



# Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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June 12, 2008



Project ID  
# **ST34**

This presentation does not contain any proprietary or confidential information

## Timeline

- Project start date: April, 2005
- Project end date: Dec., 2009
- 60 % complete

## Budget

- Expected total project funding:
  - \$1.859M (DOE)
- Funding received in FY07
  - \$400K (DOE)
- Funding received for FY08:
  - \$487.2K (DOE)

## Barriers/System Targets

- A. System Weight and Volume
  - 2010 Targets: 6 wt.% & 45 gH/L
- D. Durability/Operability
  - 2010 Target: Life of 1000 cycles
- E. Charging/Discharging Rates
  - 2010 Target: Fill time of 3 min for 5 kg H<sub>2</sub>
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

## Partners

- Participant in DOE MHCoe – collaborations with partners in all five sub-group Projects [primarily with Caltech, NIST, GE Global, U. Hawaii, SNL, U. Utah, HRL, ORNL in FY-07 & FY-08]
- Washington U. and Caltech in support a DOE/BES H<sub>2</sub> Storage Project on solid state NMR studies of light element hydrides
- International: IFE (Norway), Tohoku U. (Japan), and AIST (Japan)

## ***Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage***

- (1) Validation of storage properties and reversibility in light element hydrides**
  - Nanophase, destabilized hydrides based upon LiH, MgH<sub>2</sub>, & LiBH<sub>4</sub>
  - Complex hydrides (e.g., amides/imides, borohydrides, & AlH<sub>3</sub>-based hydrides)
  - Samples provided by numerous MHCoE partners
- (2) Support developing lighter weight and thermally efficient hydride storage vessels.**

### **FY07/FY08 Milestones:**

- Evaluate behavior of destabilized MgH<sub>2</sub>/LiBH<sub>4</sub> and Li-Sc-B-H systems against targets:
  - Reversibility
  - Kinetics
  - H<sub>2</sub> storage parameters (i.e., capacities, pressures, etc.)
- Characterize phases & chemical bonding via MAS-NMR (Caltech) to better understand basic chemisorption processes.
  - Li amides/imides/alanates
  - Borohydrides
  - Other hydrides provided by MHCoE partners
- Have postponed extended cycling tests to assess lifetime potential & durability since no destabilized/catalyzed hydrides was found with viable kinetics and reversibility to justify this commitment.

# JPL Has Been Supporting Many MHCoe Projects

**DOE/EERE**

**Metal Hydride Center of Excellence (MHCoe)**

**Coordinating Council**

**Sandia National Laboratory (SNL)- Lead Laboratory**

**Project Groups**

**A**

**Destabilized  
Hydrides**

- Stanford (POC)
- Caltech
- **JPL**
- UIUC
- U. Hawaii
- U. Pitt/CMU
- HRL
- U. Utah
- Intematix
- NIST

**B**

**Complex  
Anionic  
Materials**

- **SNL(POC)**
- GE
- U. Hawaii
- UIUC
- **JPL**
- ORNL
- NIST
- UNR
- Utah
- UTRC

**C**

**Amides/  
Imides  
(M-N-H)**

- **Utah (POC)**
- GE
- UNR
- ORNL
- U. Hawaii
- **JPL**
- Caltech
- SRNL

**D**

**Alanes  
(AlH<sub>3</sub>)**

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- **JPL**

**E**

**Engineering  
Analysis &  
Design**

- **SRNL(POC)**
- NIST
- **JPL**
- GE
- SNL

## Perform Analysis and Characterization of Selected Hydrides to Explain Fundamental Processes:

- **Volumetric measurements are used to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides.**
- **Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) measurements being performed at Caltech Solid State NMR Facility (Dr. Son-Jong Hwang, lead) to assess the phase compositions and chemical bonding parameters.**
- **Examinations of structures by neutron scattering and diffraction, etc. in collaboration with MHCoe partner NIST.**
- **Using Raman spectroscopy measurements at Caltech to determine mechanisms of desorption processes .**
- **Interacting with MHCoe theory teams (i.e., U. Pittsburgh, GA Tech, and UMSL) on phases and destabilization behavior.**

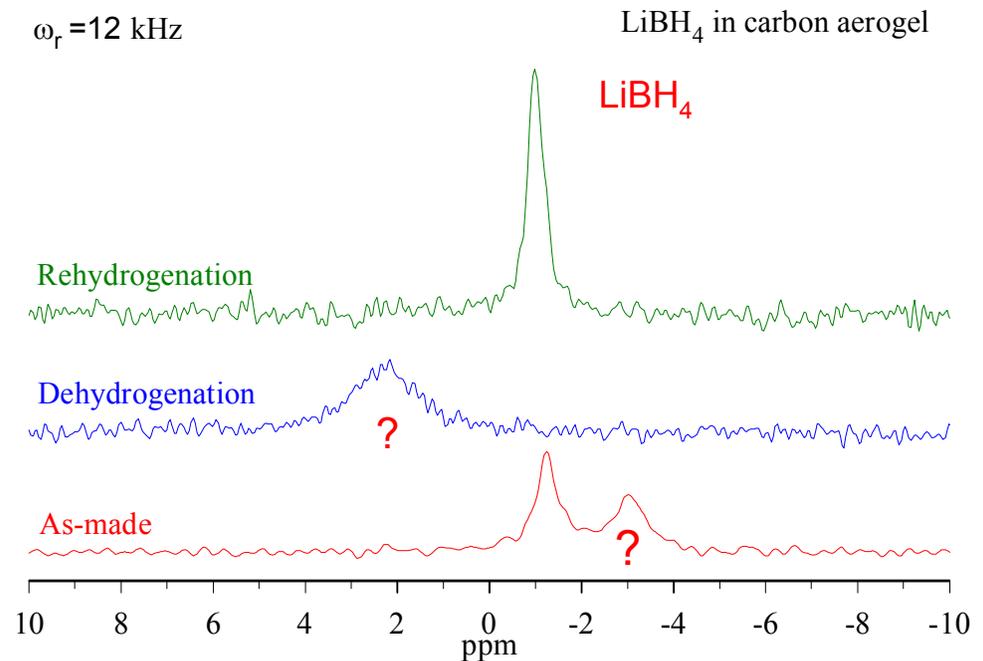
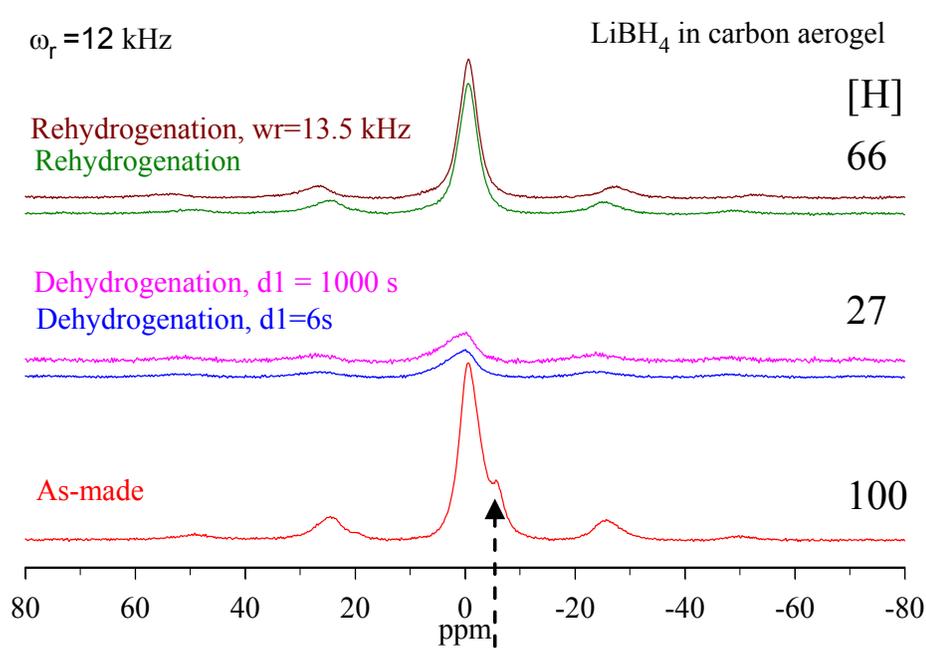
Sample ID (HRL)	Chemical species	Processing Description
SO542-113-59	LiBH <sub>4</sub> /CA	As-made in 25 nm carbon Aerogel (44.7 wt%)
SO542-113-59-used	LiBH <sub>4</sub> /CA	Dehydrogenation at 400 °C
SO542-113-59-used-a	LiBH <sub>4</sub> /CA	Rehydrogenation at 100 bar H <sub>2</sub> , at 400 °C for 2 hours

