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
- Project End Date: 8/31/13

(1 year no-cost extension to 8/31/14)

- ~100% complete

Budget

- Total Project Value: $2,714,400
- Cost Share: $554,400
- DOE Share: $2,160,000
- DOE Funding Spent*: $2,092,372
- *as of 3/31/14

Barriers

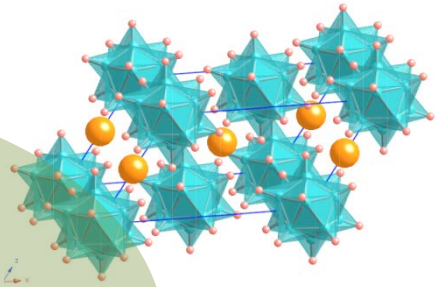
- Barriers addressed
  - O. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

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

Computational Screening of Reactions – Thermodynamics and Kinetics

- **Tools for Computational Prediction of New Materials/Reactions**
  - (High-Throughput) Density Functional Theory:
    - Open Quantum Materials Database (OQMD) - Wolverton
  - Crystal Structure Prediction:
    - Prototype Electrostatic Ground State (PEGS) – Majzoub and Ozolins
  - Prediction of Decomposition Pathways:
    - Grand Canonical Linear Programming (GCLP) – Ozolins and Wolverton

Note: None of these tools were developed in the current project. They were either developed previously or in other projects, but utilized/leveraged here.

Computational Screening of Reactions – Thermodynamics and Kinetics

We have used DFT+computational tools to look for reactions in many systems:

- **B-N-H** (Phys. Rev. B **83**, 064112 (2011); **84**, 099902 (2011))
- **Li-Mg-N-H** (Advanced Materials **19**, 3233 (2007))
- **Li-Al-N-H** (in prep, 2013)
- **Li-Mg-Al-H** (Phys. Rev. B **79**, 184102 (2009))
- **Mg-B-N-H** (in press, 2014)
- **Ca-B-N-H** (Phys. Rev. B **84**, 134103 (2011))
- **Li-Zn-B-H, Na-Zn-B-H** (Phys. Rev. B **83**, 144111 (2011); submitted, 2013)
- **Li-Mg-Ca-B-H** (J. Amer. Chem. Soc. **131**, 230 (2009))
- **Li-Mg-B-N-H** (unpublished)

Rather than doing this one system at a time…
Can we just compute <u>all possible storage reactions</u>, involving all known crystalline phases?

High-Throughput Discovery of <u>All Possible</u> Storage Reactions

Open Quantum Materials Database (OQMD)

- **<u>Open</u>** – An online (oqmd.org), freely available database…
- **<u>Quantum</u>** – … of self-consistently DFT-calculated properties…
- **<u>Materials</u>** – … for ~30,000 experimentally observed and 250,000 hypothetical structures…
- **<u>Database</u>** – … built on a standard and extensible database framework.

Scan over hundreds of possible alloy systems; For each system, need to compute (quickly) ground state hull of all combinations of known phases at all stoichiometries.

Saal, Kirklin, Aykol, Meredig, and Wolverton "*Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Mechanical Database (OQMD)*", JOM **65**, 1501 (Nov. 2013)

Technical Accomplishments: High-Throughput Discovery of <u>All Possible</u> Thermodynamic Storage Reactions

How many thermodynamically-allowed H_2 storage reactions are there?

- Any compound in the ICSD with elements from
  {H, Li, B, N, Na, Mg, Al, Si, K, Ca, Sc, Ti} (and unit cell < 60 atoms)
  832 total phases considered, 171 contained hydrogen

- <u>Total Reactions</u>
  4212 reactions (with ΔH < 150 kJ/mol H_2)
- <u>Reactions w/ good enthalpy</u>
  434 reactions with ΔH between 20-40 kJ/mol H_2
- <u>Reactions w/ high capacity</u>
  108 reactions with > 6 wt. % H_2
  43 reactions with > 8 wt. % H2
- <u>Reactions w/ good enthalpy and high capacity</u>
  22 reactions with ΔH 20-40 kJ/mol H_2, > 6 wt. %
  7 reactions with ΔH 20-40 kJ/mol H_2, > 8 wt. %

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)

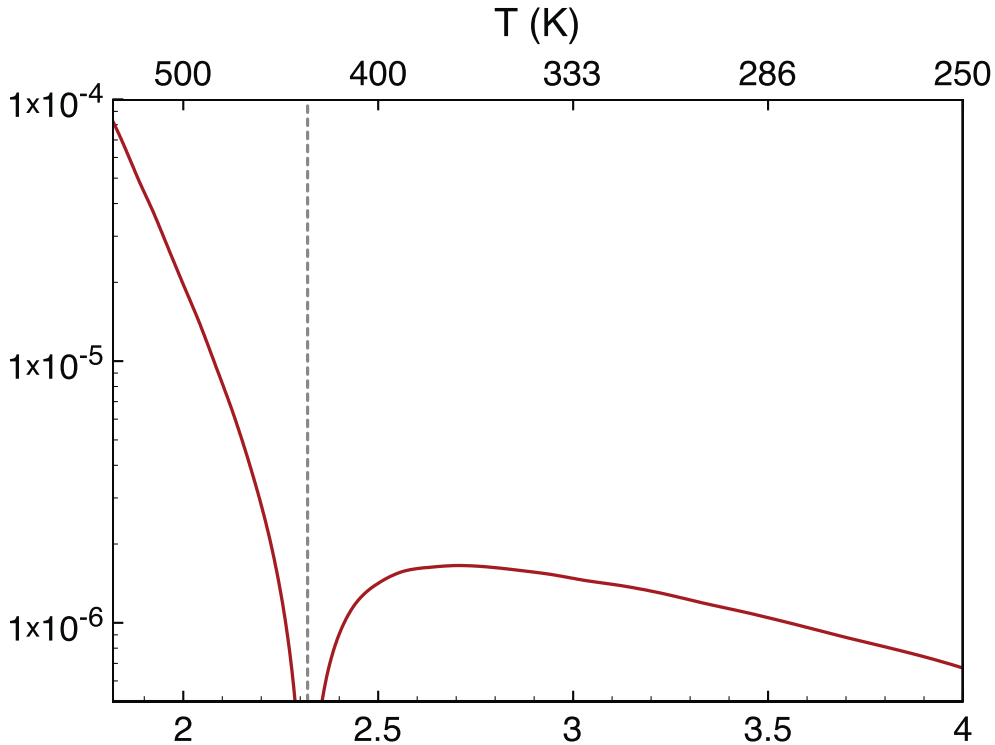
Reactions	Wt.% H_2	Vol. H_2 (g H_2/L)	ΔH^{300K} (kJ/mol H_2)	ΔS^{300K} (J/mol-K)
$2(NH_4)_2B_{12}H_{12} \rightarrow 4BN + B_{20}H_{16} + 12H_2$	**6.81**	**62**	**17**	**104**
$5Mg(BH_4)_2 + 2LiBH_4 \rightarrow 5MgH_2 + Li_2B_{12}H_{12} + 13H_2$	**8.37**	**66**	**24**	**104**
$6Mg(BH_4)_2 \rightarrow 5MgH_2 + MgB_{12}H_{12} + 13H_2$	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

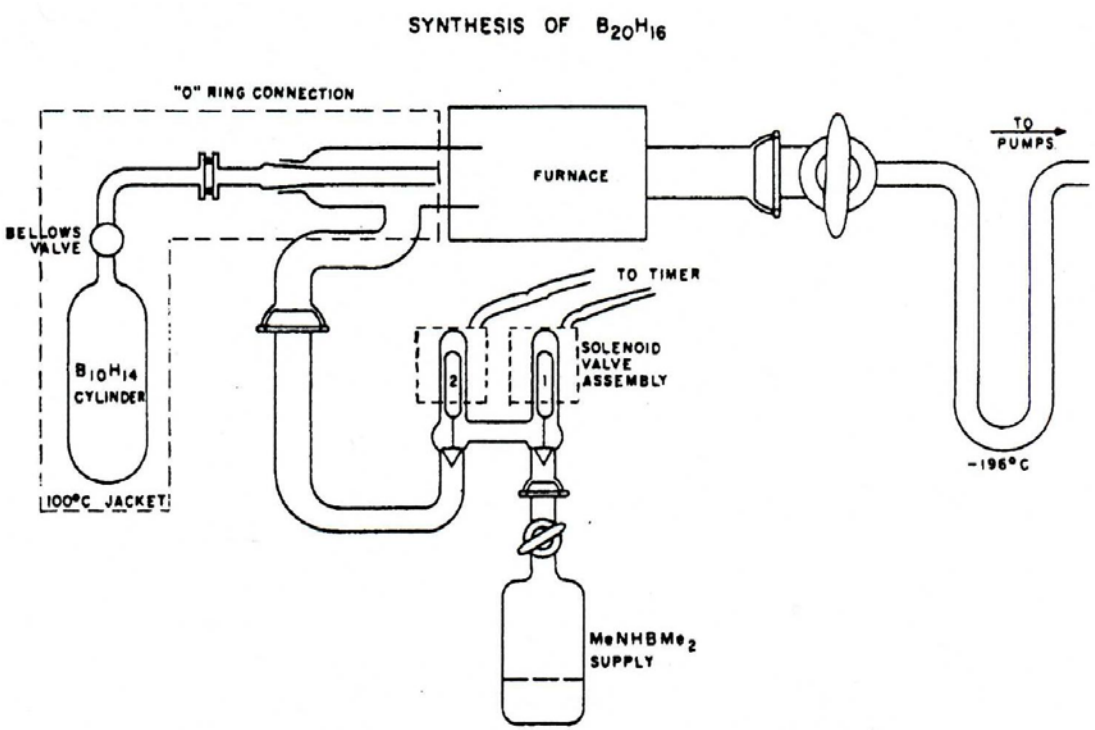
Technical Accomplishments (previous): Interstitial H_2 flux in $B_{20}H_{16}$ and mass transport activation energy



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 ($B_{20}H_{16}$)
(subcontract with S. Shore, OSU)

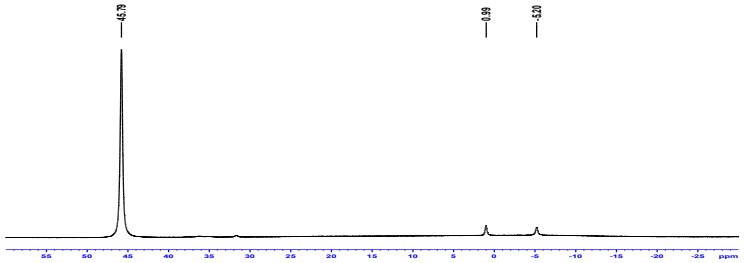


- Several methods have been reported for the preparation of icosaborane-16 ($B_{20}H_{16}$) but they were carried out under extreme conditions and with low yields 9 to 15%.
- No commercial source is available.
- The method we used in this project is the modified catalytic pyrolysis of decaborane-14 ($B_{10}H_{14}$). The reported yields for this procedure range from 10 to 15 % [1].

