

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

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Jet Propulsion Laboratory  
California Institute of Technology

Project ID  
# **STP\_38\_Reiter**

This presentation does not contain any proprietary or confidential information

## Timeline

- Project start date: April, 2005
- Project end date: Dec., 2009
- 80 % complete

## Budget

- Expected total project funding:
  - \$1.859M (DOE)
- Funding received in FY08:
  - \$487.2K (DOE)
- Funding received for FY09:
  - \$500.0K (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 four sub-group Projects, primarily with Caltech, SNL, ORNL, U. Utah, HRL, NIST, Ohio State, U. Hawaii in FY08-09
- Limited collaboration on inter-Center activities with Hydrogen Storage Engineering Center of Excellence (HSECoE)
- International: IFE (Norway), Tohoku U. (Japan), and AIST (Japan)

## Overall Goal/Primary Objective

*Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage through the 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, as opportunities are presented

## Tasks

### 1. *Phase Identification:*

Perform NMR characterizations of phase relations for Li-Mg-Al-N-H, Li-B-Mg-H, and Li-Sc-B-H systems, with attention to suitability for cycling, as per:

- Reversibility
- Kinetics, towards meeting DOE delivery and refueling targets
- H<sub>2</sub> storage parameters, with attention to approaching the 2010/2015 goals

### 2. *Reaction Pathways:*

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

### 3. *Cycling Stability:*

Extended cycling tests had been postponed through early FY2008 since no primary candidate was identified; progress has been made to accomplish this investigation with Ca(BH<sub>4</sub>)<sub>2</sub> in FY2009.

### 4. *Hydride Bed Design:*

This engineering sub-task was postponed and then shifted out of MHCoE into the new Hydrogen Storage Engineering Center of Excellence (HSECoE) for FY2009.

- Milestones (excerpted from 2008 Annual Operating Plan where appropriate)

Milestone	Date	Status
Perform NMR characterization study of reaction pathways and bonding in the M-B-H (M=Ca, Mg, Li) system <b>(Task 2)</b>	3/08	40%: milestone added late in FY2008; work will continue into FY2009
Complete NMR characterization studies of phase relations for Li-Mg-Al-N-H system, Li-B-Mg-H, and Li-Sc-B-H phases <b>(Task 1)</b>	6/08	90%: Li-Sc-B-H paper submitted, Li-Mg-Al-N-H work continues (U. Utah), focusing on Li-B-Mg-H in early FY2009
Complete initial degradation study on either a destabilized system (i.e., Li-Mg-Al-N-H) or a more promising TBD complex hydride <b>(Task 3)</b>	9/08	15%: Task shifted to FY2009; planning for extended cycling of $\text{Ca}(\text{BH}_4)_2$
Generate a Review Report on the state-of-art metal hydride storage vessels from literature sources including assessment of models that can analyze and predict hydride bed behavior <b>(Task 4)</b>	9/08	25%: (MHCoE Project E discontinued during FY2008)
Perform detailed 2-phase system engineering and thermal performance modeling studies on metal hydride demonstrator beds <b>(Task 4)</b>	9/08	50%: (MHCoE Project E discontinued during FY2008)

- Engineering (Project E) work has shifted to the new Hydrogen Storage Engineering Center of Excellence (HSECoE) in FY2009

**DOE**

Coordinating Council (2008-2009)

Bruce Clemens (Stanford, POC A), Craig Jensen (UH, POC B), Zak Fang (Utah, POC C),  
Jim Wegrzyn (BNL, POC D), Don Anton (SRNL), J.-C. Zhao (OSU)  
Jay Keller (SNL) and Lennie Klebanoff (SNL)