HRL\_SO542\_1H

<sup>1</sup>H MAS NMR

HRL\_SO542\_6Li\_bd

<sup>6</sup>Li MAS NMR

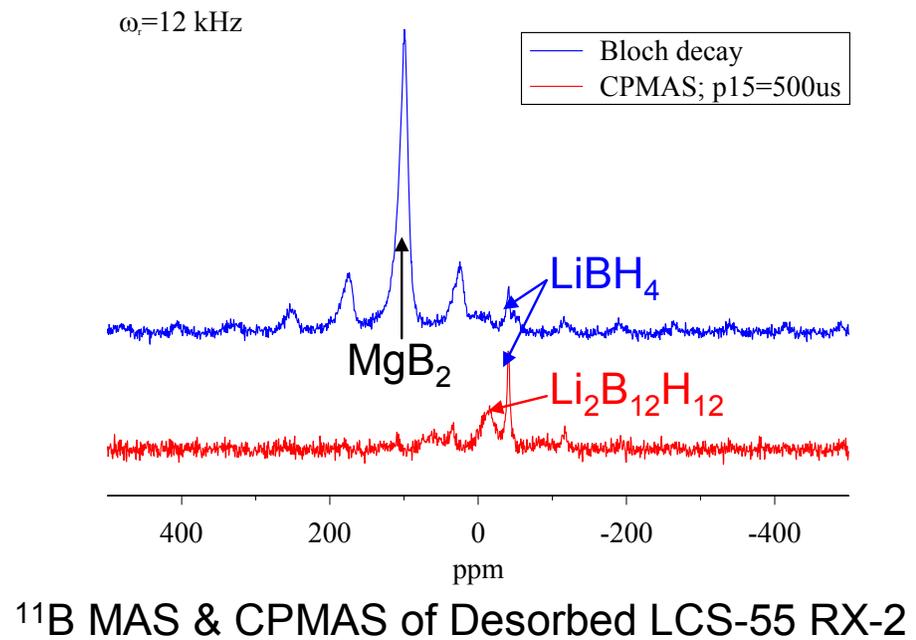
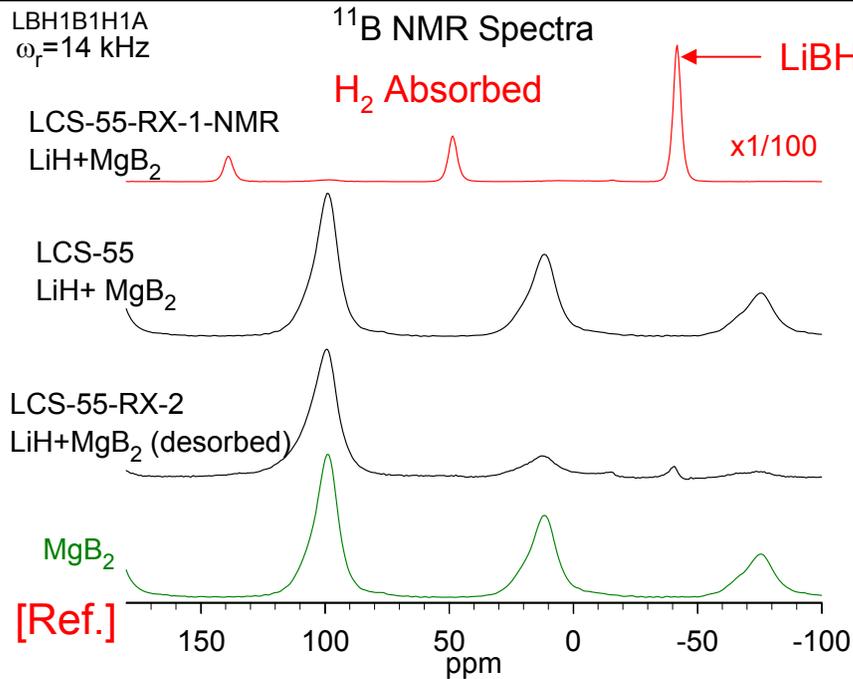


- Two proton peaks in the 'as-made' sample indicate distinct hydrogen species within the scaffold where the bulk LiBH<sub>4</sub> peak recovers while the other unknown peak (at -5 ppm) disappears after cycling.
- <sup>6</sup>Li NMR spectrum for LiBH<sub>4</sub> on CA scaffold also suggest two different sites. The -3 ppm peak might be Li ions interacting with the surface. Re-hydrogenation gives the LiBH<sub>4</sub> phase without the -3 ppm peak.
- Partial reversibility of LiBH<sub>4</sub> was noted in <sup>11</sup>B spectra (not shown) – some B<sub>12</sub>H<sub>12</sub><sup>2-</sup> species & B formed.



J. J. Vajo, et al., J. Phys. Chem. B **109** (2005) 3719

Samples	Code	Treatment	Comments
LiH+MgB <sub>2</sub>	LCS-55	As ball milled	From J. Vajo [HRL]
LiBH <sub>x</sub> +MgH <sub>2</sub>	LCS-55: RX-1	Absorbed H <sub>2</sub>	Saturated hydrides
MgB <sub>2</sub> + LiH + LiBH <sub>x</sub>	LCS-55: RX-2 + SiO <sub>2</sub>	Desorbed H <sub>2</sub> : diluted for NMR	Incomplete desorb reaction