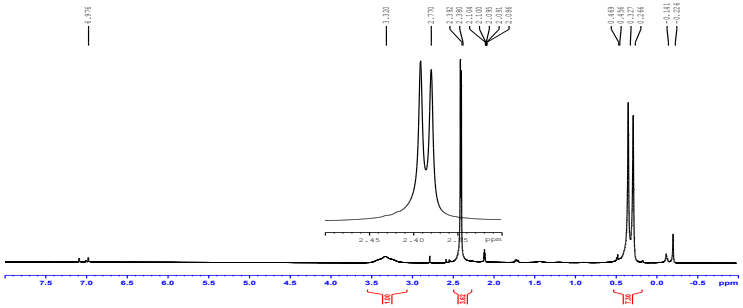
Chemistry of Boranes. XXI Icosaborane-16 : N. E. MILLER, J. A. FORSTNER, E. L. MUETTERTIES, *Inorganic Chemistry*,**3**,1690(1964)

Technical Accomplishments:
Synthesis of icosaborane-16 ($B_{20}H_{16}$) – (Shore, OSU)

- **The synthesis of catalyst, methylaminodimethylborane ($NHMeBMe_2$)**



^{11}B NMR spectrum of $MeHN{=}BMe_2$ in d_8-toluene

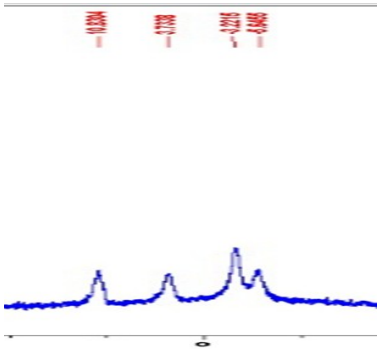


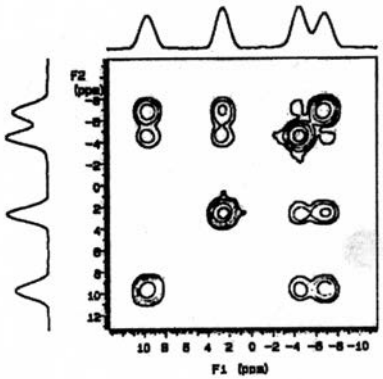
^{1}H NMR spectrum of $MeHN{=}BMe_2$ in d_8-toluene

- **The synthesis of icosaborane-16**

- **The collection and characterization of icosaborane-16**

^{11}B NMR spectrum of icosaborane-16 in CH_2Cl_2 (prepared in Dr.Shore's group) (NMR peaks: 10.8 , 3.7 , -3.2 , -5.6)





^{11}B NMR 2D spectrum of icosaborane-16[2]

[2]. D.Hnyk, et al, *Collect. Czech. Chem. Commun.* , **Vol.75**, No.11, pp. 1115-1123,2010.

Synthesis of icosaborane-16 ($B_{20}H_{16}$) – (Shore, OSU)

Notes about synthesis

- We obtained 46mg product, which the yield is about 5%.
- Ran out of funds/time before characterization other than NMR could be performed.
- We have employed all of the conditions of experiment described in the published paper on the B20 synthesis but produce yields significantly less than those reported in the literature.
- Possible that the material for the catalyst, which we purchased, is not good, or perhaps problems with the temperature for making the catalyst active as listed in the literature.

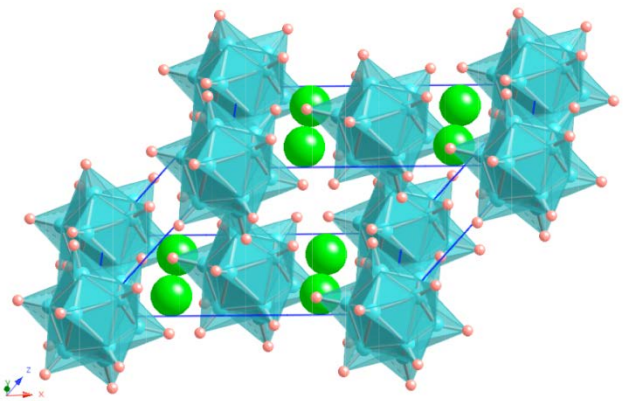
Icosaborane-16 ($B_{20}H_{16}$) – Conclusions and Suggested Future Work

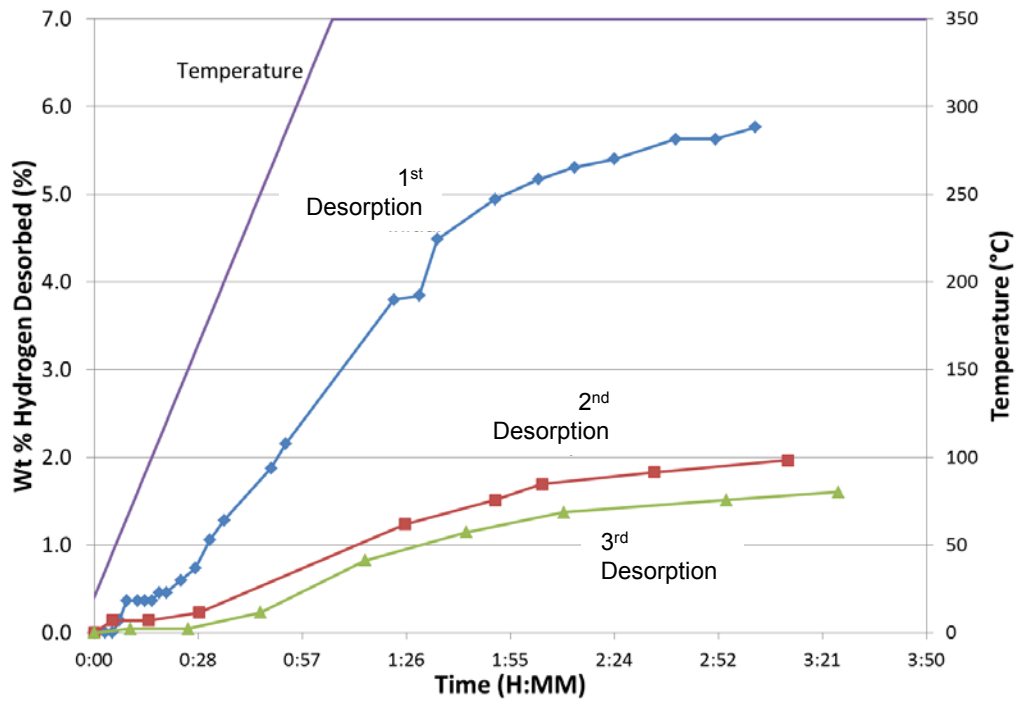
- $B_{20}H_{16}$ unique and potentially very interesting: *<u>Only</u> H_2 storage reaction of known compound with 1) high capacity, 2) good thermodynamics, and 3) predicted fast mass transport kinetics*
- Of course, there are drawbacks, but because of this unique combination of characteristics, recommend that more future work on this reaction is warranted.
- Synthesis proved difficult, with low yield.
- Future experimental work should try to validate predicted beneficial attributes of material; if validated, more focused effort should be performed to overcome any potential drawbacks (e.g., low yield synthesis, low-cost synthesis, possible kinetic limitations)

(Previous) Technical Accomplishments: Experimental Testing of Predicted Reactions

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

$Li_2B_{12}H_{12}$



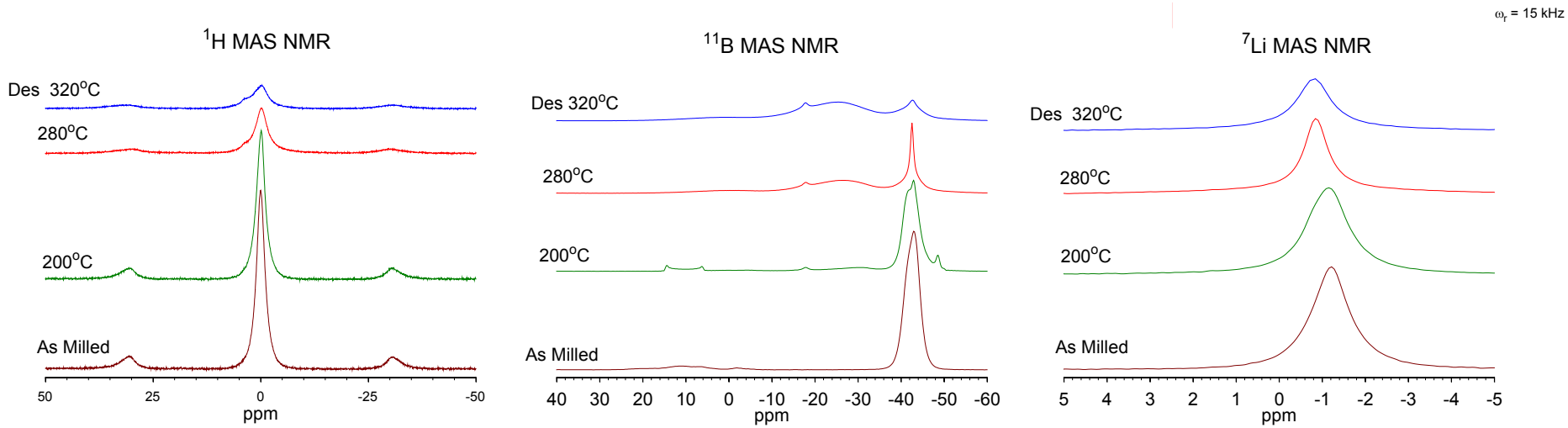


What are (non-crystalline) reaction products? Do they inhibit reversibility?

