

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

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Ohio St. Univ.



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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

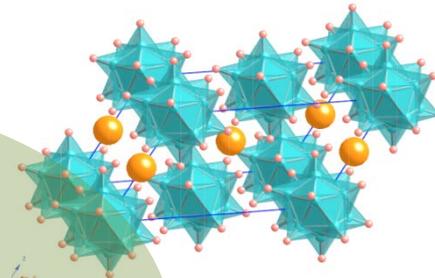
**Hydrogen Storage
Measurements and
Auto Perspective**

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.



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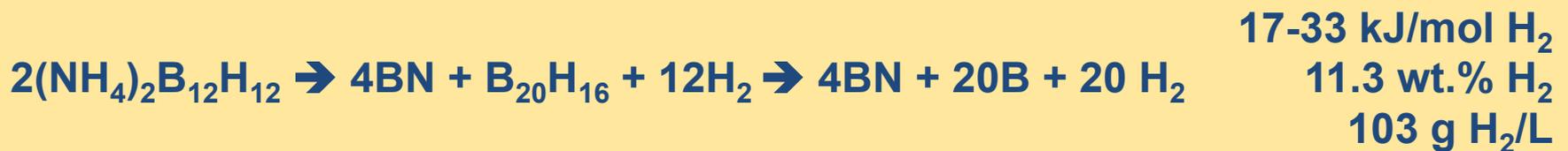
Technical Accomplishments (previous):

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)	ΔH ^{300K} (kJ/mol H ₂)	ΔS ^{300K} (J/mol-K)
2(NH₄)₂B₁₂H₁₂ → 4BN + B₂₀H₁₆ + 12H₂	6.81	62	17	104
5Mg(BH₄)₂ + 2LiBH₄ → 5MgH₂ + Li₂B₁₂H₁₂ + 13H₂	8.37	66	24	104
6Mg(BH ₄) ₂ → 5MgH ₂ + MgB ₁₂ H ₁₂ + 13H ₂	8.10	65	29	100
B₂₀H₁₆ → 20B + 8H₂	6.95	77	33	111
5MgH ₂ + MgB ₁₂ H ₁₂ → 6MgB ₂ + 11H ₂	7.46	81	44	115

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



Technical Accomplishments:

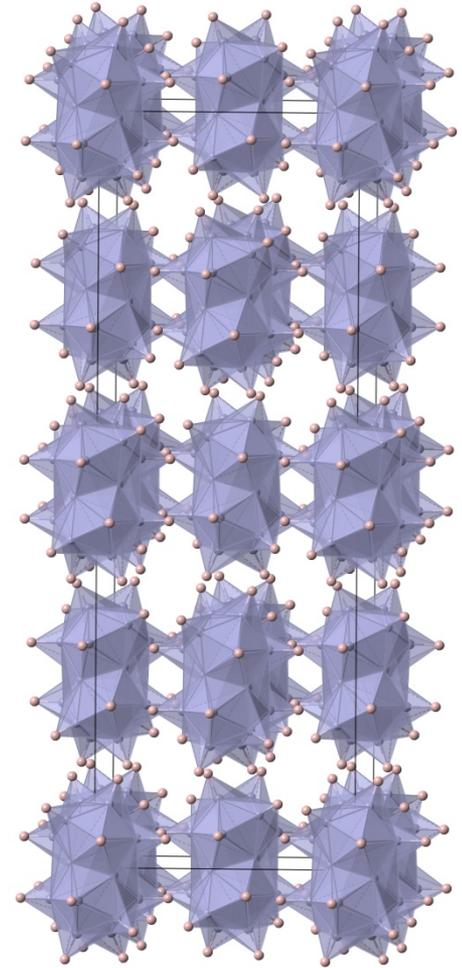
Thermodynamics of $B_{20}H_{16}$ to $20B + 8H_2$

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

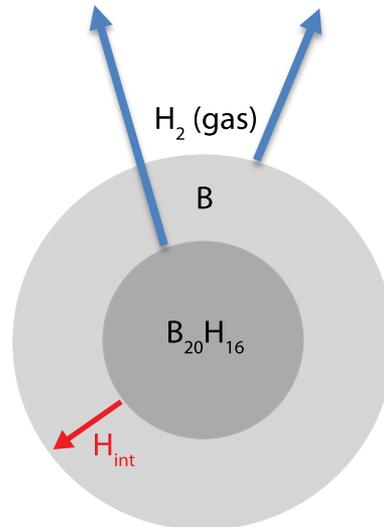
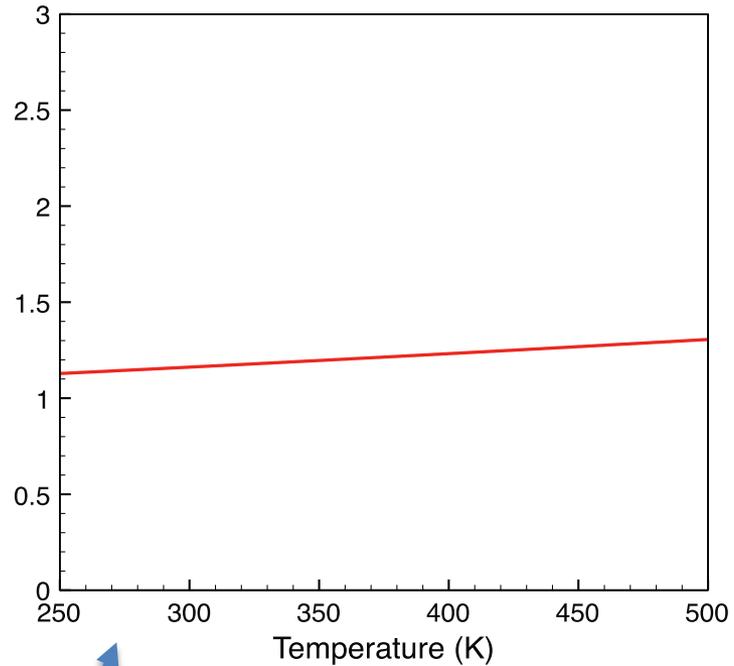
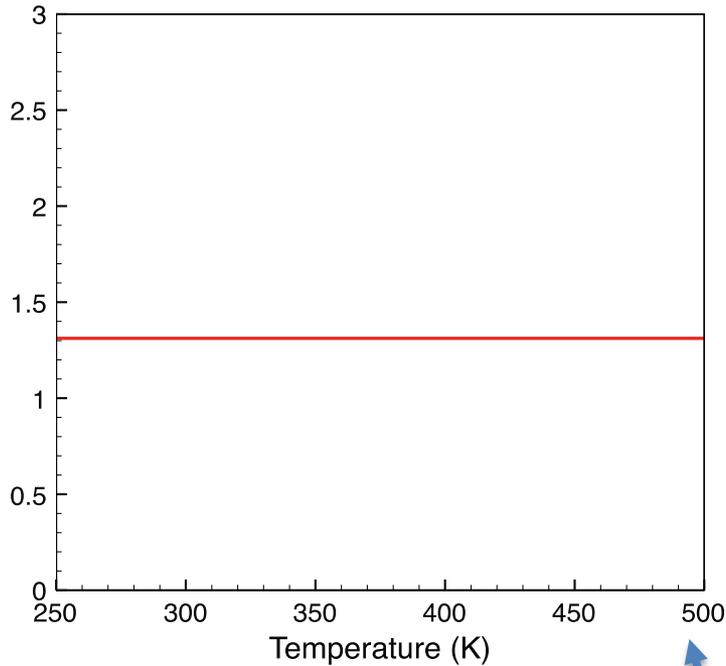
$B_{20}H_{16} \rightarrow 20B + 8H_2$	
H ₂ content	6.90 wt. %
T _{crit}	20°C
ΔH^{0K}	27 kJ/mol H ₂
ΔH^{300K}	33 kJ/mol H ₂
ΔS^{300K}	111 J/K·mol H ₂

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. % H₂
- Nothing is known about kinetics of hydrogen release or uptake

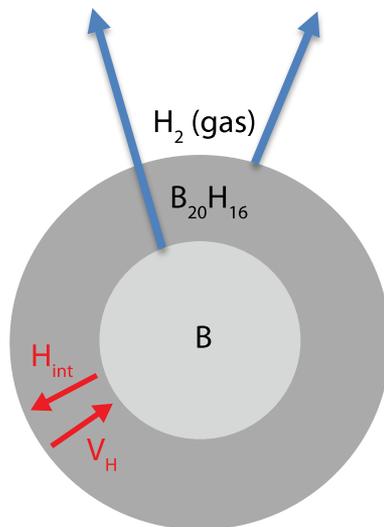
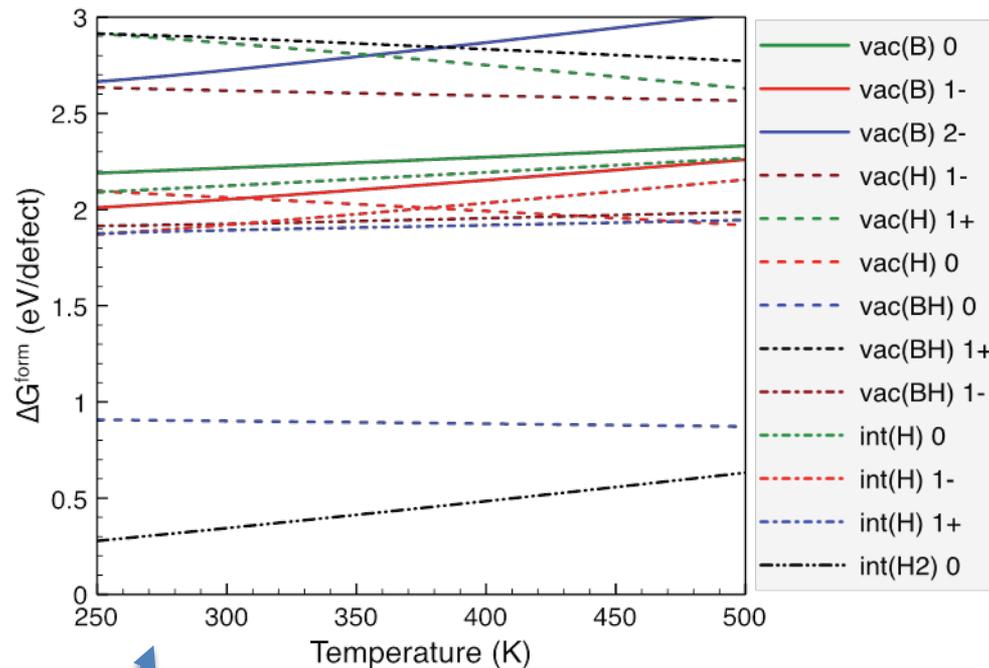
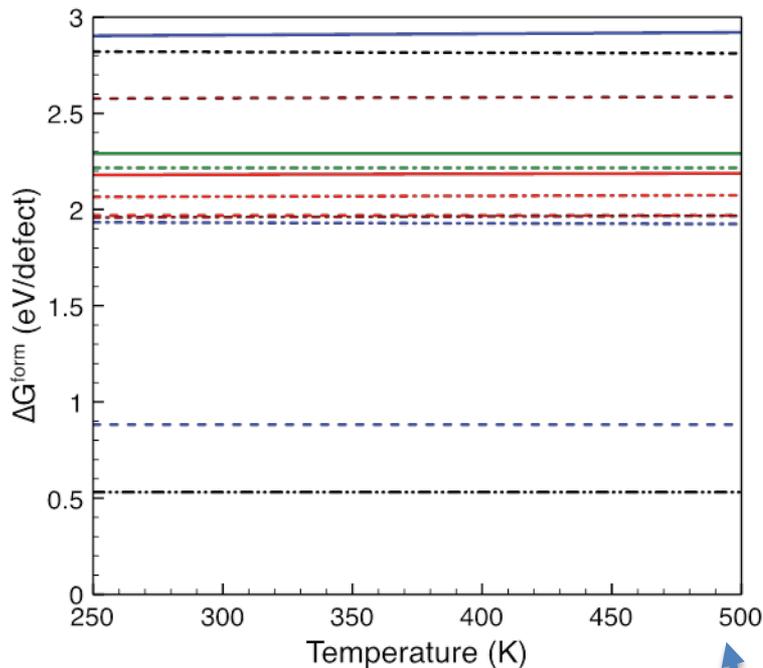