## Project Groups

**A**

### Destabilized Hydrides

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

**B**

### Complex Anionic Materials

- UH (POC)
- SNL
- OSU
- UIUC
- **JPL**
- ORNL
- NIST
- UNR
- Utah
- UTRC

**C**

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

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

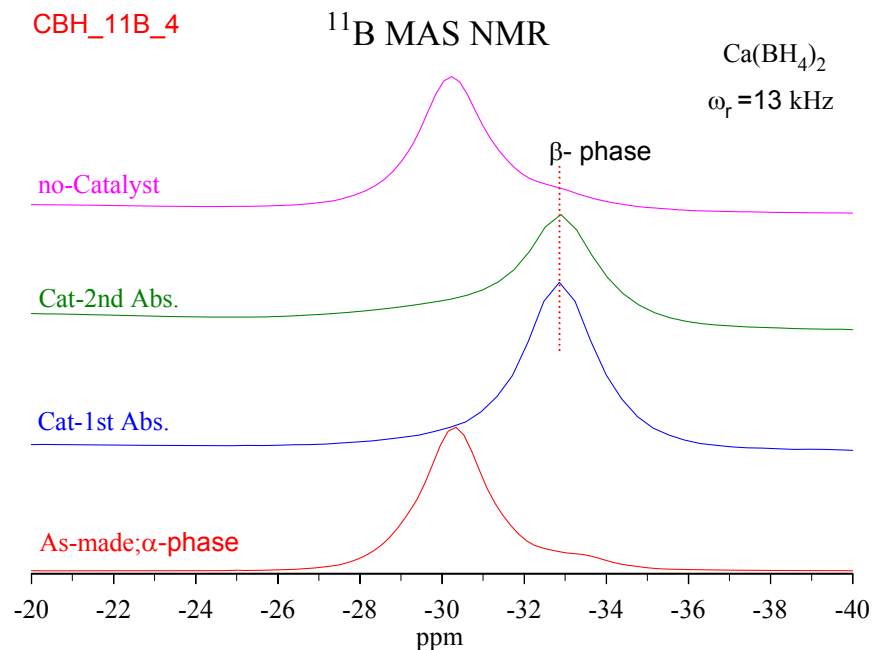
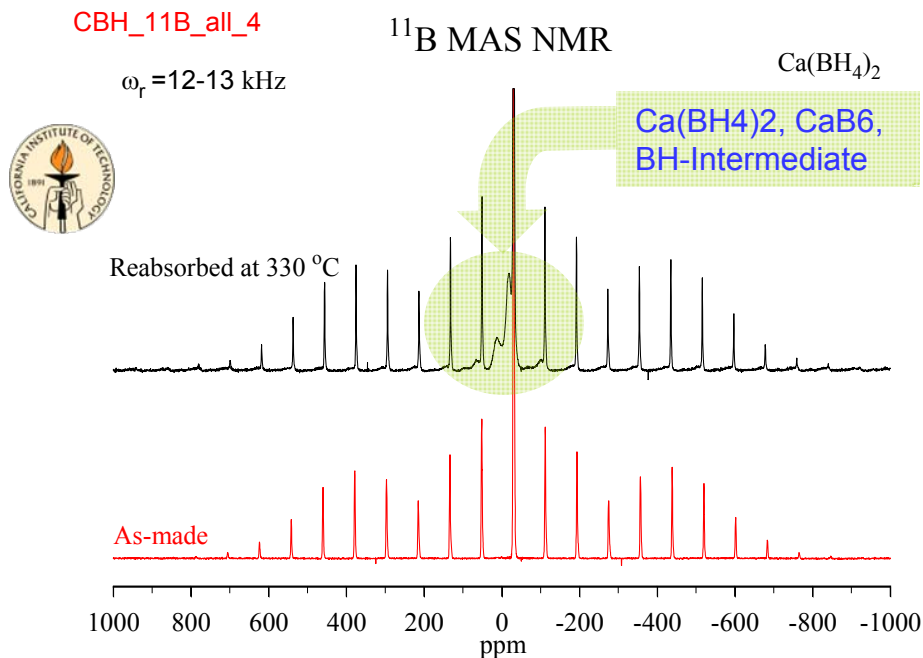
**D**

### Alane (AlH<sub>3</sub>)

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

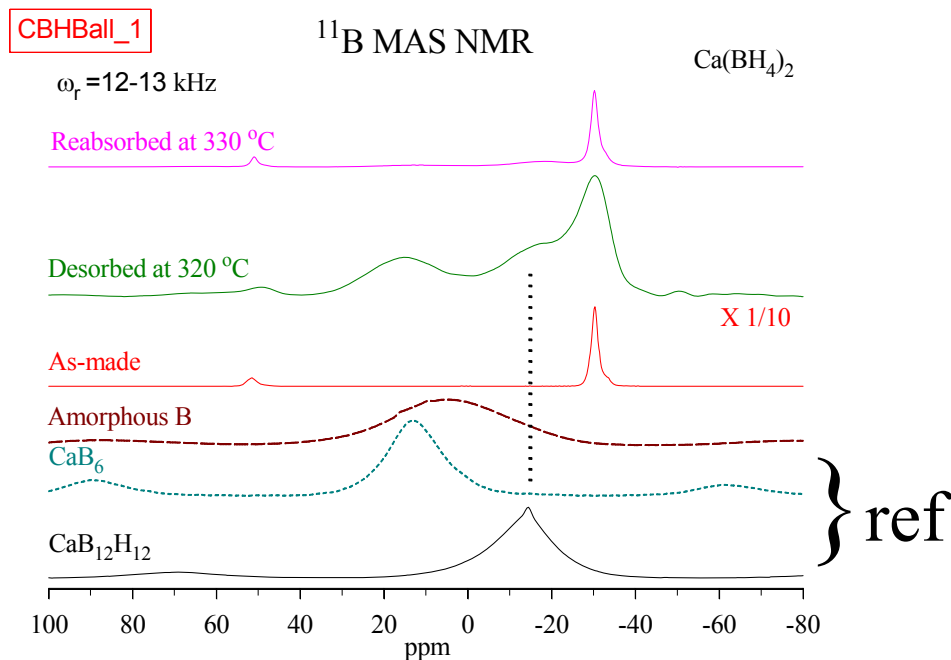
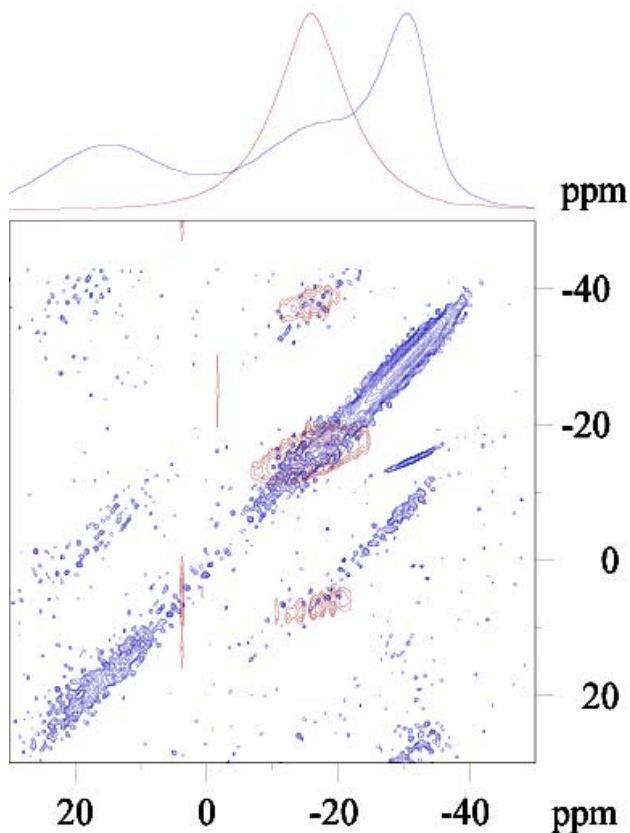
**Note: Original Project E (eng.) discontinued with HSECoE**

