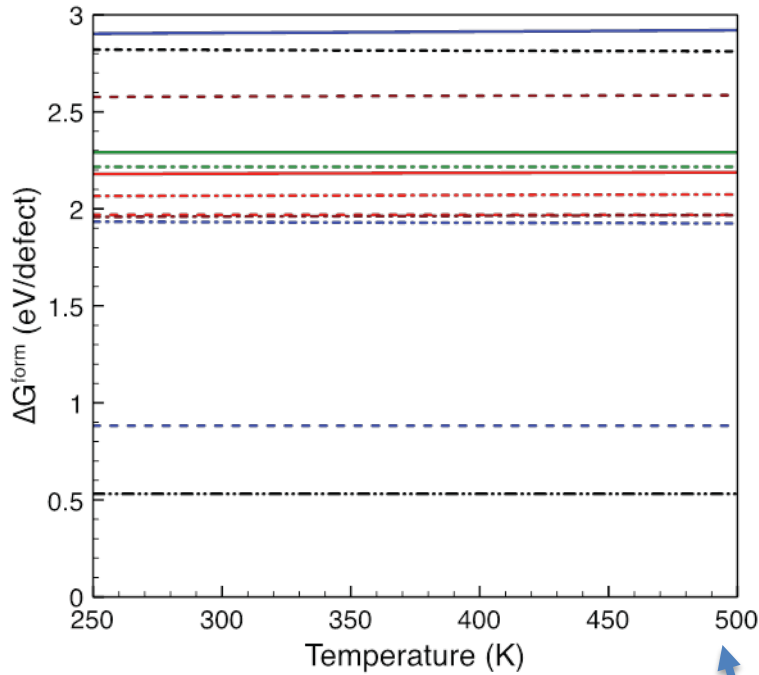- **Nothing is known about kinetics of hydrogen release or uptake**

# Defect energetics in solid phases (B)



H$_2$ (gas)

B

B$_{20}$H$_{16}$

H$_{int}$
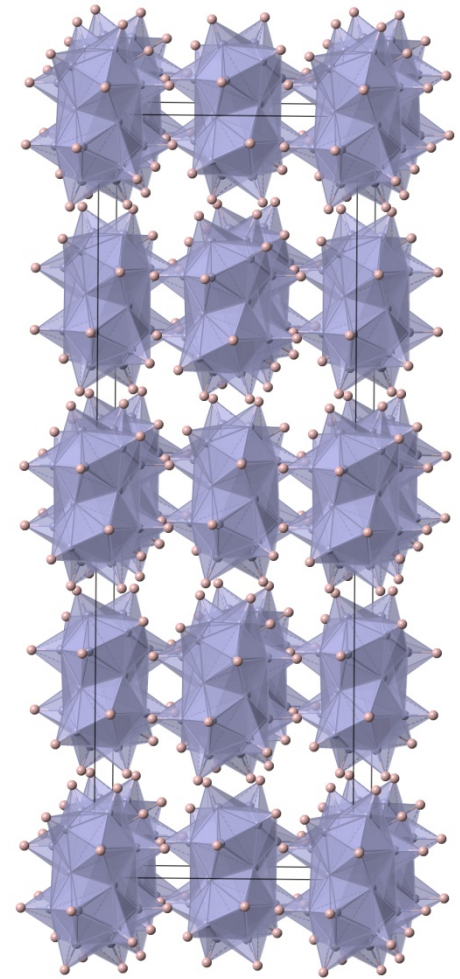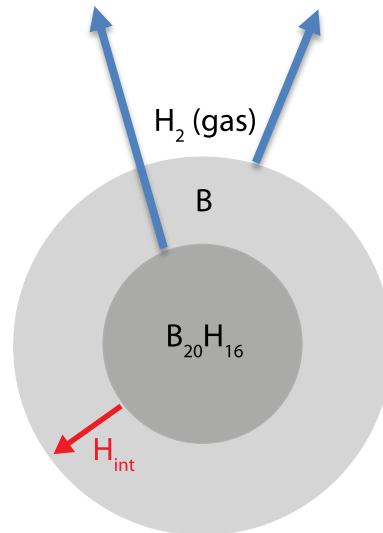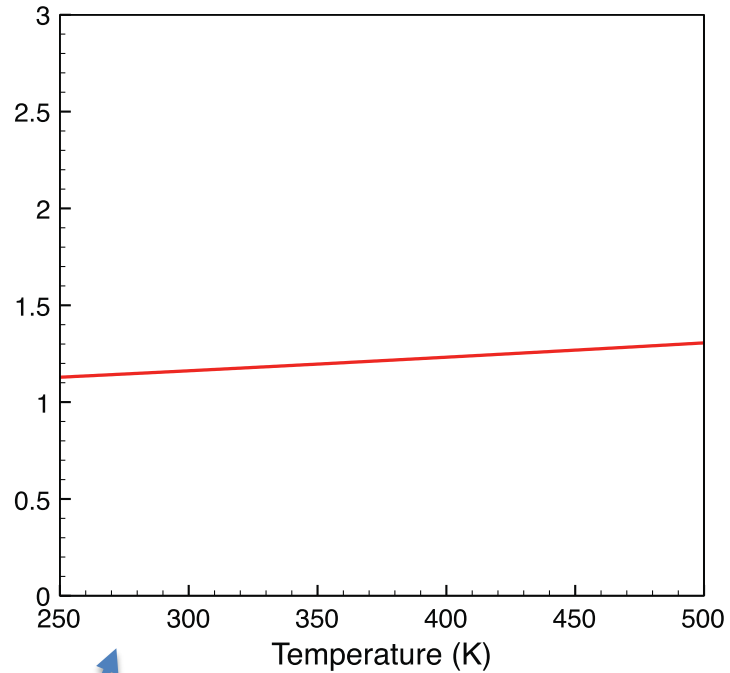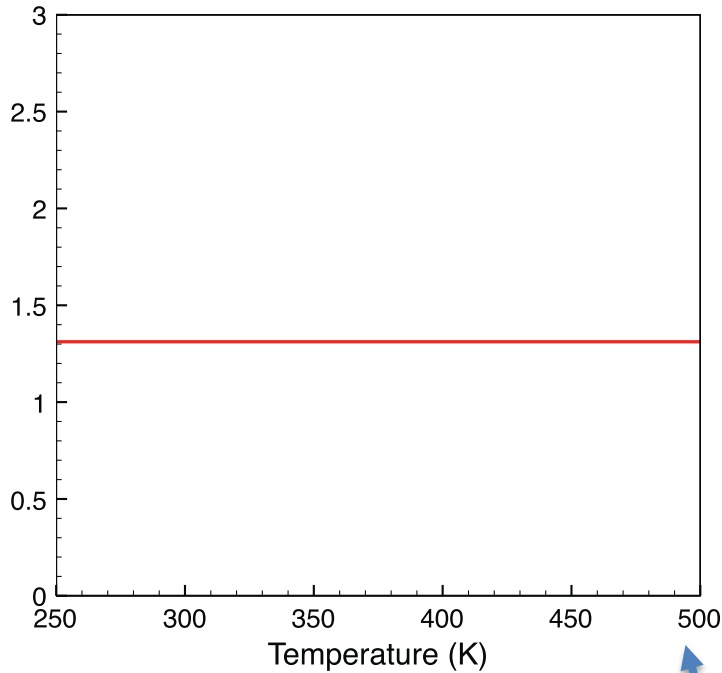
- **Formation energy of interstitial H$_2$ in boron is high so mass flux will be low**

# Defect energetics in solid phases (B$_{20}$H$_{16}$)



Legend:
- vac(B) 0
- vac(B) 1-
- vac(B) 2-
- vac(H) 1-
- vac(H) 1+
- vac(H) 0
- vac(BH) 0
- vac(BH) 1+
- vac(BH) 1-
- int(H) 0
- int(H) 1-
- int(H) 1+
- int(H2) 0

H$_2$ (gas)

B$_{20}$H$_{16}$

B

H$_{int}$

V$_H$

- **Formation energy of interstitial H$_2$ in B$_{20}$H$_{16}$ is lowest of all defects**

# Interstitial $H_2$ flux in $B_{20}H_{16}$ and mass transport activation energy

T (K)
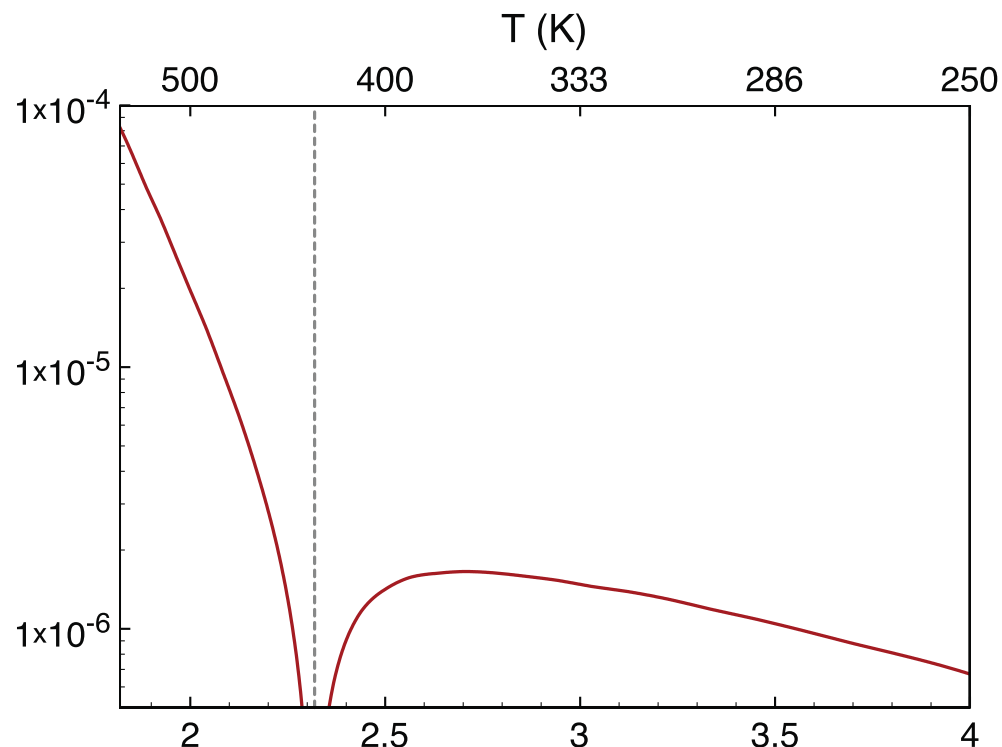


| Activation energy for mass transport | |
|---|---|
| Rehydrogenation | 6 kJ/mol |
| Dehydrogenation | 63 kJ/mol |

- **Low activation energy for interstitial $H_2$ in $B_{20}H_{16}$**

- **Mass transport is likely to be fast in this system while it is rate limiting in many others**

