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

C. Wolverton (PI), H. Kung
Northwestern Univ.

V. Ozolins
UCLA

J. Yang, M. Veenstra
Ford Motor Company

S. Hwang
Caltech

S. Shore
Ohio St. Univ.

ST028

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

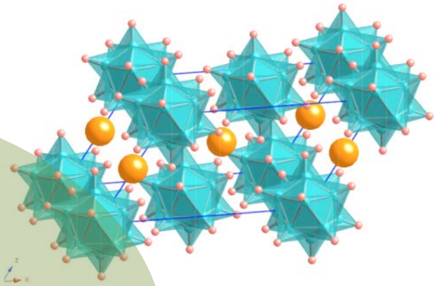
- Barriers addressed
  - O. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

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 $\Delta H < 150$ 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)

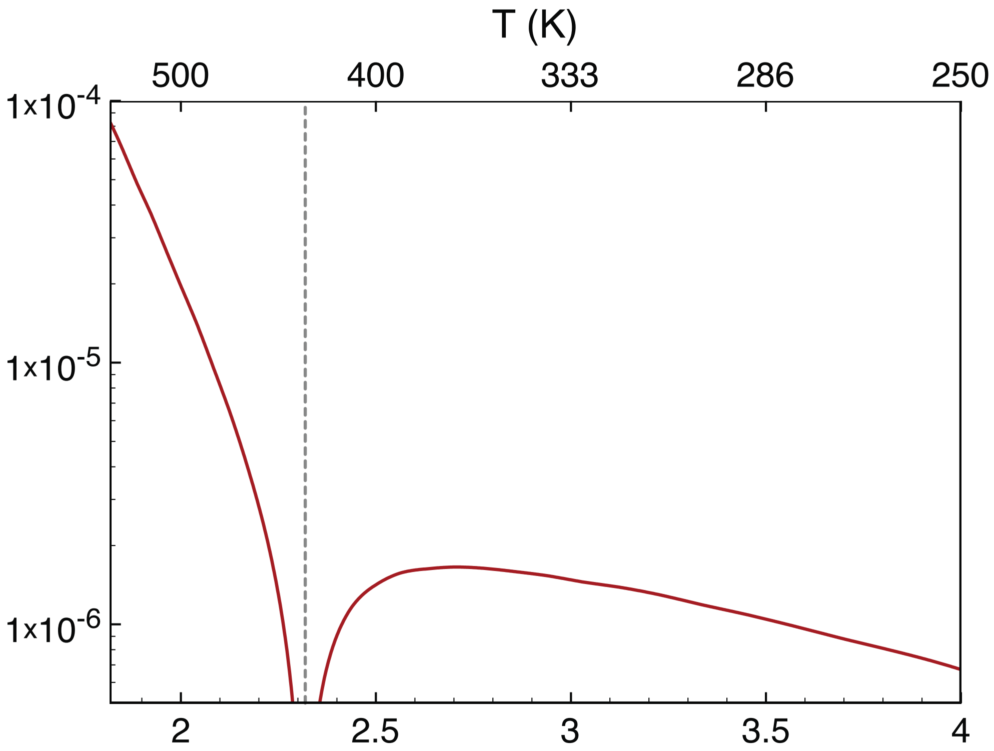
Reactions	Wt.% H_2	Vol. H_2 ($g\ H_2/L$)	ΔH^{300K} ($kJ/mol\ H_2$)	ΔS^{300K} (J/mol-K)
$2(NH_4)_2B_{12}H_{12} \rightarrow 4BN + B_{20}H_{16} + 12H_2$	**6.81**	**62**	**17**	**104**
$5Mg(BH_4)_2 + 2LiBH_4 \rightarrow 5MgH_2 + Li_2B_{12}H_{12} + 13H_2$	**8.37**	**66**	**24**	**104**
$6Mg(BH_4)_2 \rightarrow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

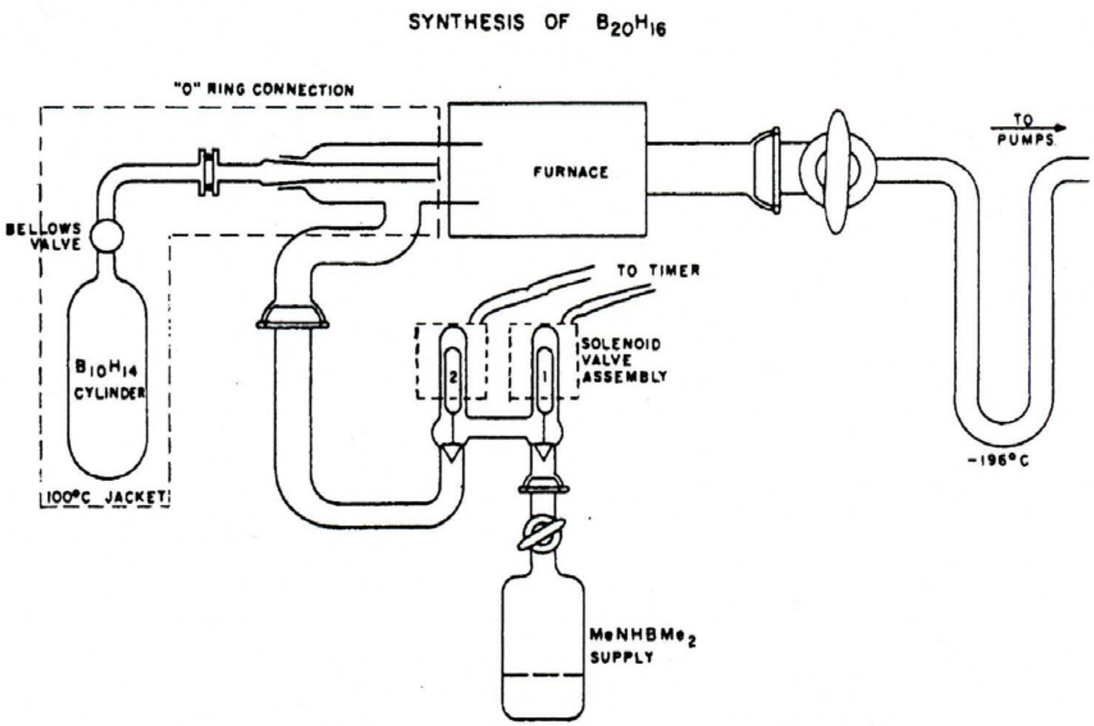


Activation energy for mass transport	
Rehydrogenation	6 kJ/mol
Dehydrogenation	63 kJ/mol

- **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)

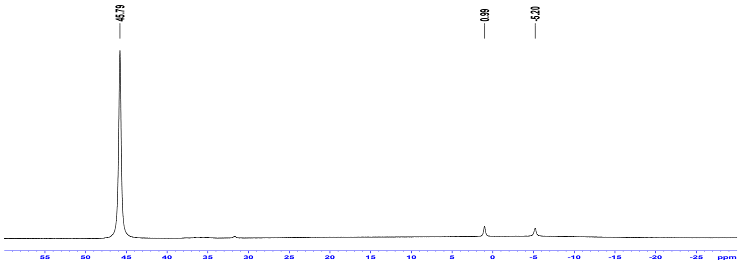


- Several methods have been reported for the preparation of icosaborane-16 ($B_{20}H_{16}$) but they were carried out under extreme conditions and with low yields 9 to 15%.
- No commercial source is available.
- The method we used in this project is the modified catalytic pyrolysis of decaborane-14 ($B_{10}H_{14}$).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

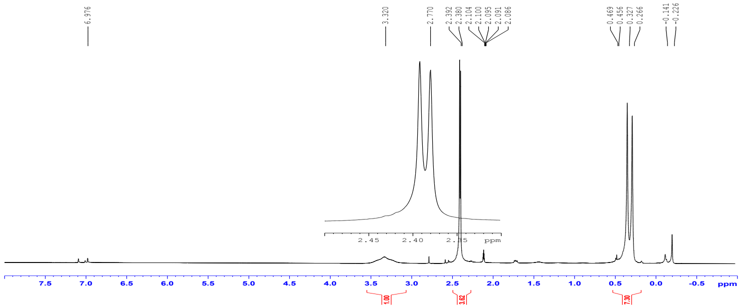
Chemistry of Boranes. XXI Icosaborane-16 : N. E. MILLER, J. A. FORSTNER, E. L. MUETTERTIES, *Inorganic Chemistry*,**3**,1690(1964)

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

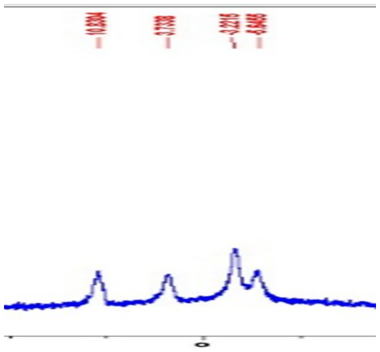


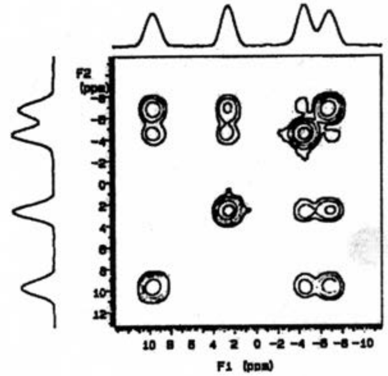
^{1}H NMR spectrum of $MeHN{=}BMe_2$ in *d*$_8$-toluene

- **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.