Defect energetics in solid phases (B)



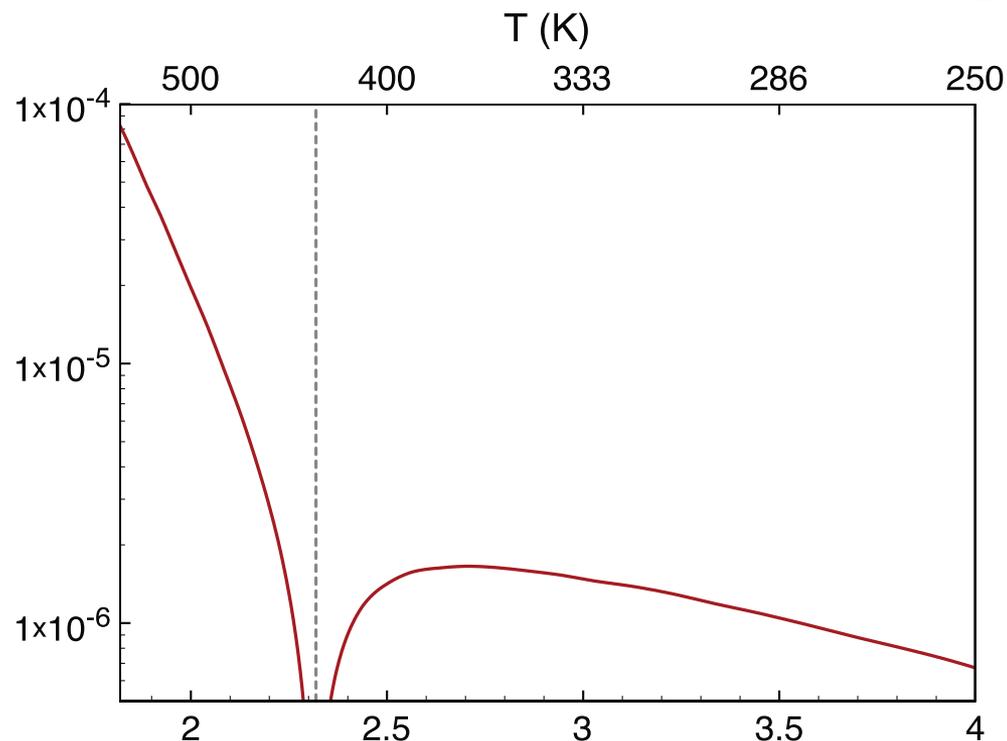
- **Formation energy of interstitial H₂ in boron is high so mass flux will be low**

Defect energetics in solid phases ($B_{20}H_{16}$)



- Formation energy of interstitial H₂ in $B_{20}H_{16}$ is lowest of all defects

Interstitial H₂ flux in B₂₀H₁₆ and mass transport activation energy



Activation energy for mass transport

Rehydrogenation 6 kJ/mol

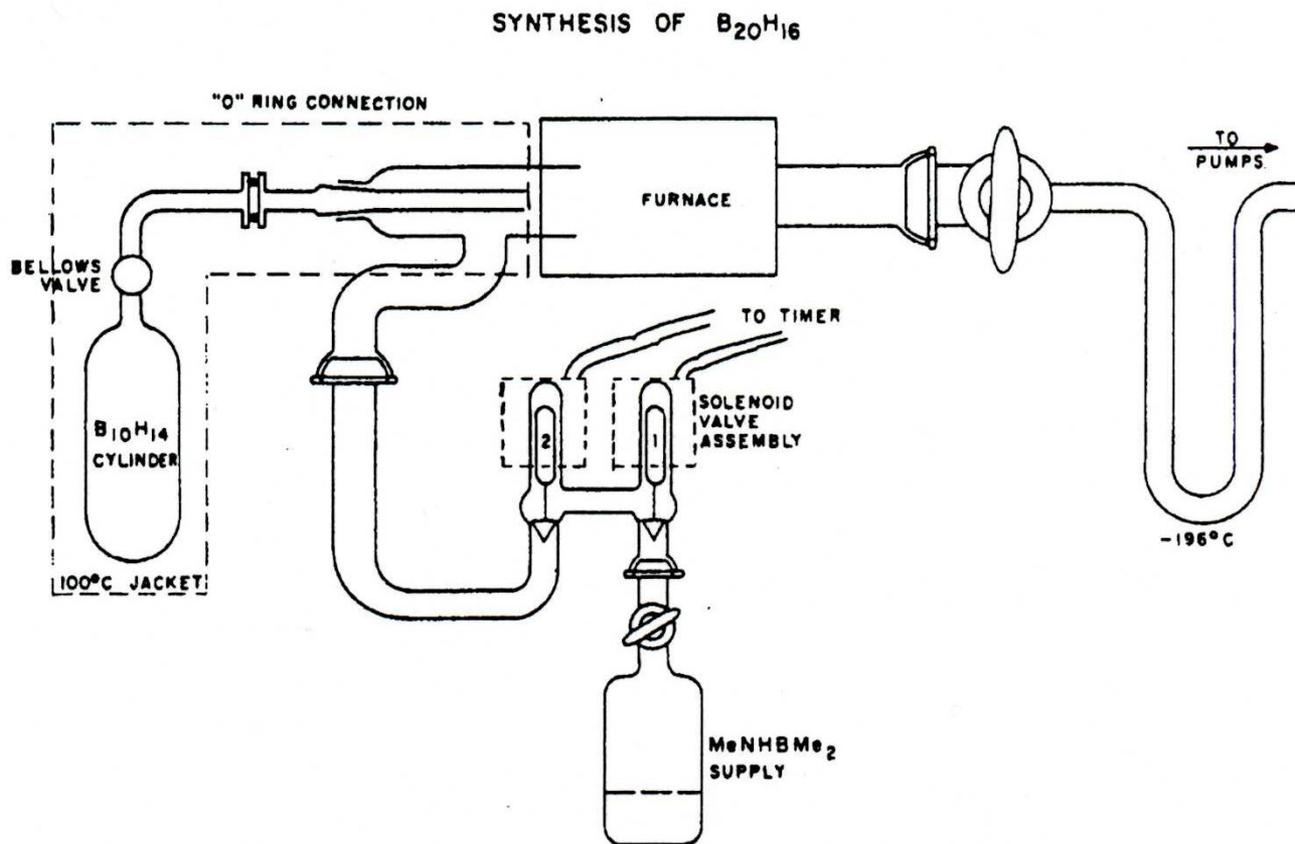
Dehydrogenation 63 kJ/mol

- Low activation energy for interstitial H₂ in B₂₀H₁₆
- Mass transport is likely to be fast in this system while it is rate limiting in many others
- B₂₀H₁₆ 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:

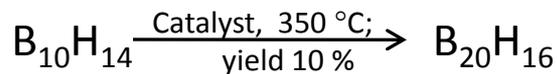
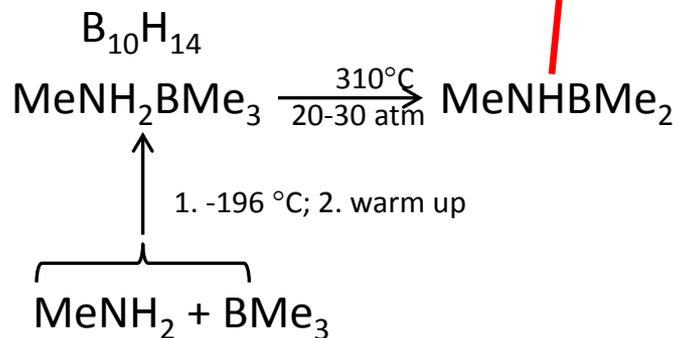
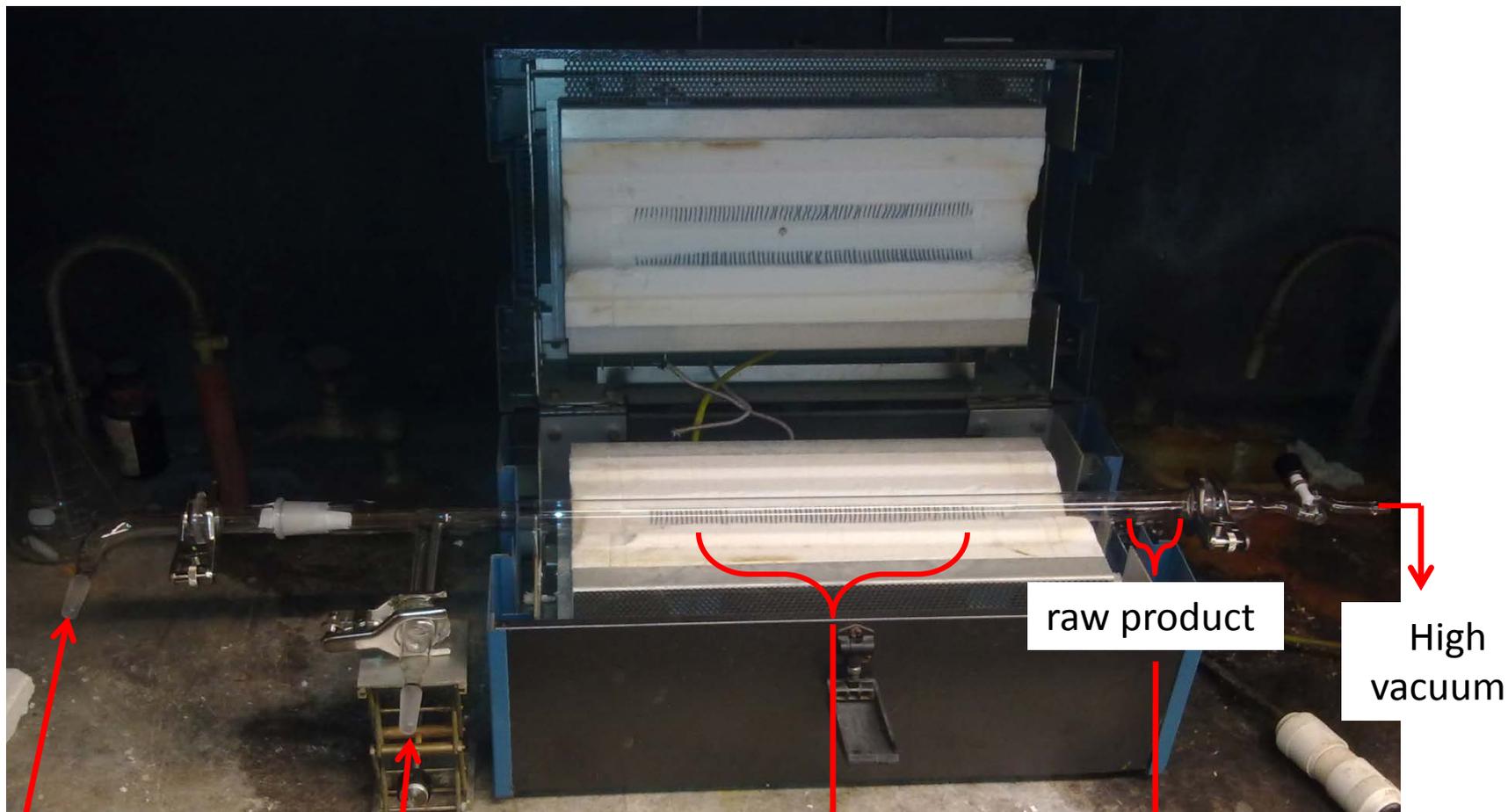
Synthesis of icosaborane-16 ($B_{20}H_{16}$)

(new subcontract with S. Shore, OSU)



Chemistry of Boranes. XXI Icosaborane-16 : N. E. MILLER, J. A. FORSTNER, E. L. MUETTERTIES,
Inorganic Chemistry, **3**, 1690(1964)

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



repeated
sublimation

pure product

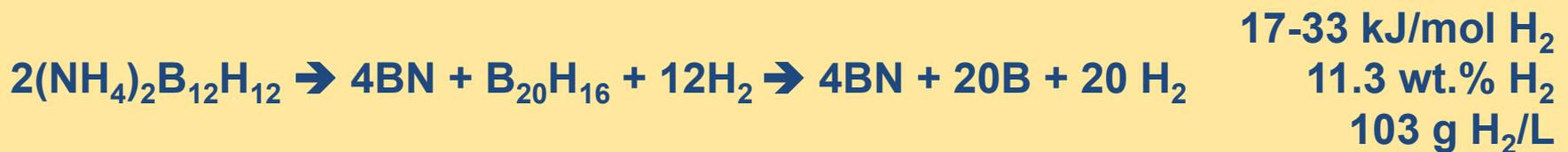
Technical Accomplishments:

Novel, High-Capacity Predicted Reactions

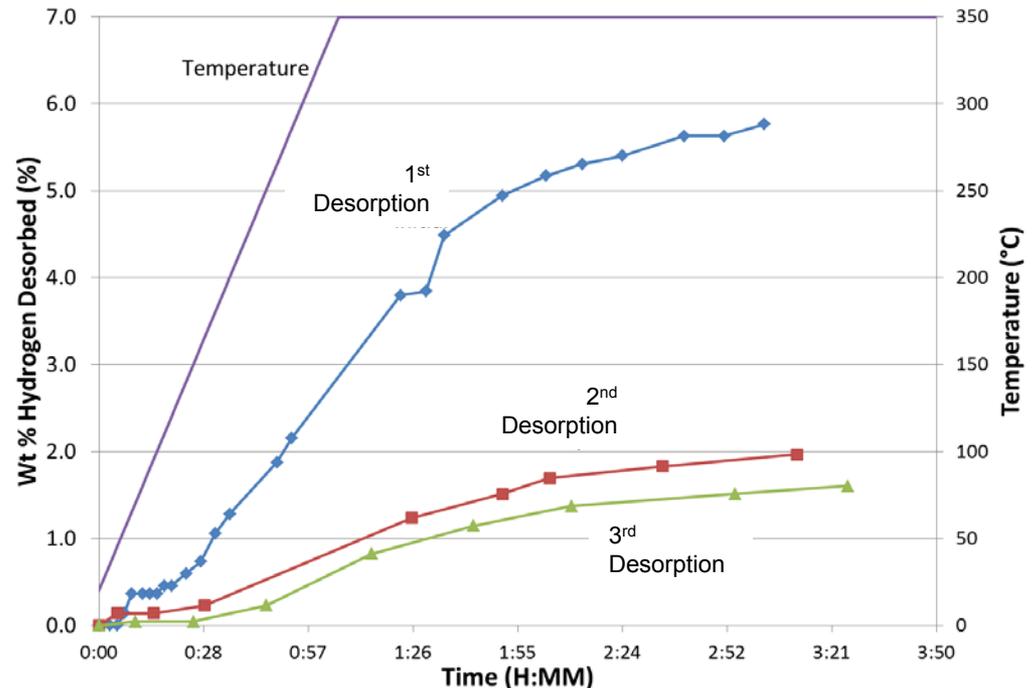
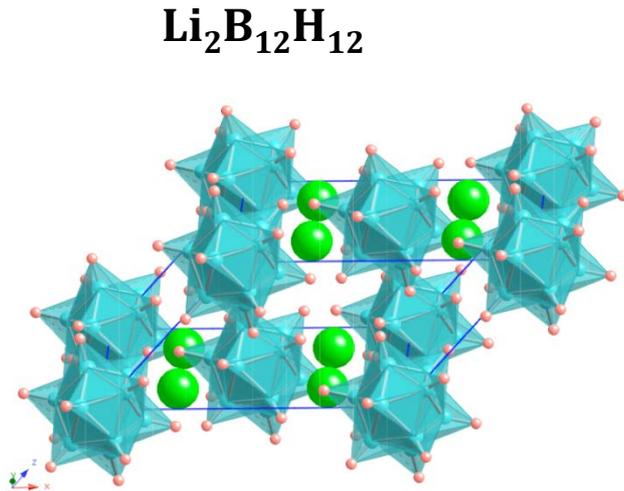
- High-throughput computational screen through all possible high capacity reactions with suitable thermodynamics in Li-Mg-B-N-H quinary.
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$5\text{Mg}(\text{BH}_4)_2 + 2\text{LiBH}_4 \rightarrow 5\text{MgH}_2 + \text{Li}_2\text{B}_{12}\text{H}_{12} + 13\text{H}_2$	8.37	66	24	104
$6\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{MgH}_2 + \text{MgB}_{12}\text{H}_{12} + 13\text{H}_2$	8.10	65	29	100
$\text{B}_{20}\text{H}_{16} \rightarrow 20\text{B} + 8\text{H}_2$	6.95	77	33	111
$5\text{MgH}_2 + \text{MgB}_{12}\text{H}_{12} \rightarrow 6\text{MgB}_2 + 11\text{H}_2$	7.46	81	44	115

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



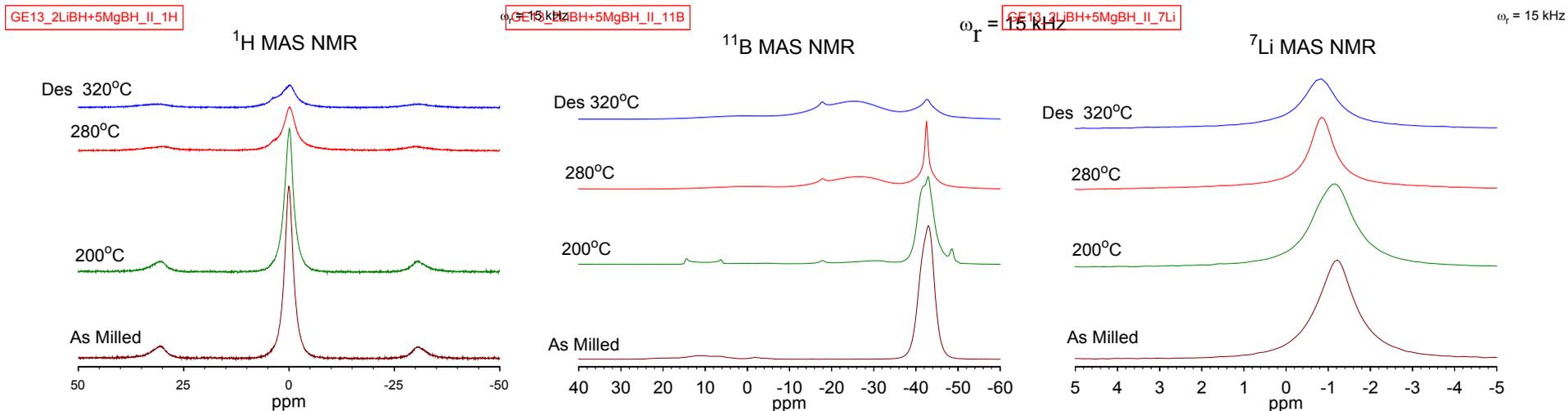
(Previous) Technical Accomplishments: Experimental Testing of Predicted Reactions



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 $2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$