- **$B_{20}H_{16}$ extremely promising – *first H2 storage reaction of known compound with 1) high capacity, 2) good thermodynamics, and 3) predicted fast mass transport kinetics!***
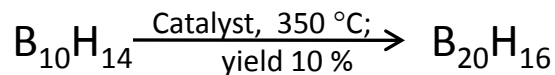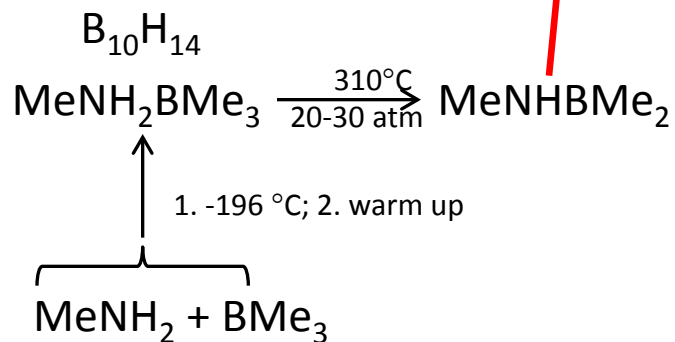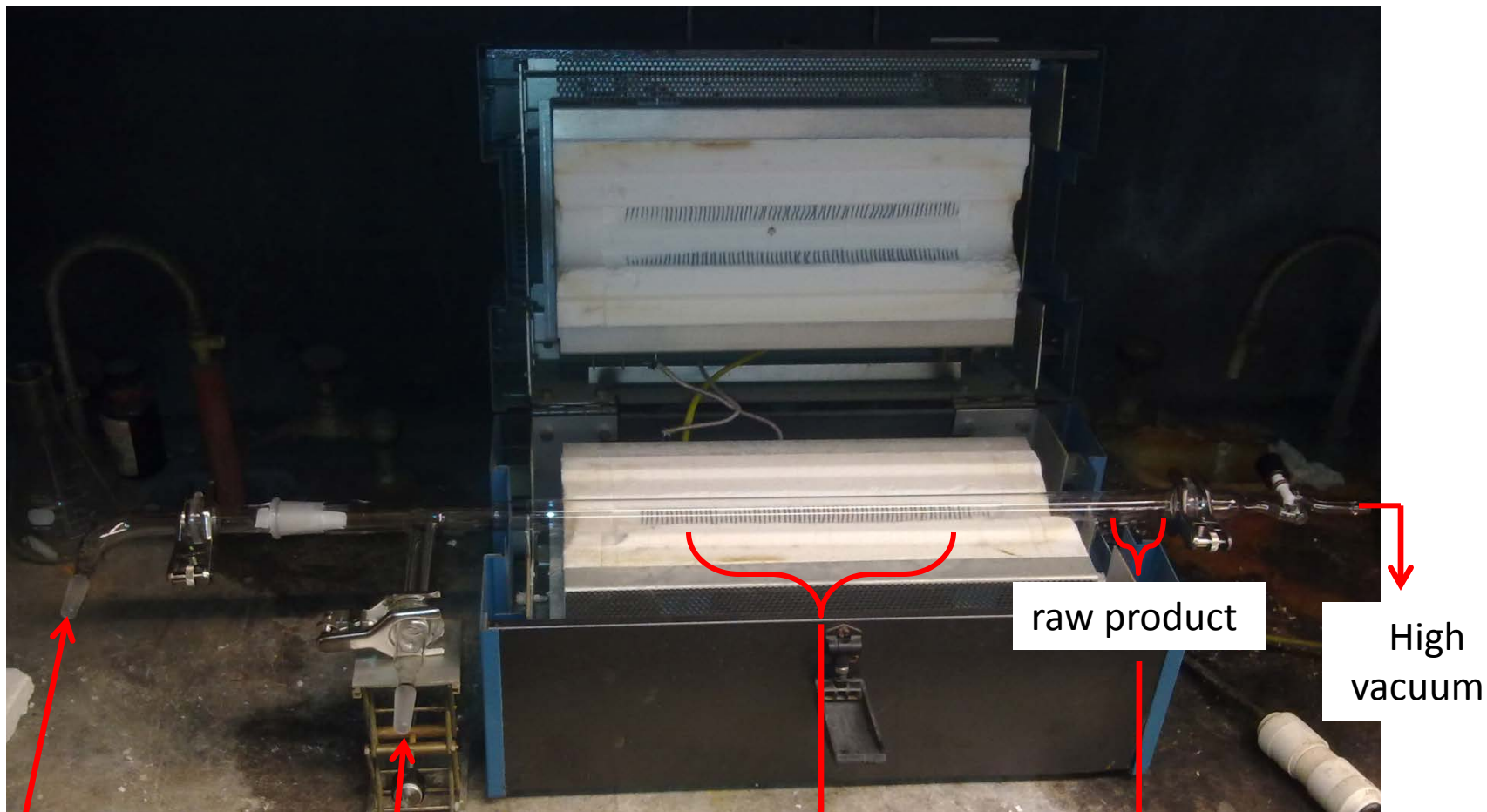
# Technical Accomplishments:
# Synthesis of icosaborane-16 ($B_{20}H_{16}$)
## (new subcontract with S. Shore, OSU)



SYNTHESIS OF $B_{20}H_{16}$
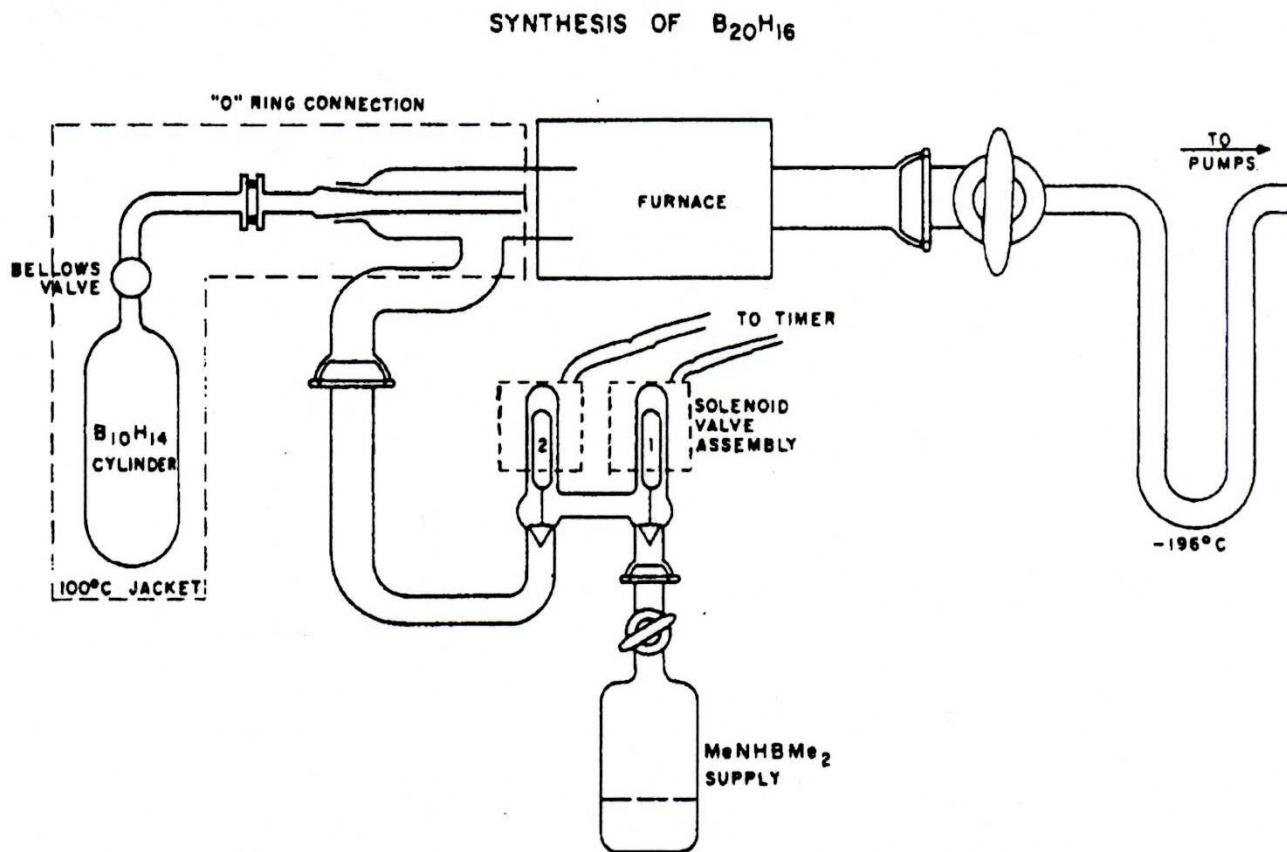
Chemistry of Boranes. XXI Icosaborane-16 : N. E. MILLER, J. A. FORSTNER, E. L. MUETTERTIES, *Inorganic Chemistry*,**3**,1690(1964)

# Synthesis of icosaborane-16 ($B_{20}H_{16}$)



raw product

High vacuum

$B_{10}H_{14}$

$MeNH_2BMe_3 \xrightarrow[\text{20-30 atm}]{310°C} MeNHBMe_2$

1. -196 °C; 2. warm up

$MeNH_2 + BMe_3$

$B_{10}H_{14} \xrightarrow[\text{yield 10 \%}]{\text{Catalyst, 350 °C;}} B_{20}H_{16}$
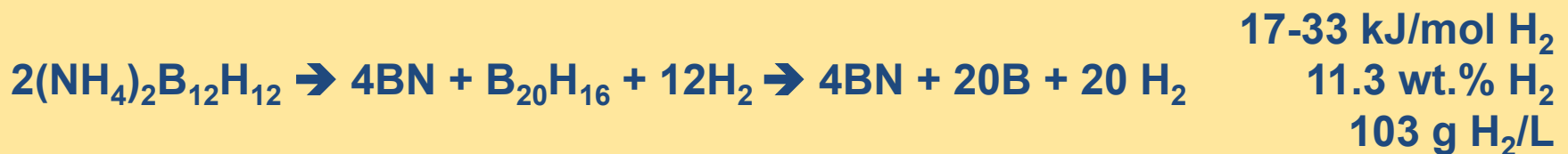
repeated sublimation

pure product

# Technical Accomplishments:
# Novel, High-Capacity Predicted Reactions

- High-throughput computational screen through all possible high capacity reactions with suitable thermodynamics in Li-Mg-B-N-H quinary.

- We focus on the reactions in bold (grayed out reactions were known previously and have been studied experimentally)

| Reactions | Wt.% $H_2$ | Vol. $H_2$ (g $H_2$/L) | $\Delta H^{300K}$ (kJ/mol $H_2$) | $\Delta S^{300K}$ (J/mol-K) |
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| **2(NH$_4$)$_2$B$_{12}$H$_{12}$ ➔ 4BN + B$_{20}$H$_{16}$ + 12H$_2$** | **6.81** | **62** | **17** | **104** |
| **5Mg(BH$_4$)$_2$ + 2LiBH$_4$ ➔ 5MgH$_2$ + Li$_2$B$_{12}$H$_{12}$ + 13H$_2$** | **8.37** | **66** | **24** | **104** |
| 6Mg(BH$_4$)$_2$ ➔ 5MgH$_2$ + MgB$_{12}$H$_{12}$ + 13H$_2$ | 8.10 | 65 | 29 | 100 |
| **B$_{20}$H$_{16}$ ➔ 20B + 8H$_2$** | **6.95** | **77** | **33** | **111** |
| 5MgH$_2$ + MgB$_{12}$H$_{12}$ ➔ 6MgB$_2$ + 11H$_2$ | 7.46 | 81 | 44 | 115 |

- Combination of 1$^{st}$ and 4$^{th}$ reactions above gives a very high capacity reaction:

**2(NH$_4$)$_2$B$_{12}$H$_{12}$ ➔ 4BN + B$_{20}$H$_{16}$ + 12H$_2$ ➔ 4BN + 20B + 20 H$_2$**

**17-33 kJ/mol $H_2$**
**11.3 wt.% $H_2$**
**103 g $H_2$/L**

# (Previous) Technical Accomplishments: Experimental Testing of Predicted Reactions

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



$Li_2B_{12}H_{12}$
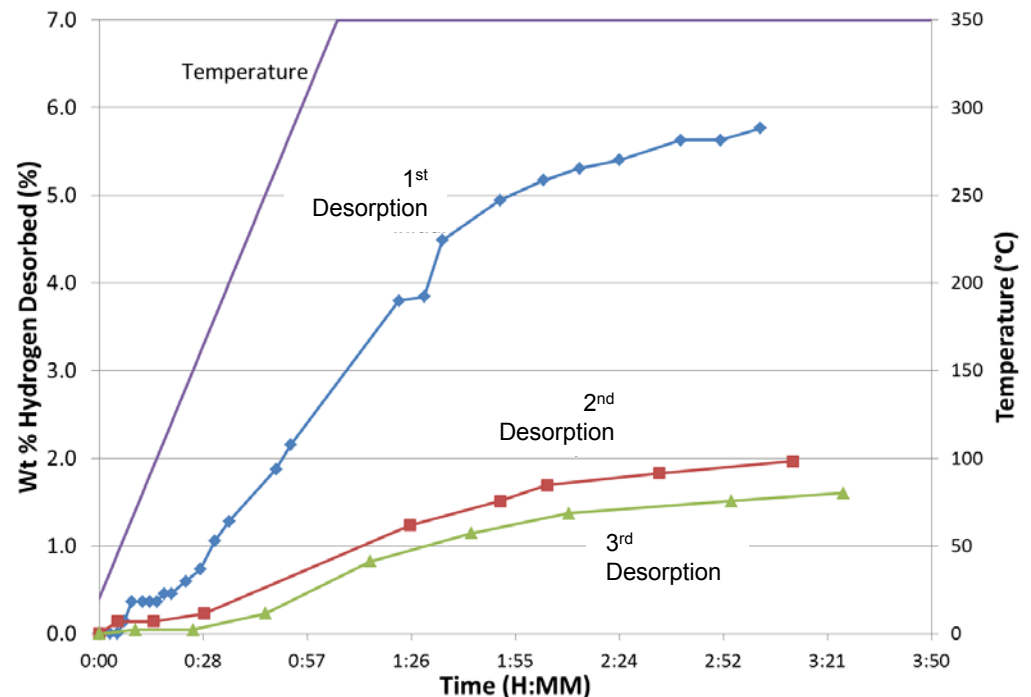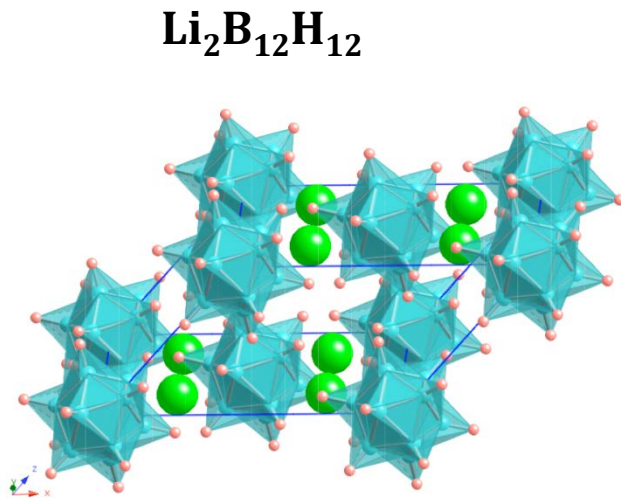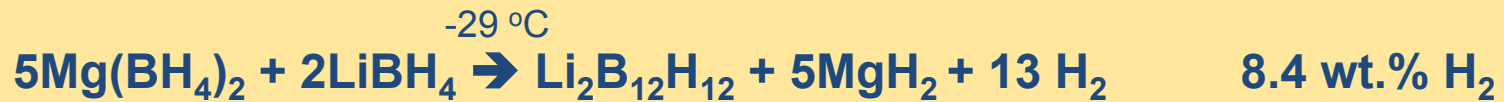


What are (non-crystalline) reaction products?  Do they inhibit reversibility?
*Following advice of AMR reviewers, initiated NMR subcontract with S. Hwang, Caltech*

# Technical Accomplishments: NMR Experiments of Mixed borohydride system $2LiBH_4 + 5Mg(BH_4)_2$

## Solid state NMR characterization upon $H_2$ desorption reactions
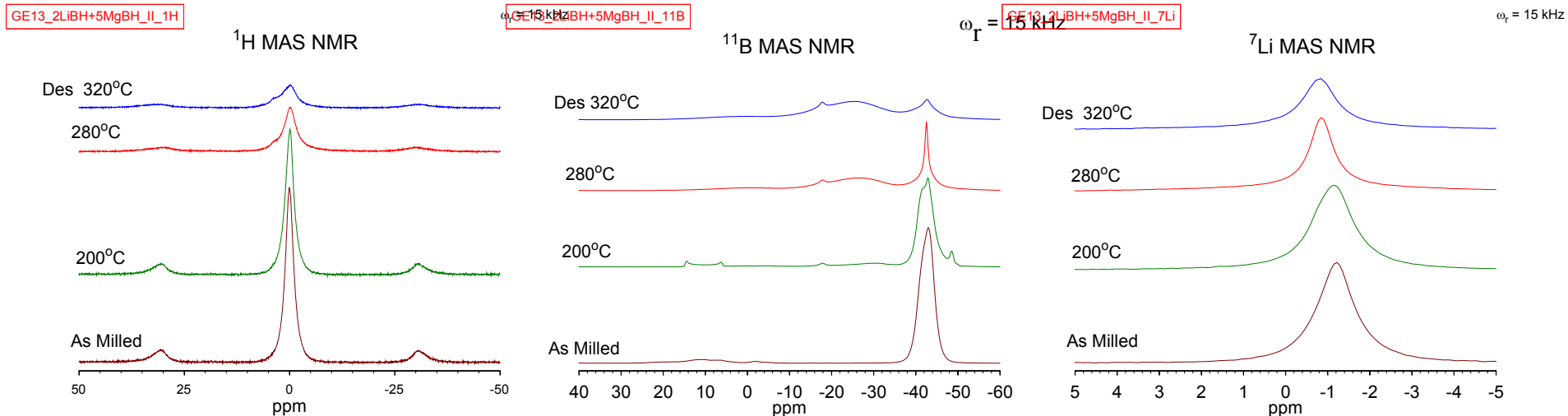


- Multinuclear and high resolution (MAS) solid state NMR experiments
- Samples include the as-milled mixture of 2:5 borohydrides and solid residue after $H_2$ desorption.
- $^1H$ and $^{11}B$ NMR show decrease of $BH_4$ (~ -41 ppm peak for both $LiBH_4$ and $Mg(BH_4)_2$)
- Desorbed borane species was mainly characterized by a broad -26 ppm peak (see following slides) after thermal heating above 280 C.
- Note that -26 ppm peak cannot be due to $Li_2B_{12}H_{12}$ of which resonance is expected at -15 ppm.

# What are B-containing reaction products observed in NMR?
## Computational screen of reaction products in $Mg(BH_4)_2$
### (from last year)
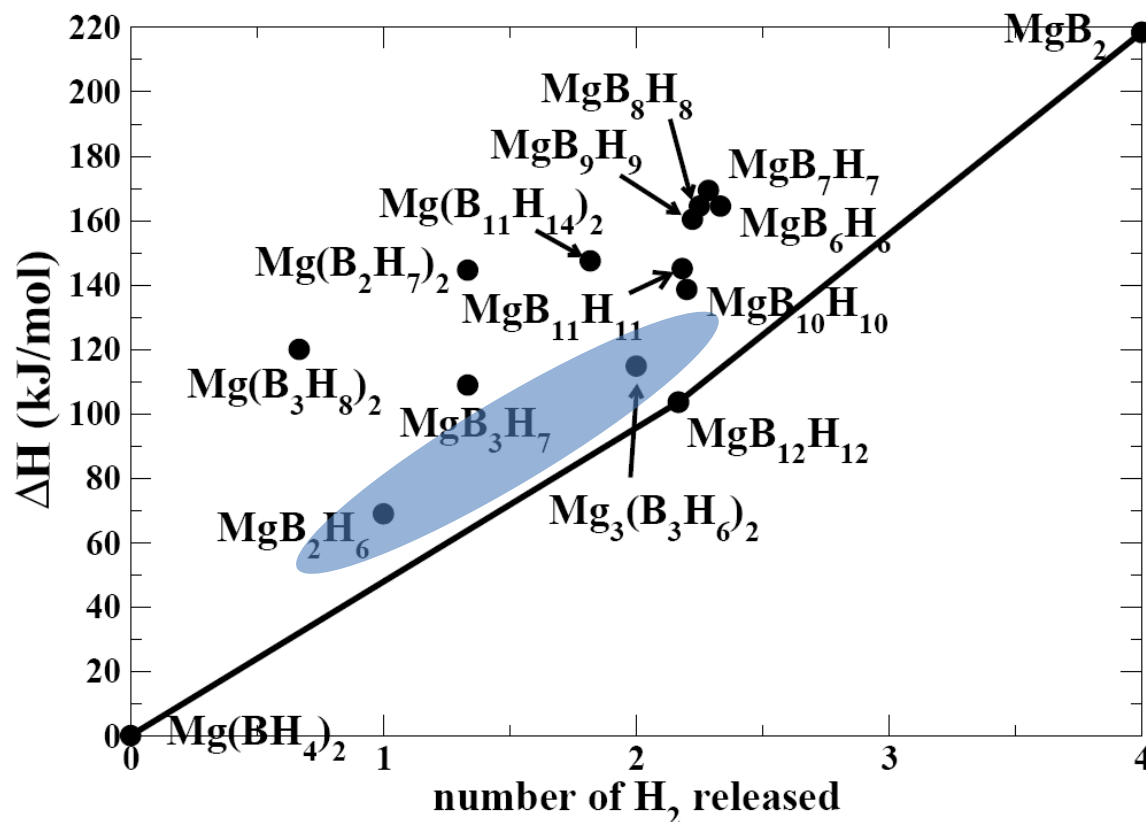


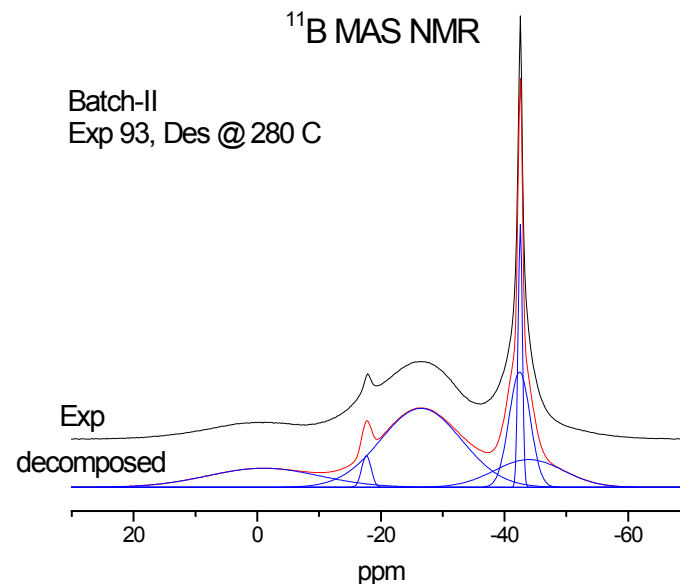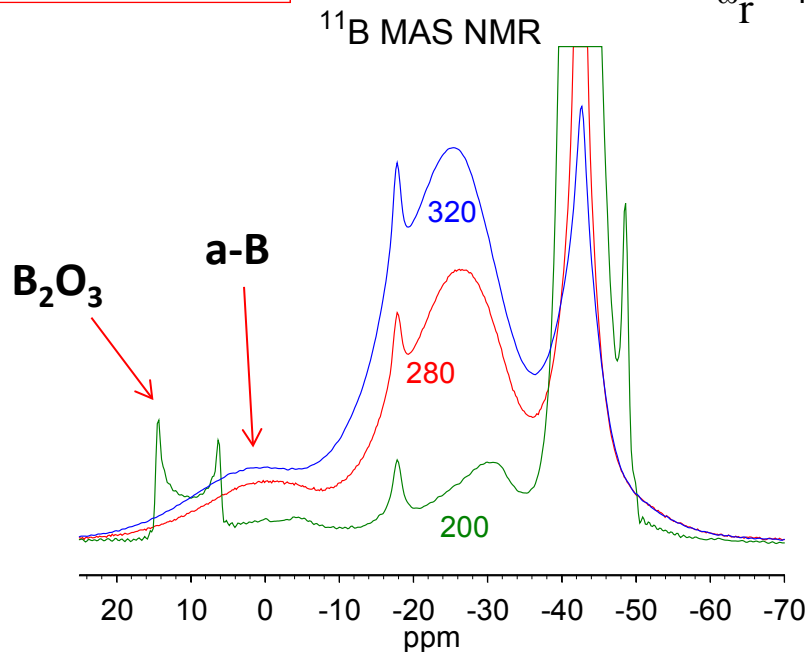**All $[B_nH_m]$ intermediates have higher reaction energies than $MgB_{12}H_{12}$.**
**Only the reactions to $MgB_2H_6$ and $Mg_3(B_3H_6)_2$ are close to the $MgB_{12}H_{12}$ convex hull.**