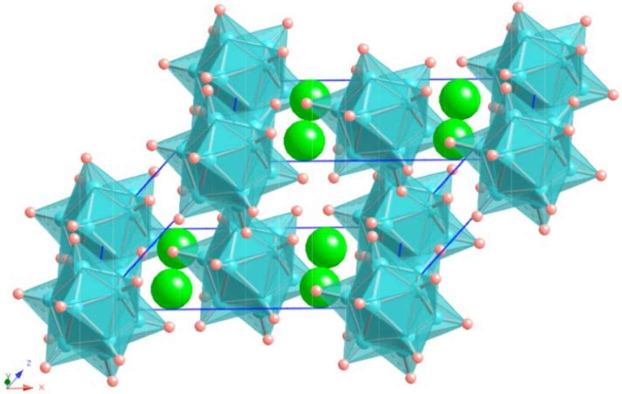
Icosaborane-16 ($B_{20}H_{16}$) – Conclusions and Suggested Future Work

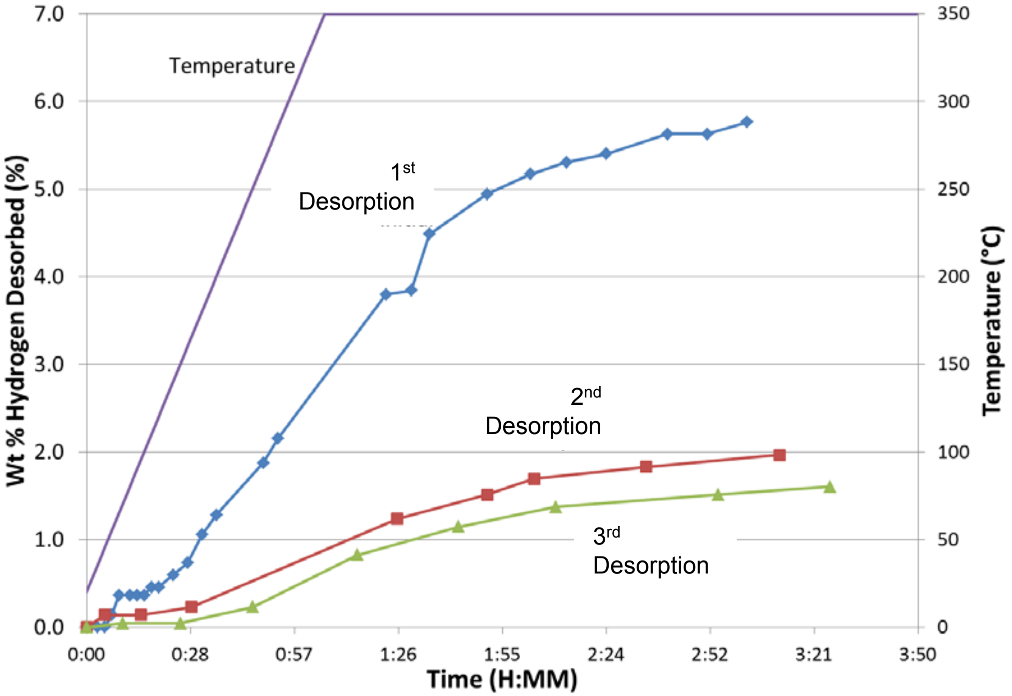
- $B_{20}H_{16}$ unique and potentially very interesting: *Only* H_2 *storage reaction of known compound with 1) high capacity, 2) good thermodynamics, and 3) predicted fast mass transport kinetics*
- Of course, there are drawbacks, but because of this unique combination of characteristics, recommend 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

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

$Li_2B_{12}H_{12}$



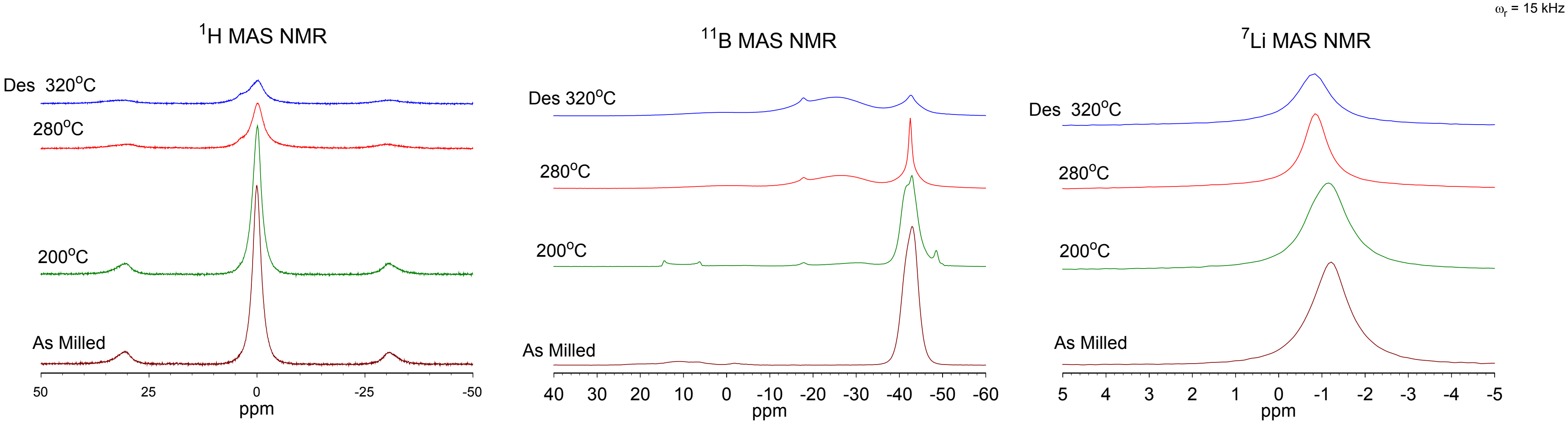


What are (non-crystalline) reaction products? Do they inhibit reversibility?

(NMR subcontract with S. Hwang, Caltech)

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

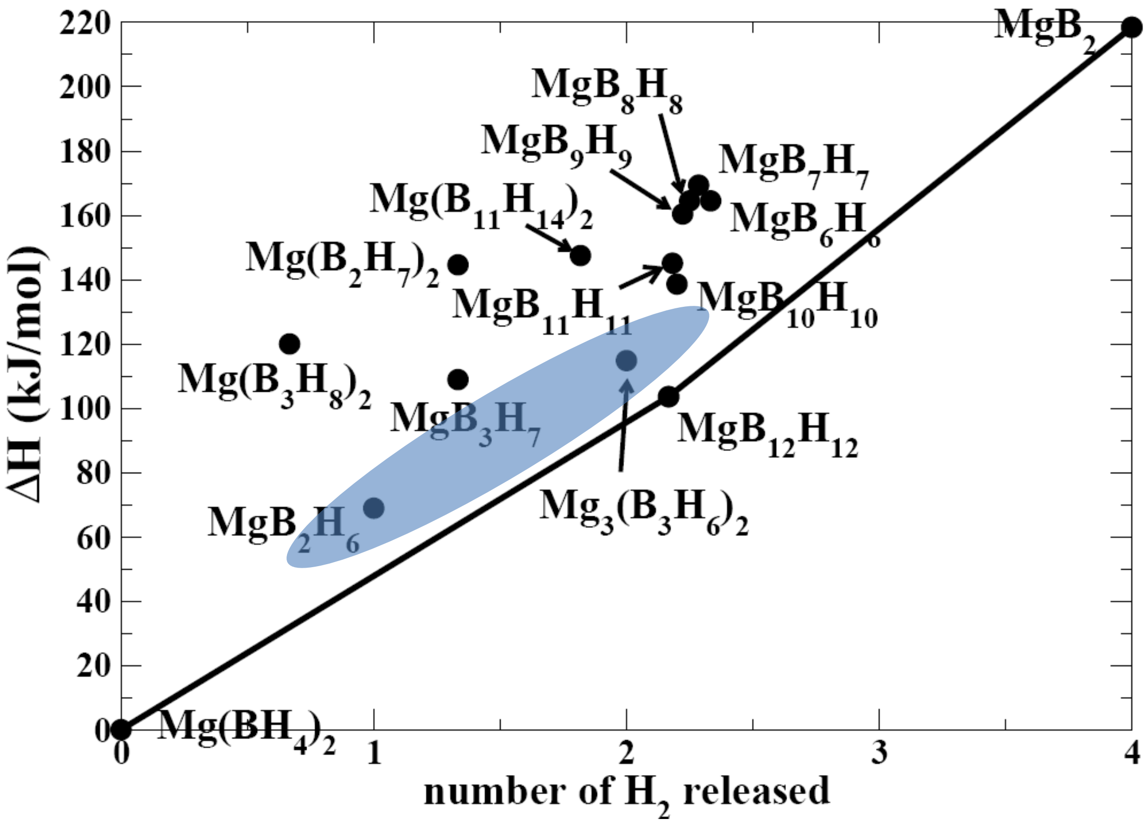
Solid state NMR characterization upon H_2 desorption reactions



- 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.
- ^{1}H 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 $Mg(BH_4)_2$