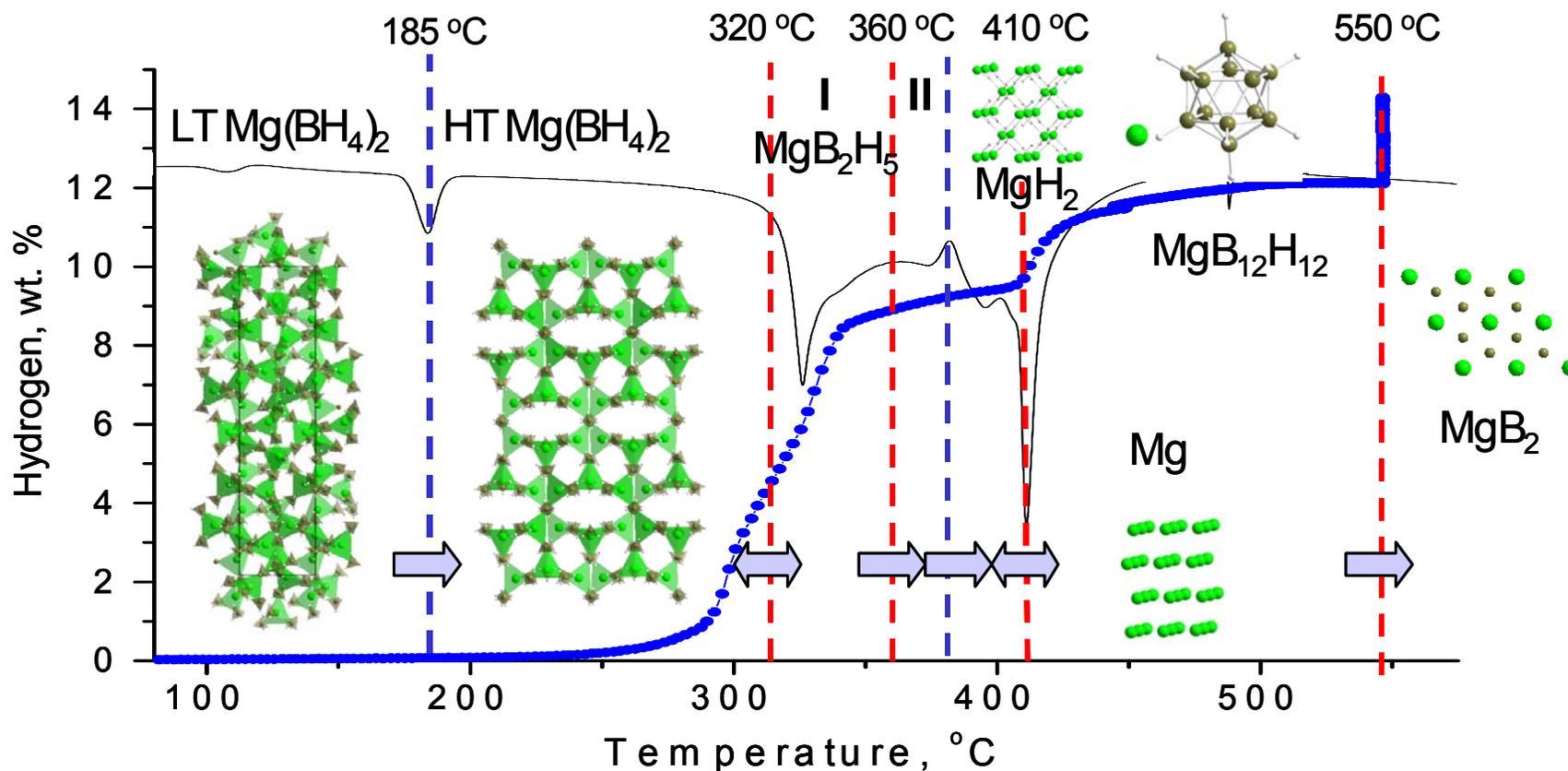
NMR shows residual amounts of B<sub>12</sub>H<sub>12</sub><sup>-2</sup> along with LiBH<sub>4</sub>: Incomplete reversibility under these cycling conditions.

Reaction down selected to “No-Go”, except for Aerogel scaffolding studies (HRL).

## JPL Objectives:

Support phase characterizations and bonding properties for new borohydrides [i.e.,  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ , &  $\text{LiSc}(\text{BH}_4)_4$ ] and their desorption processes via NMR measurements in collaboration with Caltech, SNL, GE Global, NIST, U. Hawaii.

## $\text{Mg}(\text{BH}_4)_2$ Decomposition Pathway

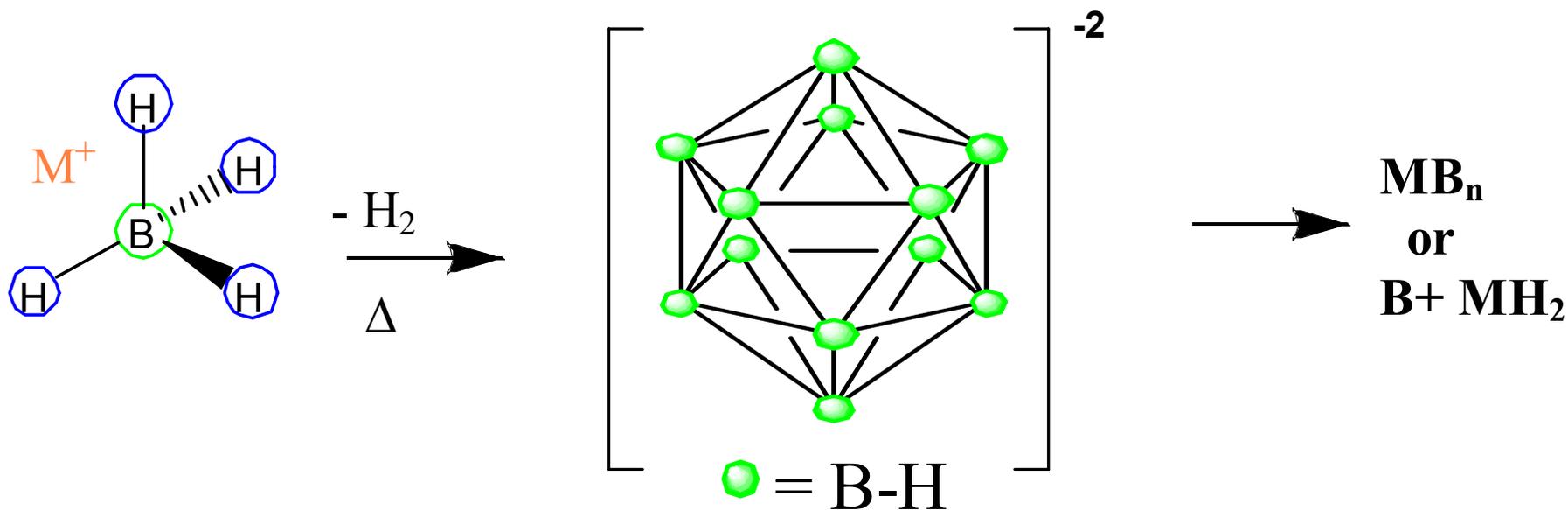


NMR has been a key method to establish phase identification!



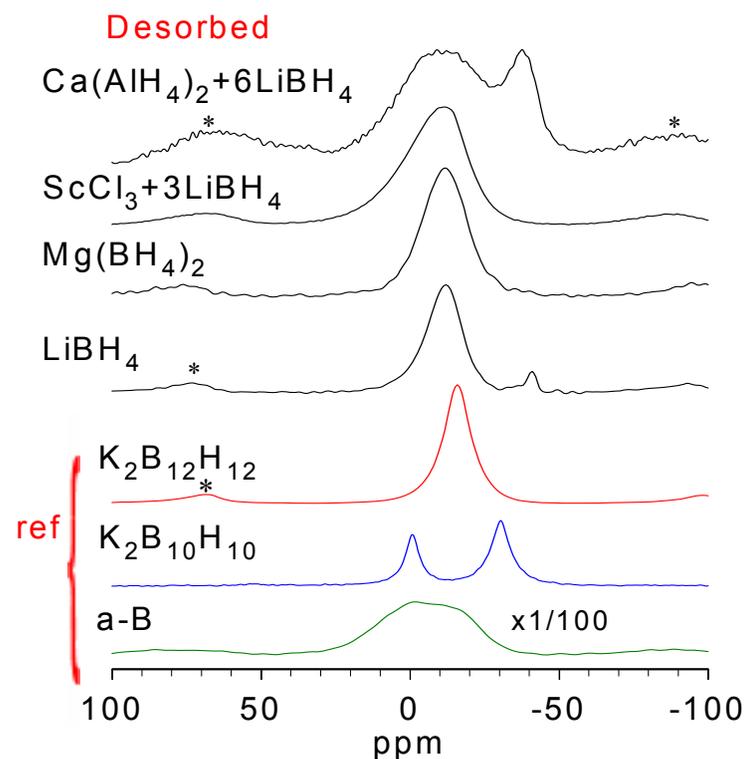
**Boron phases NOT identifiable via X-ray/Neutron diffraction ("Amorphous")**

**Solid state  $^{11}\text{B}$  NMR identified the formation of  $\text{M}_{2/n}\text{B}_{12}\text{H}_{12}$  phases as major intermediate species in hydrogen desorption reaction of various  $\text{M}(\text{BH}_4)_n$  systems before further conversion to either  $\text{MB}_n$  or  $\text{B}+\text{MH}_n$ .**