Y. Zhang et al., Phys. Rev. B (2010); J. Phys. Chem. C (2012)

# Borane species detected by $^{11}$B NMR

$\omega_r$ = 15 kHz

$^{11}$B MAS NMR

B$_2$O$_3$   a-B

320
280
200



$^{11}$B MAS NMR

Batch-II
Exp 93, Des @ 280 C

Exp
decomposed



- Besides the sharp -17.7 ppm and a broad peak at -1 ppm (amorphous boron), **the main -26 ppm peak represents the major boron species**.
- Possible species for of -26 ppm peak:
diborane dianion[2,3] - **Li$_2$B$_2$H$_6$ , MgB$_2$H$_6$**
- -17.7 and -48.6 ppm: Li$_2$B$_5$H$_9$ or MgB$_5$H$_9$ like[3]

| shift (ppm) | line width(Hz) | rel Intensity |
|---|---|---|
| -1.00 | 2880 | 0.15 |
| -17.66 | 240 | 0.02 |
| -26.50 | 2080 | 0.45 |
| -42.45 | 545.9664 | 0.17 |
| -42.54 | 109.0432 | 0.08 |
| -43.94 | 1786.133 | 0.13 |

[1]Hermanek, S. *Chemical Reviews* **1992,** *92* (2), 325-362.
[2]Godfroid, R. A. et al, JACS **1994,** *116* (26), 12107-12108.
[3]Yan, Y. et al, Mater Trans, **2011**, 52,1443.

# 2LiBH$_4$+5Mg(BH$_4$)$_2$

- At lower temperatures, a $^{11}$B peak at -30.5 ppm appeared (200 °C).
- The peak could possibly be assigned to B$_3$H$_8$ formation [2]. However, its formation was not in significant quantity (see green line in the stack plot), and other sharp peaks at -48.6 ppm and -17.8 ppm were accompanied.
- After heating at 200 °C, the reduction in hydrogen content measured by $^1$H NMR was less than 10% (see [H] plot). [H] plot for the new batch showed noticeable difference from the first batch that contains boron oxide in large fraction.

GE13_2LiBH+5MgBH_1H_2

H content from $^1$H MAS NMR
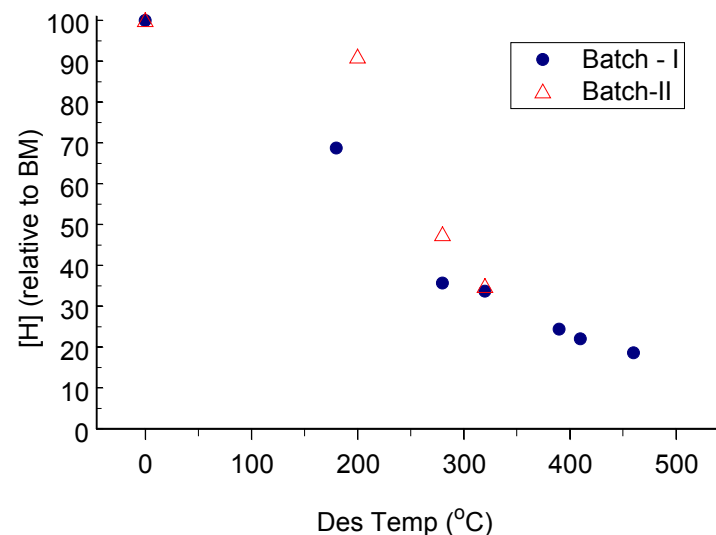


- Yan, Y et al proposed the following reaction route for B$_{12}$H$_{12}$$^{2-}$ formation.
- Assigning -26 ppm peak for B$_2$H$_6$$^{2-}$, and -17.8 and -48.6 ppm peaks for B$_5$H$_9$$^{2-}$, the sequence of products is inconsistent.
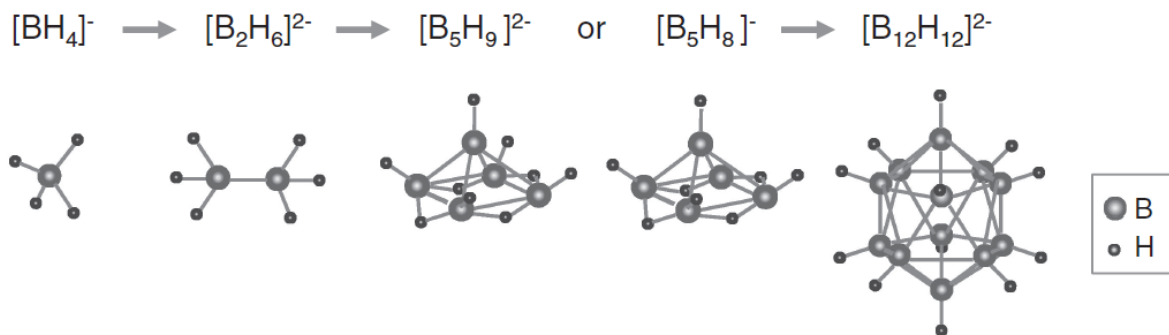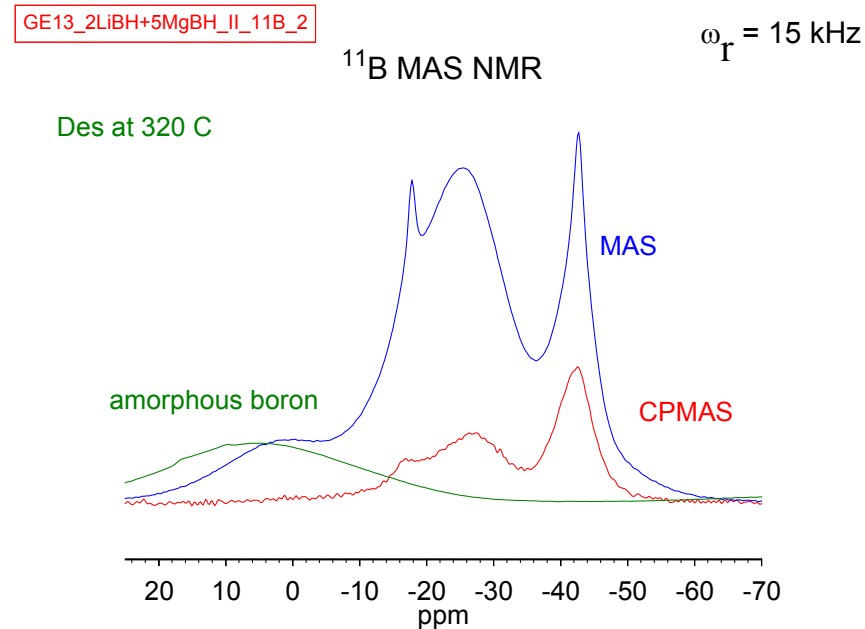
$[BH_4]^- \longrightarrow [B_2H_6]^{2-} \longrightarrow [B_5H_9]^{2-}$  or  $[B_5H_8]^- \longrightarrow [B_{12}H_{12}]^{2-}$



- B
- H

Fig. 4  Schematic illustration of formation process of $[B_{12}H_{12}]^{2-}$ from $[BH_4]^-$.

Hill, T. G.; Godfroid, R. A.; White, J. P.; Shore, S. G., *Inorganic Chemistry* **1991,** *30* (14), 2952-2954.
Yan, Y. et al, Mater Trans, **2011**, 52,1443.

# $^{11}$B CPMAS NMR:
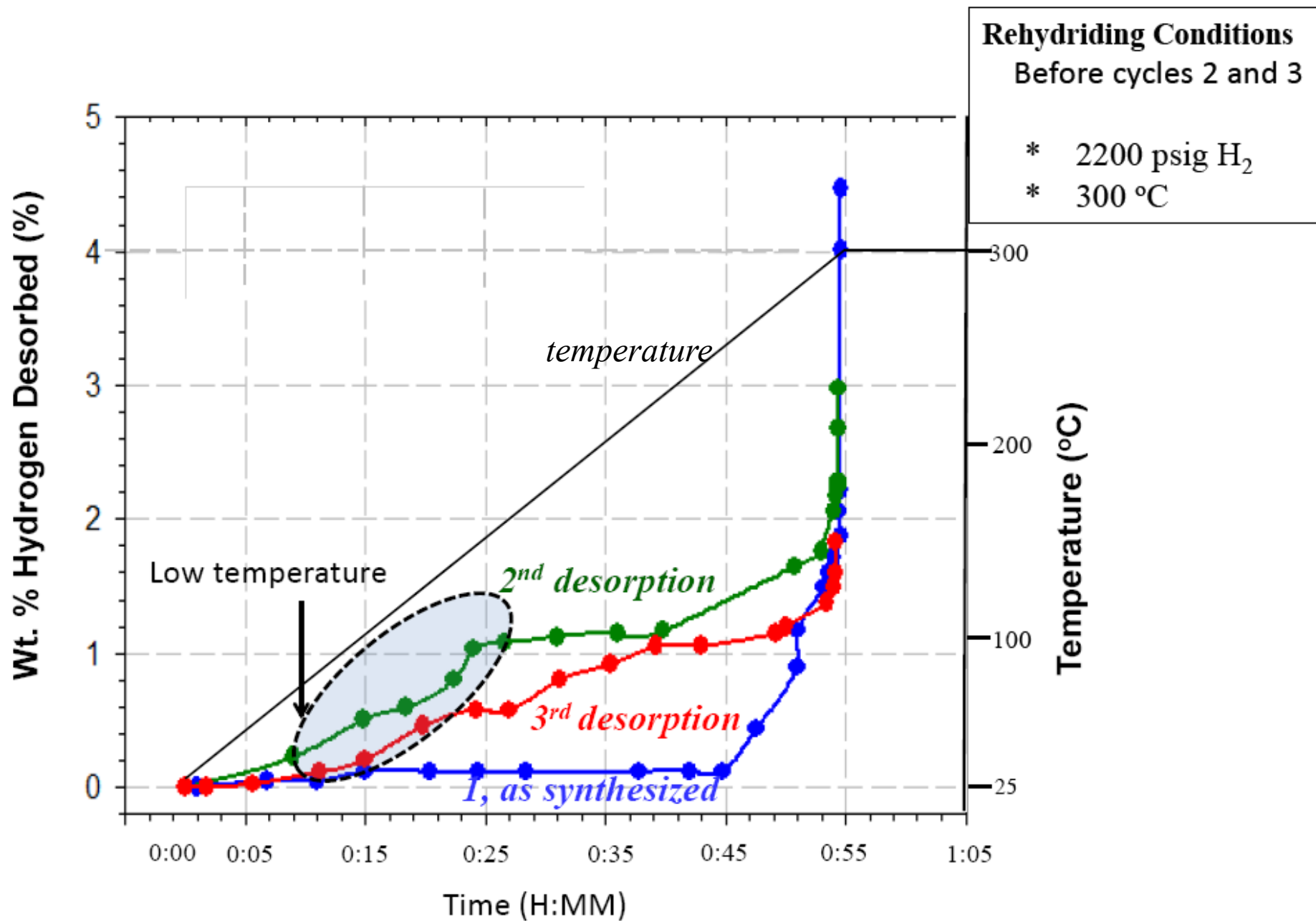# the formation of amorphous boron

- **The peak near 0 ppm is assigned as amorphous boron at the moment. The peak appears at nearly the same position of $^{11}$B spectrum of neat amorphous boron (Aldrich). $^{1}$H-$^{11}$B CPMAS (cross-polarization) NMR also supports the nature of the boron species which bears no direct B-H chemical bonds.**