Solid state NMR characterization upon H_2 desorption reactions

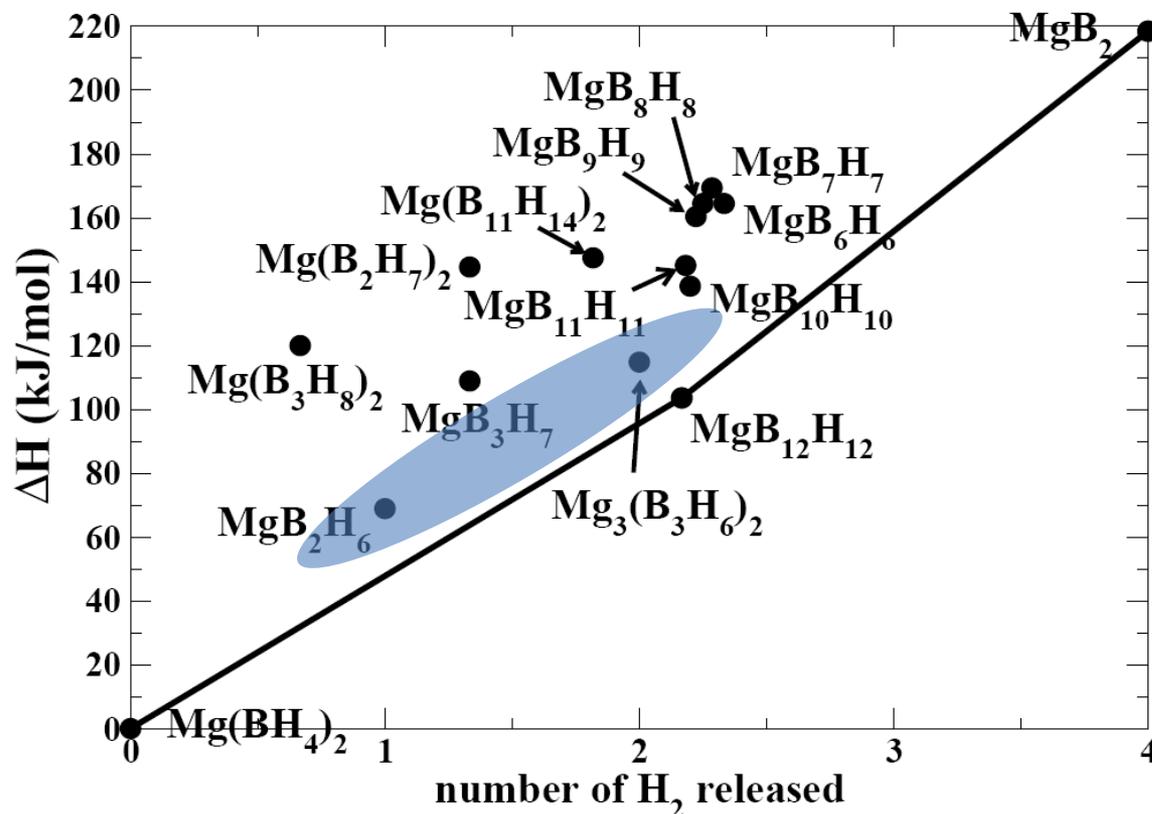


- Multinuclear and high resolution (MAS) solid state NMR experiments
- Samples include the as-milled mixture of 2:5 borohydrides and solid residue after H_2 desorption.
- ^1H and ^{11}B NMR show decrease of BH_4 (~ -41 ppm peak for both LiBH_4 and $\text{Mg}(\text{BH}_4)_2$)
- Desorbed borane species 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 $\text{Li}_2\text{B}_{12}\text{H}_{12}$ of which resonance is expected at -15 ppm.

What are B-containing reaction products observed in NMR?

Computational screen of reaction products in $\text{Mg}(\text{BH}_4)_2$

(from last year)

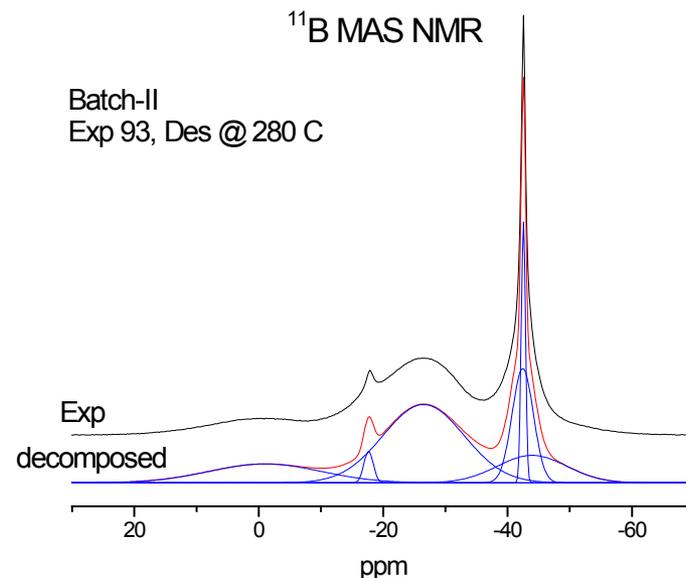
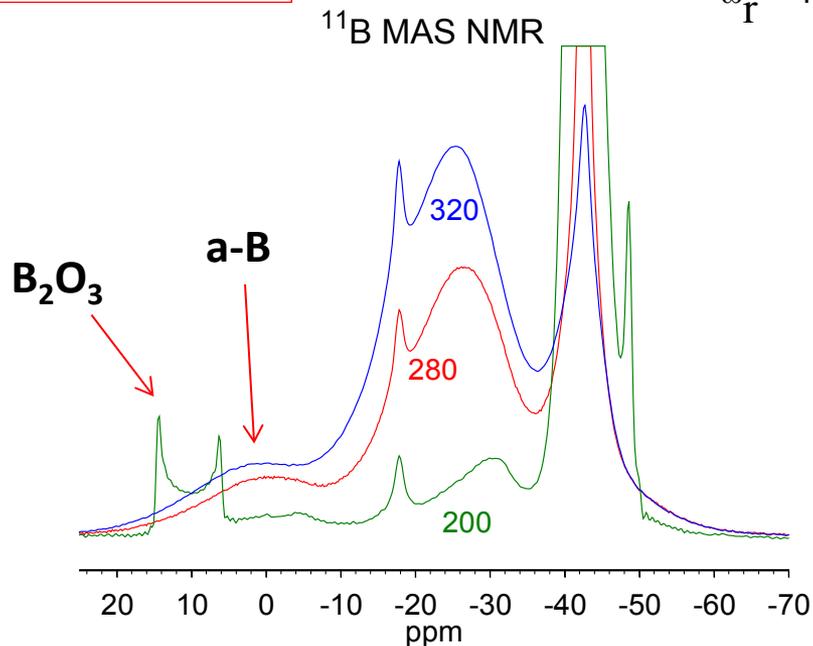


All $[\text{B}_n\text{H}_m]$ intermediates have higher reaction energies than $\text{MgB}_{12}\text{H}_{12}$.
Only the reactions to MgB_2H_6 and $\text{Mg}_3(\text{B}_3\text{H}_6)_2$ are close to the $\text{MgB}_{12}\text{H}_{12}$ convex hull.

Borane species detected by ^{11}B NMR

GE13_2LiBH+5MgBH_II_11B_1

$\omega_r = 15$ kHz



- 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} - $\text{Li}_2\text{B}_2\text{H}_6$, MgB_2H_6
- 17.7 and -48.6 ppm: $\text{Li}_2\text{B}_5\text{H}_9$ or MgB_5H_9 like³

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

¹Hermanek, S. *Chemical Reviews* **1992**, 92 (2), 325-362.

²Godfroid, R. A. et al, *JACS* **1994**, 116 (26), 12107-12108.

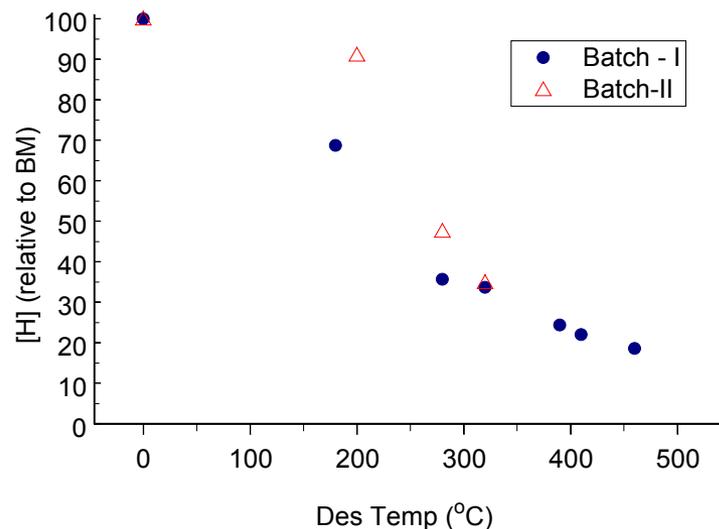
³Yan, Y. et al, *Mater Trans*, **2011**, 52,1443.

$2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$

- At lower temperatures, a ^{11}B peak at -30.5 ppm appeared (200 °C).
- The peak could possibly be assigned to B_3H_8 formation². 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 ^1H 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 ^1H MAS NMR



- Yan, Y et al proposed the following reaction route for $\text{B}_{12}\text{H}_{12}^{2-}$ formation.
- Assigning -26 ppm peak for $\text{B}_2\text{H}_6^{2-}$, and -17.8 and -48.6 ppm peaks for $\text{B}_5\text{H}_9^{2-}$, the sequence of products is inconsistent.

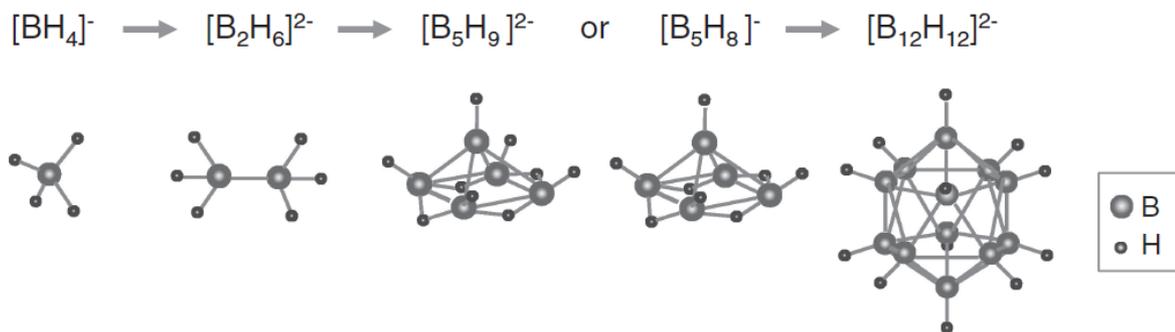


Fig. 4 Schematic illustration of formation process of $[\text{B}_{12}\text{H}_{12}]^{2-}$ from $[\text{BH}_4]^-$.