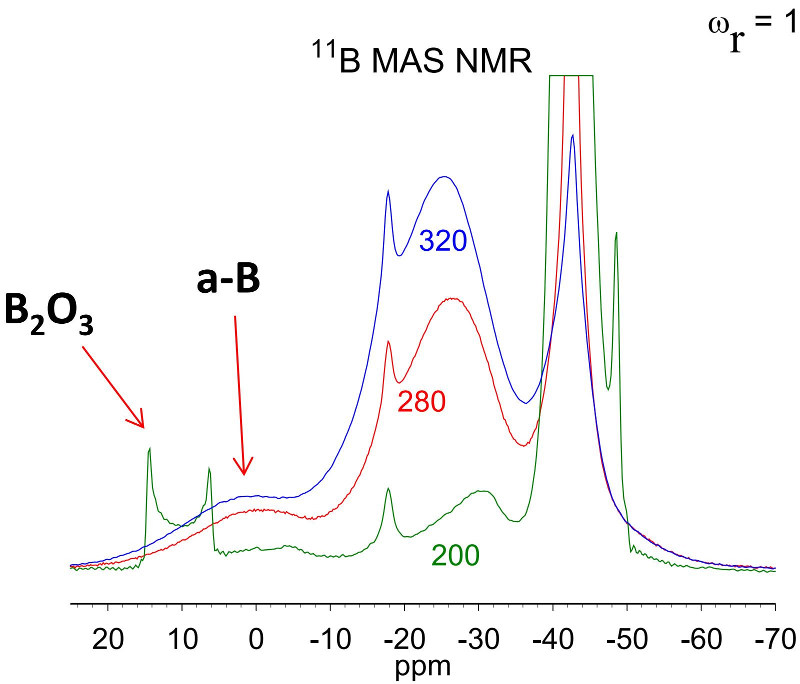
(from 2012)

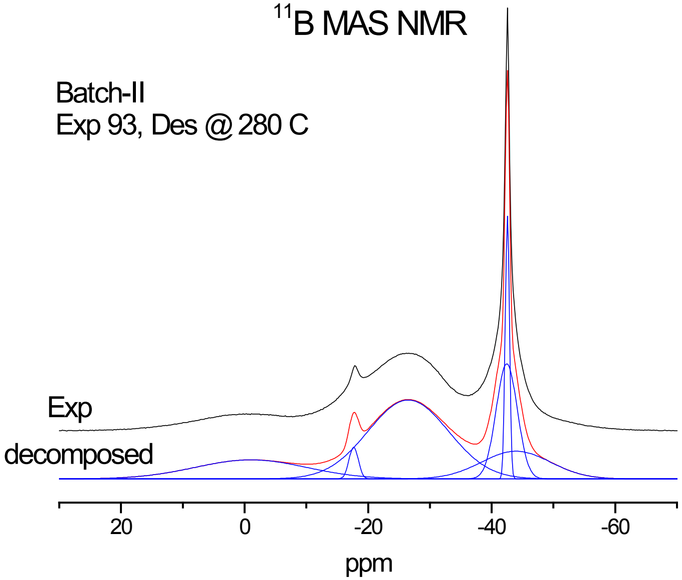


All $[B_nH_m]$ intermediates have higher reaction energies than $MgB_{12}H_{12}$.
Only the reactions to MgB_2H_6 and $Mg_3(B_3H_6)_2$ are close to the $MgB_{12}H_{12}$ convex hull.

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**

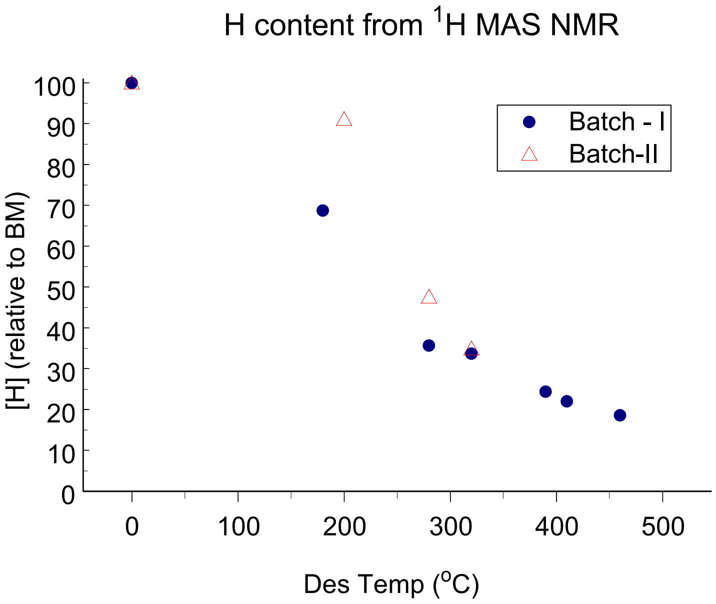
- -17.7 and -48.6 ppm: $Li_2B_5H_9$ or MgB_5H_9 like[3]

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.

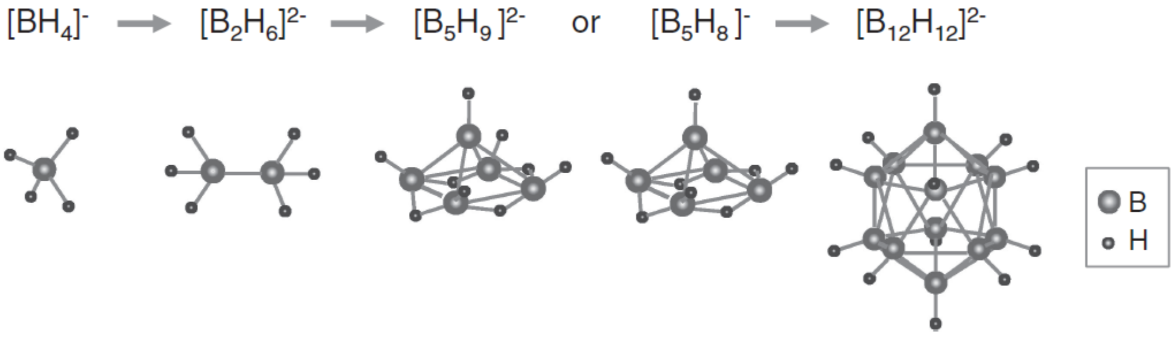


Fig. 4 Schematic illustration of formation process of $[B_{12}H_{12}]^{2-}$ from $[BH_4]^-$.

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

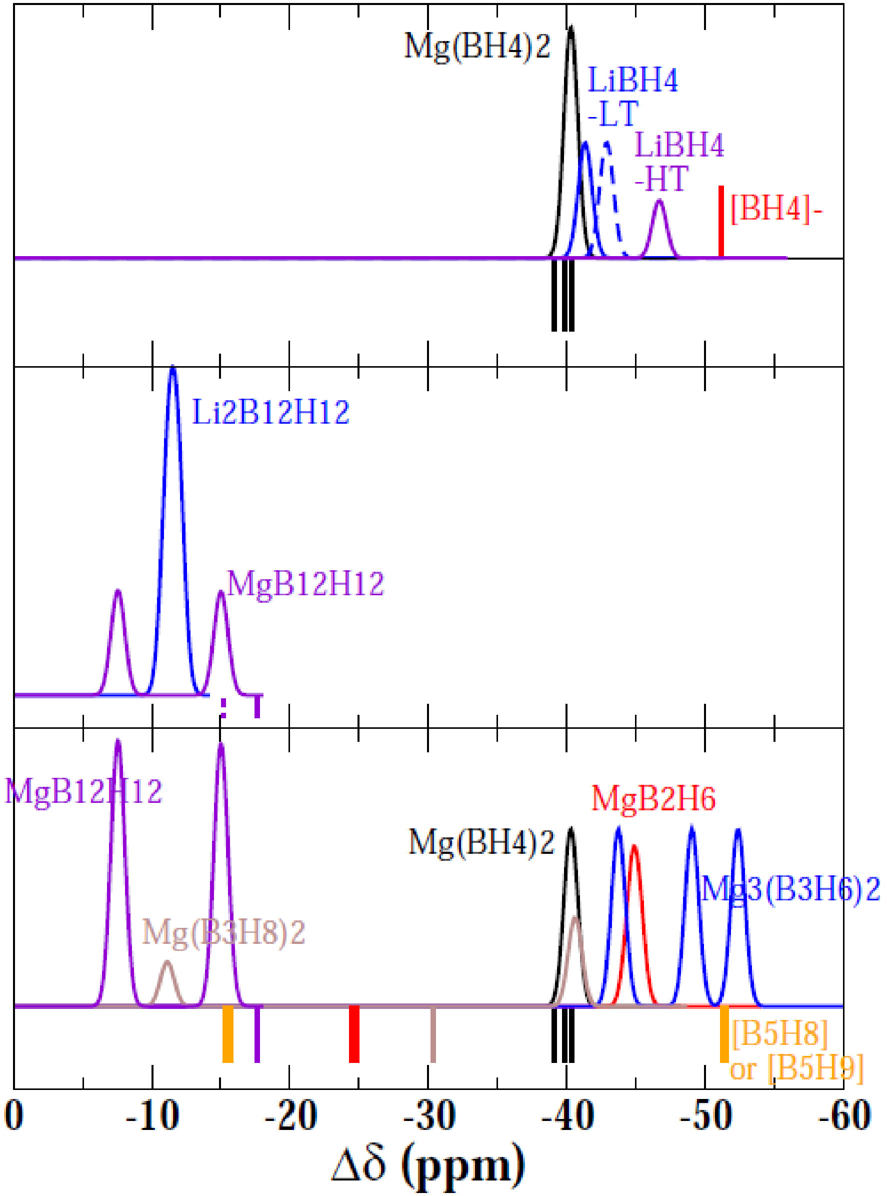
DFT-NMR calculations of possible $Mg(BH_4)_2$ decomposition products:

$Mg(BH_4)_2$, $MgB_{12}H_{12}$, 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).