- **Somewhat surprising to see the formation of amorphous boron – not thermodynamically expected (from calculations)**
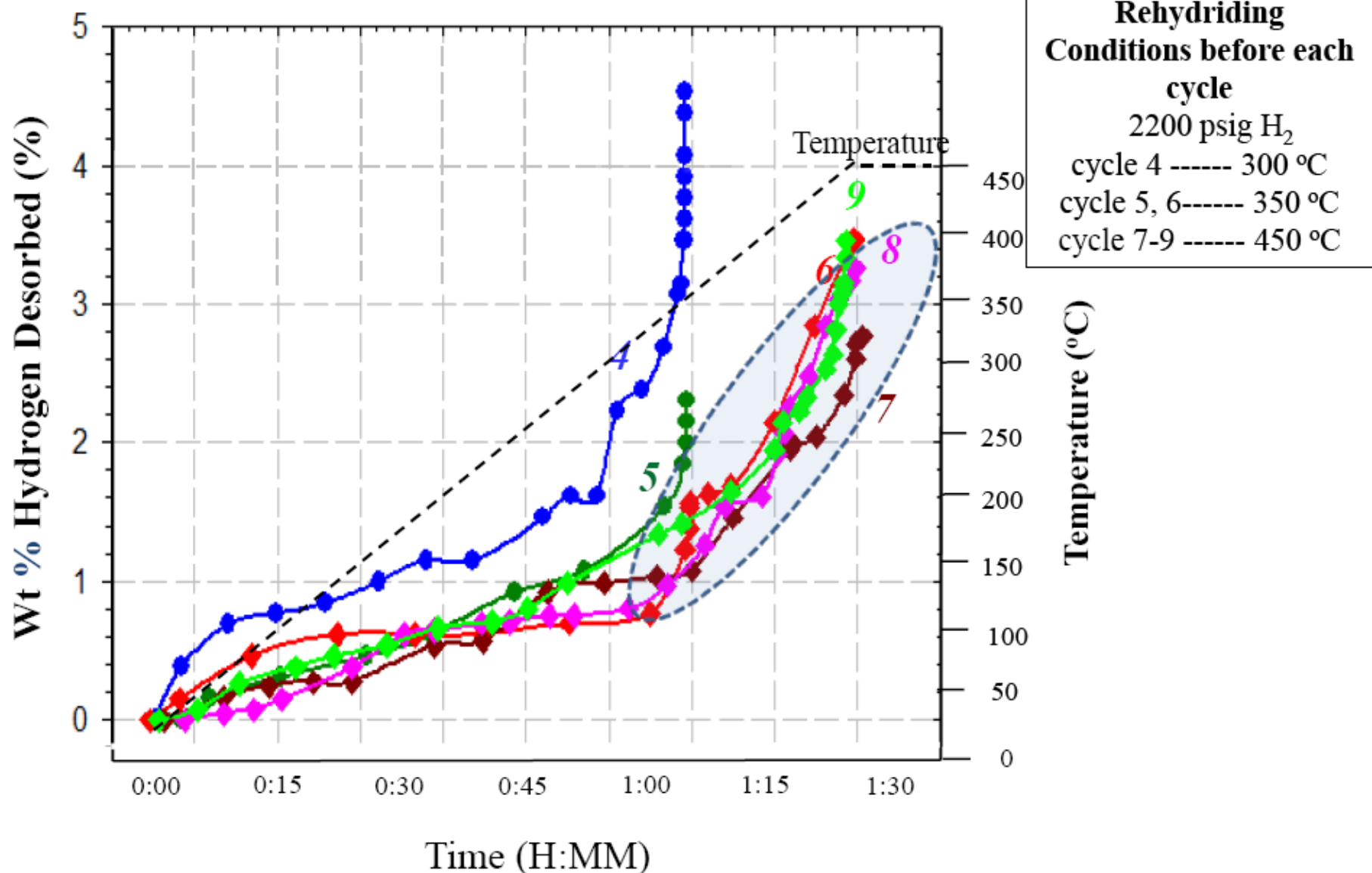
- **We still have much to learn in this highly-promising reaction system.**

GE13_2LiBH+5MgBH_II_11B_2

$\omega_r$ = 15 kHz

$^{11}$B MAS NMR

Des at 320 C

MAS

amorphous boron

CPMAS

20  10  0  -10  -20  -30  -40  -50  -60  -70
ppm

# LiBH$_4$-carbon composite hydrogen desorption profiles



**Rehydriding Conditions**
Before cycles 2 and 3

* 2200 psig H$_2$
* 300 ºC

temperature

Low temperature

2$^{nd}$ desorption

3$^{rd}$ desorption

1, as synthesized

Wt. % Hydrogen Desorbed (%)

Temperature (ºC)

Time (H:MM)

# LiBH$_4$-carbon composite H$_2$ desorption cycles 4-9



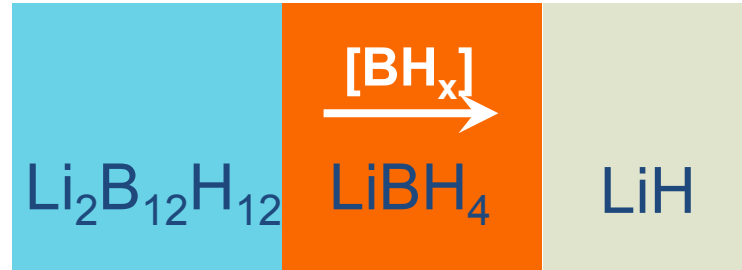**Steady and reversible performance can be attained after several dehydriding/rehydriding cycles.**

# Technical Accomplishments:
# New Theoretical Predictions

- Kinetics of high-capacity borohydride reactions almost always limiting factor - thermodynamic problems solved by appropriate combinations, i.e., $2LiBH_4 + 5Mg(BH_4)_2$

- ***All computational efforts now focused on calculations of kinetic barriers (diffusion, mass transport, surface dissociation, etc.)***

- Diffusion & mass transport (required for fast kinetics)
  - ➤ Mass transport in $LiBH_4$
  - ➤ Al diffusion in $B_{20}H_{16}$

- $H_2$ kinetic studies on $MgB_2(0001)$ surface: dissociation and diffusion

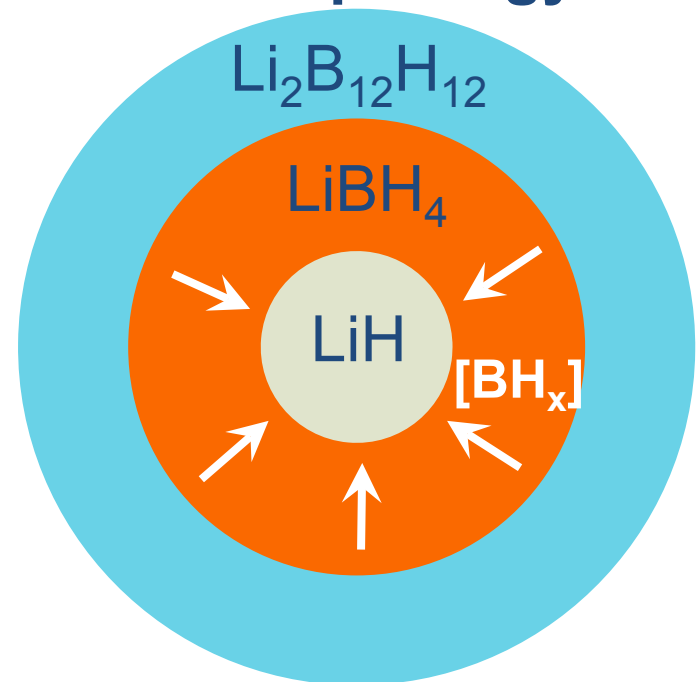# Technical Accomplishments
# Mass transport in borohydrides