(NMR subcontract with S. Hwang, Caltech)

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

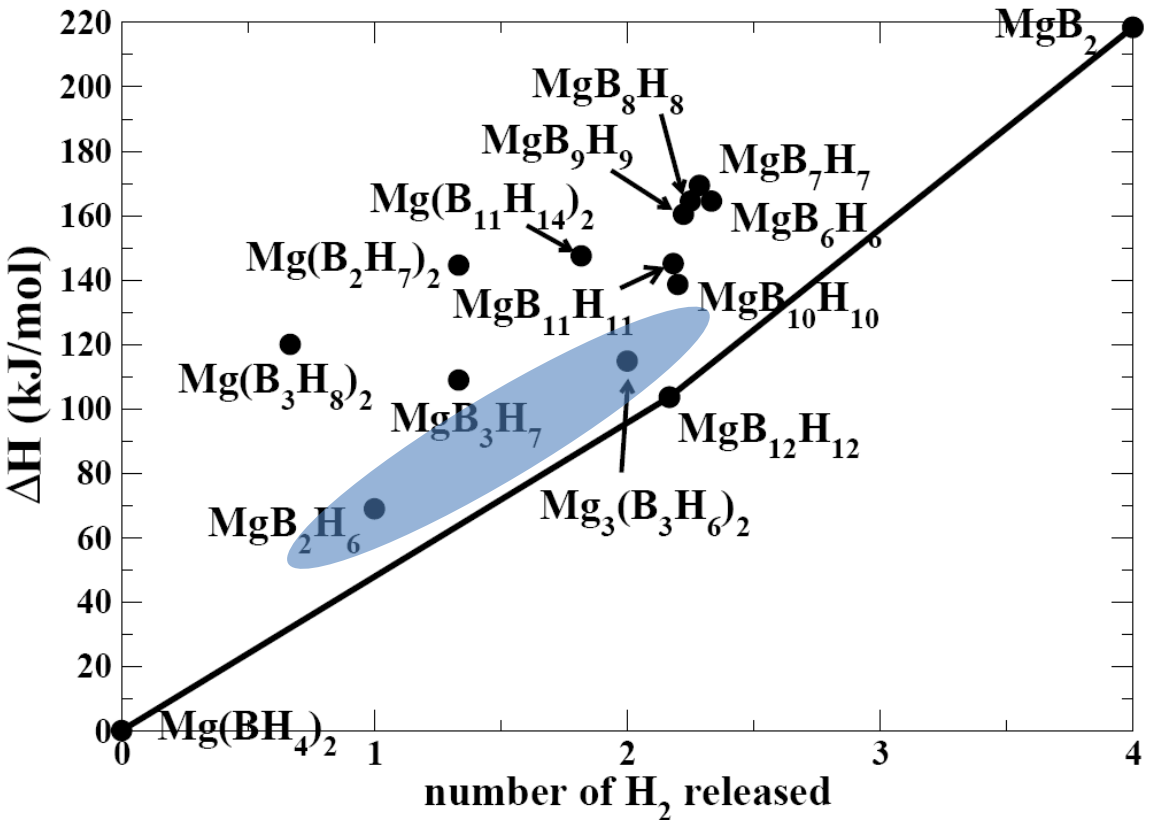
Solid state NMR characterization upon H_2 desorption reactions



- 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 $Mg(BH_4)_2$

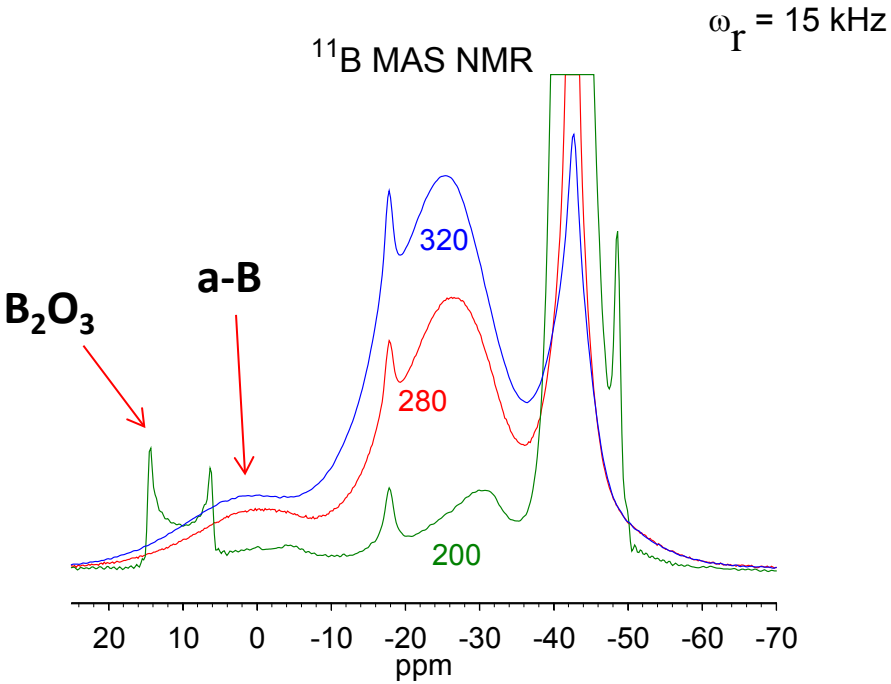
(from 2012)

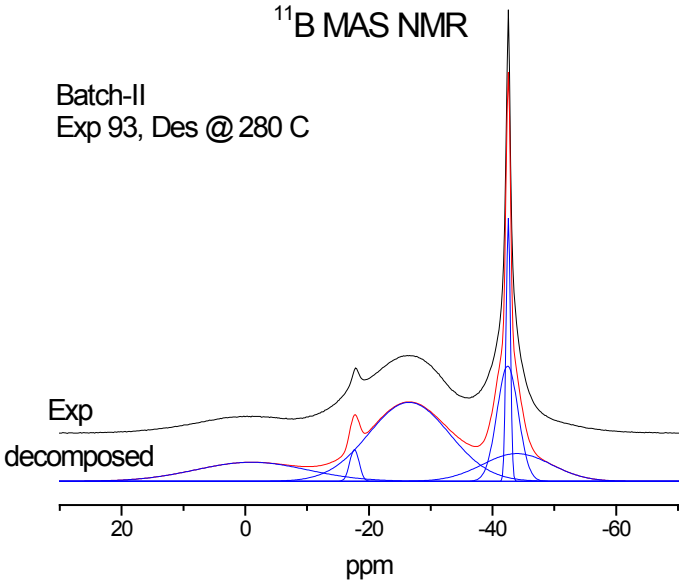


All $[B_nH_m]$ intermediates have higher reaction energies than $MgB_{12}H_{12}$.
Only the reactions to MgB_2H_6 and $Mg_3(B_3H_6)_2$ are close to the $MgB_{12}H_{12}$ convex hull.

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

Borane species detected by ^{11}B NMR





- 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] - **$Li_2B_2H_6$, MgB_2H_6**

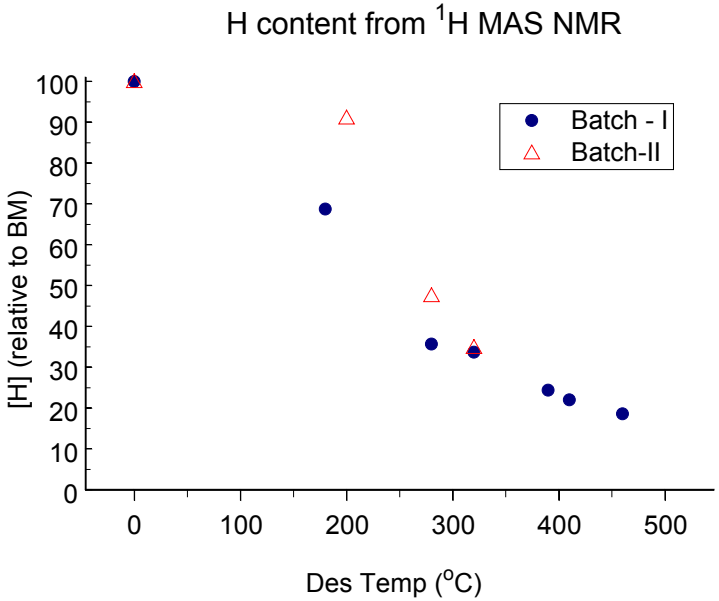
- -17.7 and -48.6 ppm: $Li_2B_5H_9$ or MgB_5H_9 like[3]

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_3H_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 ^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.



- Yan, Y et al proposed the following reaction route for $B_{12}H_{12}^{2-}$ formation.
- Assigning -26 ppm peak for $B_2H_6^{2-}$, and -17.8 and -48.6 ppm peaks for $B_5H_9^{2-}$, the sequence of products is inconsistent.

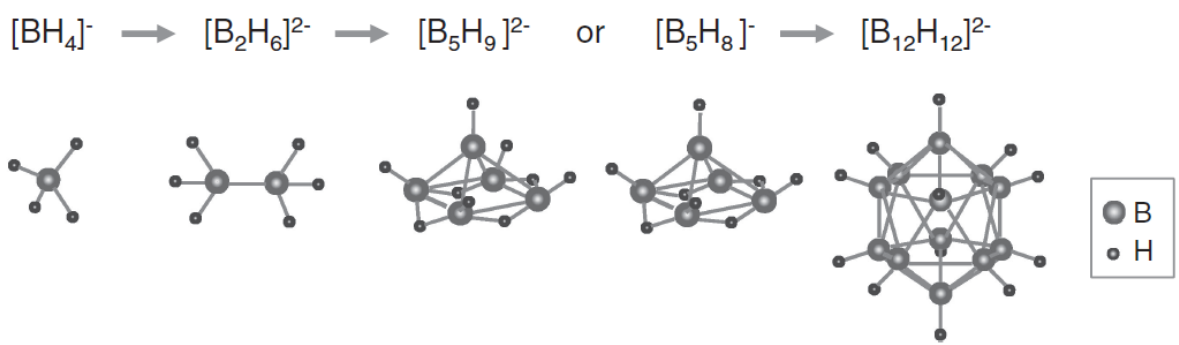


Fig. 4 Schematic illustration of formation process of $[B_{12}H_{12}]^{2-}$ from $[BH_4]^-$.

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.