- **Multi-disciplinary Analysis and Characterization of Selected Hydrides to Elucidate Fundamental Processes**
- **Thermo-volumetric measurements**
  - Determinations of fundamental hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides
- **“Magic Angle” Spinning Nuclear Magnetic Resonance (MAS-NMR)**
  - Measurements are performed at Caltech Solid State NMR Facility (CSNF, Dr. Son-Jong Hwang, lead) to assess the phase compositions and chemical bonding parameters
  - NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods
- **Neutron scattering spectroscopy**
  - Examinations of structures by neutron scattering and diffraction, etc. in collaboration with MHCoe partner NIST
- **Raman spectroscopy**
  - Measurements made at Caltech to determine mechanisms of desorption processes
- **Theoretical collaborations**
  - Interactions with MHCoe theory teams (i.e., UCLA/UMSL, etc.) on phases and destabilization behavior



- NMR shows the crystalline phase  $\text{Ca}(\text{BH}_4)_2$  after absorption via the powder pattern from the spinning sidebands and chemical shift position
- Following hydrogenation at 330 °C, about 57 % of boron is now present as  $\alpha$ - $\text{Ca}(\text{BH}_4)_2$ : the Intermediate ~ 30%,  $\text{CaB}_6$  ~ 13 %
- The use of catalyst (samples provided by SNL) showed change of crystalline polymorphs of the recovered powder ( $\alpha \rightarrow \beta$ ). This interesting result shows various additional transformations among different polymorphs around the reaction temperature





- NMR identifies Desorption/Absorption of  $\text{Ca}(\text{BH}_4)_2$  at low temperatures ( $<350\text{ }^\circ\text{C}$ ) typically show residual  $\text{Ca}(\text{BH}_4)_2$ , Ca-B-H intermediate ( $-20\text{ ppm}$ ), and  $\text{CaB}_6$
- The Ca-B-H intermediate is not yet fully characterized while its chemical shift is very close to  $\text{CaB}_{12}\text{H}_{12}$  (sample provided from SNL). Dissolution of the desorbed material in water did not show the presence of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  phase, unlike  $\text{LiBH}_4$  or  $\text{MgBH}_4$  cases<sup>1</sup>

<sup>1</sup> Hwang, S.-J. et al. *The Journal of Physical Chemistry C* **2008**, 112, 3164