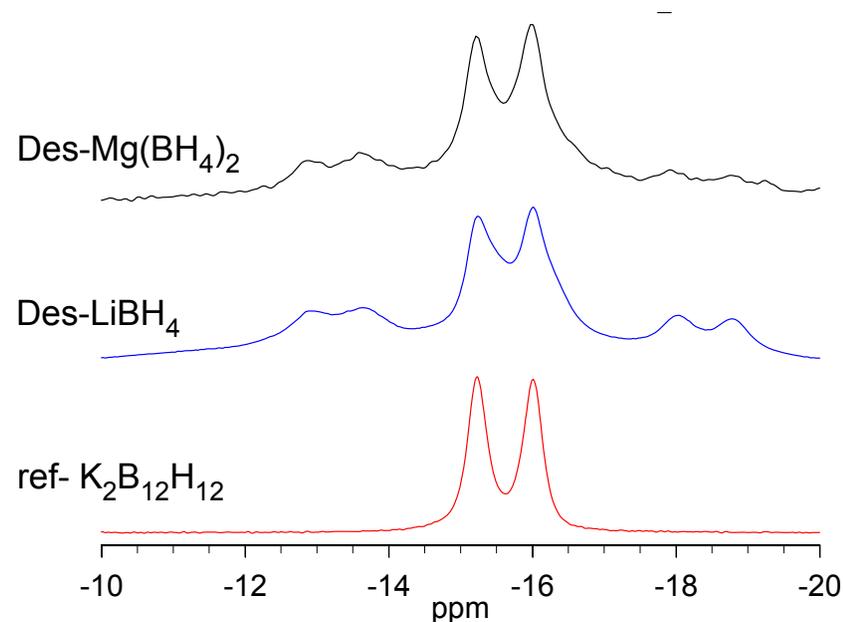


S.-J. Hwang, R. C. Bowman, Jr., J. W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J.-C. Zhao, H. Kabbour, and C. C. Ahn, *J. Phys. Chem. C Letters* **112** (2008) 3164-3169.

In collaboration with Caltech and GE,  $\text{LiBH}_4$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{Ca}(\text{AlH}_4)_2\text{-LiBH}_4$ , studied by  $^{11}\text{B}$  magic angle spinning (MAS) and cross-polarization magic angle spinning (CPMAS) after hydrogen desorption reactions at  $\sim 400^\circ\text{C}$ .



$^{11}\text{B}$  CPMAS NMR spectra of desorbed materials (contact time = 0.05 ms). Ref. spectra: amorphous boron (a-B, note the scale change (1/100)),  $\text{K}_2\text{B}_{10}\text{H}_{10}$ , and  $\text{K}_2\text{B}_{12}\text{H}_{12}$  added for comparison.

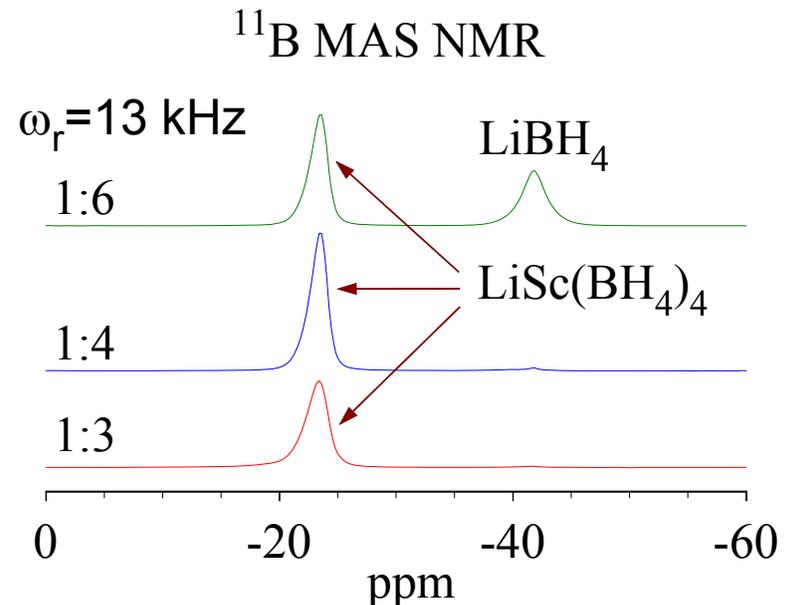
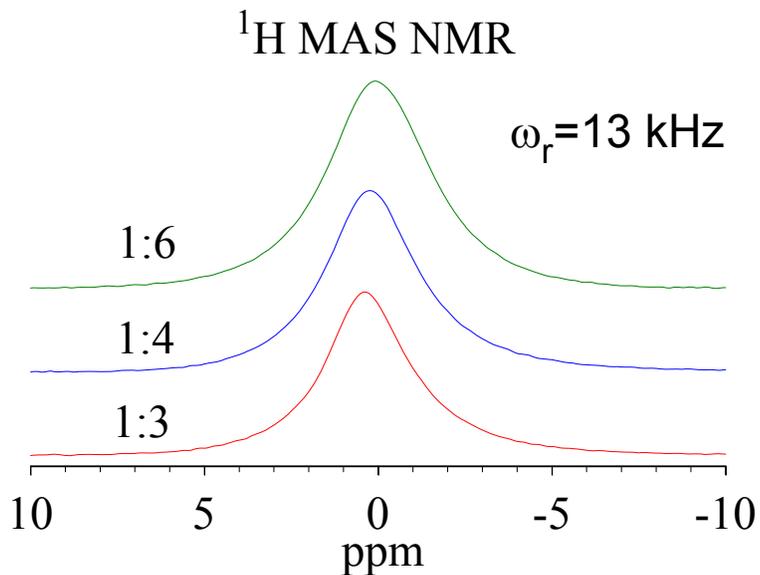


$^{11}\text{B}$  solution NMR spectra after powders from desorption reactions were dissolved in  $\text{H}_2\text{O}$ .

- Ref:  $\text{K}_2\text{B}_{12}\text{H}_{12}$  compound dissolved in water.
- $[\text{B}_{12}\text{H}_{12}]^{2-}$  unit present in the dissolved  $\text{LiBH}_4$  and  $\text{Mg}(\text{BH}_4)_2$  decomposition products.
- $J(\text{B-H}) = 125\text{ Hz}$  is confirming signature of B-H chemical bond in  $[\text{B}_{12}\text{H}_{12}]^{2-}$  unit