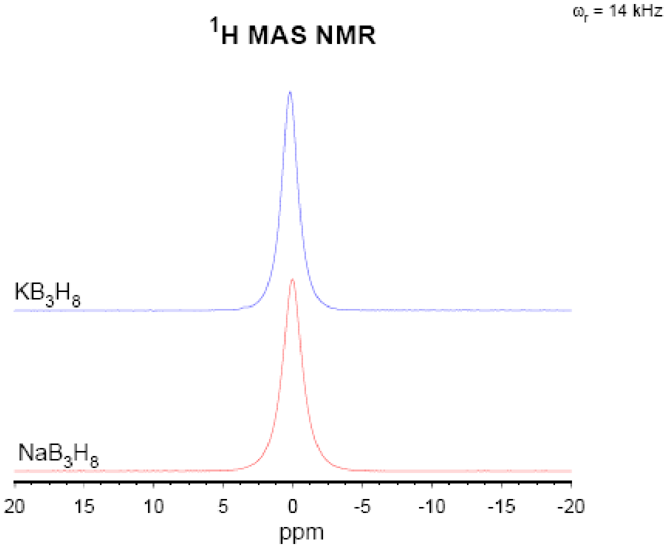


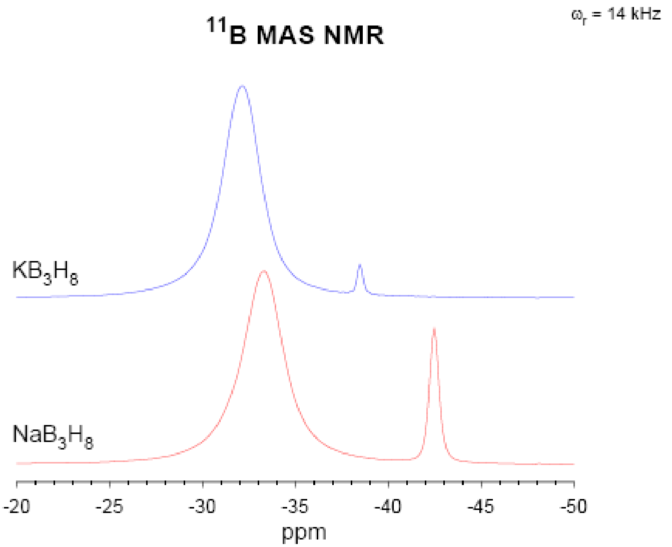
Technical Accomplishments

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

^{1}H 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 ^{1}H MAS NMR spectra are shown below.



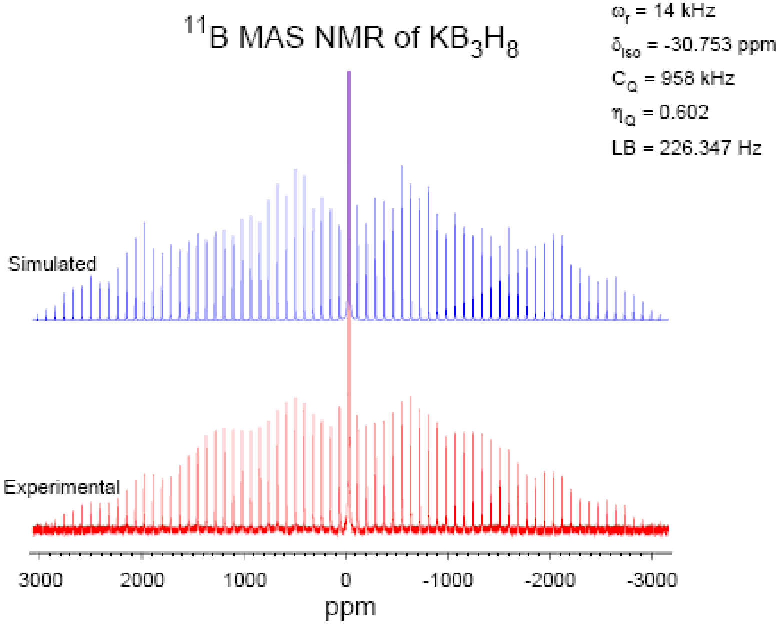


- Both samples show the presence of minor contaminant (~-40 and ~-43 ppm) which are nominally supposed to be BH_4^- ion, and their NMR shift positions match with $NaBH_4$ and KBH_4.

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.

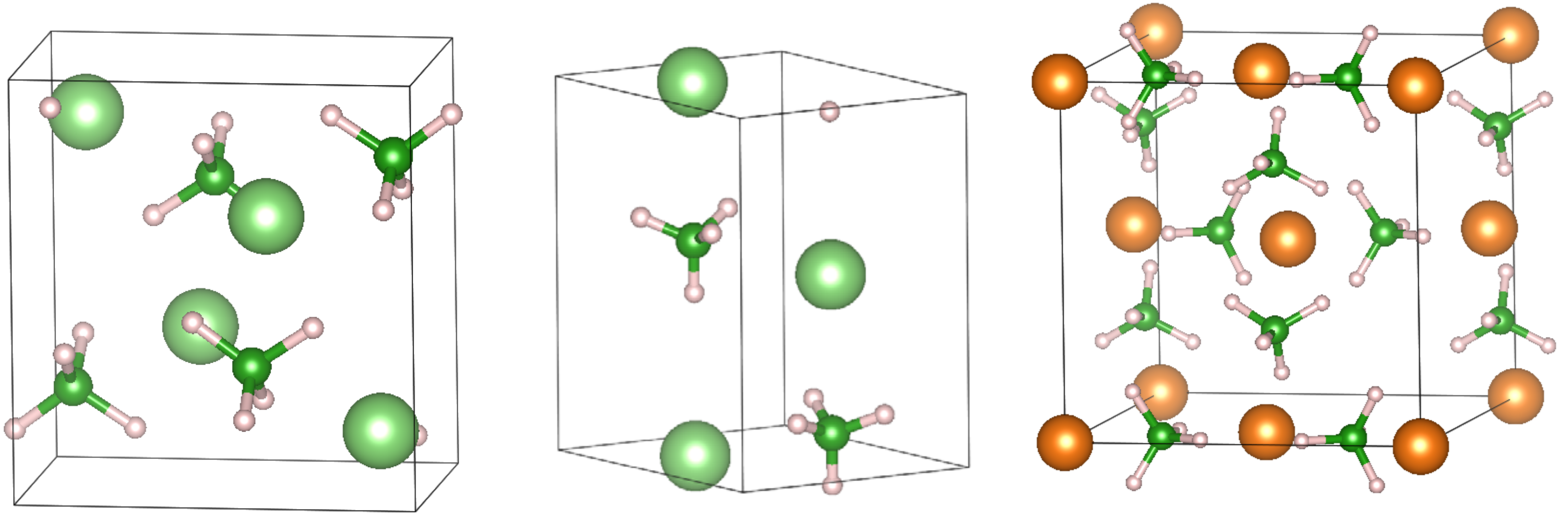


[1] Reynhardt and Lourens, J. Phys. C: Solid St. Phys. 13, 1980, 2675.

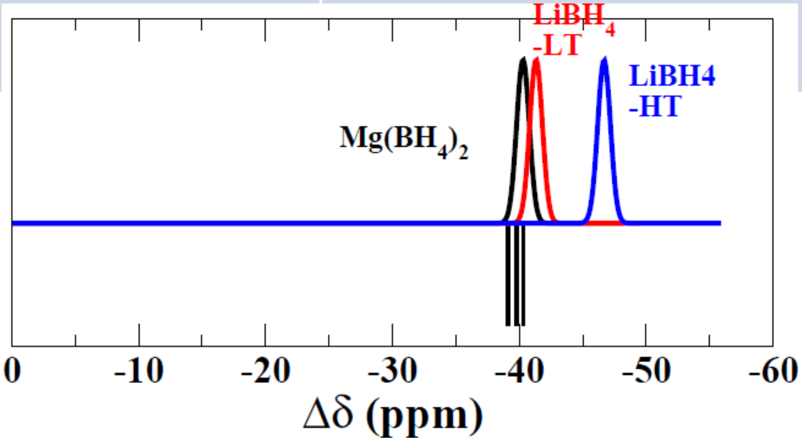
[2] Paine RT et al, Chem Phys Lett, 1975, 32, 566.