Technical Accomplishments: ^{11}B NMR calculations – Using DFT to help interpret NMR experimental data

Collaboration w/ C. Pickard, UCL

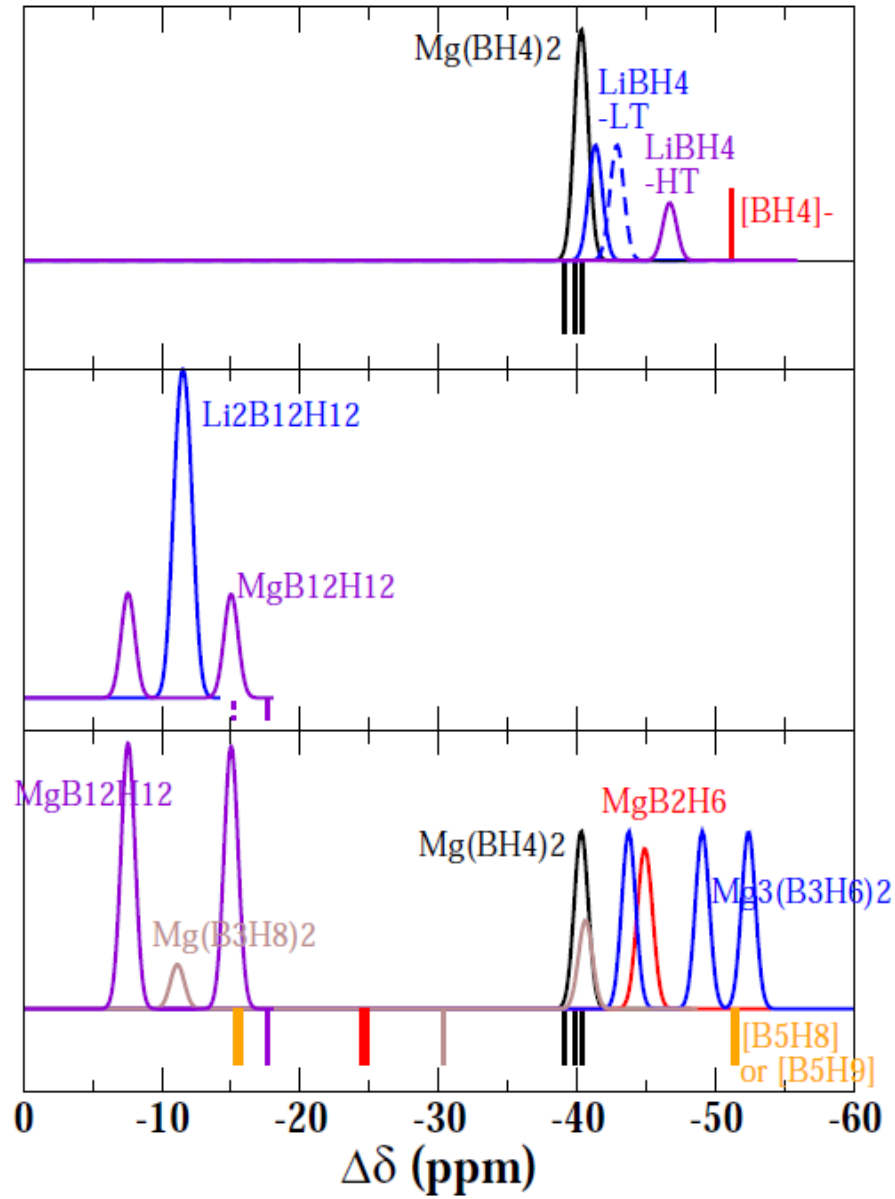
DFT-NMR calculations of possible $Mg(BH_4)_2$ decomposition products:

$Mg(BH_4)_2$, $MgB_{12}H_{12}$, MgB_2H_6, $Mg(B_3H_8)_2$, $Mg_3(B_3H_6)_2$

The theoretically calculated ^{11}B NMR of $[B_{12}H_{12}]$ is in good agreement with the experimental measurements.

From experimental NMR measurements (Cal. Tech.), there has a strong peak around -50 ppm, which is also present in our theoretical $Mg_3(B_3H_6)_2$ NMR calculations. Thus, the agreement is in accord with our previous theoretical prediction of $Mg_3(B_3H_6)_2$ as a possible decomposition product.

The experimental NMR suggested $[B_nH_m]$ region (~-30ppm) needs further investigation (see subsequent slides).

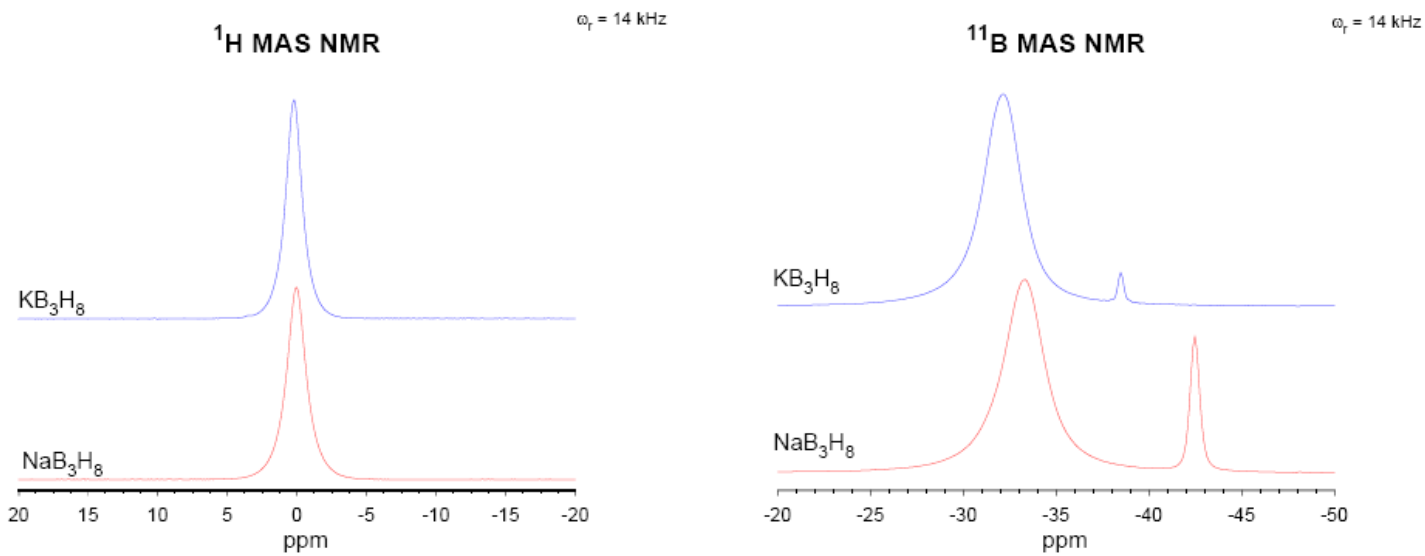


Technical Accomplishments

To clarify role of possible B_3H_8 products, NMR experiments and calculations performed for <u>known</u> pure B_3H_8 compounds, NaB_3H_8 and KB_3H_8. Samples provided by J.C. Zhao and X. Chen, Ohio State

^1H and ^{11}B MAS NMR of MB_3H_8

The center band line shapes of both Na and K version of $B_3H_8^-$ as well as the corresponding ^1H MAS NMR spectra are shown below.

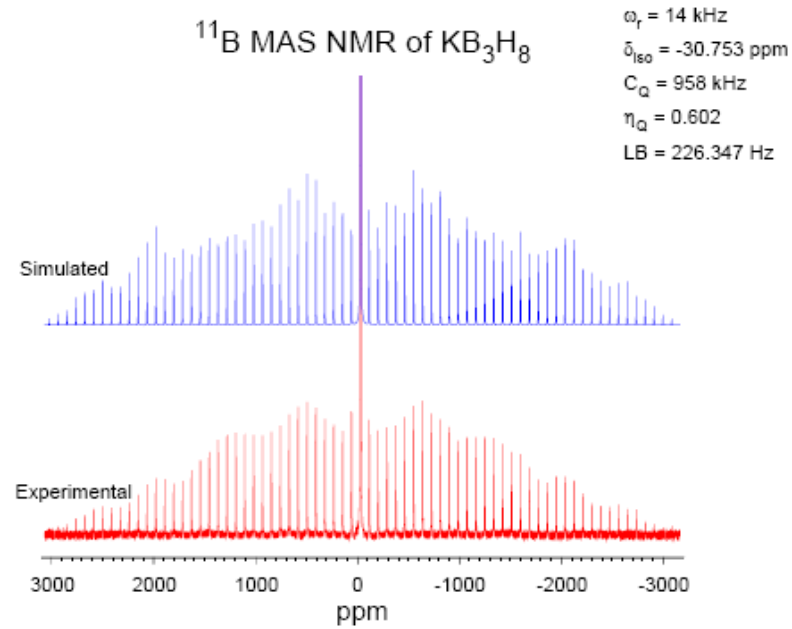


- Both samples show the presence of minor contaminant (~-40 and ~-43 ppm) which are nominally supposed to be BH_4^- ion, and their NMR shift positions match with $NaBH_4$ and KBH_4.

Technical Accomplishments

^{11}B NMR of KB_3H_8

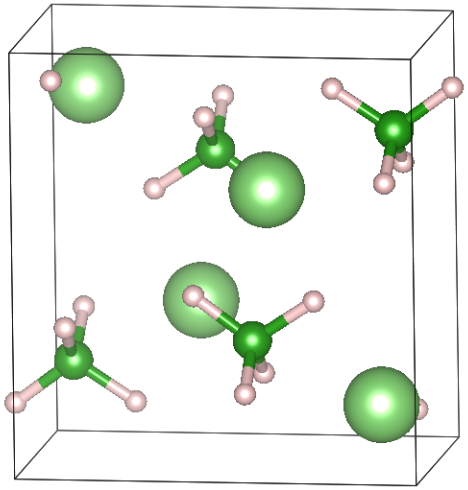
- According to literature[1], while B atoms are stationary below 316 K (phase transition to isotropic phase), but NMR sees all borons equivalent due to an exchange mechanism, and our exp ^{11}B NMR is also showing one B environment and consistent with previous reports.
- C_Q and η_Q are in agreement with literature[2] values (0.96 MHz and 0.76, respectively)
- ^{11}B appears to experience bit more distortion around B coordination (higher C_Q and η) compared to NaB_3H_8.
- ^{39}K NMR was not attempted since its resonance frequency is too low at our magnet.

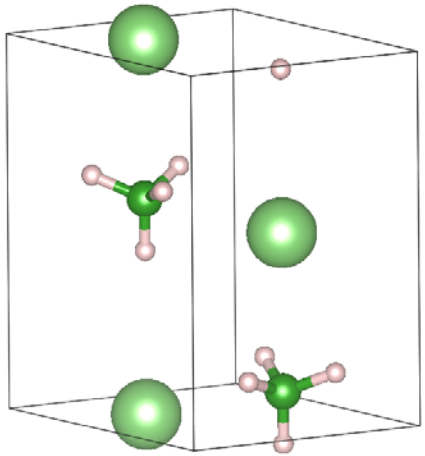


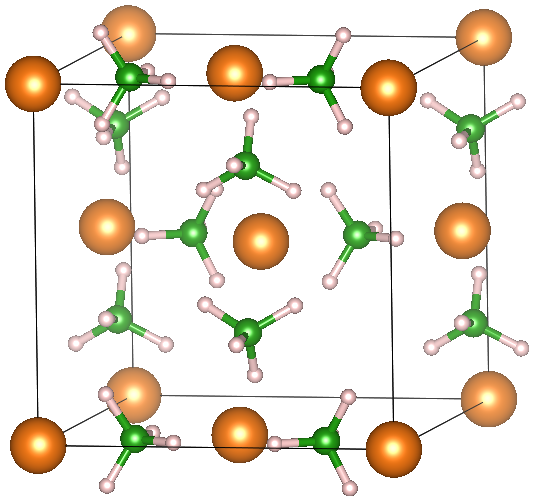
[1]Reynhardt and Lourens, J. Phys. C: Solid St. Phys. 13, 1980, 2675.
[2]Paine RT et al, Chem Phys Lett, 1975, 32, 566.