# Mass fluxes in LiBH$_4$
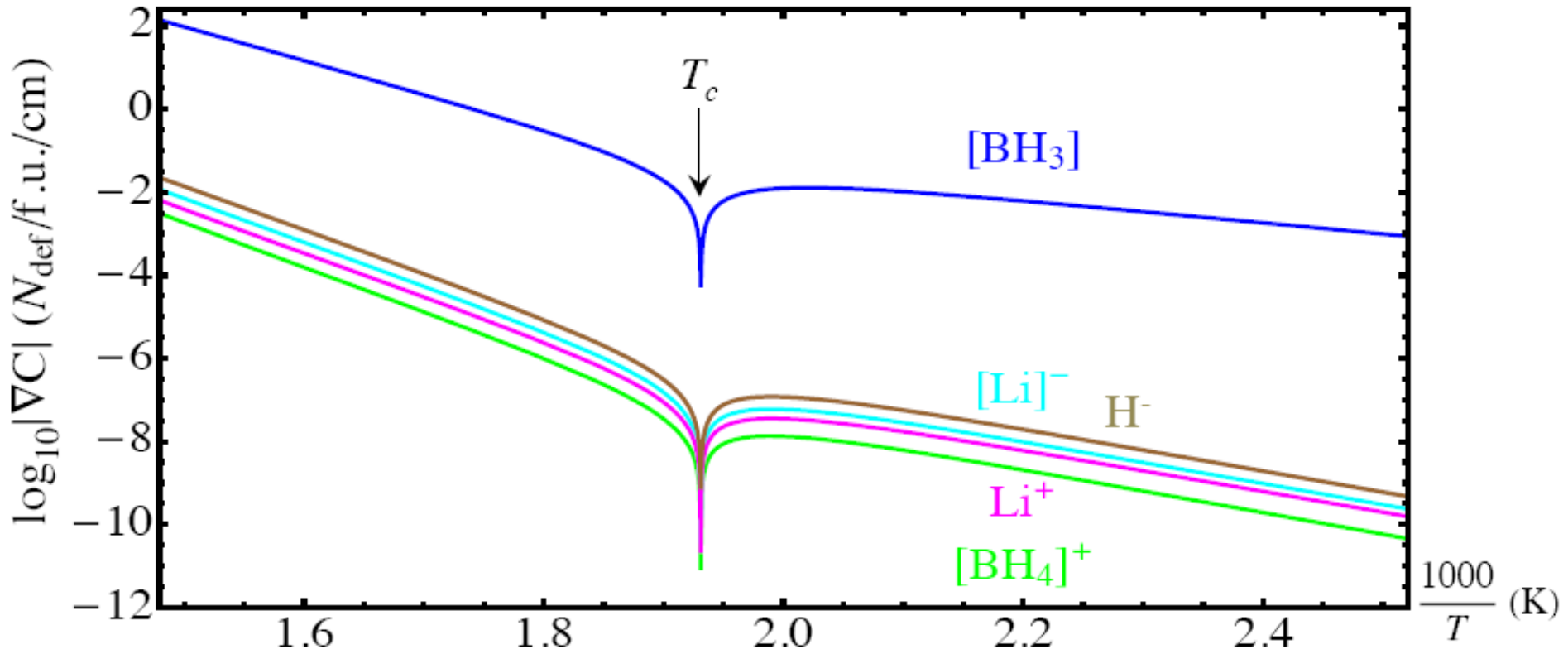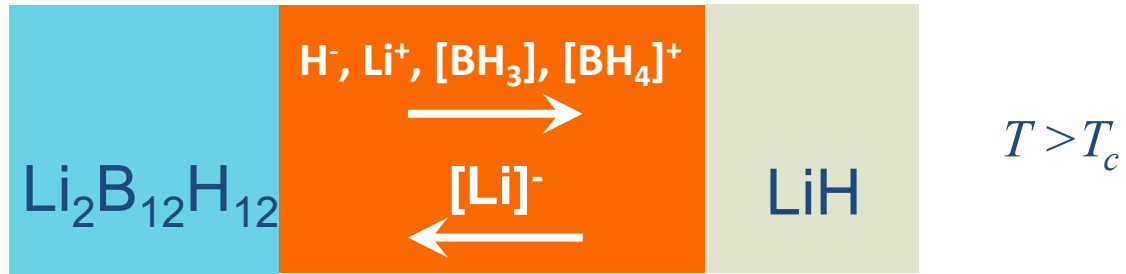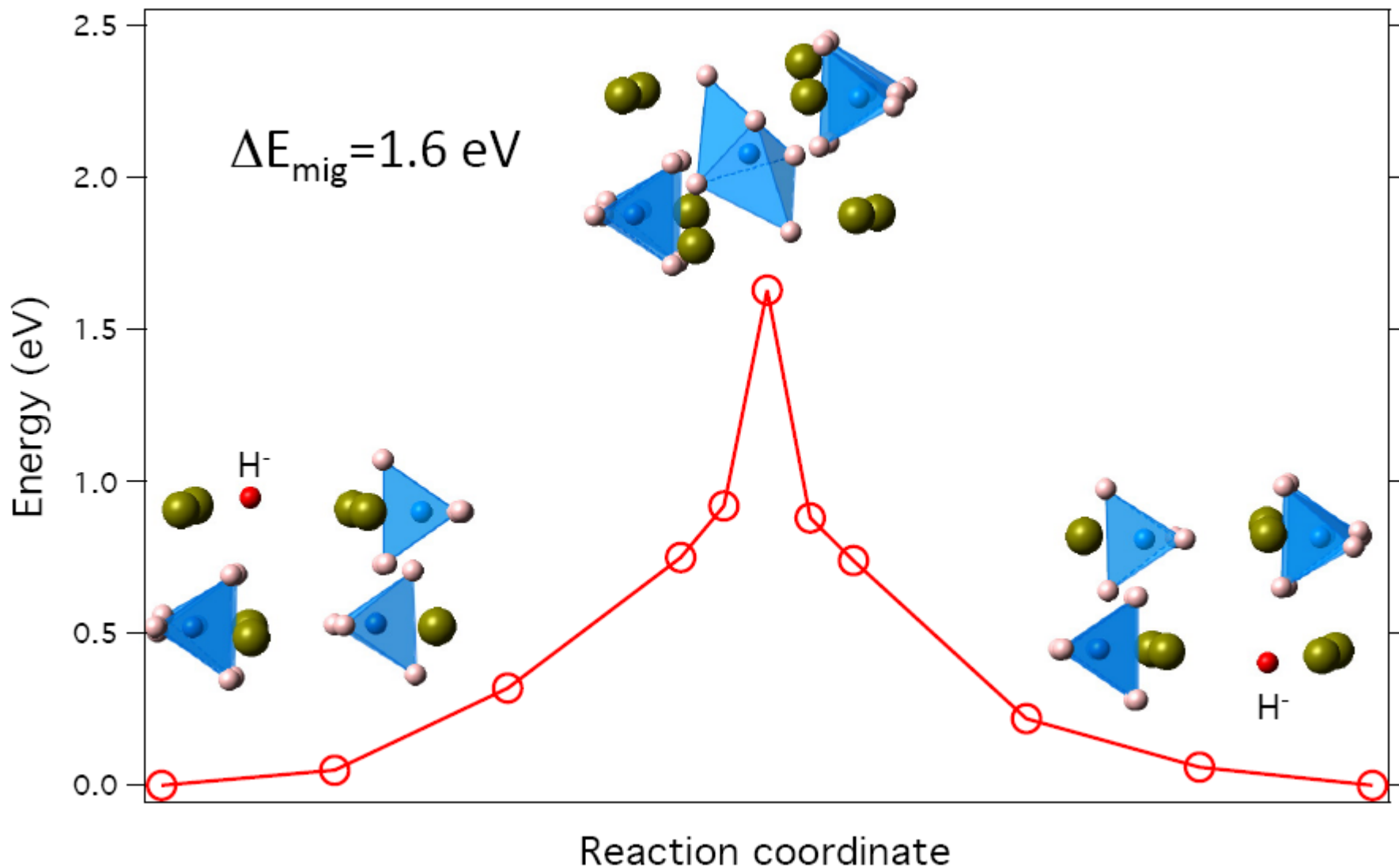


The BH$_3$ vacancy has the largest concentration gradient.
But how about D?

$$\vec{J} = -D\vec{\nabla}C$$
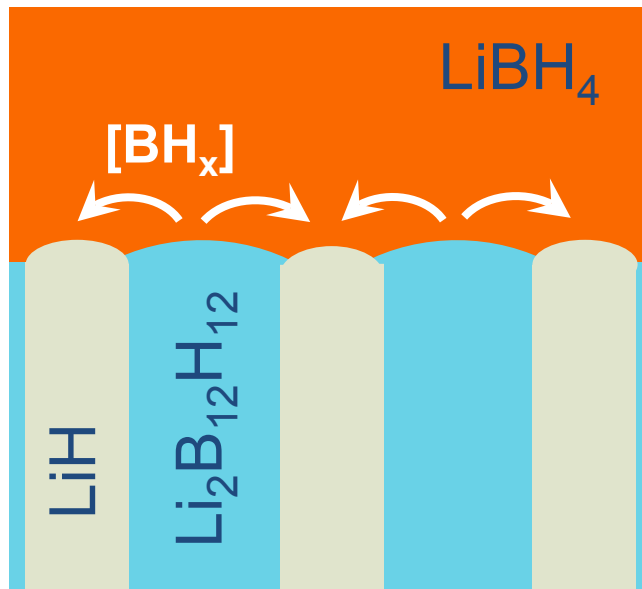
# Diffusion of [BH$_3$] vacancies in LiBH$_4$



$\Delta E_{mig} = 1.6$ eV

**The [BH$_3$] vacancy migration barrier in LiBH$_4$ is very high, 1.6 eV.**

# Native defects in LiH and Li$_2$B$_{12}$H$_{12}$
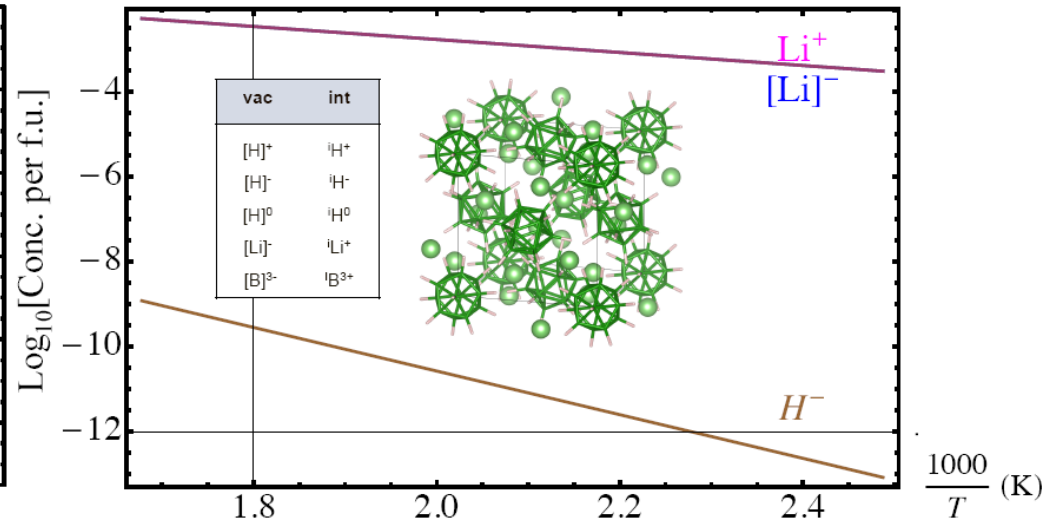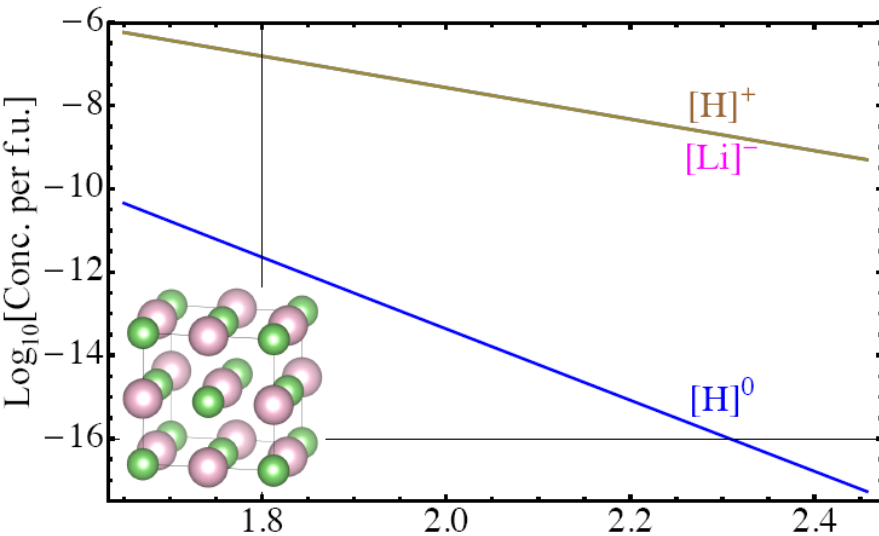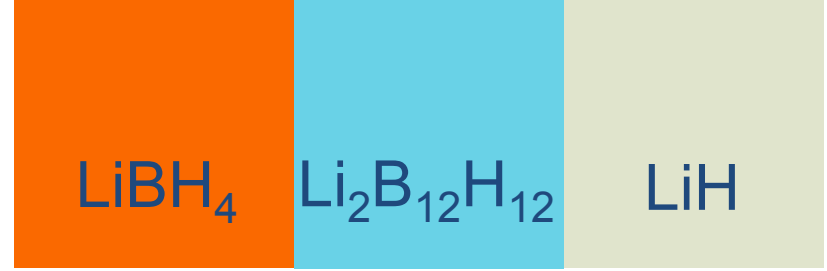


**Concentration gradients are ~10$^5$ times smaller than in LiBH$_4$**

# Collaborations

PI's/co-PI's

Chris Wolverton (Northwestern, lead)
Harold Kung (Northwestern)
Vidvuds Ozolins (UCLA)
Mike Veenstra (Ford, no-cost)
Jun Yang (Ford, no-cost)
S. G. Shore (OSU, subcontract)
S. Hwang (Caltech, subcontract)

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

- Complete synthesis of $B_{20}H_{16}$. (subcontract); Perform desorption experiments for this compound; extend NMR experiments to determine reaction products (if non-crystalline). Perform computations of observed reaction products to confirm results and provide predictions of thermodynamics/kinetics

- If $B_{20}H_{16}$ does not exhibit fast kinetics, computations suggest this would not be due to mass transport, but rather other effects (e.g., nucleation). In this event, perform "product seeding" experiments on this compound to try and accelerate product nucleation.