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

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



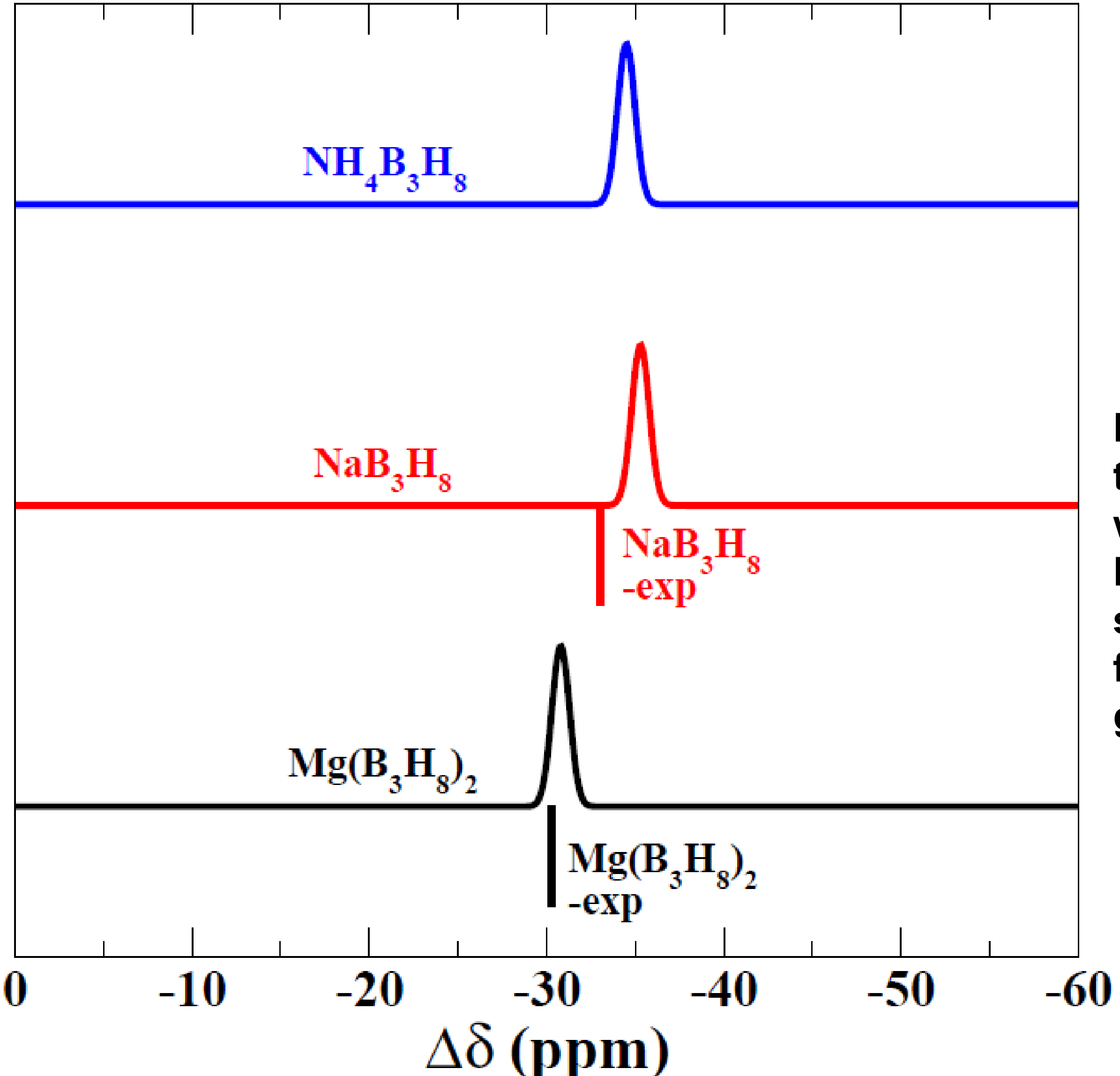
MBH_4	$LiBH_4$-LT	$LiBH_4$-HT	$Mg(BH_4)_2$
^{11}B Chemical shielding (δ) (ppm)	141.9	147.3	140.80

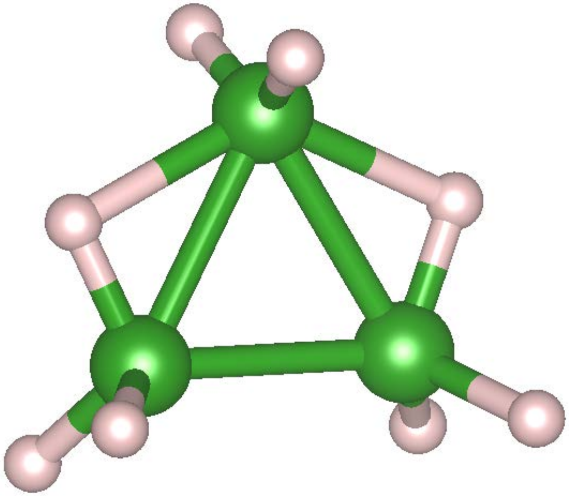


$\Delta\delta=\delta_{ref}-\delta$
$\Delta\delta_{exp}\approx$-40ppm
=>
$\delta_{ref}\approx$100.6 ppm

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

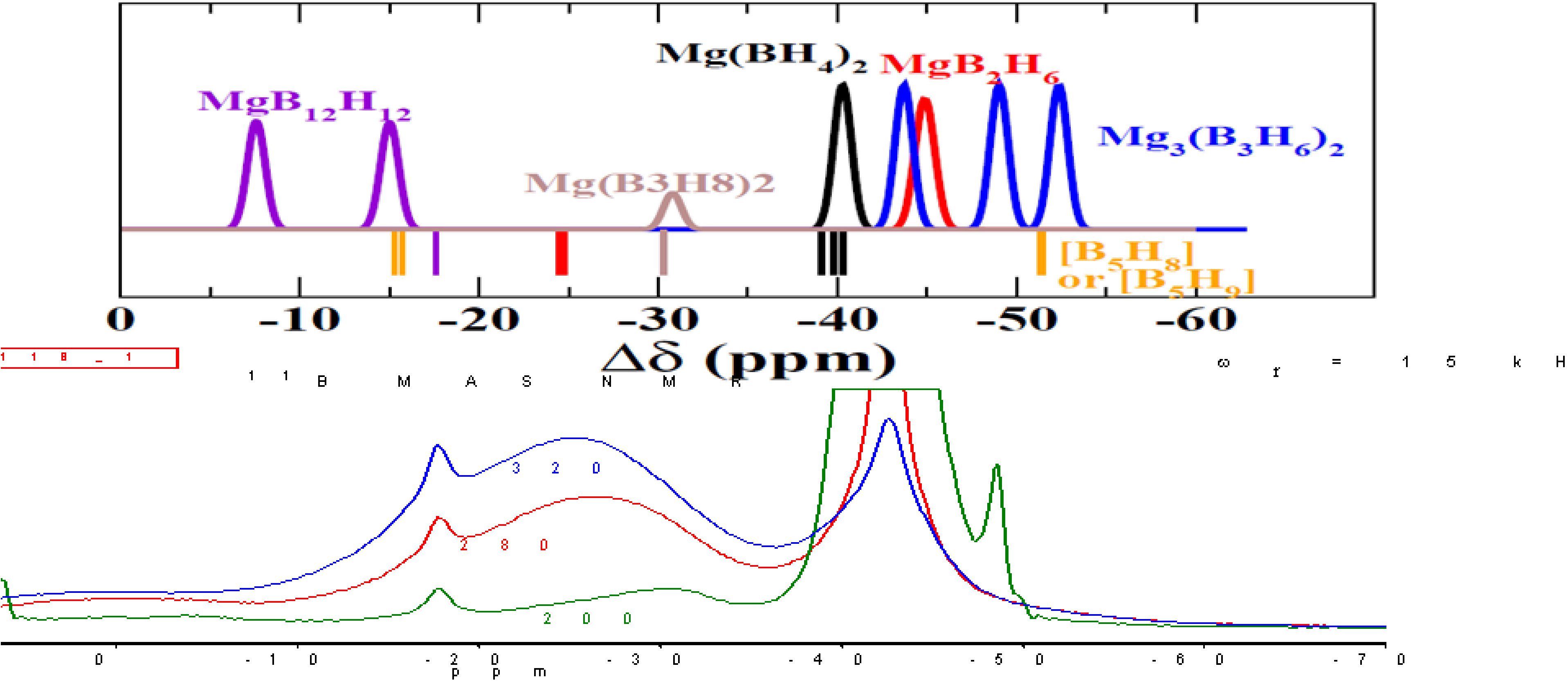




DFT calculations of B3H8 show two 11B peaks, consistent with the two B environments. But, experimental measurements show only one peak, due to the fast H exchange within the anion group.

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.