^{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). ^1H - ^{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)

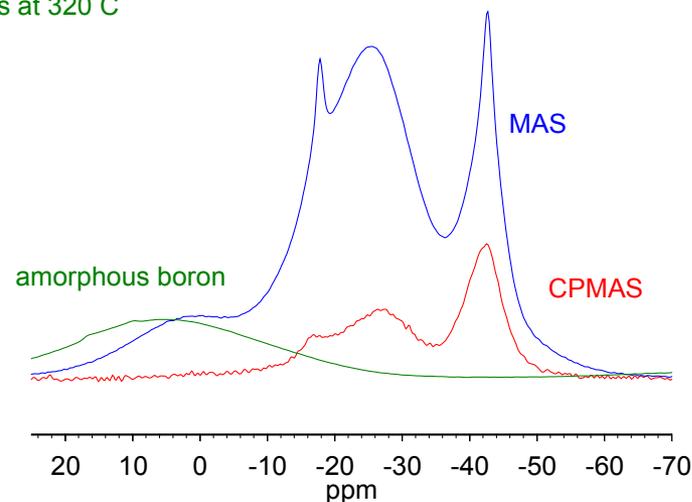
- We still have much to learn in this highly-promising reaction system.

GE13_2LiBH+5MgBH_II_11B_2

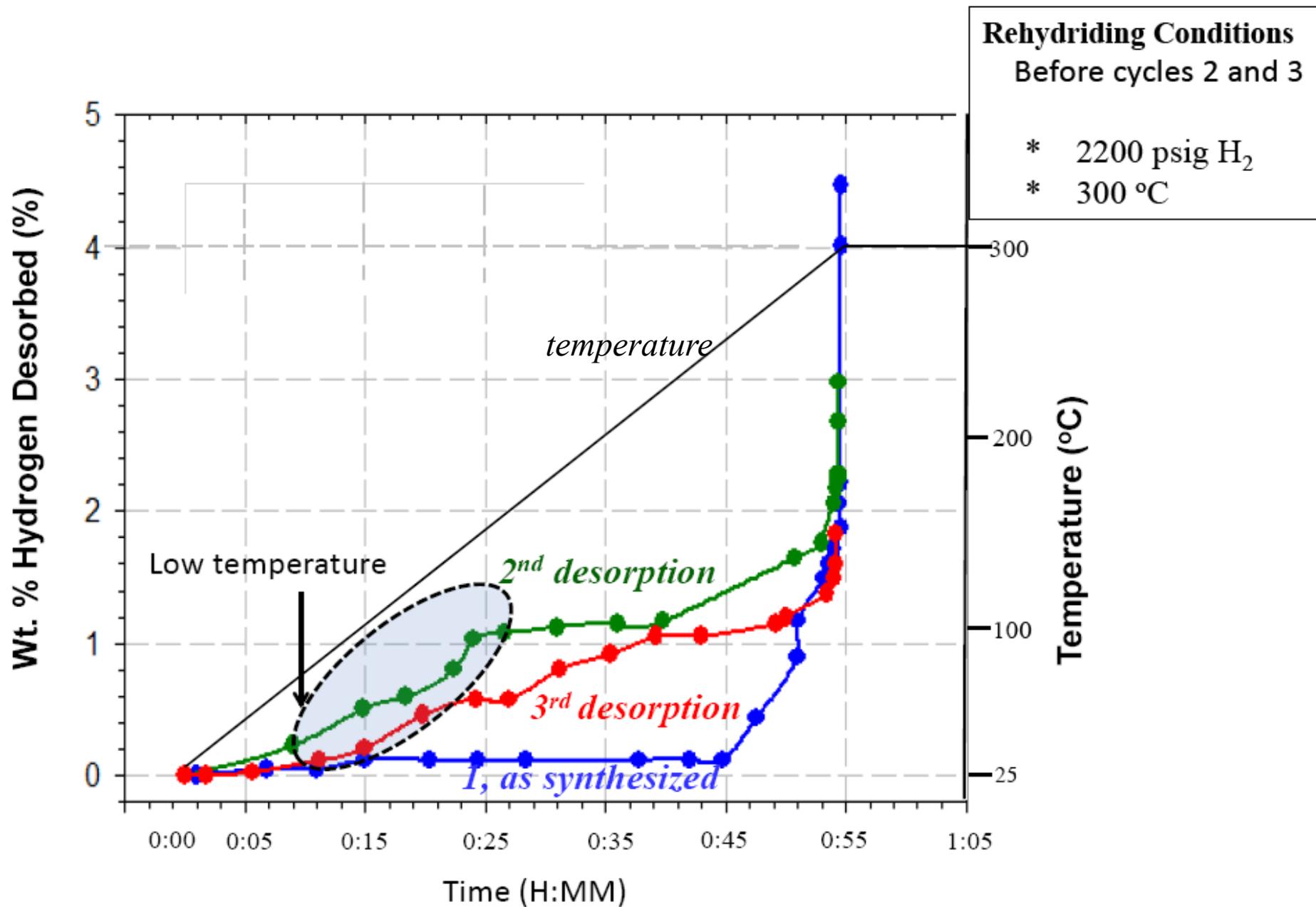
^{11}B MAS NMR

$\omega_{\text{r}} = 15 \text{ kHz}$

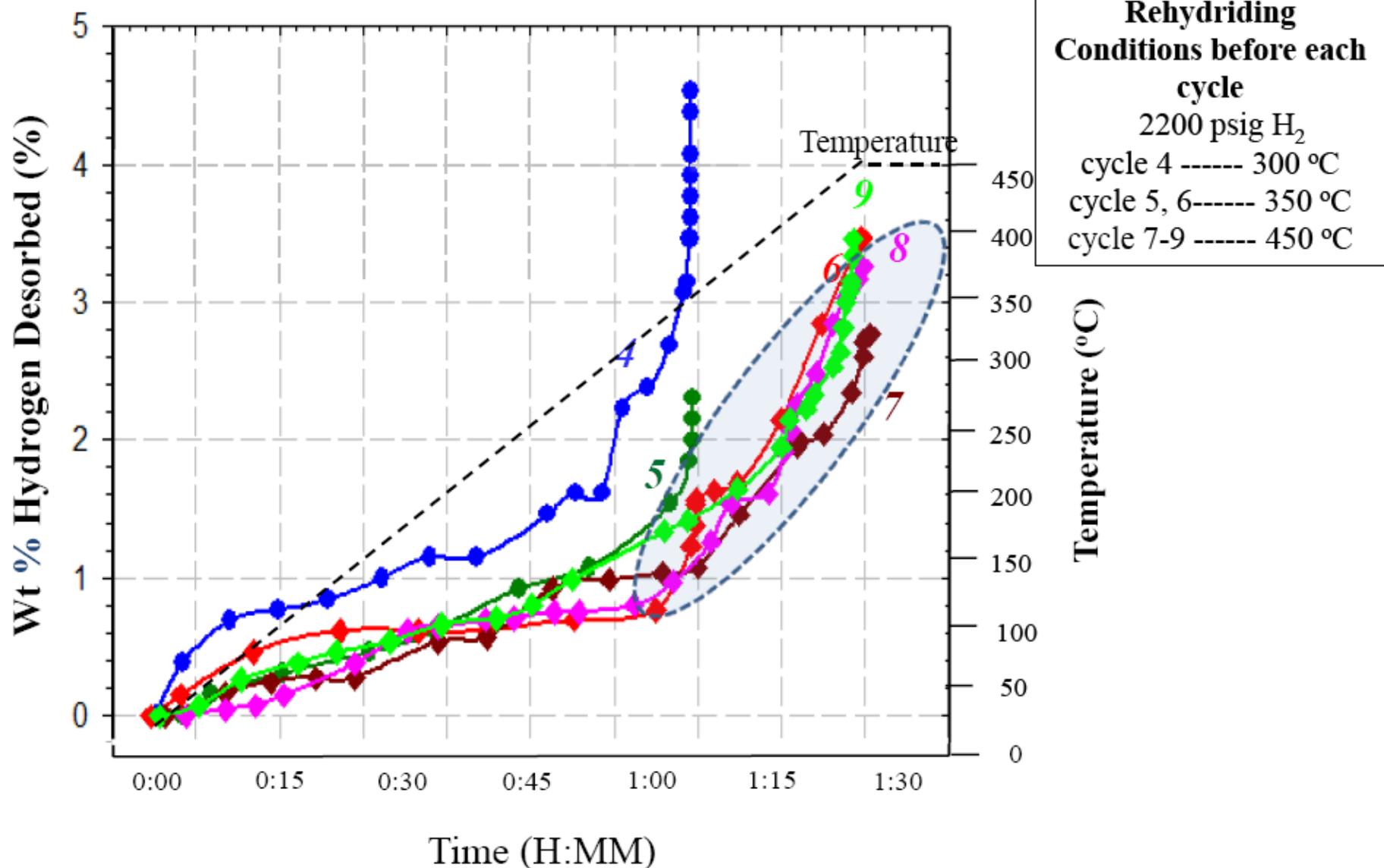
Des at 320 C



LiBH₄-carbon composite hydrogen desorption profiles



LiBH₄-carbon composite H₂ desorption cycles 4-9



Steady and reversible performance can be attained after several dehydrating/rehydrating cycles.

Technical Accomplishments: New Theoretical Predictions

- Kinetics of high-capacity borohydride reactions almost always limiting factor - thermodynamic problems solved by appropriate combinations, i.e., $2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$
- ***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 $\text{B}_{20}\text{H}_{16}$
- H_2 kinetic studies on $\text{MgB}_2(0001)$ surface: dissociation and diffusion