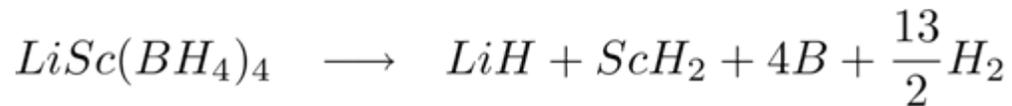
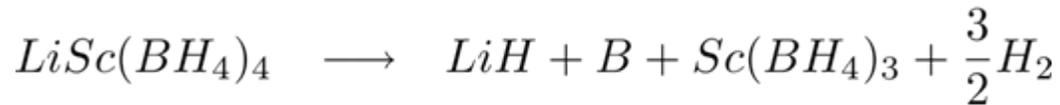
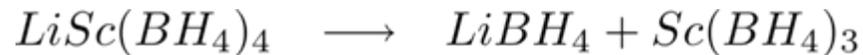
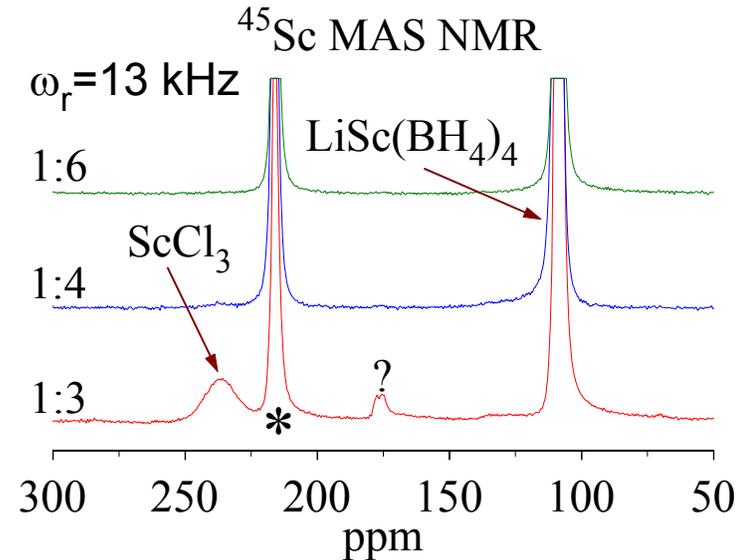
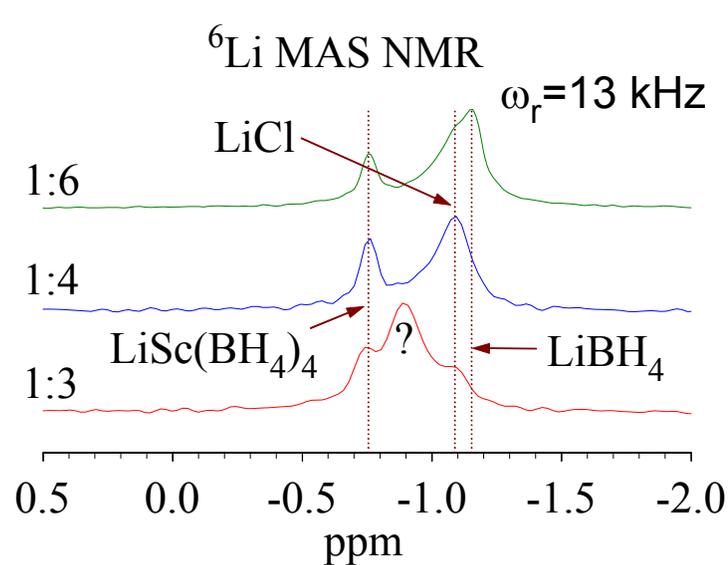
- Approach used by Y. Nakamori & S. Orimo to make  $M(\text{BH}_4)_n$  &  $M'M(\text{BH}_4)_n$
- Caltech: Anhydrous  $\text{ScCl}_3$  and  $\text{LiBH}_4$  (Aldrich,  $\geq 90\%$ ) mixed with five 0.5" diameter SS balls in a Fritsch-pulverisette 6 planetary mill at 500 rpm for 3 hours

ratio ( $\text{ScCl}_3 + x\text{LiBH}_4$ )	non-ionic route	ionic route
1:3	$\text{ScCl}_3 + 3\text{LiBH}_4 = \text{Sc}(\text{BH}_4)_3 + 3\text{LiCl}$ .	$\text{ScCl}_3 + 3\text{LiBH}_4 = \frac{3}{4} \text{LiSc}(\text{BH}_4)_4 + \frac{9}{4} \text{LiCl} + \frac{1}{4} \text{ScCl}_3$ .
1:4	$\text{ScCl}_3 + 4\text{LiBH}_4 = \text{Sc}(\text{BH}_4)_3 + 3 \text{LiCl} + \text{LiBH}_4$	$\text{ScCl}_3 + 4\text{LiBH}_4 = \text{LiSc}(\text{BH}_4)_4 + 3 \text{LiCl}$ .
1:6	$\text{ScCl}_3 + 6\text{LiBH}_4 = \text{Sc}(\text{BH}_4)_3 + 3 \text{LiCl} + 3\text{LiBH}_4$	$\text{ScCl}_3 + 6\text{LiBH}_4 = \text{LiSc}(\text{BH}_4)_4 + 3 \text{LiCl} + 2\text{LiBH}_4$ .



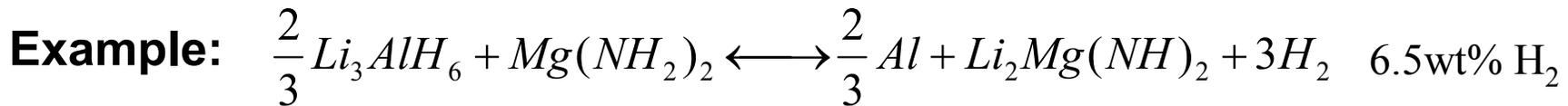
MAS proton &  $^{11}\text{B}$  spectra for ball milled mixtures of  $\text{ScCl}_3/\text{LiBH}_4$  in the ratios 1:3, 1:4, and 1:6. Peak assignments were obtained from combined analyses of spectra for all nuclei.

MAS and CPMAS spectra of  $^6\text{Li}$  and  $^{45}\text{Sc}$  nuclei (also  $^{11}\text{B}$ ) for  $\text{ScCl}_3/\text{LiBH}_4$  in the ratios 1:3, 1:4, and 1:6 show **only  $\text{LiSc}(\text{BH}_4)_4$**  phase is formed. The “?” in  $^6\text{Li}$  and  $^{45}\text{Sc}$  spectra are from a species without protons (i.e., probably  $\text{Li}_3\text{ScCl}_6$ ).

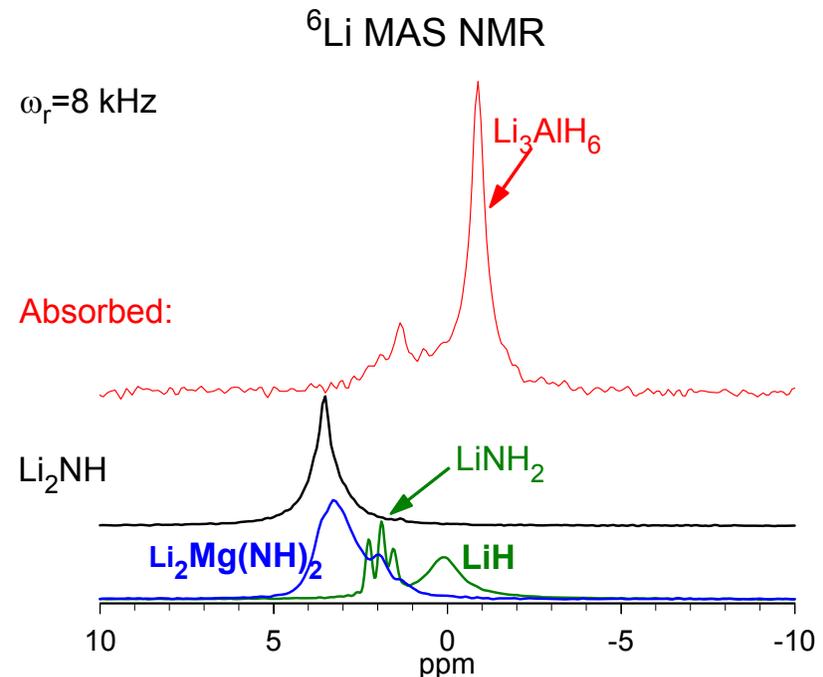
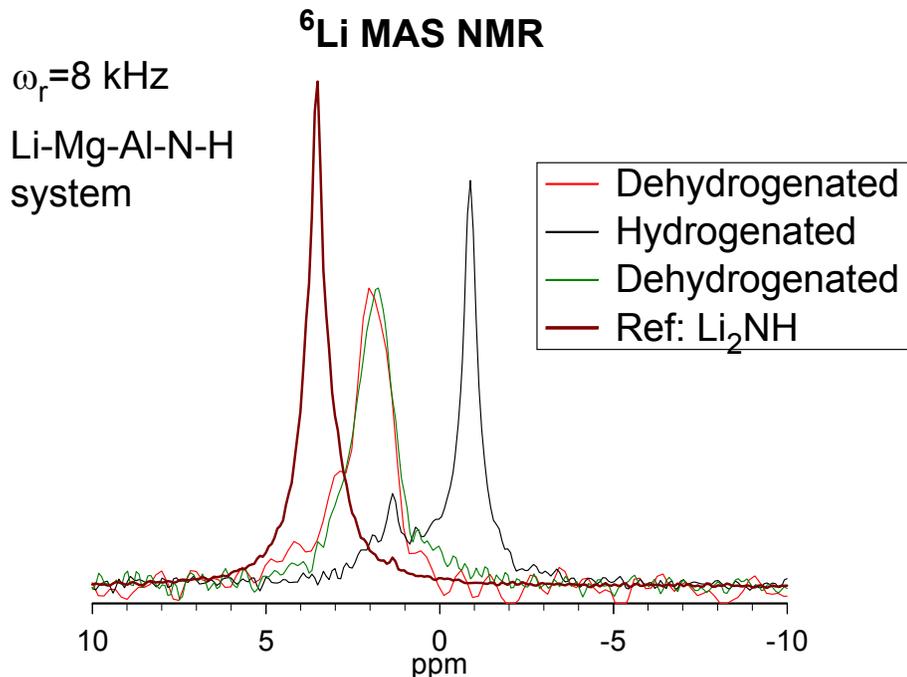