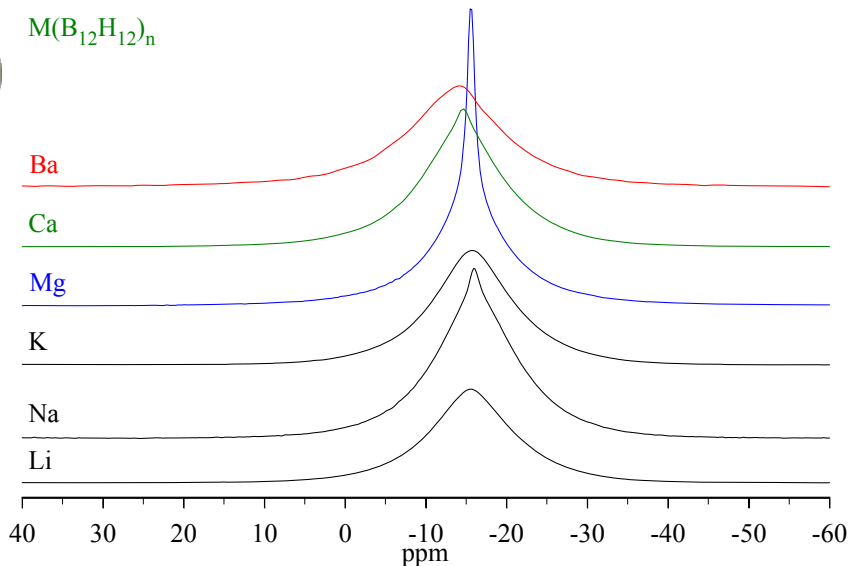
M\_DoBo\_11B

$^{11}\text{B}$  MAS NMR

$\omega_r = 13\text{-}15$  kHz

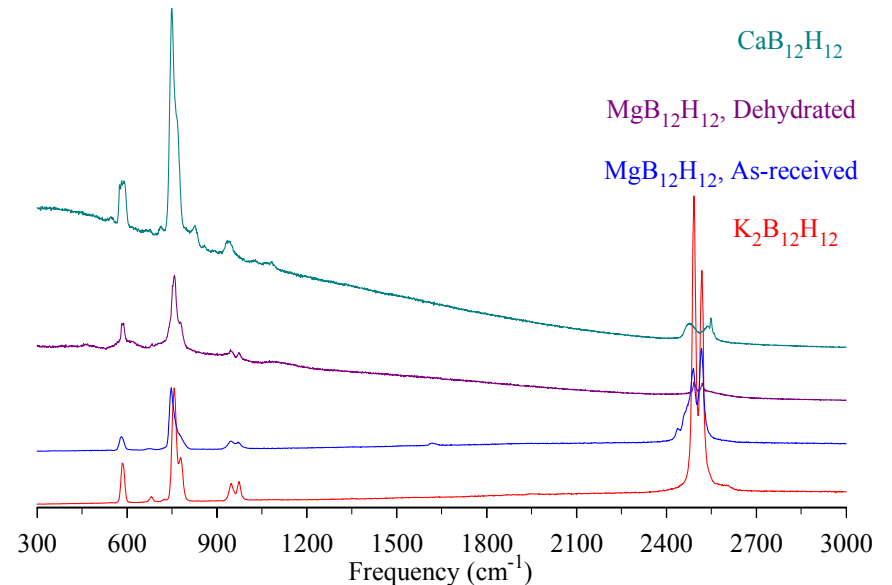


$M(B_{12}H_{12})_n$



Raman\_DB

Raman Spectra

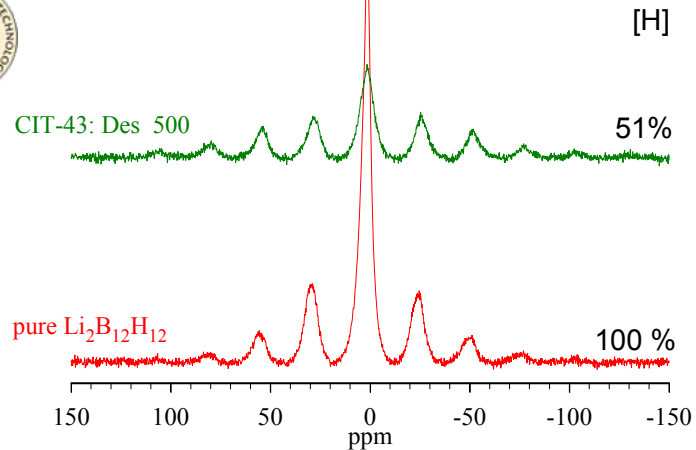


- Various dodecaborane samples were characterized by NMR and other spectroscopic tools in collaboration with SNL, S. Jalisatgi (U. Missouri-Columbia), J.-C. Zhao (OSU), T. Udovic (NIST)
- $^{11}\text{B}$  MAS NMR spectra show characteristic down field shifts for  $M =$  alkali metal vs alkali earth metal cations, and quadrupole coupling constants were varied in  $\sim 100$  kHz range; the  $\text{BH}_4$  icosahedrons becomes highly mobile (sharp center NMR line as for Mg) as water molecules are introduced to the crystalline phases
- Removal of crystalline water becomes a challenging issue for certain metals (e.g. Mg)
- NMR remains an excellent tool for characterizing the details of these complex B-H systems

DoBoH1

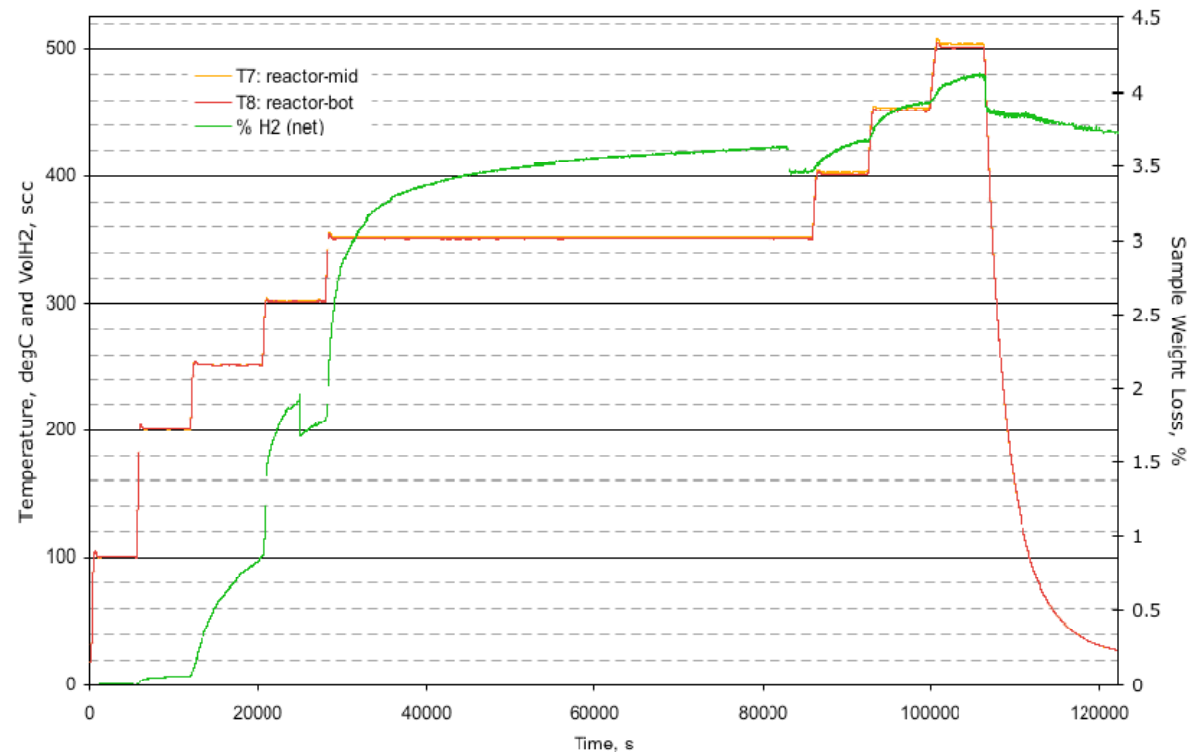
$^1\text{H}$  MAS NMR

$\omega_r = 13$  kHz  
 $d1 = 1000$ s



- Dehydrogenation to 500 ° C of 525 mg of material yields an initial 3.7% loss, with most activity occurring between 300-400 ° C

- Direct dehydrogenation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  material was attempted in order to elucidate reaction pathways in the M-B-H system (M = Li, Mg, Ca)