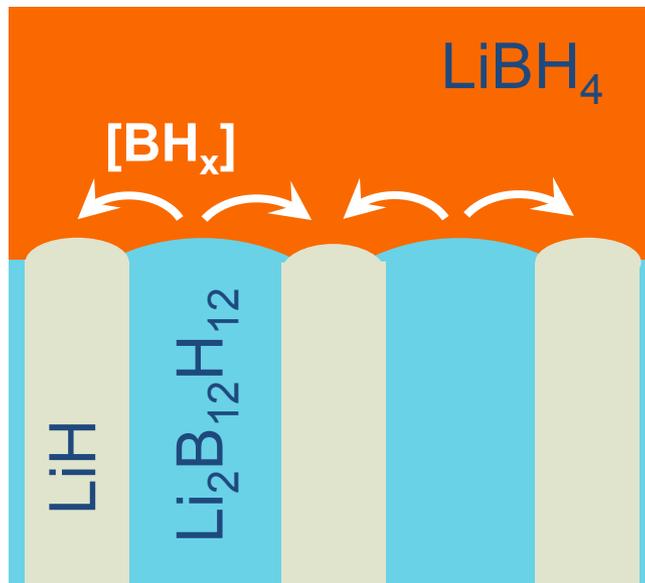
Technical Accomplishments

Mass transport in borohydrides

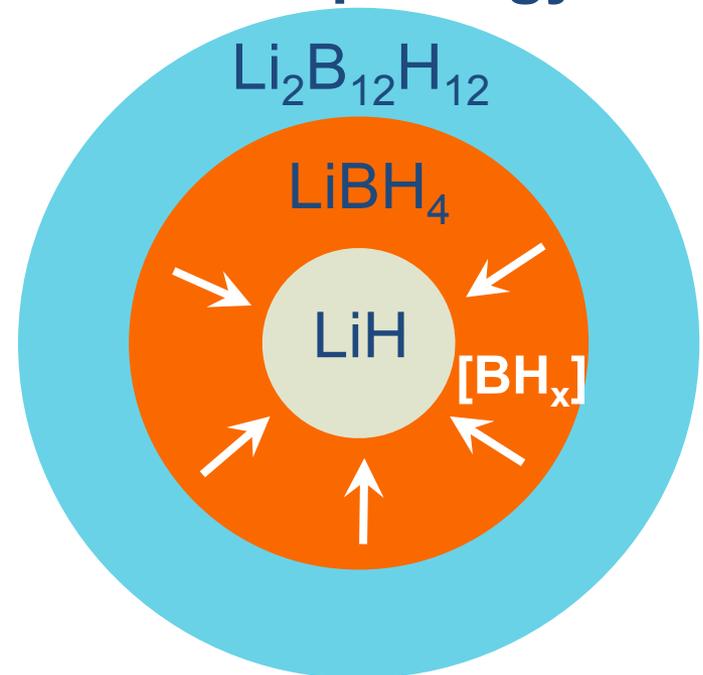
1D morphology



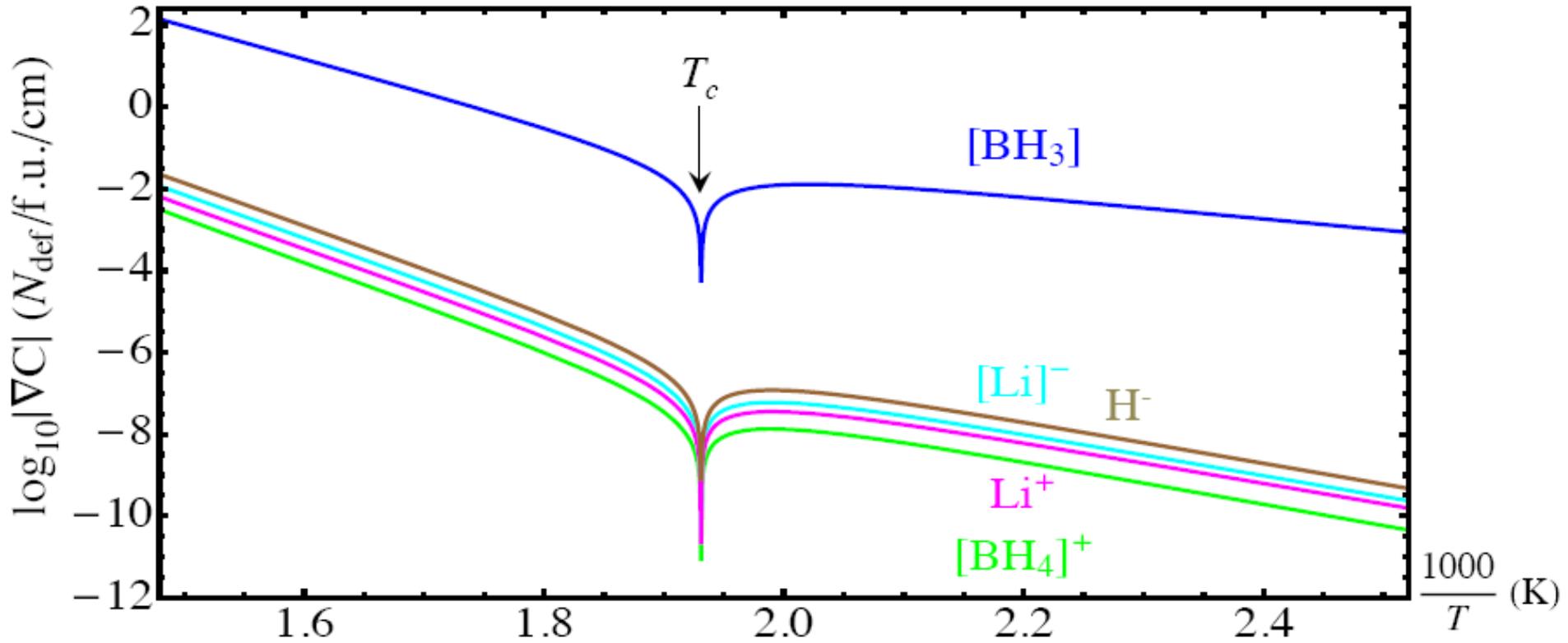
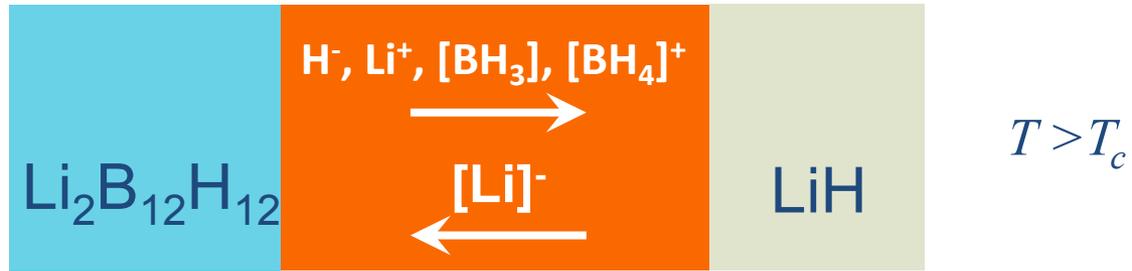
2D morphology



3D morphology



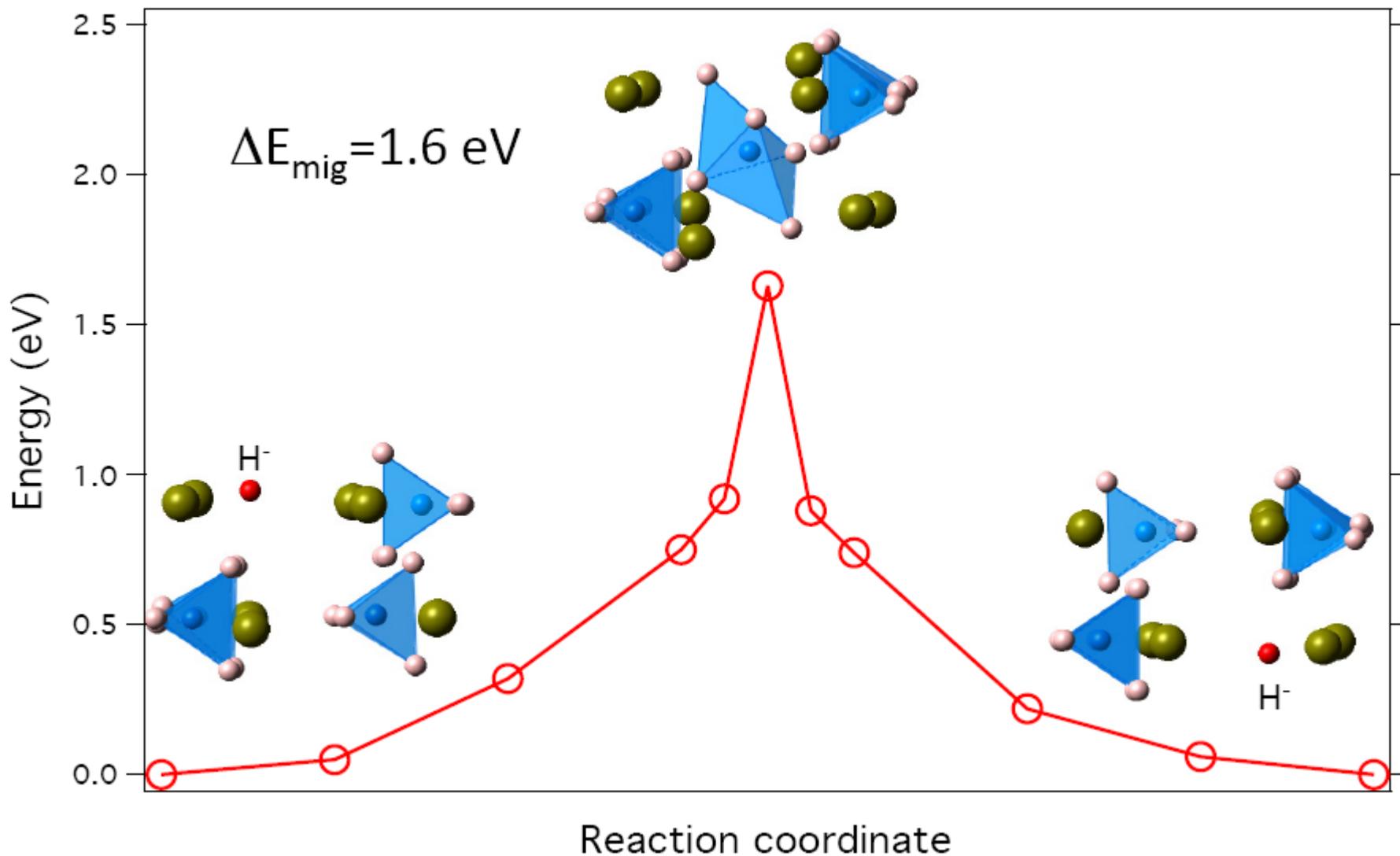
Mass fluxes in LiBH_4



The BH_3 vacancy has the largest concentration gradient.
 But how about D ?