- Extend NMR experiments to "recharged" $2LiBH_4+5Mg(BH_4)_2$ samples, to determine portion(s) of the reaction that are reversible.

- Computational efforts to continue on kinetics, defects, diffusion/mass transport in promising predicted reactions (mass transport nearly complete; focusing on other barriers now – surface reactions, nucleation)

- Potentially promising avenue for "fast kinetics" borohydrides: low melting point combinations (i.e., low-lying eutectics). Direct some computational effort to finding these low-lying eutectics (AIMD and $\lambda$-integration)

- Investigate the inclusion of various additives to LiBH4-carbon composites:1) To improve the kinetics of the hydrogen cycle, 2) To ameliorate the initial degradation in cyclability . 3) To influence the decomposition pathway so that $LiBH_4$ will decompose to more reversible reaction products.

# Summary – Technical Accomplishments

- Focused efforts on two main reactions, predicted to have high capacity and suitable thermodynamics for H2 storage applications, $2LiBH_4 + 5Mg(BH_4)_2$ and $B_{20}H_{16}$.

- $B_{20}H_{16}$ extremely promising – *first known H2 storage reaction with high capacity, good thermodynamics, and computational predicted fast mass transport kinetics!*

- Theoretically predicted that mass transport in $B_{20}H_{16}$ is fast. Subcontract at OSU focused on synthesis of $B_{20}H_{16}$ compound (future plans will focus on desorption, NMR, kinetics, and reaction products – full characterization of this material)

- $H_2$ desorption and decomposition pathways have been studied in $[2LiBH_4 + 5Mg(BH_4)_2]$ using NMR; reaction products consistent with theoretically predicted $B_2H_6$ anion; still much to explore in this system in terms of reversibility of reaction products (future plans).

- Low temperature hydrogen desorption observed for $LiBH_4$ -carbon composite. Stable cycling can be attained after a few cycles

- Using the predictive models of kinetics of mass transport, the Al mass transport in $B_{20}H_{16}$ is quite high (important for $H_2$ release from $AlB_4H_{11}$), but the mass transport in $LiBH_4$ is very low (much lower than that in $NaAlH_4$); potential avenue for borohydrides – low-lying eutectics (see future plans).

- Computational survey of dopants that lower surface dissociation or diffusion for $MgB_2$ rehydrogenation

# Publications (2012-2013)

- *Transition Metal-Decorated Activated carbon Catalysts for Dehydrogenation of NaAlH$_4$*, Sean S.-Y. Lin, Jun Yang, and Harold H. Kung,  Int. J. Hydrogen Energy **37**, 2737 (2012)

- *Theoretical prediction of metastable intermediates in the decomposition of Mg(BH$_4$)$_2$*, Yongsheng Zhang, Eric Majzoub, Vidvuds Ozolins and C. Wolverton , J. Phys. Chem. C **116**, 10522 (2012)

- *Crystal structures, phase stabilities, and hydrogen storage properties of metal amidoboranes*, Yongsheng Zhang and C. Wolverton , J. Phys. Chem. C **116**, 14224 (2012)

- *First-principles insight into the degeneracy of ground state LiBH$_4$ structures*, Yongsheng Zhang, Yongli Wang, Kyle Michel and C. Wolverton, Phys. Rev. B **86**, 094111 (2012)

- *Structure determination of an amorphous compound AlB$_4$H$_{11}$*, X.Chen, Y. Zhang, Y. Wang, W. Zhou, D. A. Knight, T. B. Yisgedu, Z. Huang, H. K. Lingam, B. Billet, T. J. Udovic, G. M. Brown, S. G. Shore, C. Wolverton and J.-C. Zhao, Chem. Sci. **3**, 3183 (2012)

- *First-principles studies at intermediate products in the decomposition of metal amidoboranes*, Yongsheng Zhang, Tom Autrey and C. Wolverton , J. Phys. Chem. C **116**, 26728 (2012).

- *Hydrogen storage properties of complex-metal hydride-carbon materials*, Sean S.-Y. Lin , Jun Yang, Harold H. Kung  and Mayfair C. Kung, Topics in Catalysis (in press, 2013).

- *The kinetics of mass transport in B20H16*, Kyle Michel, Yongsheng Zhang and C. Wolverton, (submitted, 2013)

- *Crystal Structure, Phase Stability, and Decomposition of the Quaternary Mg-B-N-H Hydrogen Storage System*, Y. Zhang,  D. Farrell, J. Yang, A. Sudik, and C. Wolverton (submitted, 2013).

# Publications (previous years)

- *Theoretical prediction of different decomposition paths for Ca(BH4)2 and Mg(BH4)2* , Yongsheng Zhang, Eric Majzoub, Vidvuds Ozolins and C. Wolverton,  Phys. Rev. B **82**, 174107 (2010)

- *First-principles prediction of phase stability and crystal structures in Li-Zn and Na-Zn mixed-metal borohydrides,* Dilpuneet S. Aidhy and C. Wolverton , Phys. Rev. B **83**, 144111 (2011)

- *Prediction of a Ca(BH4)(NH2) quaternary hydrogen storage compound from first-principles calculations*, Dilpuneet S. Aidhy, Yongsheng Zhang and C. Wolverton , Phys. Rev. B **84**, 134103 (2011)

- *First-principles prediction of high-capacity, thermodynamically reversible hydrogen storage reactions based on (NH4)2B12H12,* W. H. Sun, C. Wolverton, A. R. Akbarzadeh and V. Ozolins , Phys. Rev. B 83, 064112 (2011).
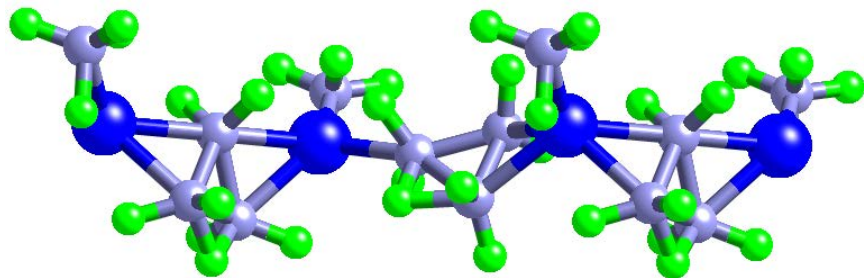
# Backup Slides
# (Extra information/results not presented due to time constraints)

# Technical Accomplishments
# mass transport in $AlB_4H_{11}$

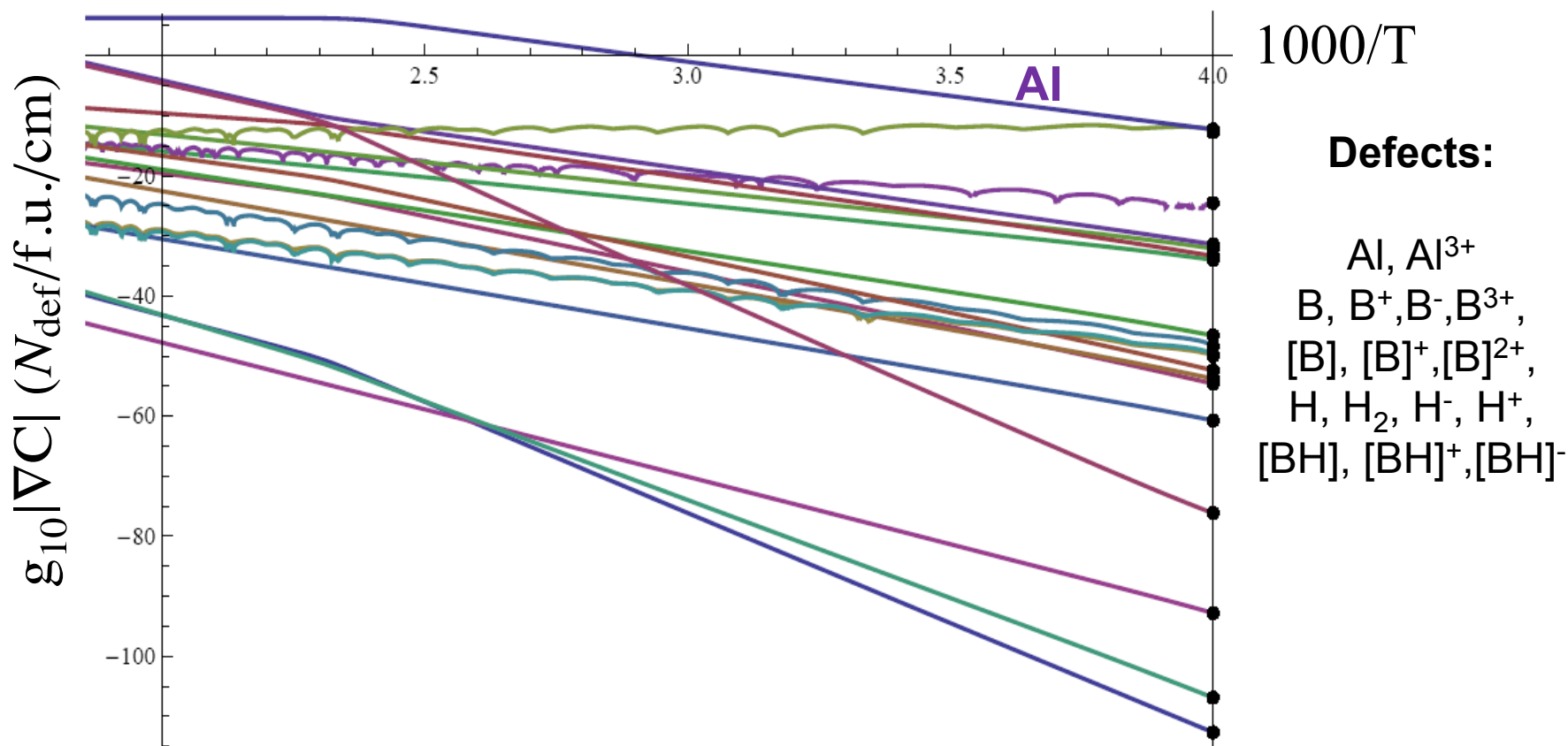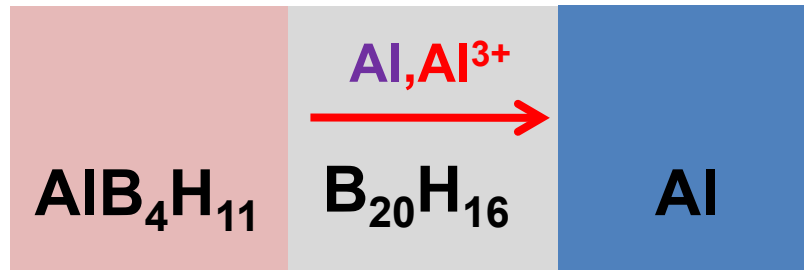- **$AlB_4H_{11}$ structure** X. Chen et al., Chem. Sci. **3**, 3183 (2012)