DoBoB1A

$^{11}\text{B}$  MAS NMR

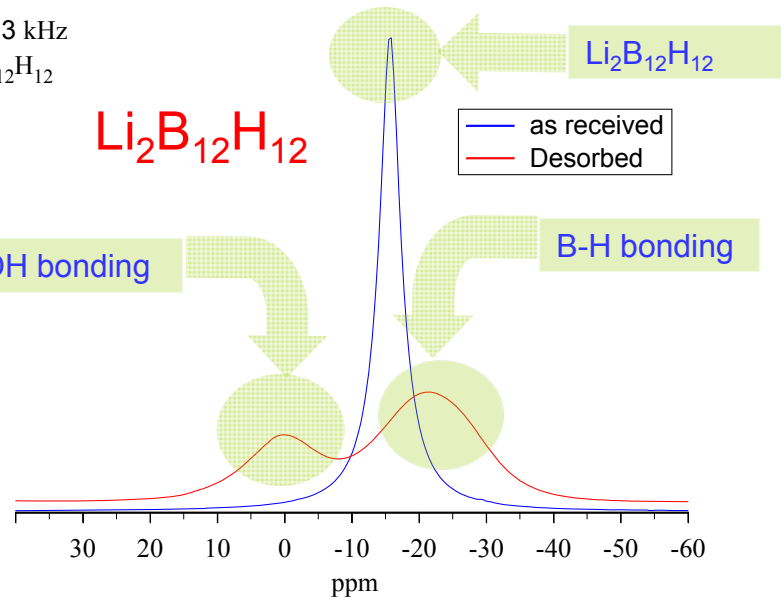
$\omega_r = 13$  kHz  
 $\text{Li}_2\text{B}_{12}\text{H}_{12}$



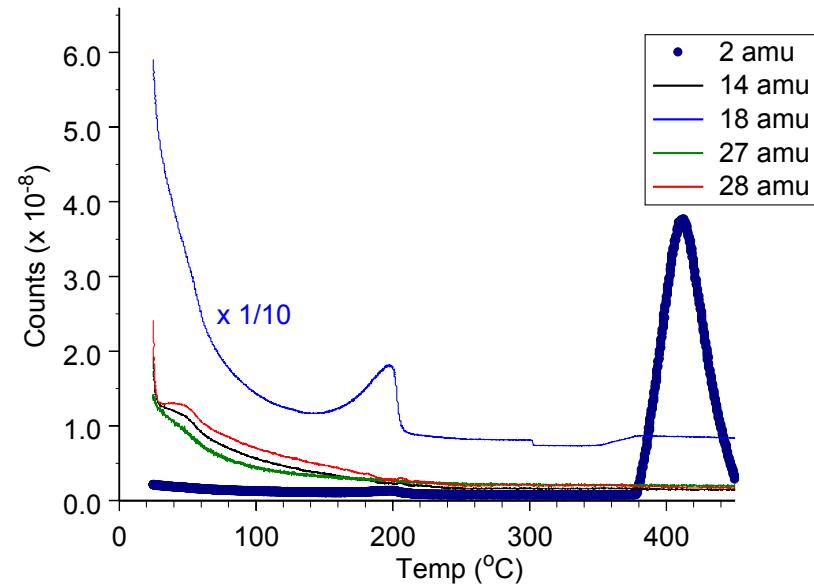
$\text{Li}_2\text{B}_{12}\text{H}_{12}$

B-OH bonding

B-H bonding

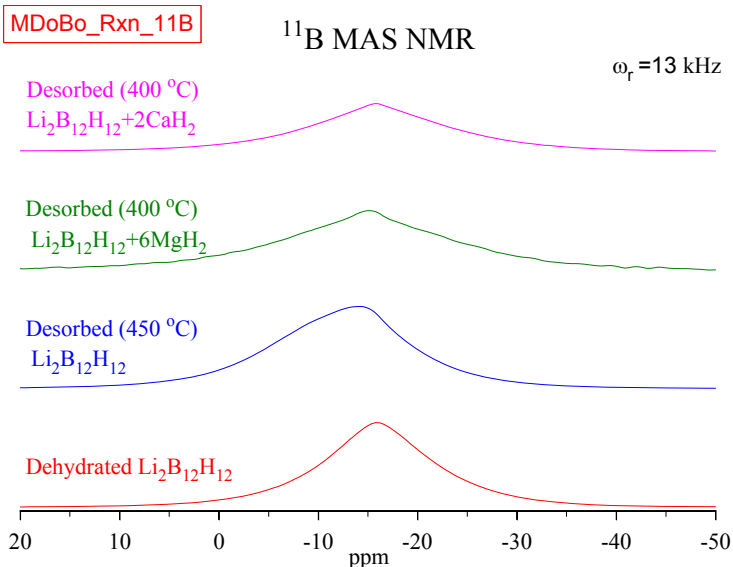
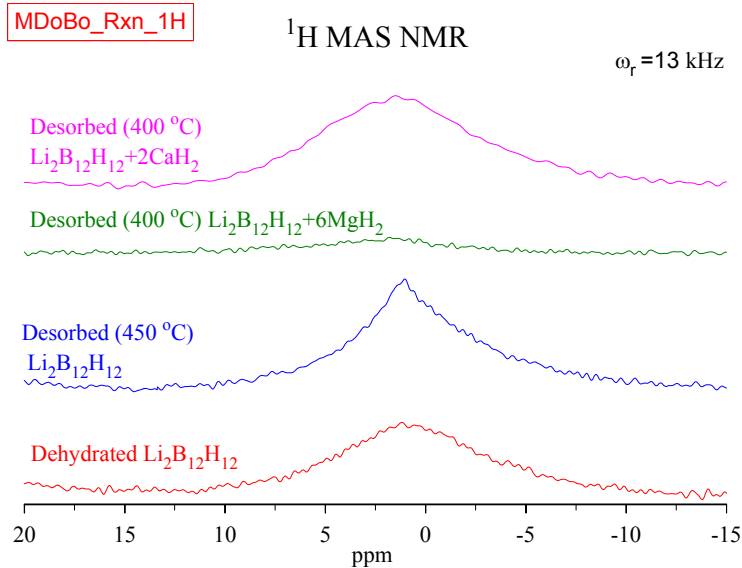