Technical Accomplishments: ^{11}B NMR – DFT calculations, collaboration with C. Pickard, UCL

^{11}B NMR reference standard calibration: δ_{ref}







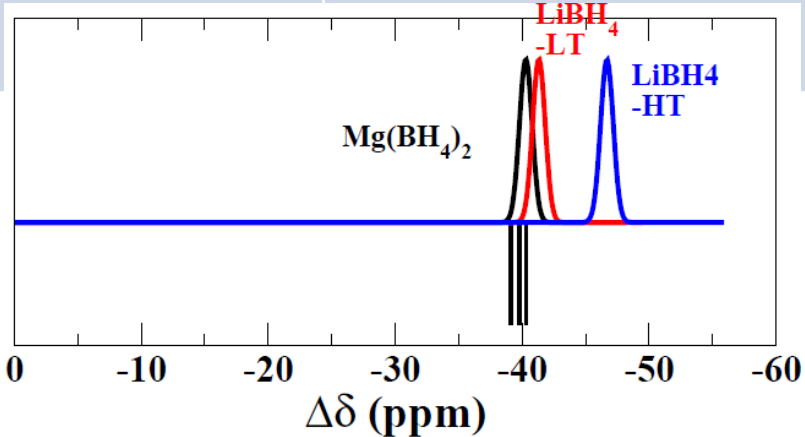
MBH_4	$LiBH_4$-LT	$LiBH_4$-HT	$Mg(BH_4)_2$
^{11}B Chemical shielding (δ) (ppm)	141.9	147.3	140.80

$\Delta\delta=\delta_{ref}-\delta$

$\Delta\delta_{exp}\approx-40$ppm

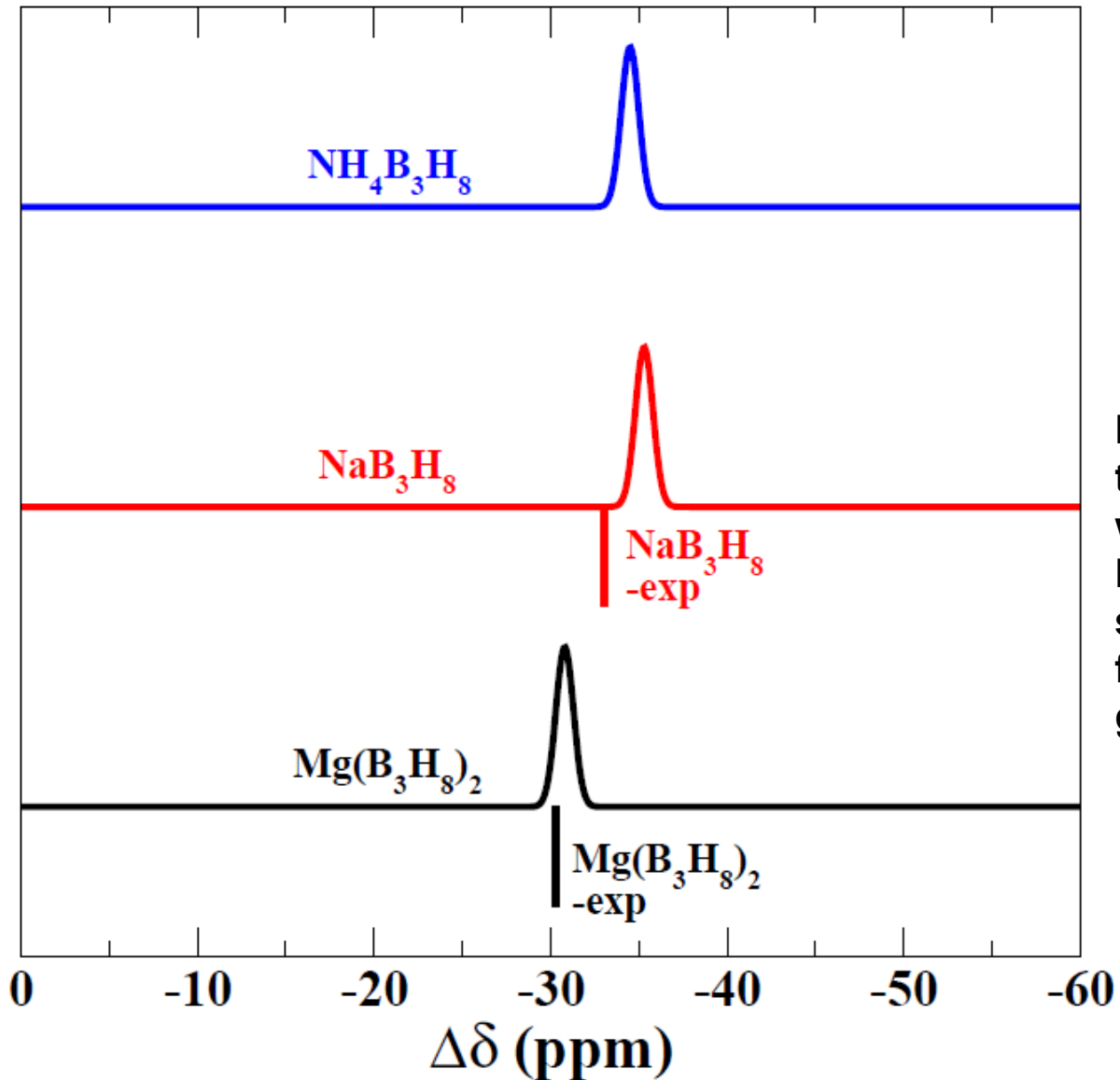
=>

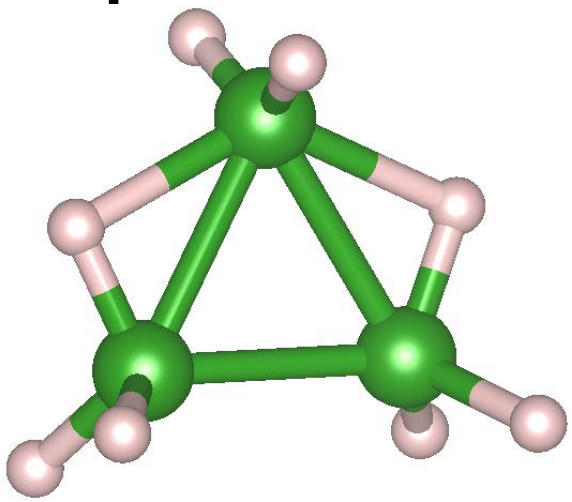
$\delta_{ref}\approx100.6$ ppm



The different ^{11}B NMR in $LiBH_4$-HT is due to the different B-H bond length.

Technical accomplishments:
$[B_3H_8]$ ^{11}B NMR: calculations vs. experiments

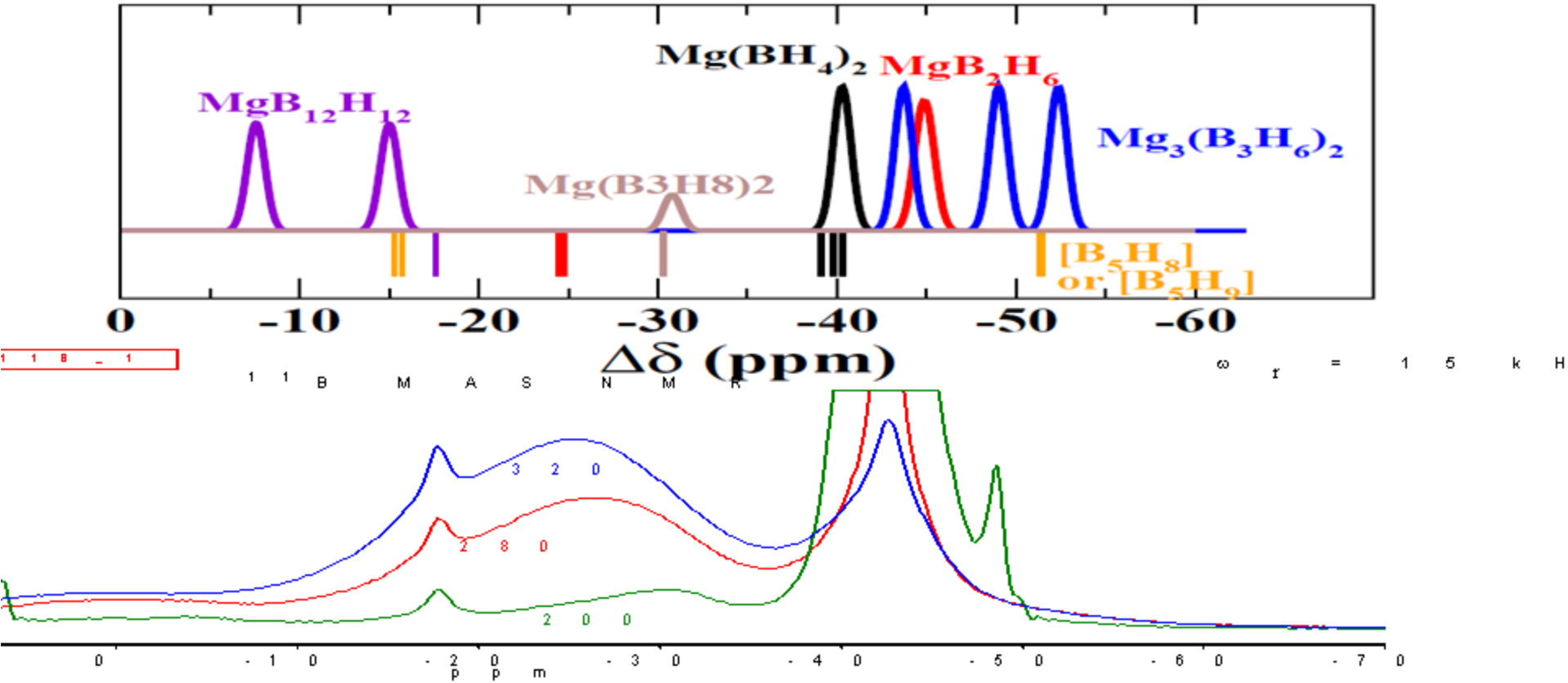




DFT calculations of B3H8 show two 11B peaks, consistent with the two B environments. But, experimental measurements show only one peak, due to the fast H exchange within the anion group.

***Averaging* these two DFT peaks are in good agreement with the experimental measurements. Thus $Mg(B_3H_8)_2$ is consistent with observed product at ~30ppm, but only present at low temperatures and in low concentrations.**

^{11}B NMR of other possible intermediates



- With the combined NMR experiments and DFT calculations, we can assign now most of the peaks in the observed products.
- The current or Ref[1] measured peak ~-25ppm is still unknown. Even though Ref[1] suggests that the peak belongs to $[B_2H_6]$, our theoretical calculations on $[B_2H_6]$ show a different peak position.