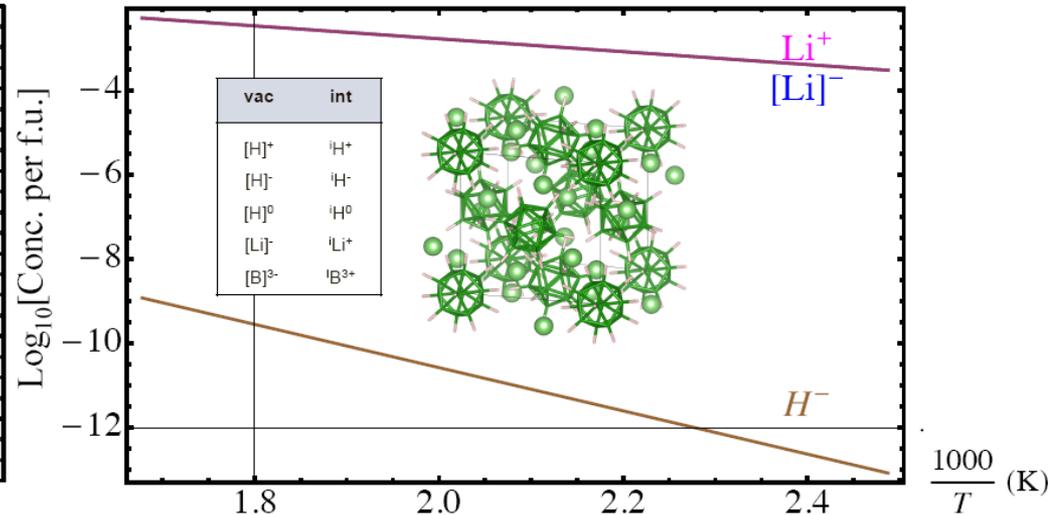
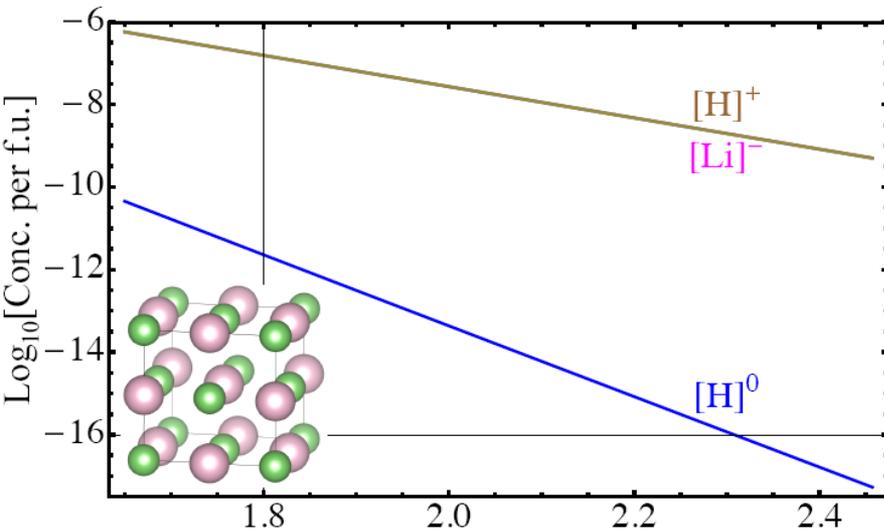
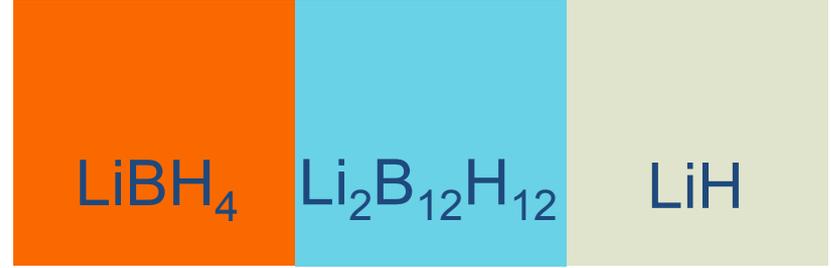
$$\mathbf{J} = -D \vec{\nabla} C$$

Diffusion of $[\text{BH}_3]$ vacancies in LiBH_4



The $[\text{BH}_3]$ vacancy migration barrier in LiBH_4 is very high, 1.6 eV.

Native defects in LiH and Li₂B₁₂H₁₂



Concentration gradients are $\sim 10^5$ times smaller than in LiBH₄

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)



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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 λ -integration)
- Investigate the inclusion of various additives to $LiBH_4$ -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, $2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2$ and $\text{B}_{20}\text{H}_{16}$.
- $\text{B}_{20}\text{H}_{16}$ 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 $\text{B}_{20}\text{H}_{16}$ is fast. Subcontract at OSU focused on synthesis of $\text{B}_{20}\text{H}_{16}$ compound (future plans will focus on desorption, NMR, kinetics, and reaction products – full characterization of this material)
- H₂ desorption and decomposition pathways have been studied in $[2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2]$ 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 $\text{B}_{20}\text{H}_{16}$ is quite high (important for H₂ release from $\text{AlB}_4\text{H}_{11}$), 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 NaAlH₄*, 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(BH₄)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 LiBH₄ structures*, Yongsheng Zhang, Yongli Wang, Kyle Michel and C. Wolverton, Phys. Rev. B **86**, 094111 (2012)
- *Structure determination of an amorphous compound AlB₄H₁₁*, 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 B₂O₃H₁₆*, 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 $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$* , 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 $\text{Ca}(\text{BH}_4)(\text{NH}_2)$ 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 $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$* , W. H. Sun, C. Wolverton, A. R. Akbarzadeh and V. Ozolins, Phys. Rev. B **83**, 064112 (2011).

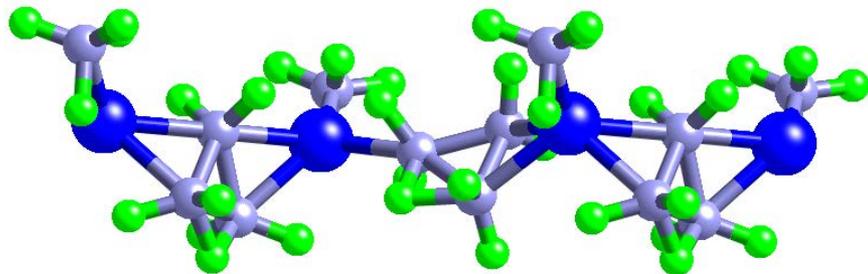
Backup Slides

(Extra information/results not presented due to time constraints)

Technical Accomplishments

mass transport in $\text{AlB}_4\text{H}_{11}$

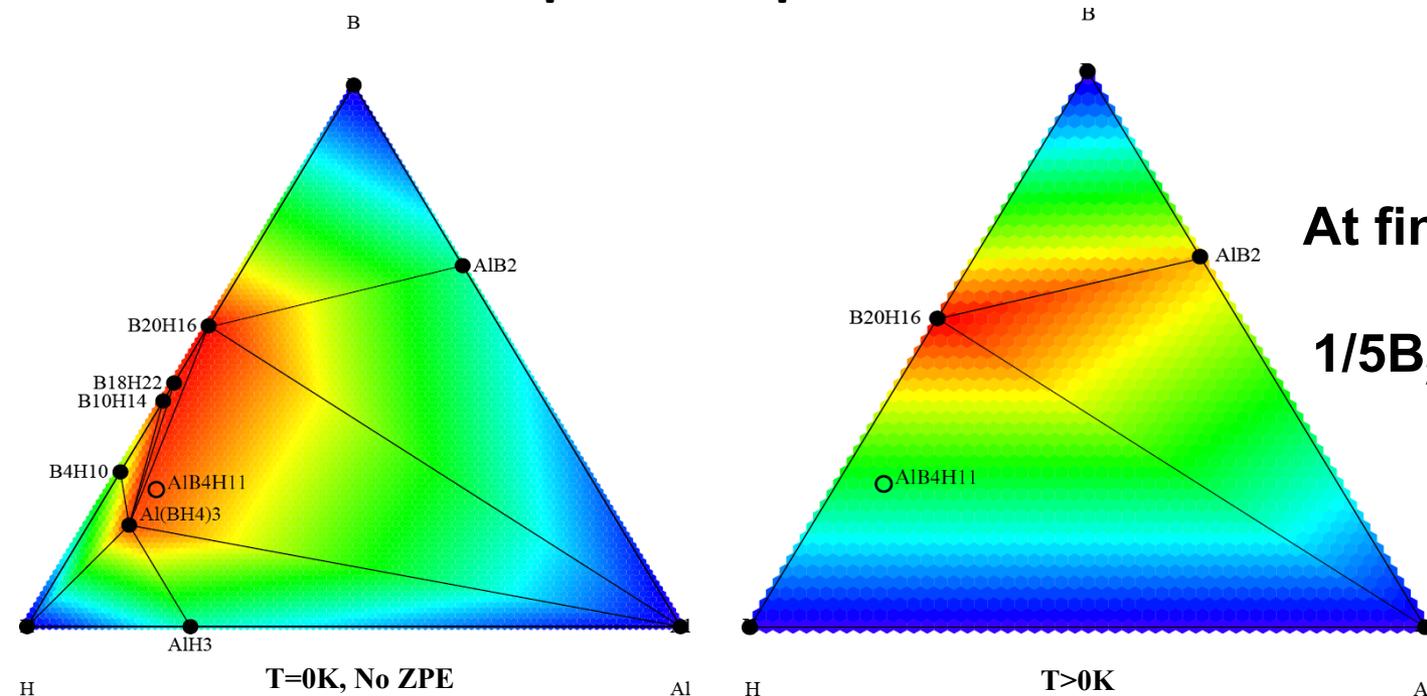
- $\text{AlB}_4\text{H}_{11}$ structure X. Chen et al., Chem. Sci. **3**, 3183 (2012)