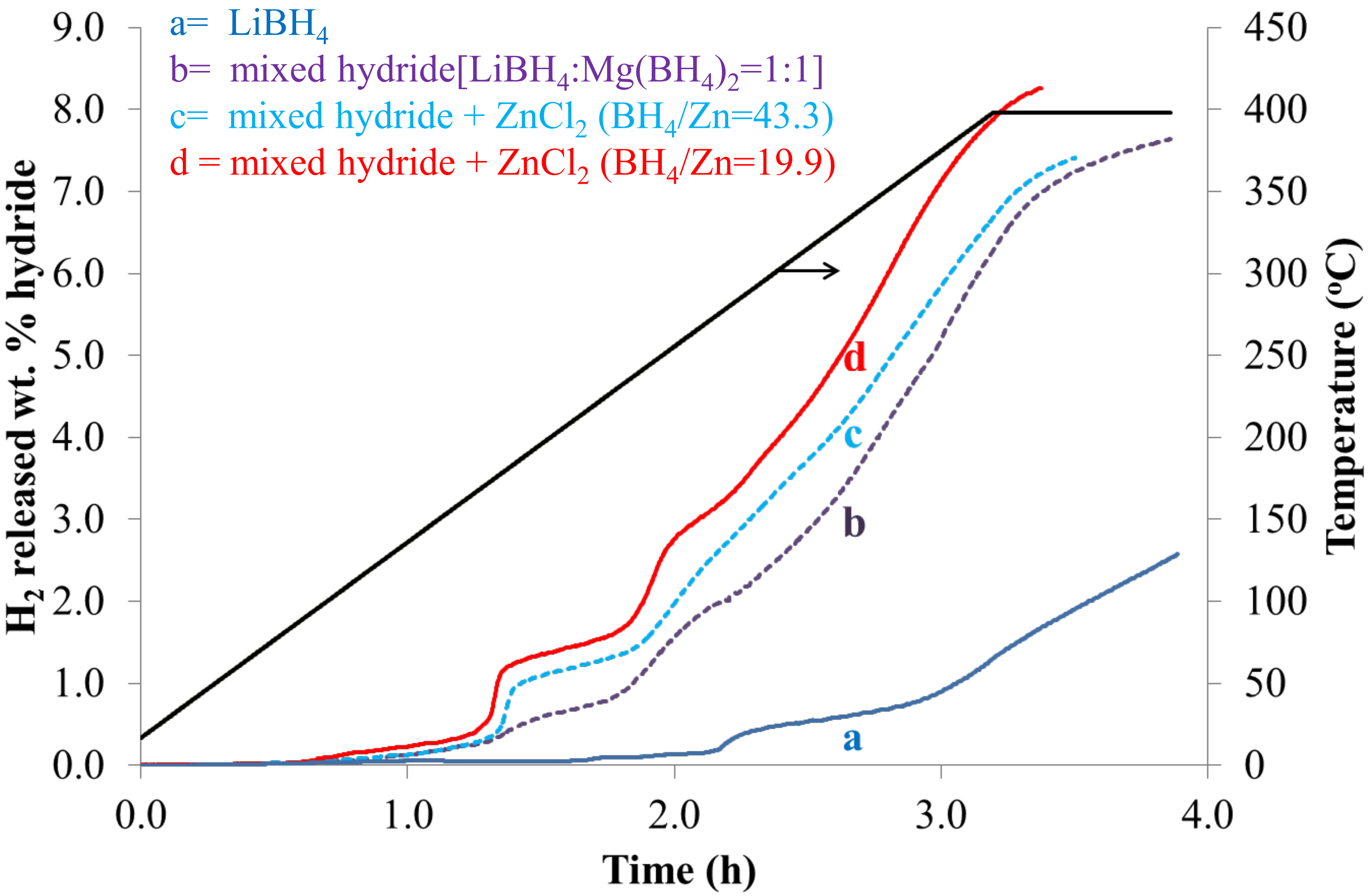
  B_2H_6 is formed by the following reaction:
  $10LiBH_4 + 5ZnCl_2 = 5Zn + 10\ LiCl + 5B_2H_6 + 5H_2$
  Corresponding reaction between $Mg(BH_4)_2$ and $ZnCl_2$ has not been reported..

  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.

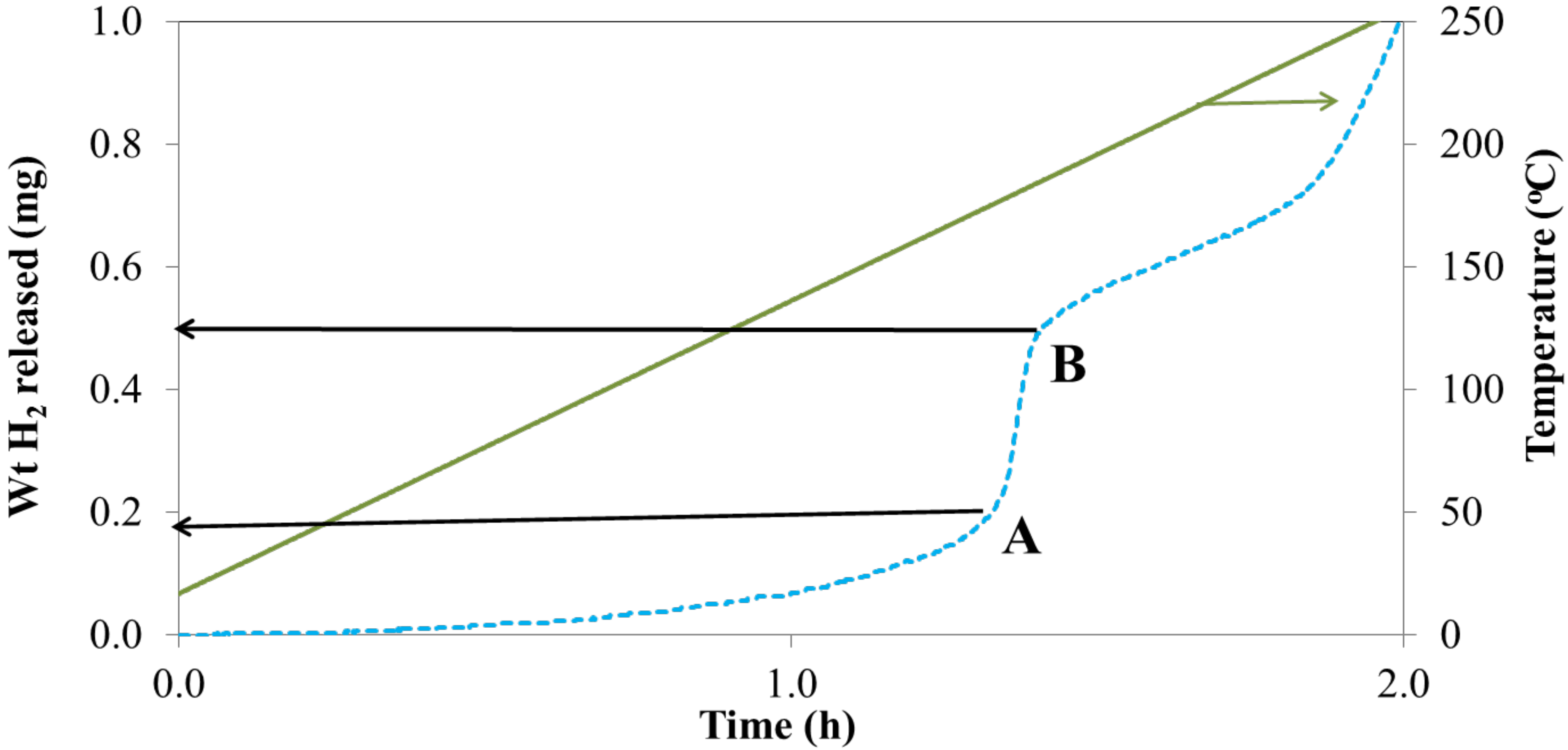
Results: $ZnCl_2$ addition increased H_2 release at low temperatures from $LiBH_4$- $Mg(BH_4)_2$ mixed hydrides. Comparing curves b, c, and d: more H_2 released with more $ZnCl_2$.



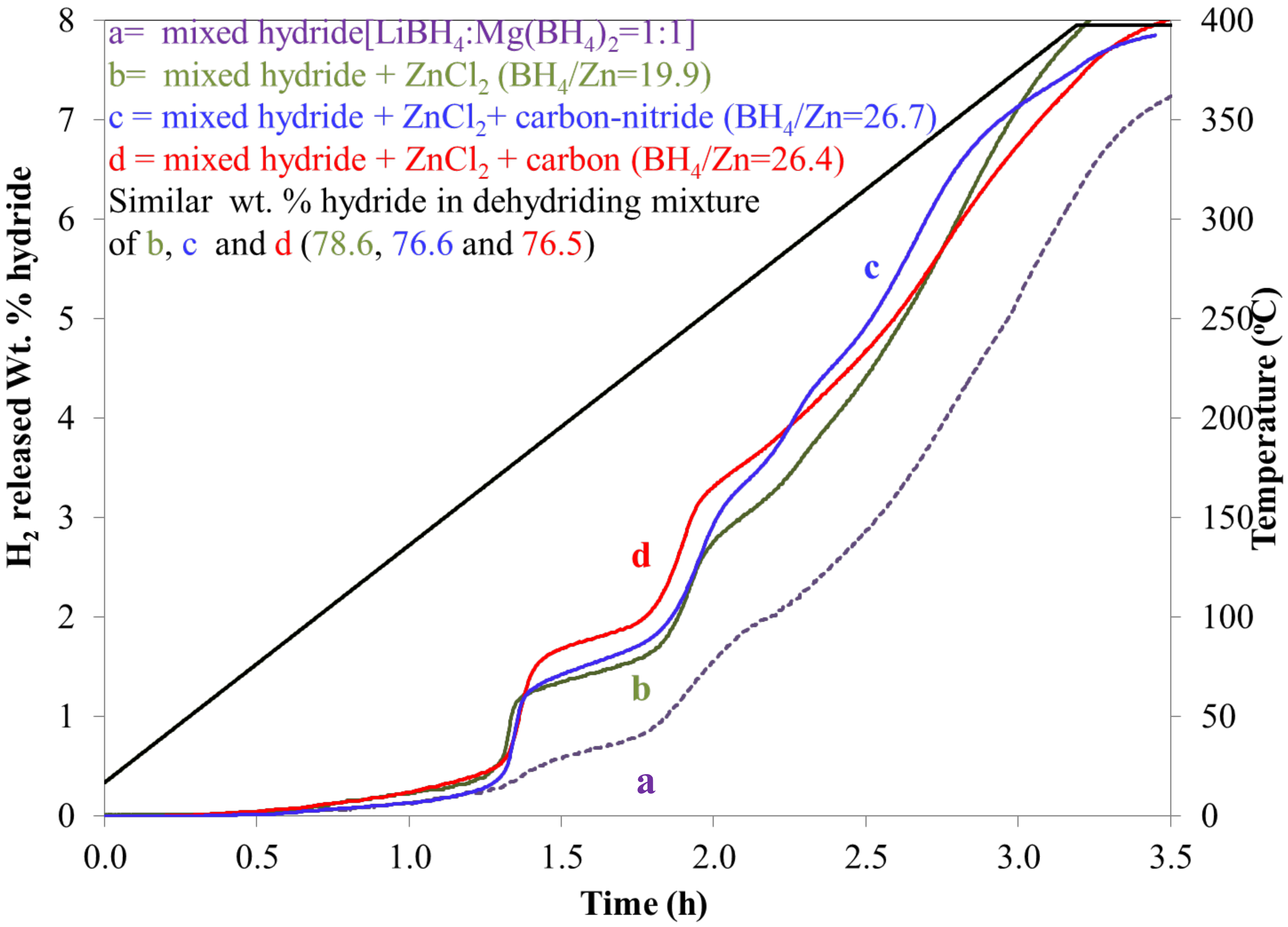
Results: Evidence that indicates little or no B_2H_6 formation.