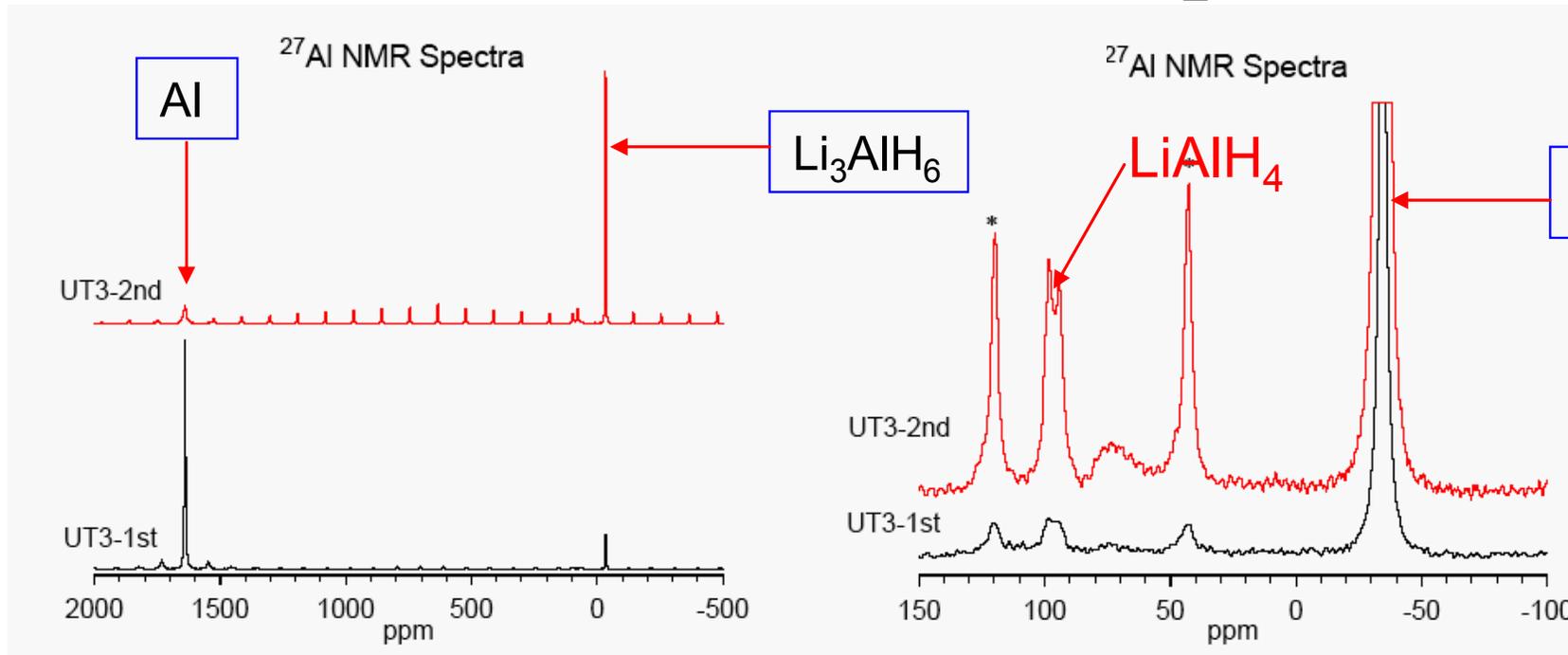
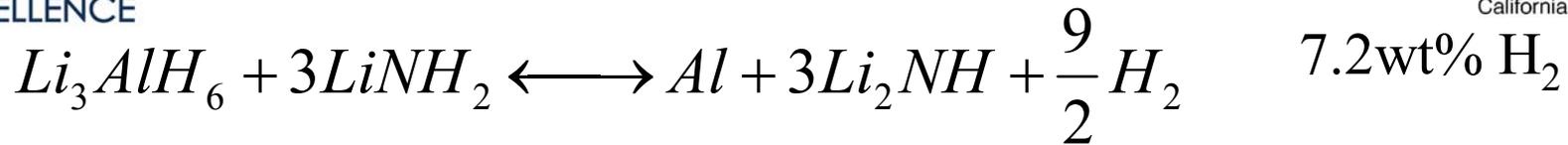
- Static DFT calculations (no phonons) T=0K
- All reaction equations +67 kJ/mol f.u. or greater (**Consistent with NMR!**)
- **BM method does NOT yield the less stable covalent  $\text{Sc}(\text{BH}_4)_3$  phase**

- Improve basic understanding of these materials
- Provide info on local chemical bonding during reaction
- Critically test and complement theoretical modeling of reaction mechanisms
- Assess reactions of amides/imides with alanates and borohydrides.



**<sup>6</sup>Li and <sup>27</sup>Al spectra indicated reversibility of the Li-Mg-Al-N-H samples from U. Utah.**





## Phase composition of UT3-2<sup>nd</sup> Sample

Components	Chemical shift (ppm)	Rel. Quantity (%)
Al(M)	1640	5.2
AlH <sub>4</sub> <sup>-</sup>	98.8	8.1
Al <sub>2</sub> O <sub>3</sub>	74.1	3.8
AlH <sub>6</sub> <sup>-3</sup>	-34.6	82.9

➤ Conversion to Li<sub>3</sub>AlH<sub>6</sub> is more than 80% based from NMR results, which also indicate LiAlH<sub>4</sub> forming when pressure is 2500 psi.

➤ Subsequent studies showing impact of reaction conditions on product yield & formation of AlN phase @ heating rates < 5 K/min.

UT3-1st: Sample UT2 after rehydrogenation at 300 °C and 2000 psi

UT3-2<sup>nd</sup>: Sample UT2 after rehydrogenation at 300 °C and 2500 psi

## Prototype Hydride Beds Development and Life Testing

### Objectives:

- Support development of more efficient hydride storage vessels to reduce storage system mass while retaining viable thermal management during H<sub>2</sub> absorption & desorption.
- Support system design and analyses using methods and analytical models established at JPL for sorption cryocooler hydride compressor beds.
- Evaluate the performance and robustness of candidate hydrides during many cycles of hydrogen absorption and desorption.

Deferred conducting cycling tests in FY-07/08 as LiBH<sub>4</sub>/MgH<sub>2</sub> and other borohydride systems are not attractive due to slow kinetics & poor reversibility – will start cycling tests only if a viable candidate is identified from current screening assessments.