[1] Y. Yang et al., Materials transactions **2011**, 52, 1443

$ZnCl_2$ assisted Dehydrogenation of 1:1 $LiBH_4$-$Mg(BH_4)_2$

Rationale:

- $LiZn_2(BH_4)_5$ was reported to have very low decomposition temperature,[1] lower than $LiBH_4$-$Mg(BH_4)_2$.
- However, decomposition of $LiZn_2(BH_4)_5$ leads to evolution of B_2H_6.[1]

Objective: To investigate the effect of the addition of $ZnCl_2$ or $ZnCl_2$/carbon mixture on the decomposition of $LiBH_4$-$Mg(BH_4)_2$.

Approach:

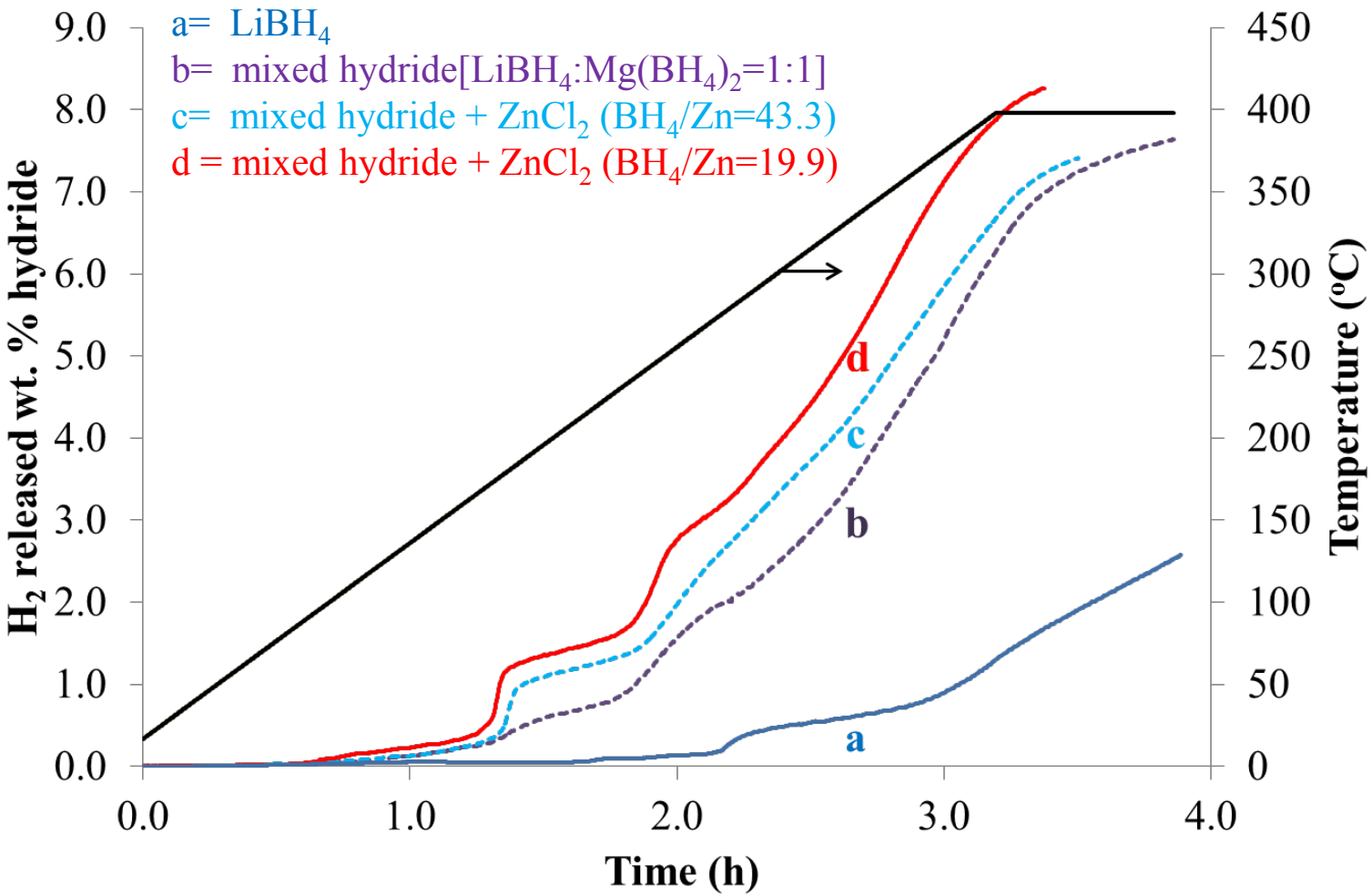
- Add small quantities of $ZnCl_2$ and to see if B_2H_6 formation is suppressed.

  B_2H_6 is formed by the following reaction:
  $10LiBH_4 + 5ZnCl_2 = 5Zn + 10\ LiCl + 5B_2H_6 + 5H_2$
  Corresponding reaction between $Mg(BH_4)_2$ and $ZnCl_2$ has not been reported..

  Suppression of B_2H_6 formation will be indicated by larger quantity of low temperature H_2 release than that shown by the equation above.
- Explore whether carbon can also suppress B_2H_6 formation. Test 2 different types of carbon: carbon molecular sieve (Y-carbon) and graphitic carbon nitride (Carbodeon Corporation)

1. Ravnsbæk et.al. Angew. Chem. Int. Ed. 2009, 48, 6659 –6663.

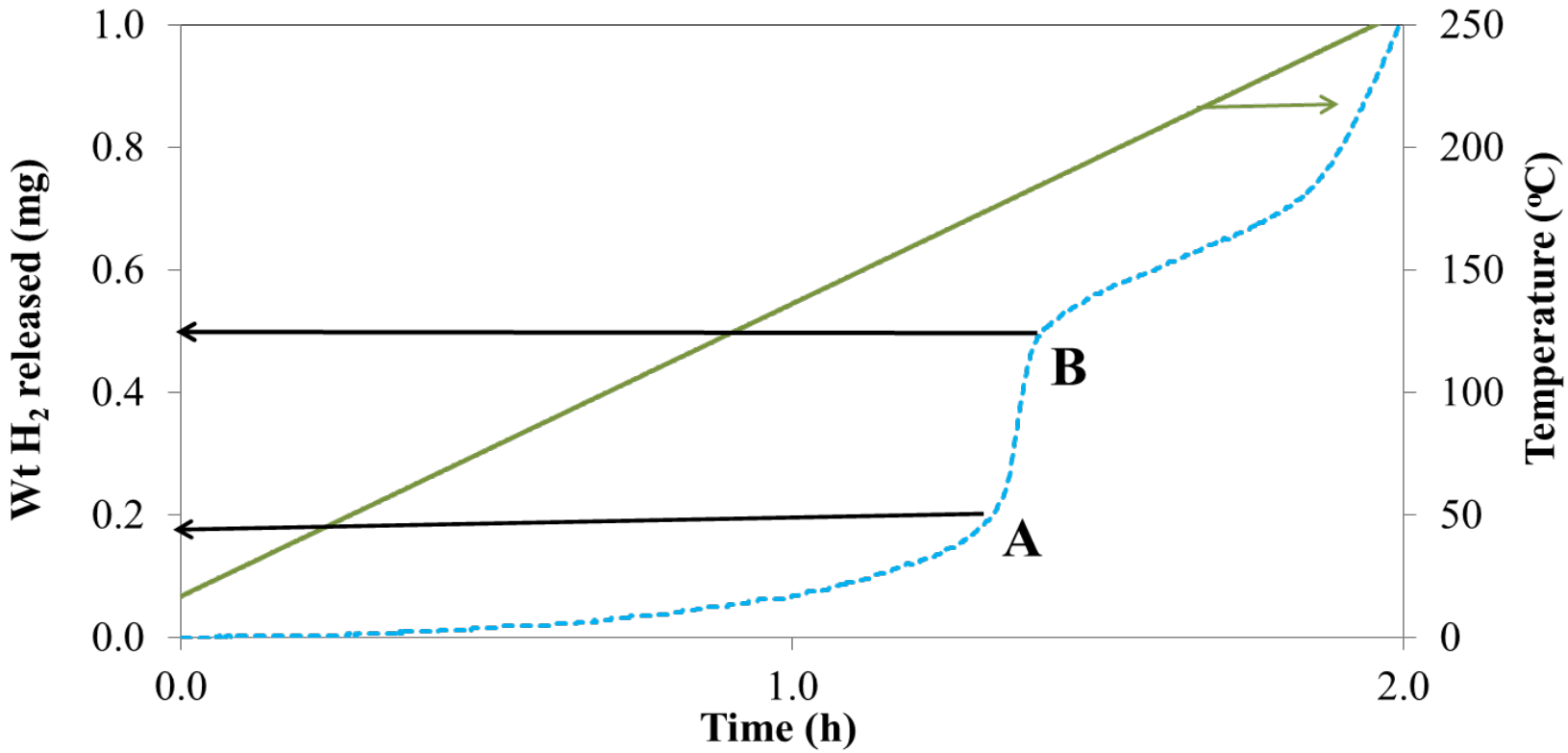
Results: $ZnCl_2$ addition increased H_2 release at low temperatures from $LiBH_4$- $Mg(BH_4)_2$ mixed hydrides. Comparing curves b, c, and d: more H_2 released with more $ZnCl_2$.