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

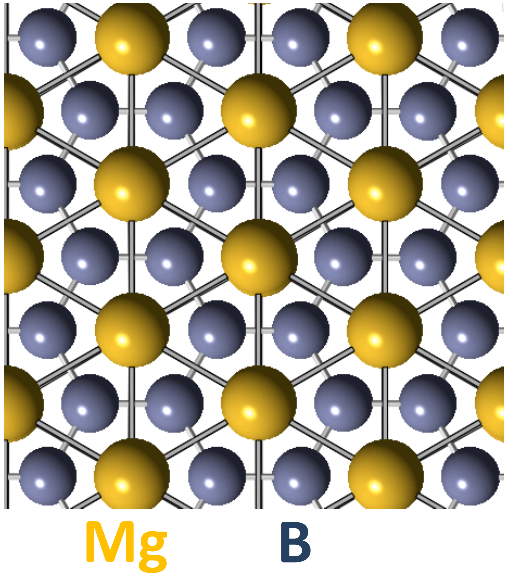


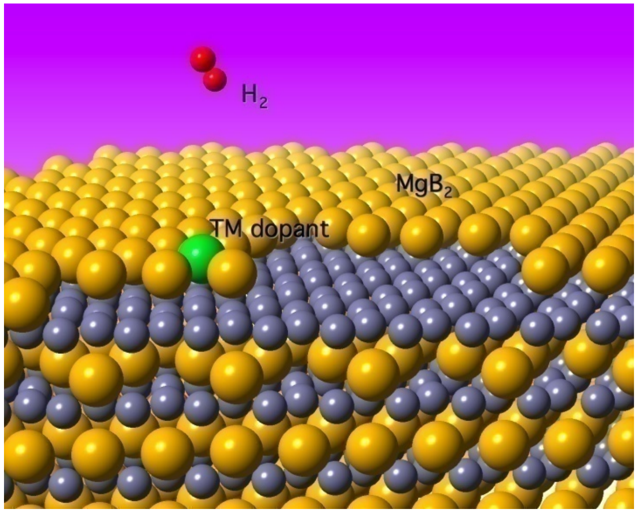
Result: addition of carbon to $ZnCl_2$ further improved low temperature H_2 released from $LiBH_4$- $Mg(BH_4)_2$



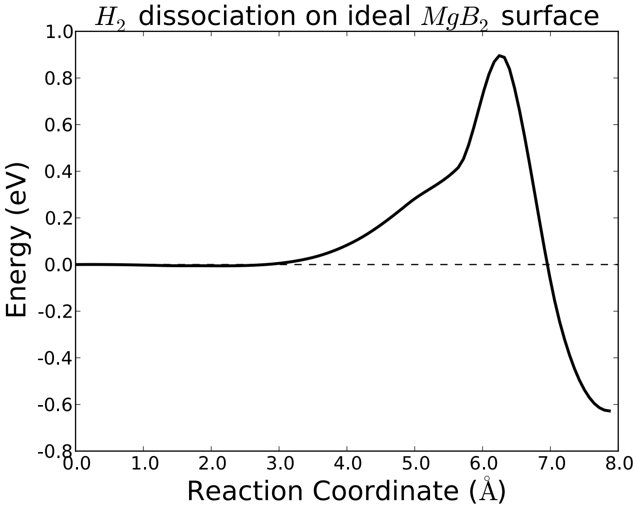
Identify the kinetic barriers for re-hydrogenation of MgB_2

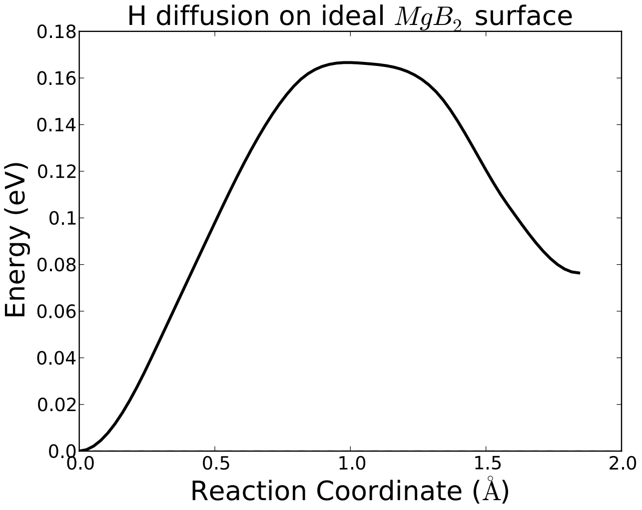
- **What are the rate-limiting steps for MgB_2 ?
(mass transport, nucleation, dissociation, diffusion, or others?)**





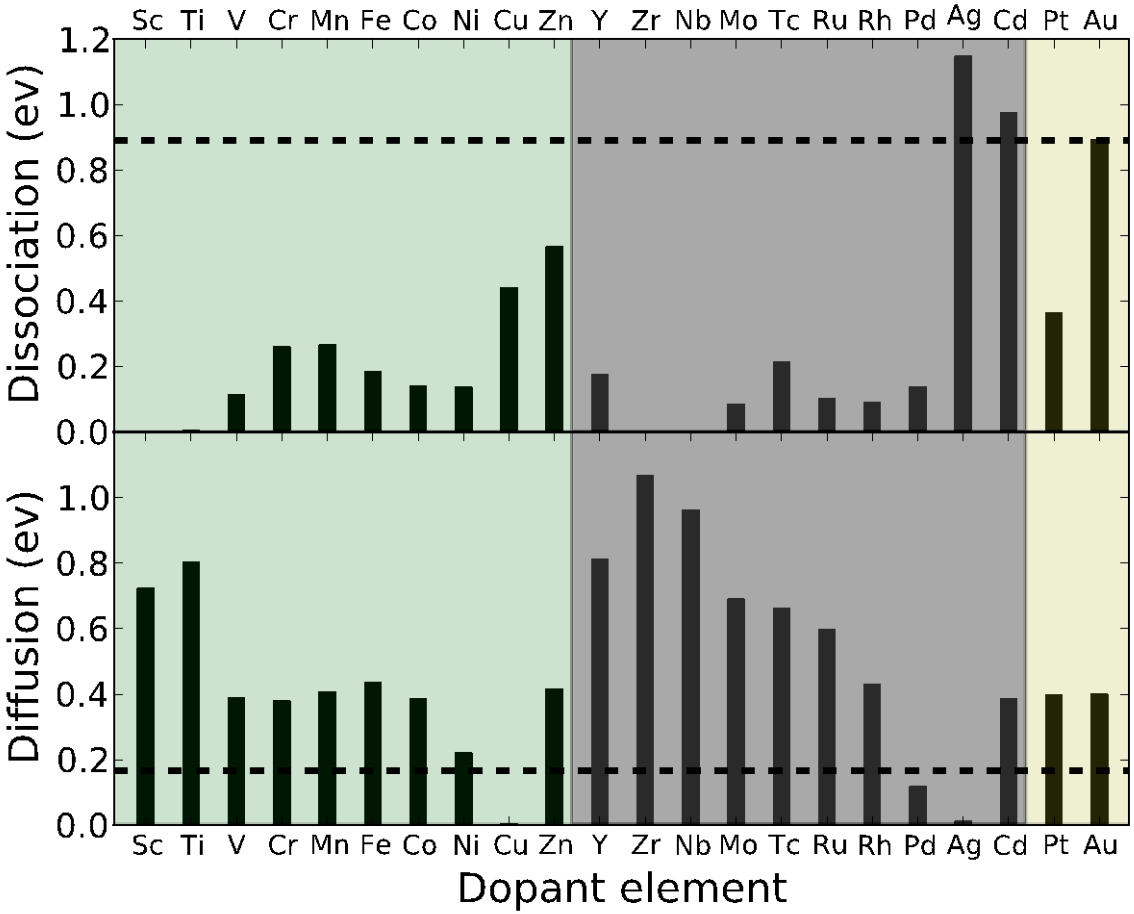
We investigated the H_2 dissociation and H diffusion on the Mg-terminated MgB_2 (0001) surface