## Accomplishments during FY07/08

### • **Completing Metal Hydride Storage Survey Report on status of the vessel design configurations and thermal analyses methodologies**

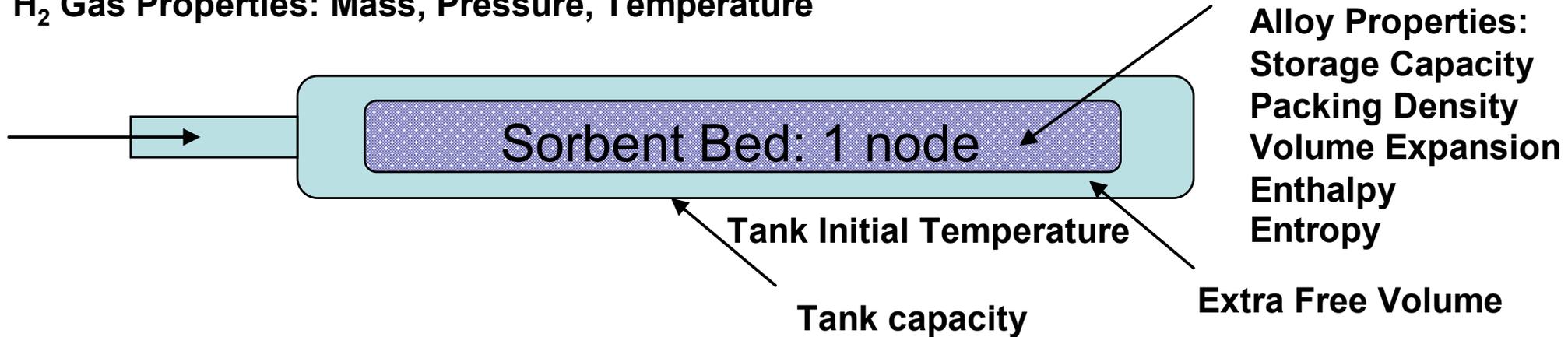
- Compiled from literature sources:
- Teaming with SRNL, UTRC, SNL, & DOE/EERE
- Progress reported at MS&T'07 Meeting, Detroit, MI (September 2007) and at DOE SSAWG Meeting, Washington DC (December 2007).
- Draft Report is planned to be completed in June 2008.

### • **Evaluate MH System thermal performance with analysis codes adapted from models previously developed for JPL sorption cryocoolers:**

- Comparisons using generic bed design configurations:
  - Known hydrides (e.g.,  $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ ,  $\text{AB}_2$ , and bcc-type alloys)
  - Light complex hydrides (e.g., alanates, etc.)
- Assess feasibility of rapid absorption filling of “Hybrid HP-LT Hydride Vessels”
  - Materials limited by heat transfer processes rather than reaction kinetics
  - Compare behavior of various  $\text{AB}_5$  and  $\text{AB}_2$  alloys.

# Excel Hydride Model to Determine Cooling For Hydride Bed Charging

H<sub>2</sub> Gas Properties: Mass, Pressure, Temperature



$$\text{Cooling Required} = \frac{Q_{\text{charging}} - Q_{\text{absorbed\_by\_hydrogen}} - Q_{\text{absorbed\_by\_alloy}}}{\text{Fueling Time}}$$

## • Model Features:

- 1 node model
- 0 order comparison of hydrides

- Heat from bed charging is dependant on alloy enthalpy and hydrogen mass absorbed by the alloy
- Heat Absorbed by Alloy & Hydrogen depend on equilibrium temperature
  - Van't Hoff Equation: P-C-T Curves not included
  - Does not account for the sloped plateaus

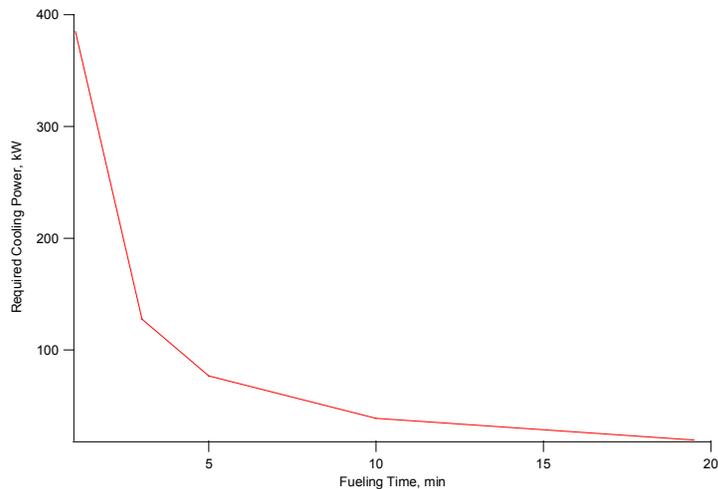
## Abilities:

- Fast back of the envelope approach to calculating required cooling for charging a hydride bed at low pressures
- Calculates hydrogen charged into the alloy
- Calculates an equilibrium temperature
- Can do a 0-order comparison of alloys without taking specific geometry into account

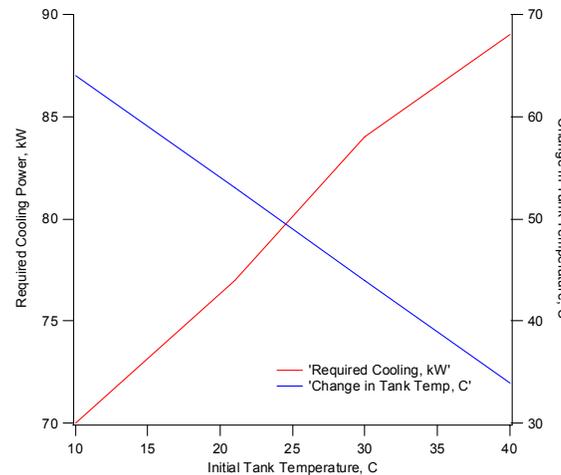
## Limitations:

- Does not include Pressure, Temperature, Concentration Curves
- Model code predicts hydrogen always absorbed by the alloy even at high temperatures (not realistic)
- Comparison between two alloys can be difficult due to limitations on pressure, temperature, and hydrogen concentration relationship

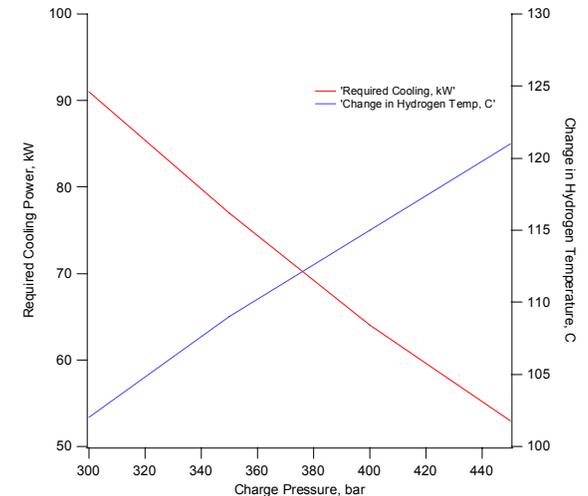
## Some Parametric Results for a Ti-Based AB<sub>2</sub> Alloy



Fueling time (min)



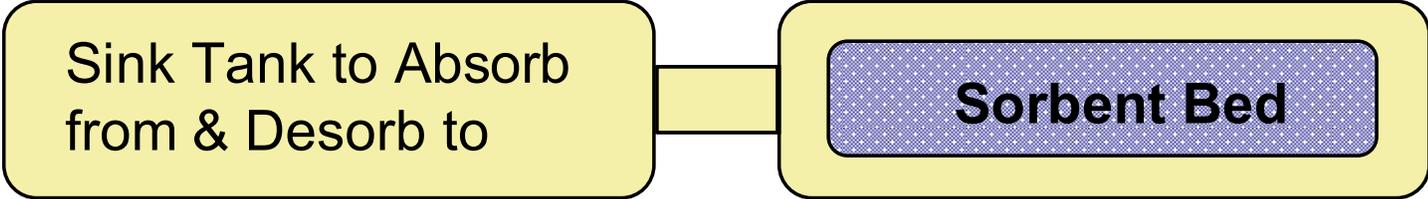
Initial Tank Temperature



Maximum H<sub>2</sub> Charge Pressure (bar)