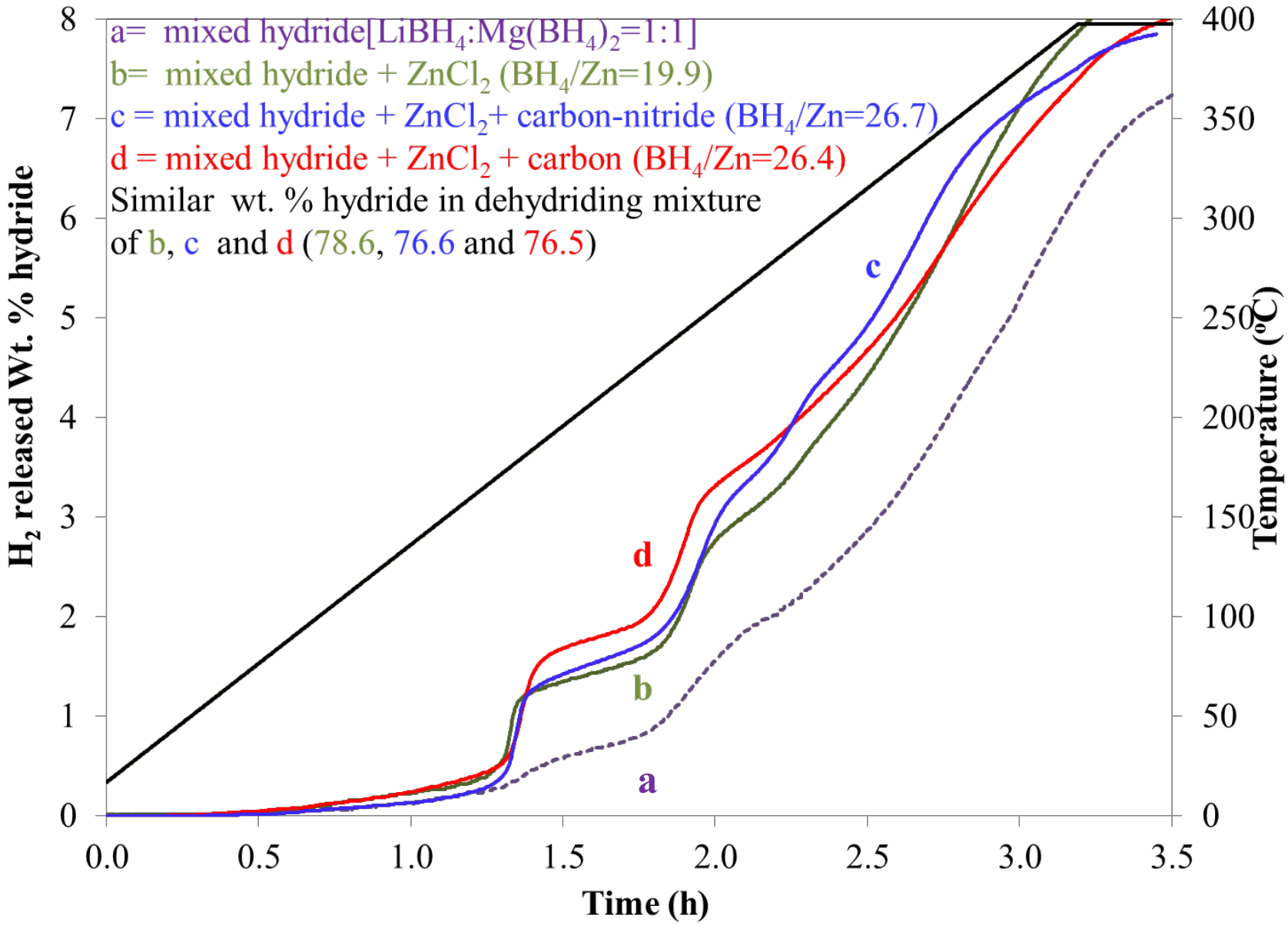
Results: Evidence that indicates little or no B_2H_6 formation.

Total amount of gas released at low temperature (up to 185 °C) is much higher than that corresponding to formation of B_2H_6 and H_2 according to reaction A. It is consistent with reaction B.

A: $10LiBH_4 + 5ZnCl_2 = 5Zn + 10LiCl + 5B_2H_6 + 5H_2$ (1 mole of B_2H_6 is treated as 1 mole of H_2)
B: $10LiBH_4 + 4ZnCl_2 = 20\ H_2$ +Zn and boron and Li decomposition products

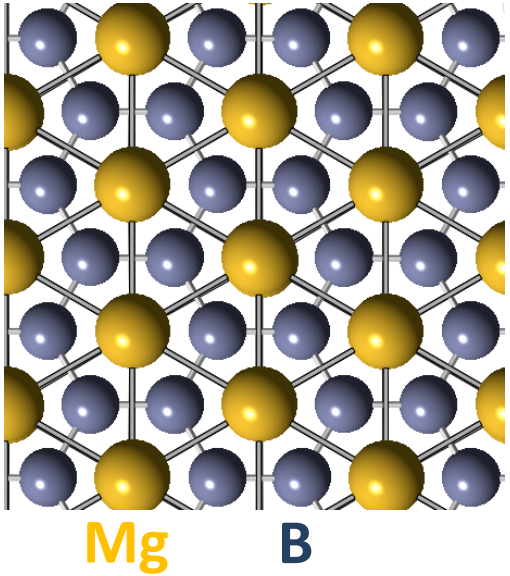


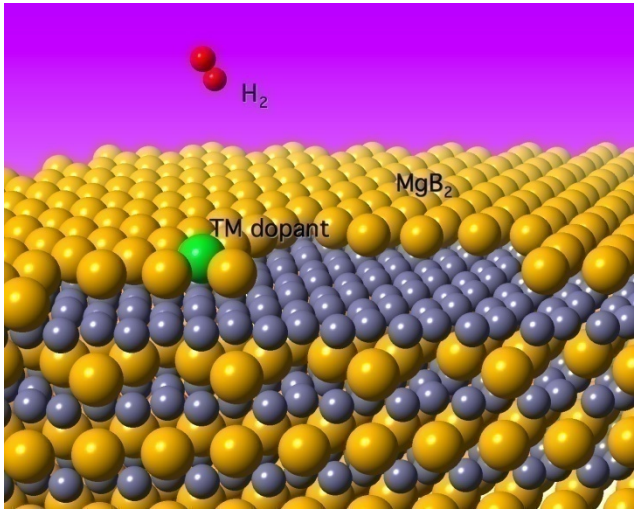
Result: addition of carbon to $ZnCl_2$ further improved low temperature H_2 released from $LiBH_4$- $Mg(BH_4)_2$



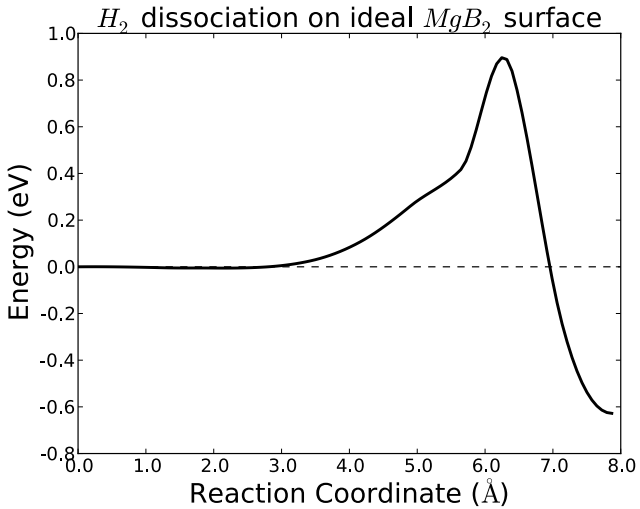
Identify the kinetic barriers for re-hydrogenation of MgB_2

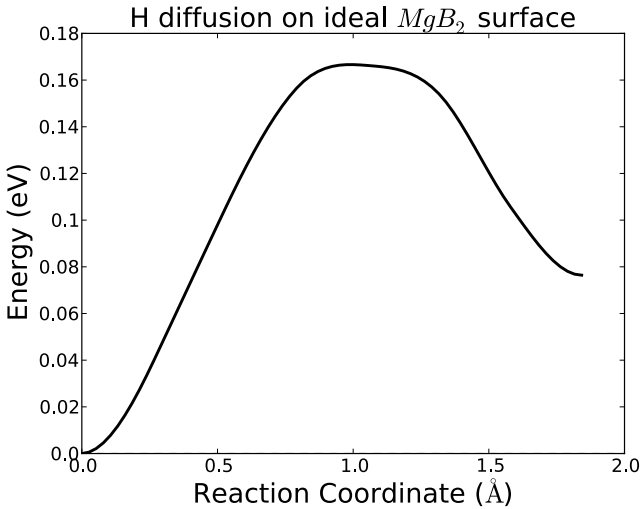
- What are the rate-limiting steps for MgB_2 ? (mass transport, nucleation, dissociation, diffusion, or others?)





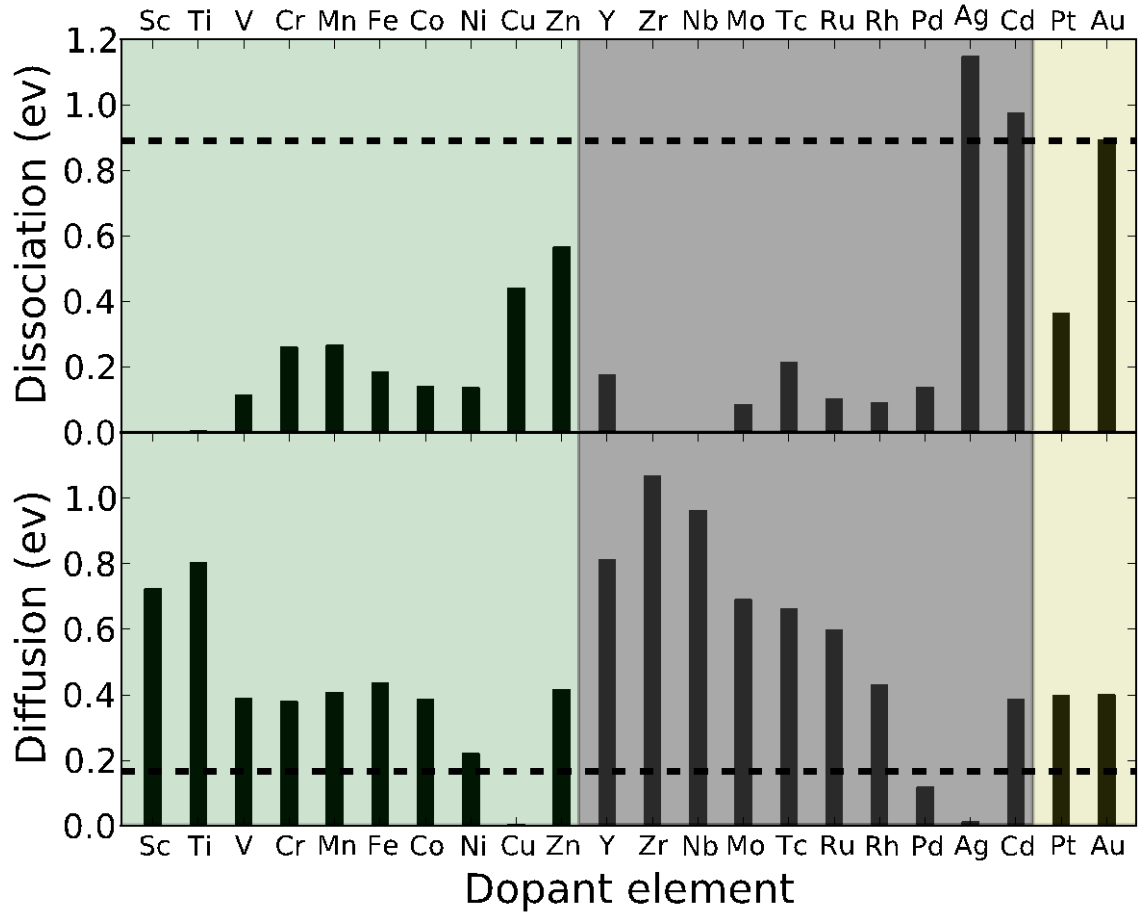
We investigated the H_2 dissociation and H diffusion on the Mg-terminated MgB_2 (0001) surface