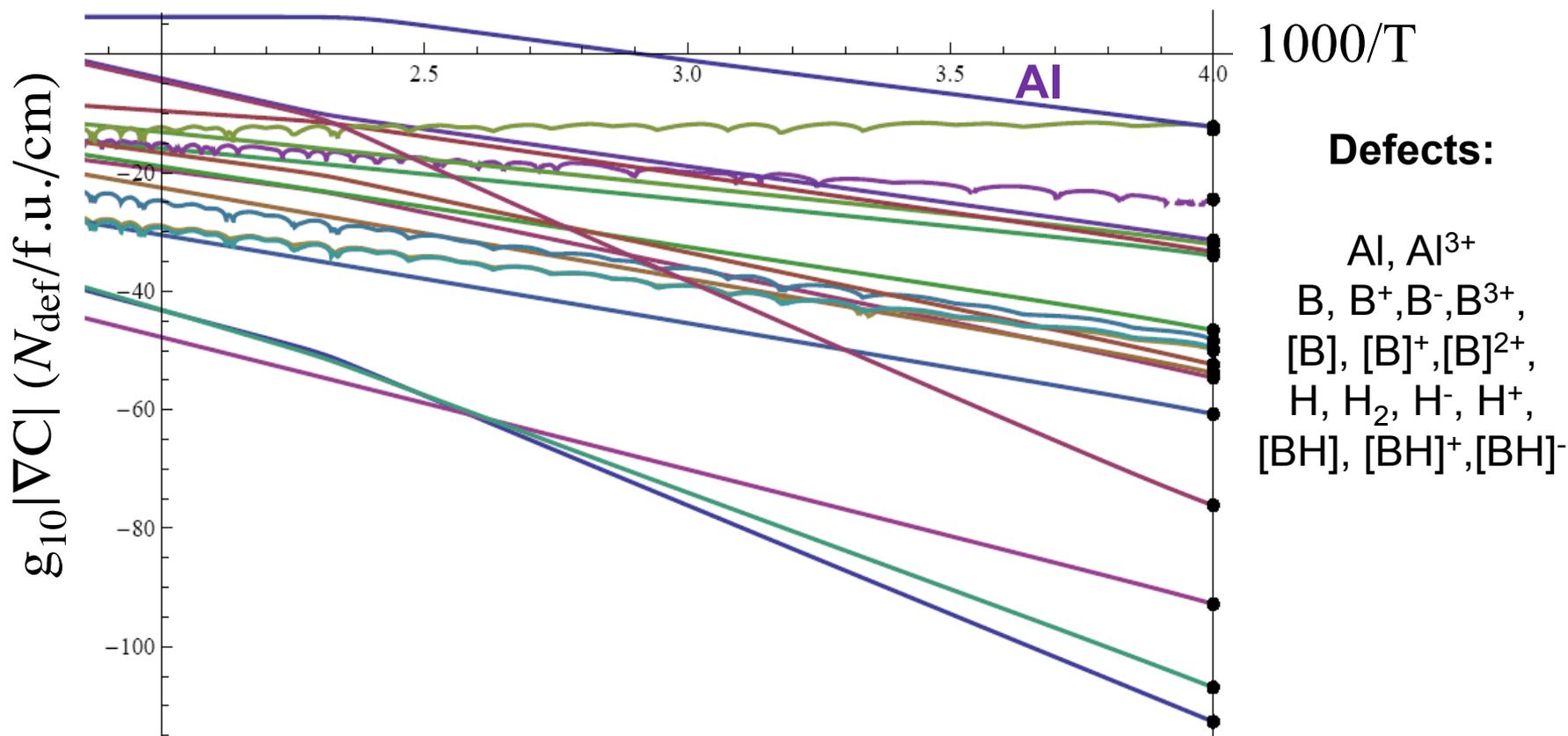
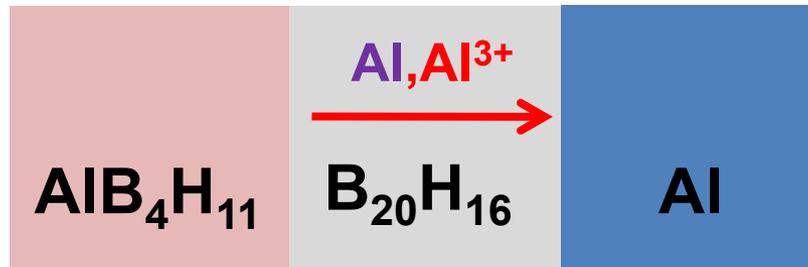
- $\text{AlB}_4\text{H}_{11}$ attractive properties

- High hydrogen content (13.5% H_2)
- Moderate stability
- Decomposition temperature $\sim 125^\circ\text{C}$
- Endothermic dehydrogenation
- Rehydrogenation at moderate conditions

- Unknown decomposition products

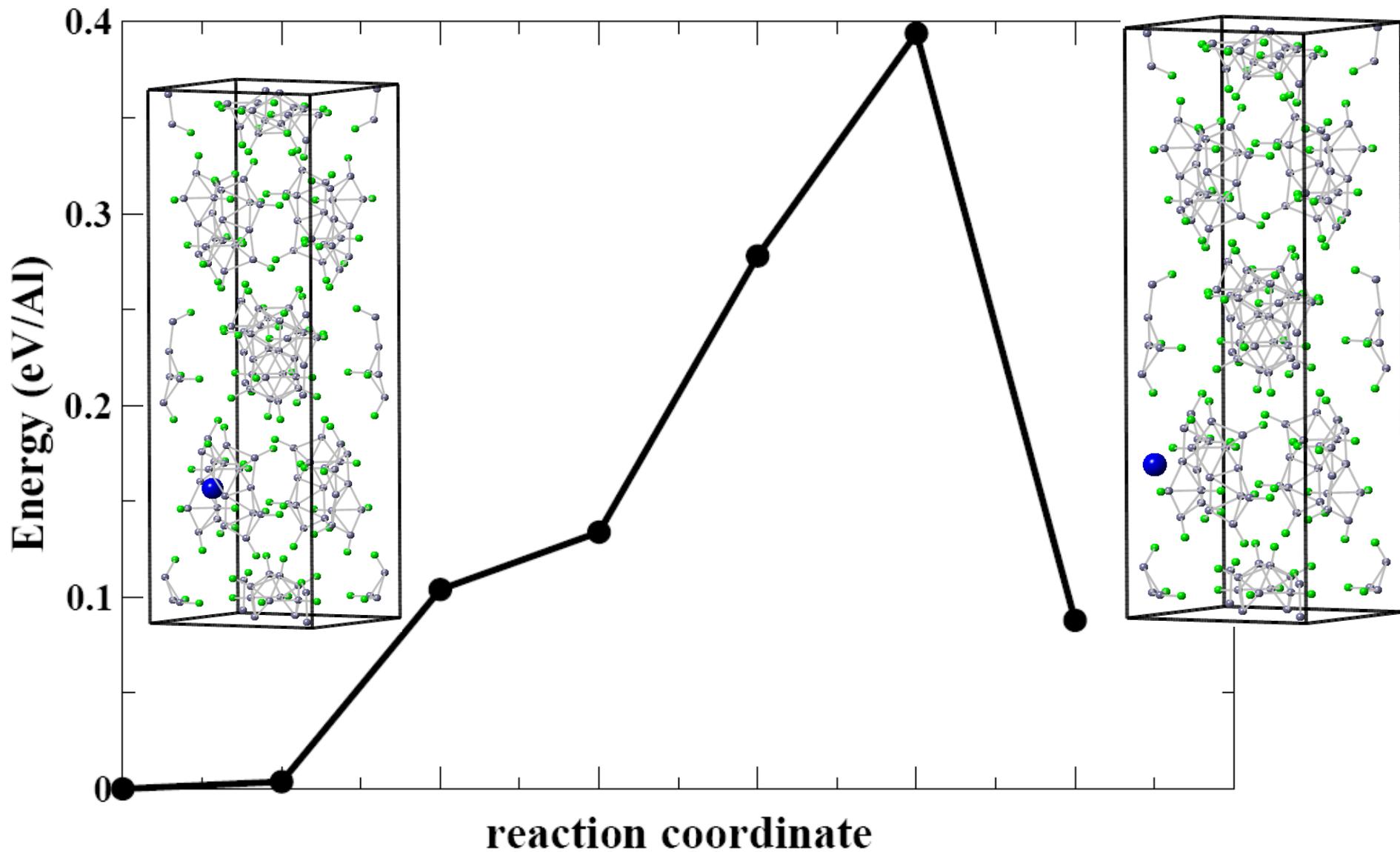


Mass fluxes in $B_{20}H_{16}$



The Al interstitial has the largest concentration gradient.

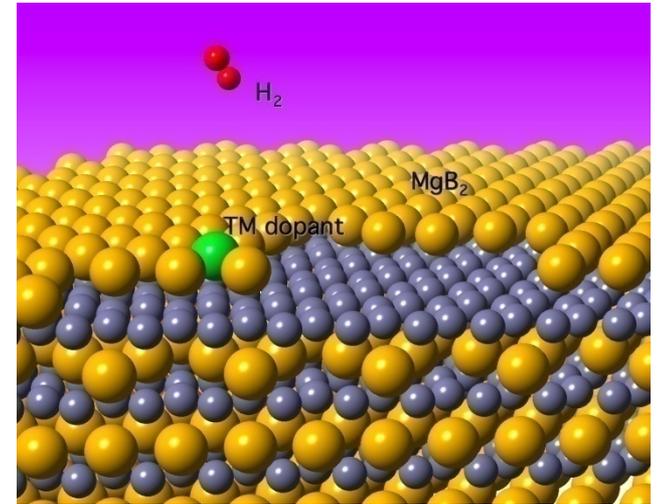
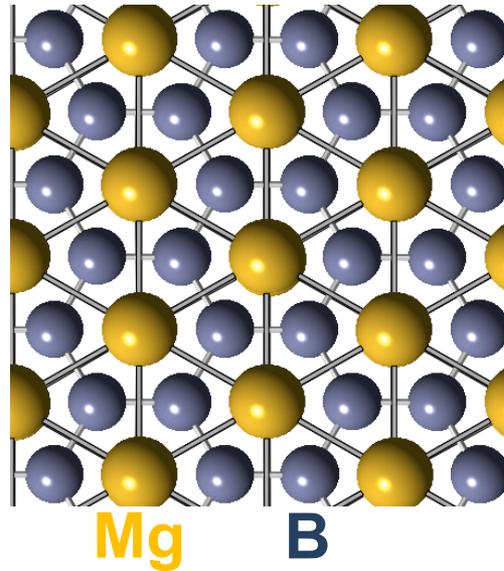
Al migration barrier in $B_{20}H_{16}$: preliminary results



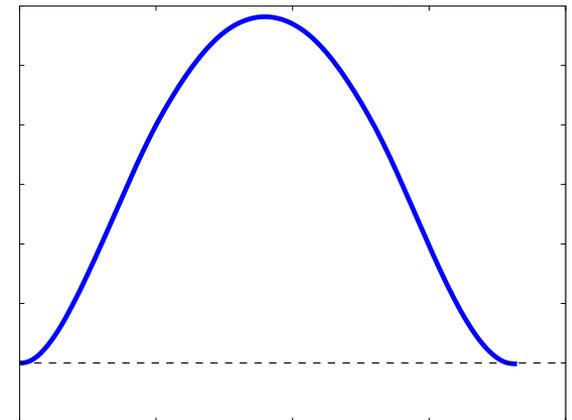
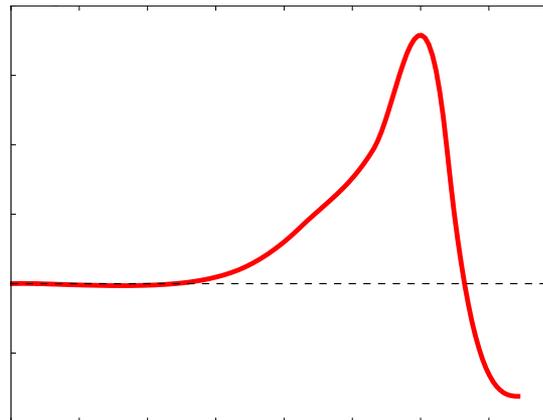
The Al migration barrier in $B_{20}H_{16}$ is low, ~ 0.4 eV.

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?)



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).