**Need to adapt basic model for including Pressure, Temperature, Concentration relationships more completely.**

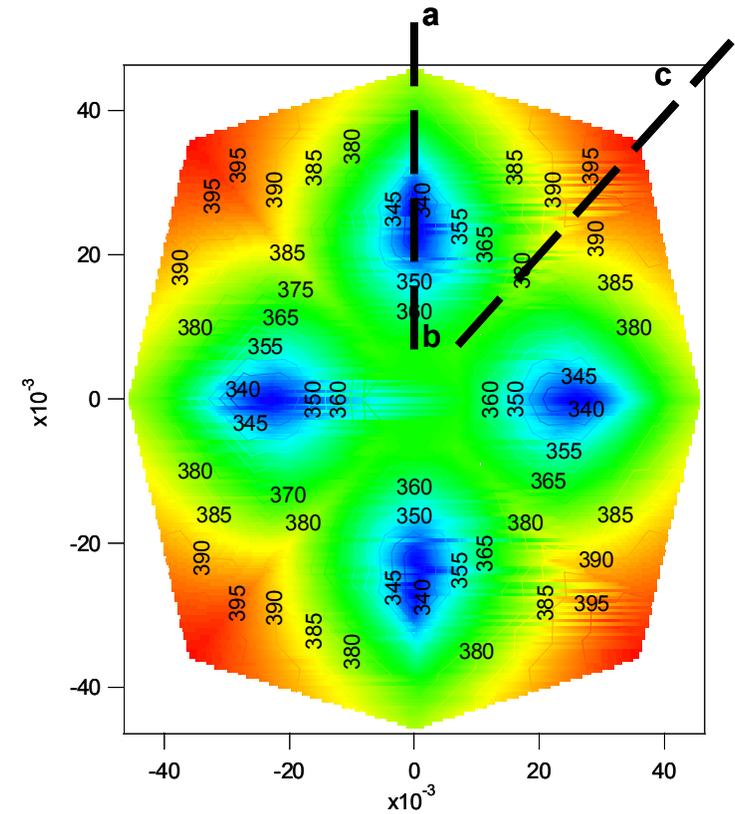
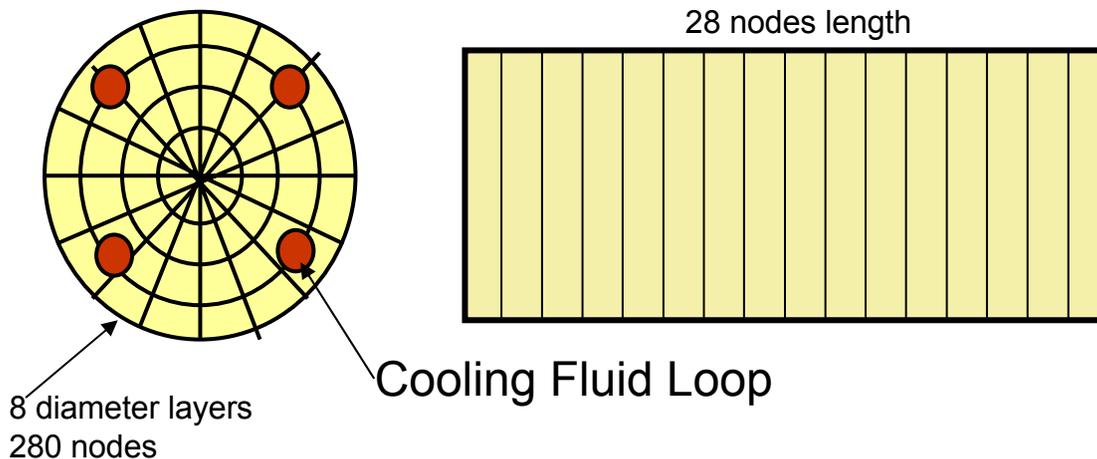
# JPL SINDA/FLUINT Model For Hydride Bed Charging



## Model Features:

- Over 7000 nodes for the hydride bed
- Detailed hydride & bed design properties
- P-C-T curves are calculated for each node

## SINDA Model Hydride Bed



Simulated temperature map shows gradients of  $\sim 50$  K within bed

Note: Details are in a back-up slide

## Destabilized Reactions (Proj. A)

- Continue reaction path investigations using NMR and Raman spectroscopies in the Li-Sc-B-H &  $\text{LiBH}_4\text{-Ca}(\text{AlH}_4)_2$  systems to understand destabilization and reversibility mechanisms.
- Extend studies of the  $\text{LiBH}_4$  encapsulated in carbon Aerogel samples to determine chemical bonding of Li and protons with host surfaces via  $^{13}\text{C}$  and  $^6\text{Li}$  MAS-NMR and CP-MAS.
- Apply NMR to identify species in destabilized complex hydride systems that lack definitive crystallographic features or have nanophase structures.

## Complex Anionic Materials (Proj. B)

- Continue detailed volumetric & NMR assessments of  $\text{Ca}(\text{BH}_4)_2$  phases (SNL), catalyzed borohydrides and alanates (SNL, U. Hawaii, IFE, and Tohoku U.), and  $\text{NaMgH}_3$  (SRNL, NIST, and Washington U.)
- Evaluate the desorption and absorption (including potential catalysts) behavior of the polyborane  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  via NMR, Raman, and neutron vibrational spectroscopy (Caltech & NIST) then look for methods to enhance reversibility of polyborane reactions.

## Amides/Imides (Proj. C)

- Continue systematic  $^{27}\text{Al}$ ,  $^6\text{Li}$ , and  $^{15}\text{N}$  MAS-NMR studies of Li-Mg-Al-N-H phases (U. Utah).
- Investigate reaction mechanisms, kinetics, diffusion, and reversibility for these materials.

## Evaluations of Alanes (Proj. D)

- Assess  $\text{AlH}_3$  phases and decomposition processes (U. Hawaii, SRNL, BNL, and IFE)

## Engineering Analysis & Design (Proj. E)

- Complete literature survey review on state-of-art hydride bed designs and performance.
- Model optimized  $\text{H}_2$  absorption of high-pressure alloy hydride beds for rapid filling rates.
- Perform accelerated cycling study if a promising hydride material can be identified.

**Approach:** JPL supporting MHCoe goals/objectives in two areas

1. Systematic characterizations of phase formation and hydride reversibility using solid state NMR and volumetric measurements (Projects A, B, C, & D)
2. Development of improved hydride storage vessels and system engineering of high performance and long life materials (Project E)

**Technical accomplishments and progress:**

- Phase characterization, kinetics (i.e., diffusion behavior), & reversibility assessments via NMR in numerous systems (i.e., Li-Mg-B-H, Li-Sc-B-H, Li-B-Ca-Al-H,  $\text{AlH}_3$ , Li-Mg-Al-N-H) that complement and extend theoretical modeling and empirical discovery studies by other MHCoe partners.
- NMR analysis is identifying amorphous/nanophase species that are not distinguishable via x-ray diffraction or vibrational spectroscopy methods (i.e., established importance of  $\text{B}_{12}\text{H}_{12}$  anions as key intermediates that limit performance of most borohydrides).
- Conducted a survey review of hydride storage vessel configurations and performance to assess state-of-art and provide explicit directions for improvements.

**MHCoe Collaborations:** Caltech, U. Utah, SNL, GE Global, HRL, NIST, U. Hawaii, SRNL, & UTRC

**Future Research:** (1) Continue intensive NMR/volumetric characterizations of promising candidates to improve their kinetics and reversibility; (2) Focus system engineering efforts onto modeling behavior during absorption and assessing degradation reactions during extended absorption/desorption cycling.