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

- **Unknown decomposition products**



**T=0K, No ZPE**



**T>0K**

**At finite temperatures:**
**$AlB_4H_{11} \rightarrow$**
**$1/5 B_{20}H_{16} + Al + 39/10 H_2$**
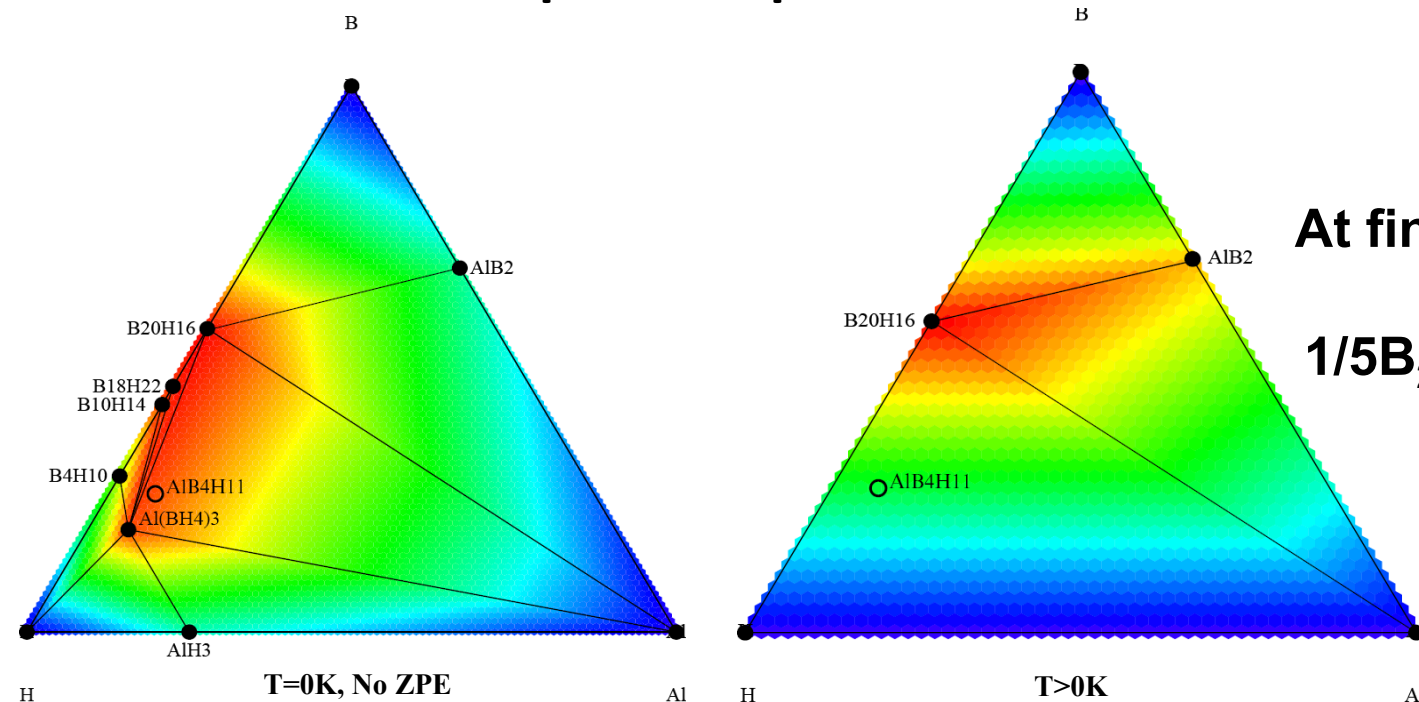
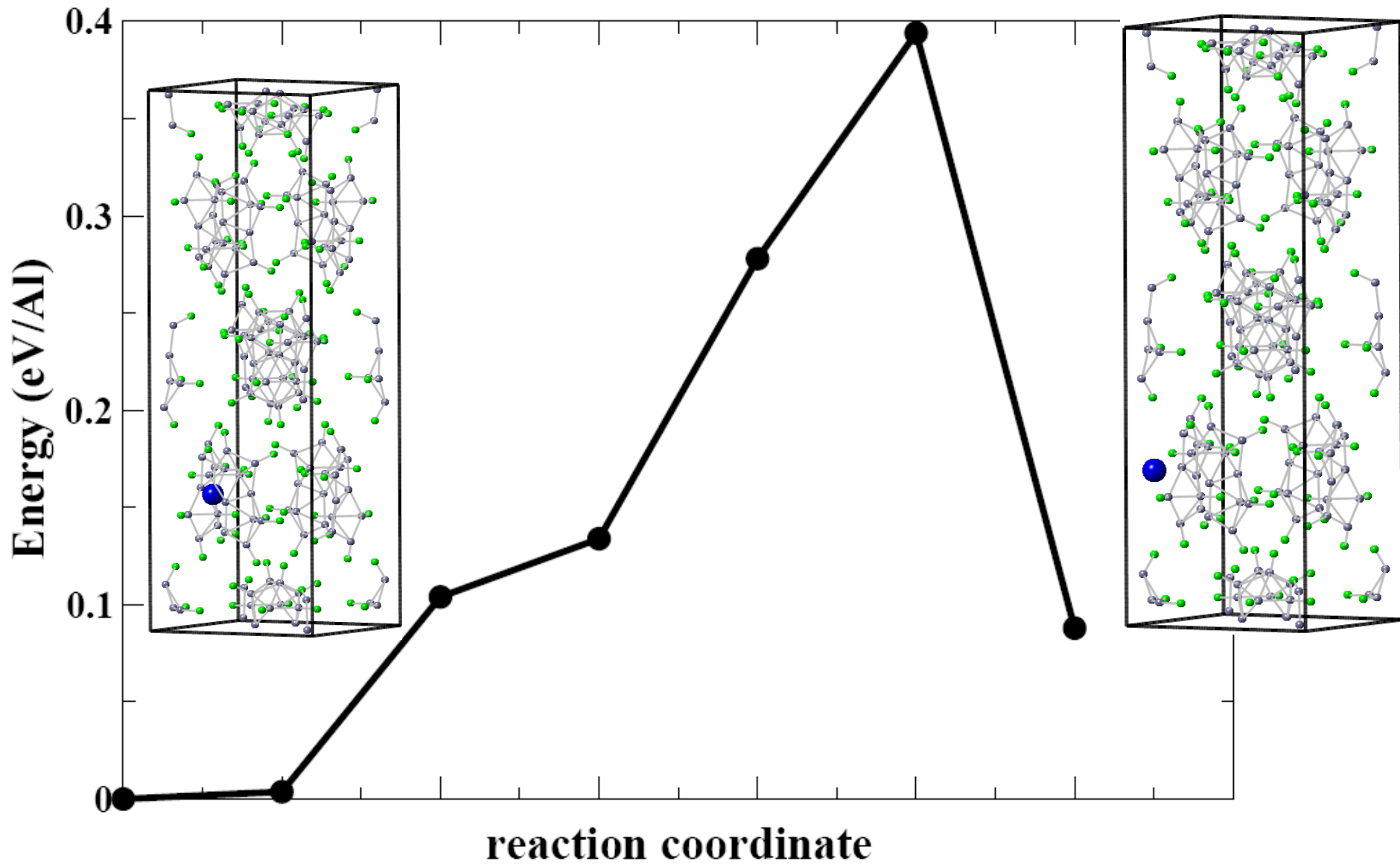# Mass fluxes in B<sub>20</sub>H<sub>16</sub>



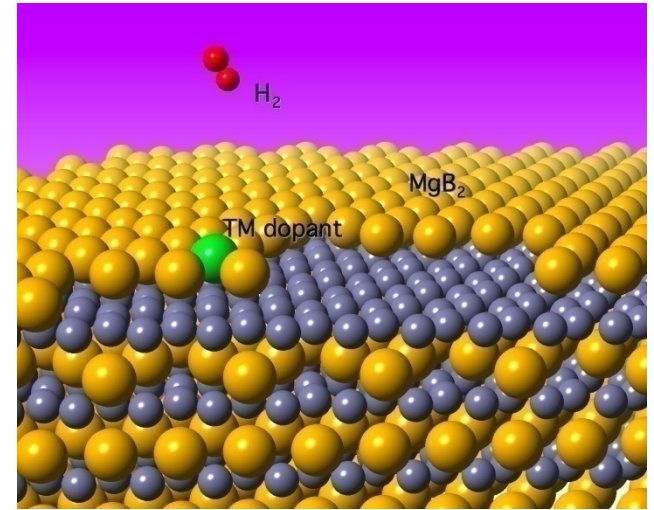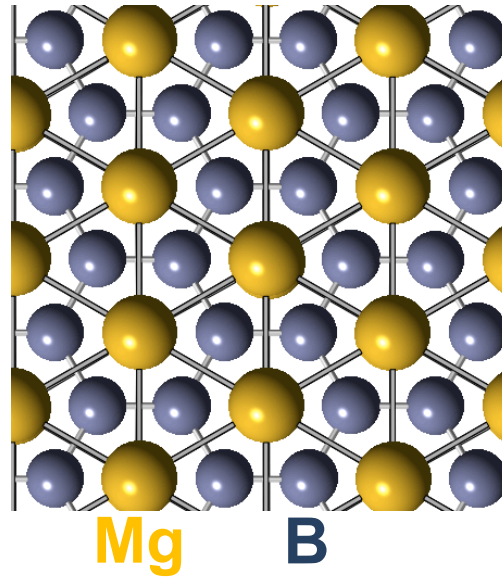The Al interstitial has the largest concentration gradient.

# Al migration barrier in $B_{20}H_{16}$: preliminary results
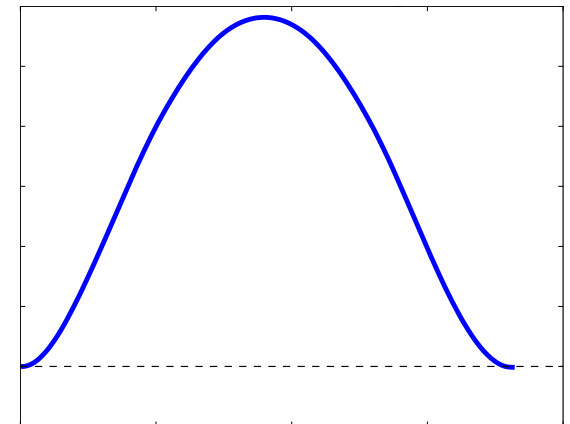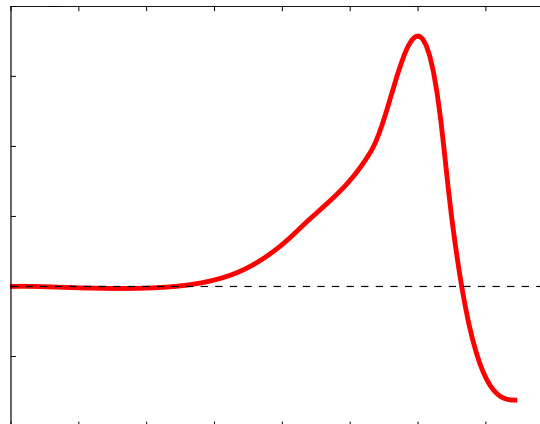


The Al migration barrier in $B_{20}H_{16}$ is low, ~0.4 eV.

# Identify the kinetic barriers for re-hydrogenation of MgB$_2$

- **What are the rate-limiting steps for MgB$_2$ ?**
  **(mass transportation, nucleation, dissociation, diffusion or etc?)**



Mg    B



**We investigated the H$_2$ dissociation and H diffusion on the Mg-terminated MgB$_2$ (0001) surface**

# Identify the kinetic barriers for re-hydrogenation of MgB$_2$

| | Disso-ciation | Diffu-sion |
|---|---|---|
| Barrier (eV) | 0.72 | 0.12 |

**Computational prediction of dopants that lower dissociation, diffusion barriers (or both).**