Identify the kinetic barriers for re-hydrogenation of MgB_2

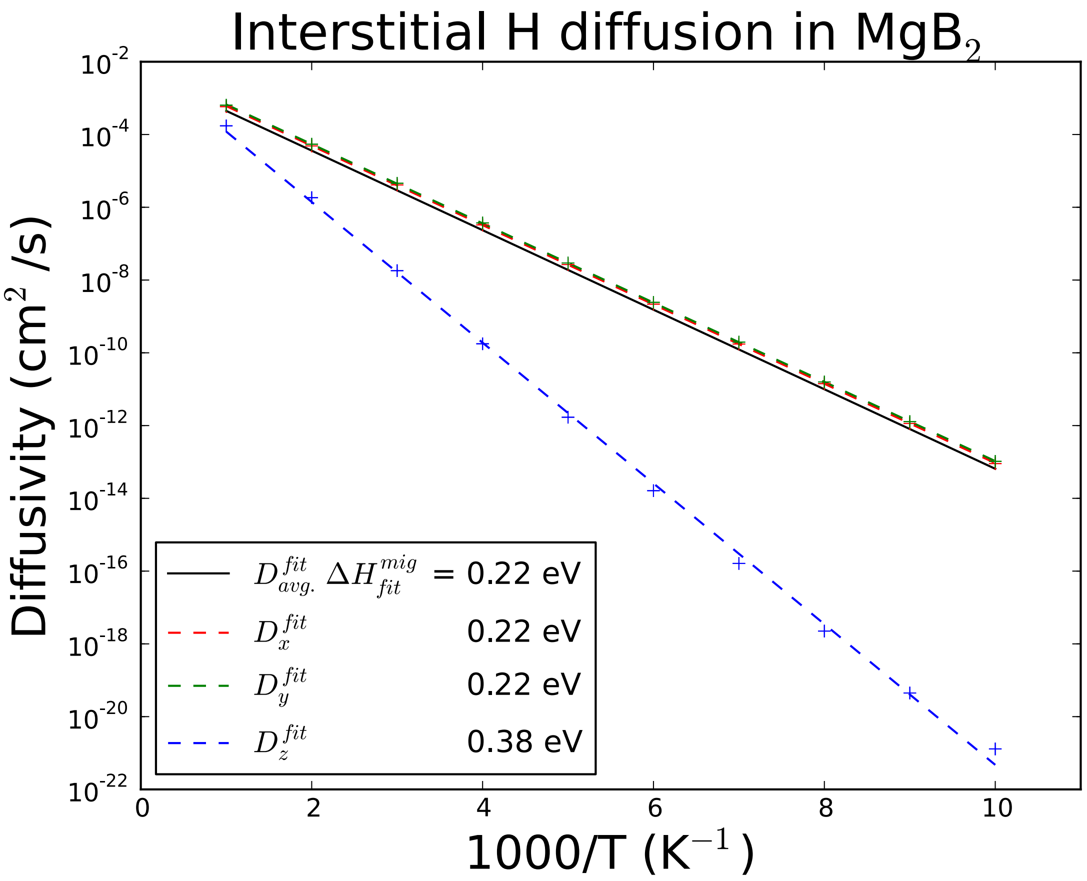
	Barriers (eV)
Dissociation	0.89
Diffusion	0.17



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



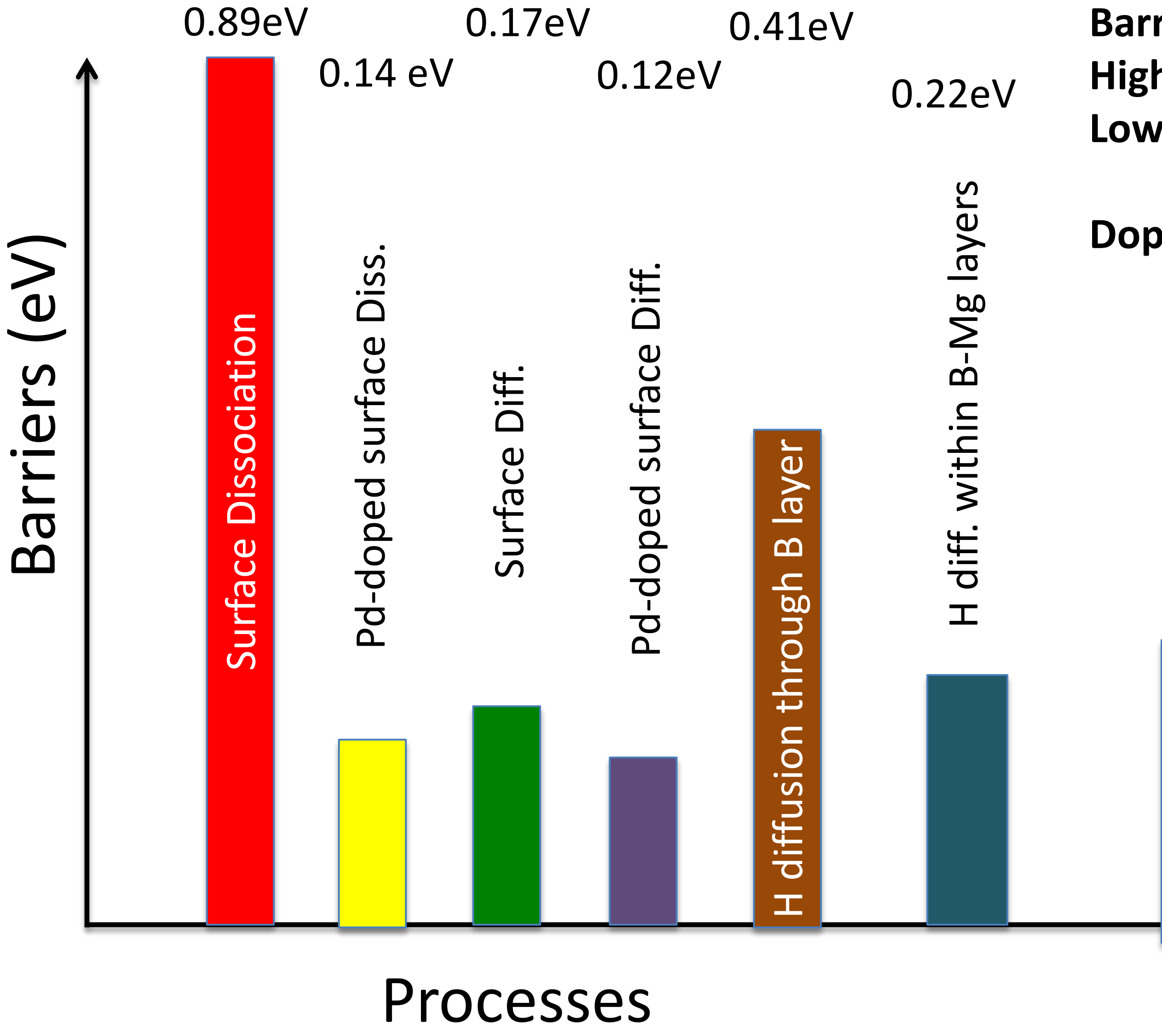
KMC calculations results:
(migration energy)

- $D_x = D_y = 0.22$ 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

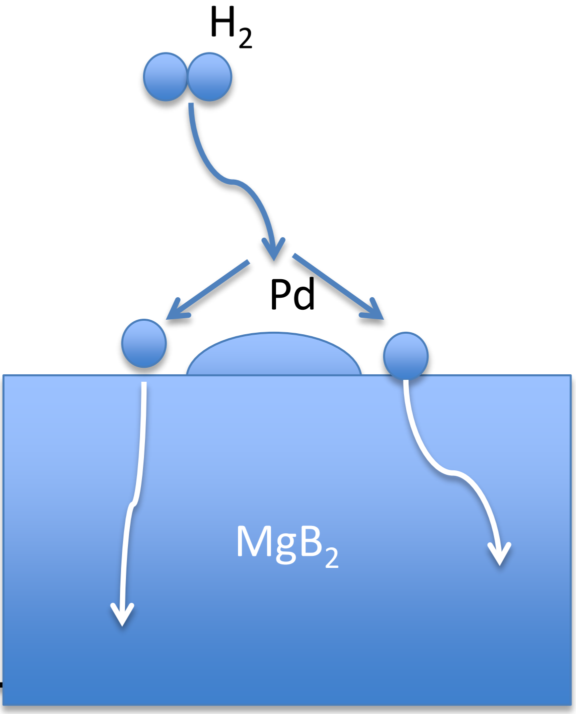


Barriers:

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

- <u>Kinetics</u> of high-capacity borohydride reactions almost always limiting factor - <u>thermodynamic</u> 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

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)

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