$\text{Li}_2(n\text{H}_2\text{O})\text{B}_{12}\text{H}_{12}$  - Mass Spec



- Based on several experiments, it appears that in the  $\text{MB}_{12}\text{H}_{12}$  system ( $\text{M} = \text{Li}, \text{Mg}, \text{Ca}$ ), high affinity with  $\text{H}_2\text{O}$  results in B-OH formation during heating, even as water is being removed
- The presence of water in these material systems proves a universal difficulty in practice as there are several hydration states in each system

MHCoE Project A: *Destabilized Hydrides*

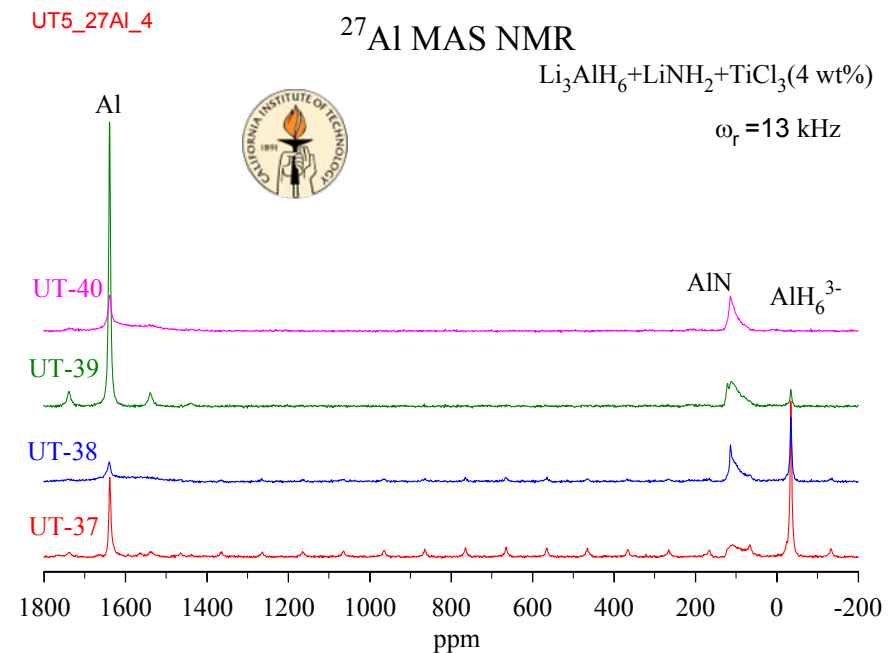


Reaction	Description	Weight (mg)
$\text{Li}_2\text{B}_{12}\text{H}_{12}$	Des 450 °C,	58.5
$\text{Li}_2\text{B}_{12}\text{H}_{12}$	Reabs 450 °C, 90 atm $\text{H}_2$	47.2
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2$	Des 400 °C	77.5
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2$	Reabs 300 °C	74.4
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 2\text{CaH}_2$	Des 400 °C	54.5

- $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2$  (M=Mg, Ca) which were reported<sup>1</sup> to have favorable  $\Delta H_{\text{react}}$  appear to show high kinetic barrier
- $^{11}\text{B}$  MAS NMR results show little change in B-H coordination from initial dodecaborane structures

<sup>1</sup> Ozolins, et.al., *J. Am. Chem. Soc.* **2009**, 131, 230.