Identify the kinetic barriers for re-hydrogenation of MgB_2

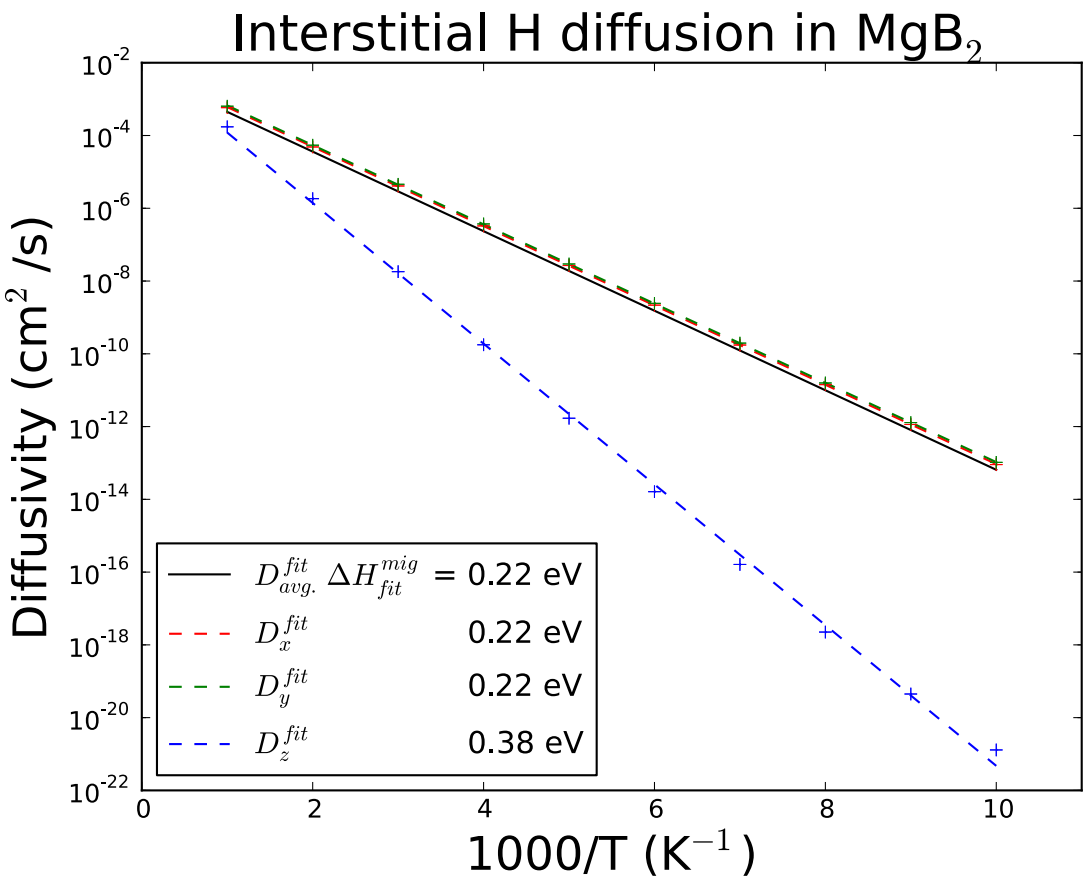
	Barriers (eV)
Dissociation	0.89
Diffusion	0.17



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

Identify the kinetic barriers for re-hydrogenation of MgB_2

We studied the interstitial H diffusion in bulk MgB_2



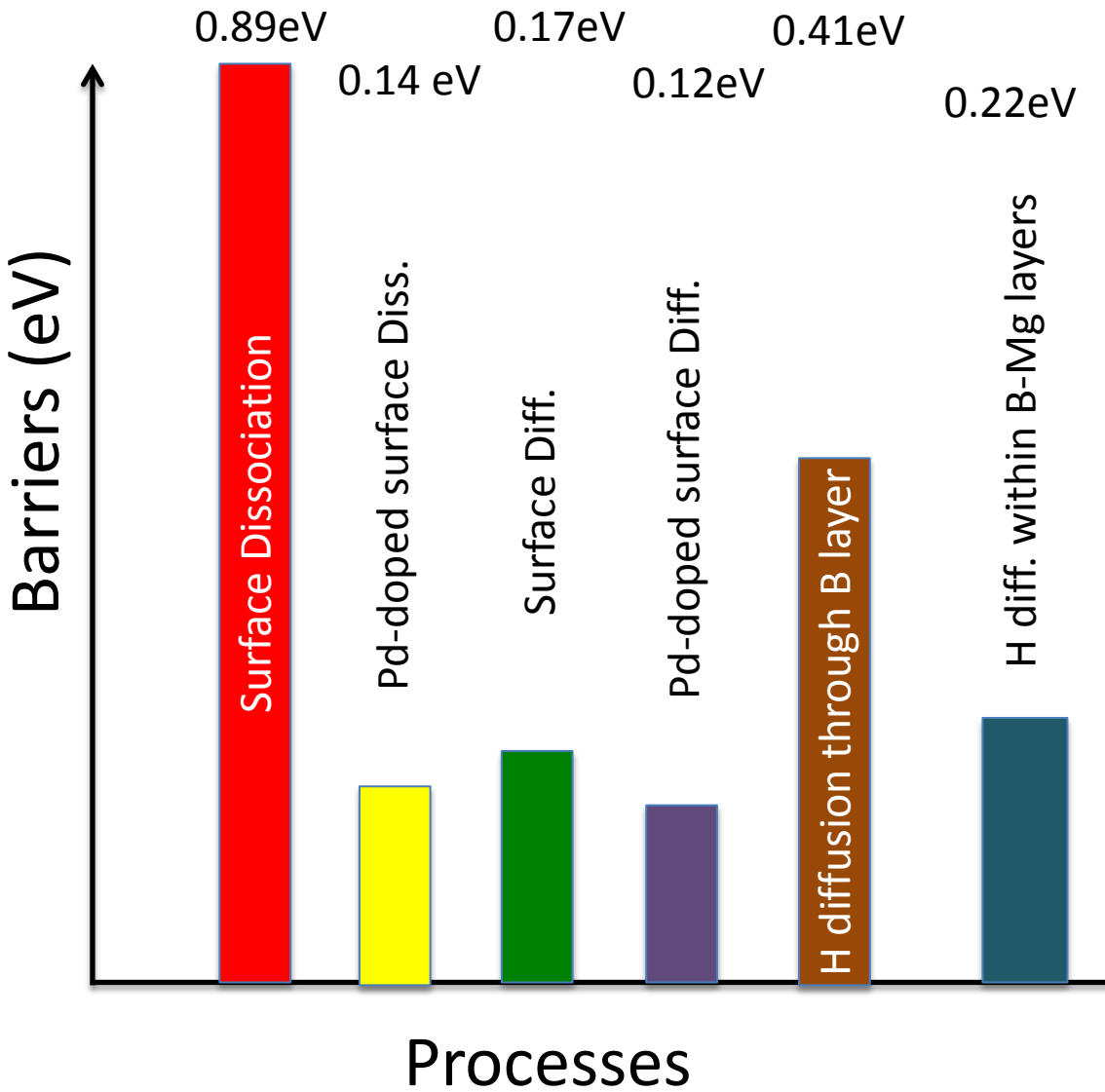
KMC calculations results:
(migration energy)

- $D_x = D_y = 0.22$ eV
- $D_z = 0.38$ eV

x, y plane: parallel Mg, B layers
z direction: perpendicular B layers

Low barriers for
H diffusion in the bulk of MgB_2

Identify the kinetic barriers for re-hydrogenation of MgB_2

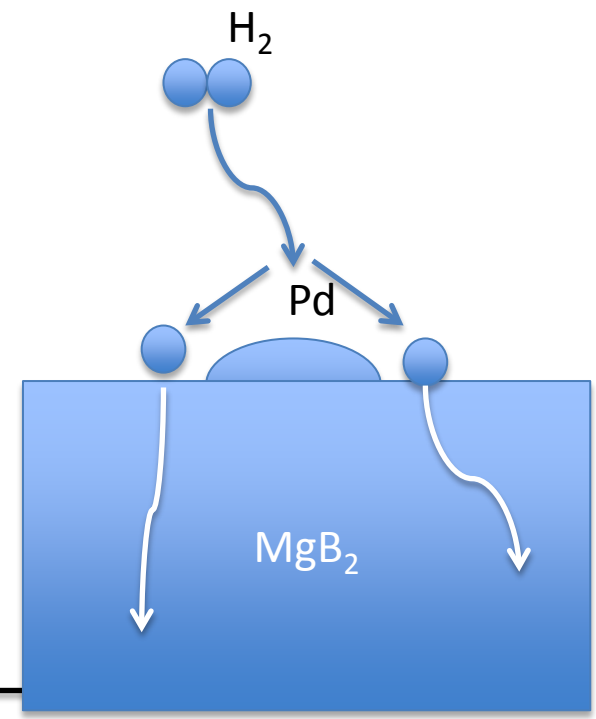


Barriers:

High: H_2 diss. on the surface

Low: H diff. in the bulk

Doping Pd can reduce diss. barrier



$2LiBH_4+5Mg(BH_4)_2$ – Conclusions and Suggested Future Work

- DFT discovery of this reaction as high capacity, and thermodynamically reversible; However, like most borohydrides, mass transport is a significant kinetic limitation to reversibility.
- Kinetics of high-capacity borohydride reactions almost always limiting factor - thermodynamic problems solved by appropriate combinations, i.e., $2LiBH_4+5Mg(BH_4)_2$
- Measurements suggest that the $2LiBH_4+5Mg(BH_4)_2$ reaction is at least partially reversible.
- Computations also suggest some strategies to reduce kinetic barriers for the hydrogenation of MgB_2.
- NMR experiments of $2LiBH_4+5Mg(BH_4)_2$ show a number of intermediates or decomposition products. Many of these were identified via a combination of experiment and DFT calculations of NMR spectra.
- Future work on this system should be focused on: 1) more clearly defining the reversible (and kinetically-limited) portions of the reaction, 2) finding a suitable catalyst to overcome kinetic limitations.

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 $MgB_2(0001)$ surfaces and bulk (see subsequent slides): dissociation and diffusion

Collaborations

PI's/co-PI's

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Summary – Technical Accomplishments

- Used computational tools and high-throughput machinery to survey high capacity, thermodynamically-reversible reactions.
- 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 (synthesis and NMR characterization performed; project ran out of time/funds before full desorption, kinetics, and reaction products could be performed)
- 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. Using combination of experiments and DFT, able to assign almost all reaction products. Still one uncertain product (~-25ppm).
- Computational survey of dopants that lower surface dissociation or diffusion for MgB_2 rehydrogenation
- Addition of ZnCl2 (and carbon) to LiBH4+Mg(BH4)2 mixture results in (slight) increase in hydrogen desorption at lower temperatures