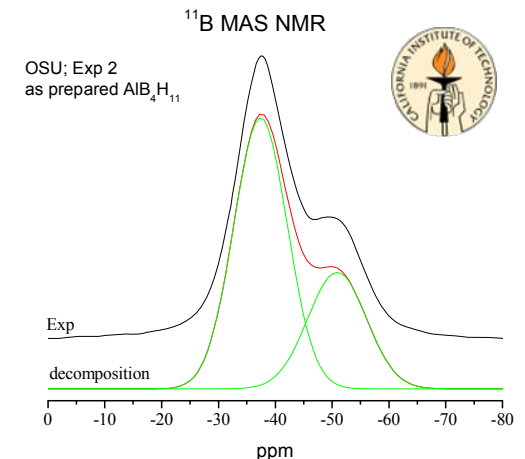
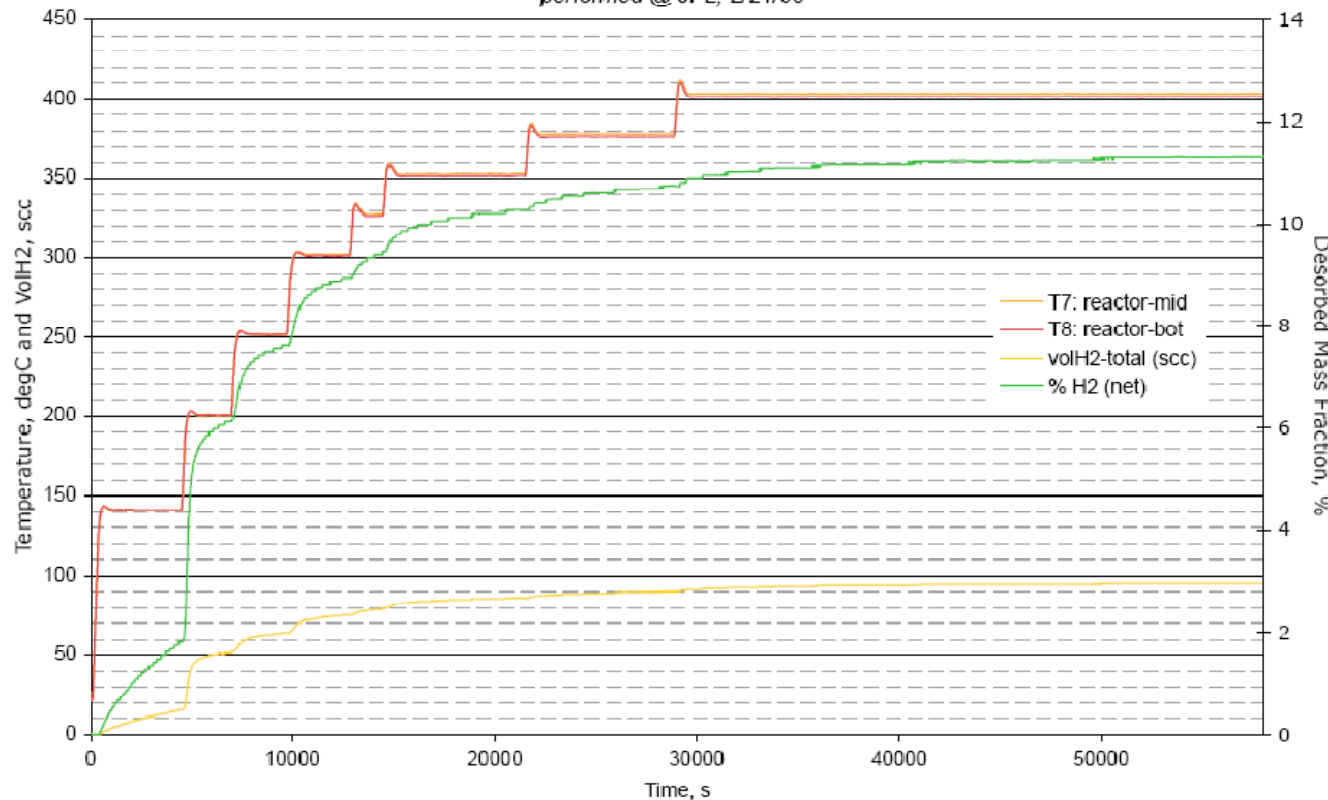
Sample	Description	Weight (mg)
UT-37	Hydrogenated at 300 °C at heating rate of 10 °C/min under 2650 psi of $\text{H}_2$	53.4
UT-38	Hydrogenated at 250 °C at heating rate of 10 °C/min under 2650 psi of $\text{H}_2$	53.8
UT-39	Hydrogenated at 300 °C at heating rate of 1 °C/min under 2650 psi of $\text{H}_2$	51.4
UT-40	Hydrogenated at 250 °C at heating rate of 1 °C/min under 2650 psi of $\text{H}_2$	61.5



- System has 7.2 wt%  $\text{H}_2$  capacity; all samples were prepared by jar-rolling/ball-milling for 80 hours, dehydrogenated at 300° C in vacuum for 6 hours (collaboration with Z. Fang at U. Utah)
- Preferential formation of AlN or  $\text{Li}_3\text{AlH}_6$  depends on heating rate<sup>1</sup>;  $\text{Li}_3\text{AlH}_6$  formation needs heating rate of 5 °C/min, and  $T_{\text{react}} > 250$  °C
- MAS-NMR proves a good probe of pathways via  $^{27}\text{Al}$  spectra

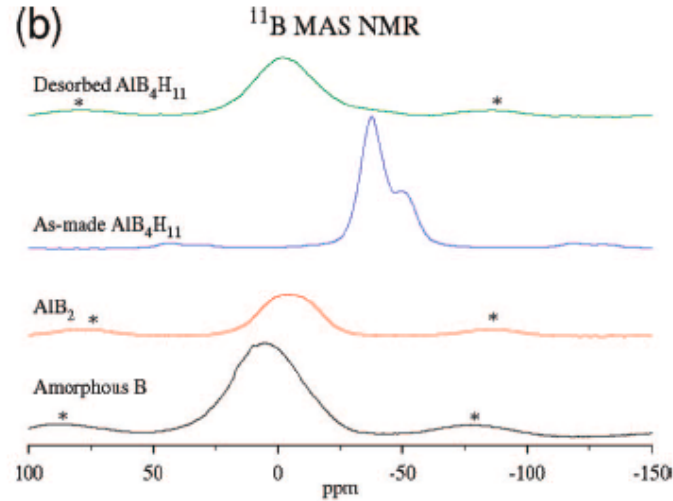
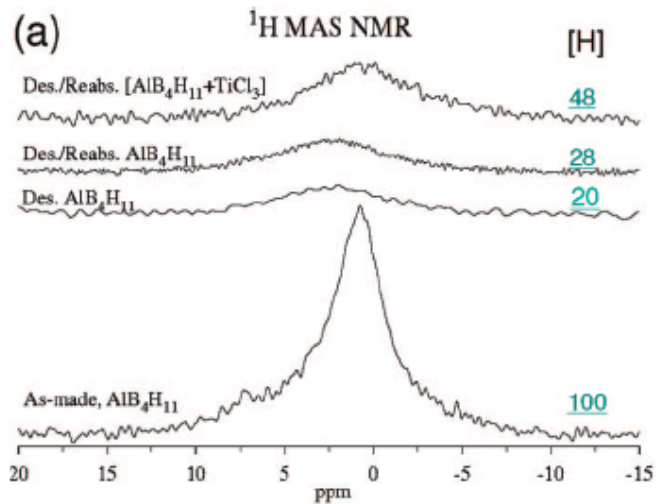
<sup>1</sup> Jun Lu, et al. J. Power Source, **2008**, 185, 1354.

AIB4H11 Dehydrogenation to 400 C  
System Temperatures, Desorbed H2 and Desorbed Mass % vs. Time  
performed @ JPL, 2/21/08

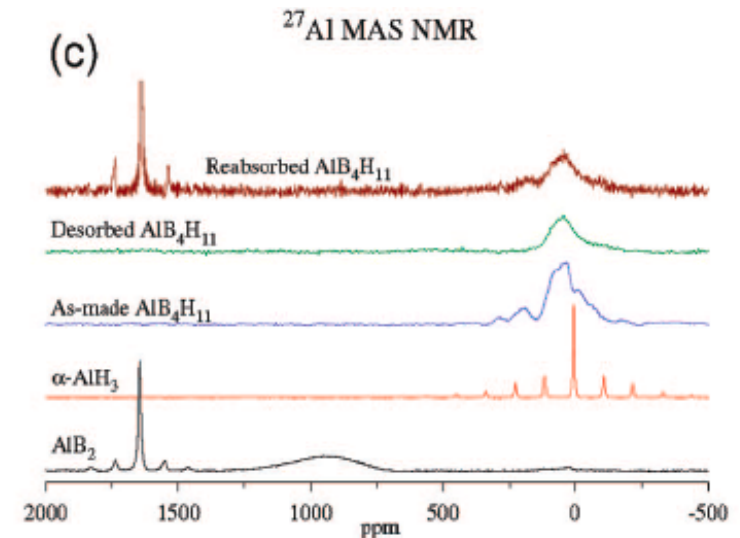


- Material provided by ORNL; effort was a collaboration among JPL, Caltech, ORNL & Ohio State
- Extensive characterization of this new material from ORNL included volumetric work showing 11.4% content (at 400°C); *significant H2 release occurred in the range 140-200°C*
- Initial NMR spectra revealed a complex boron environment in the products, including both B-H complexes and (possibly) elemental boron with other features, partially avoiding the  $\text{B}_{12}\text{H}_{12}$  route





- MAS NMR spectra collected during systematic study of the desorption/reabsorption pathways in  $\text{AlB}_4\text{H}_{11}$ <sup>1</sup>
  - (a)  $^1\text{H}$  NMR suggests partial reversibility of an  $\text{H}_2$  bearing phase
  - (b)  $^{11}\text{B}$  NMR shows the complexity of the boron environment, as compared to reference  $\text{AlB}_2$  and a-B phases
  - (c)  $^{27}\text{Al}$  NMR following reabsorption suggests the possibility of reduced Al metal, but this is a topic for further study





- With the transfer of engineering roles out of *Project E* to the new Hydrogen Storage Engineering Center of Excellence (HSECoE), JPL's roles in this area were shifted out of MHCoE in FY09
  - 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.
  - Perform literature review on hydride bed design techniques and approaches
- JPL retains engineering functions as a direct partner in HSECoE as well as informal/formal communications via the Engineering Materials Working Group (POC D. Anton, SRNL)
  - See JPL Poster in Engineering session, [stp\\_10\\_reiter](#)

- **Project A - Destabilized Hydride Systems**

- [FY09] Investigate the potential for structured carbon-based materials (aerogels, graphitic carbons, high-surface area materials) as dopants in destabilized hydride systems utilizing volumetric, NMR, and XRD techniques
  - Investigate pore size effects
  - *(potential collaborations with Caltech, SRNL, HRL, NIST)*

- **Project B - Complex Anionic Materials**

- [FY09] Continue phase transformation and reversibility studies of the  $\text{Ca}(\text{BH}_4)_2$  system in collaboration with MHCoE partners, lending support with volumetric characterizations as well as MAS-NMR, XRD, and Raman analytical techniques
  - Assess initial cycling data for  $n \sim 10$ -100 cycles
  - *(SNL, Caltech, U. Hawaii)*
- [FY09-10] Continue studies of possible destabilization routes in material systems containing the  $[\text{B}^{12}\text{H}^{12}]^{2-}$  anion, especially as it pertains to avoiding the production of this stable intermediate in the Mg-B-H, Li-B-H, Ca-B-H and mixed cation borohydride systems
  - Investigate reaction pathways and bonding
  - Consultation with theory groups
  - *(Caltech, SNL, NIST, UCLA, UMSL)*

- **Project C - Amides/Imides**

- [FY09-10] Perform systematic investigations of  $^{15}\text{N}$ -enriched amine-borohydride materials, leveraging MAS-NMR techniques for the purpose of assessing reaction kinetics, bonding dynamics, and phase transformation effects in the M-B-N-H system ( $M = \text{Li}, \text{Al}, \text{Mg}$ ), especially for mixed cation and/or ternary systems
  - *(ORNL, Ohio State, U. Utah)*

- **Approach**
  - Systematic characterizations of phase formation and hydride reversibility using solid state NMR and volumetric measurements (Projects A, B, C, & D)
- **Technical Accomplishments**
  - Phase characterization, kinetics (i.e., diffusion behavior), & reversibility assessments via MAS 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)
  - NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods
- **Collaborations**
  - Caltech, U. Utah, SNL, Ohio State, ORNL, HRL, NIST, U. Hawaii, SRNL, & UTRC
- **Future directions**
  - Continue aggressive investigations of destabilization routes in the  $\text{MB}_{12}\text{H}_{12}$  system
  - Perform systematic multi-spectroscopic study of results from  $\text{Ca}(\text{BH}_4)_2$  cycling
  - Utilize NMR methods within  $^{15}\text{N}$ -enriched amide/imide systems