

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

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Jet Propulsion Laboratory  
California Institute of Technology

Project ID  
# **ST069**

## Timeline

- Project start date: April, 2005
- Project end date: Dec., 2010
- 90 % complete

## Budget

- Expected total project funding:
  - \$1.859M (DOE)
- Funding received in FY09:
  - \$500.0K (DOE)
- Funding received for FY10:
  - \$200.0K (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. Nevada (Reno) in FY09-10
- Limited collaboration on inter-Center activities with Hydrogen Storage Engineering Center of Excellence (HSECoE)

## 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 Mg-B-H and Al-B-N-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

**DOE**

Coordinating Council (2008-2010)

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>)

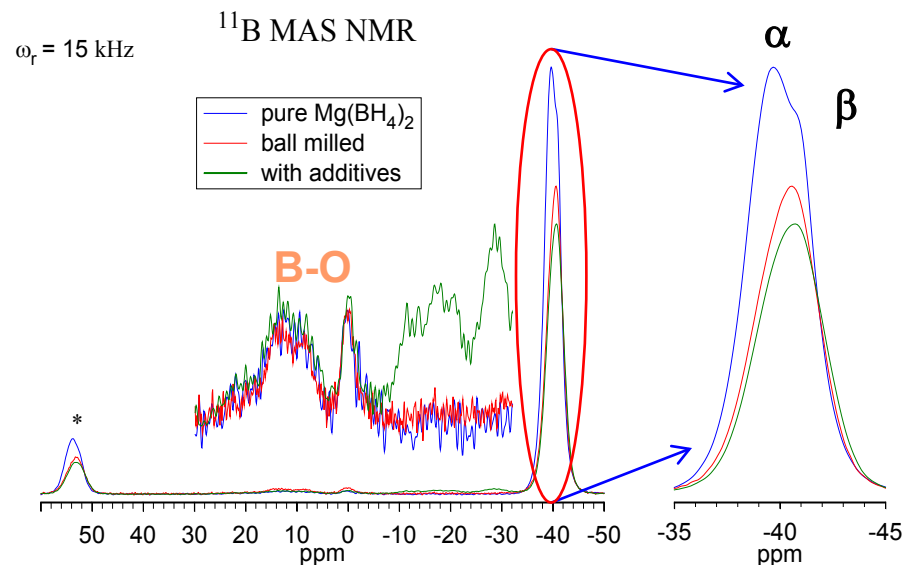
- BNL(POC)
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- **JPL**

- **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 on phases and destabilization behavior

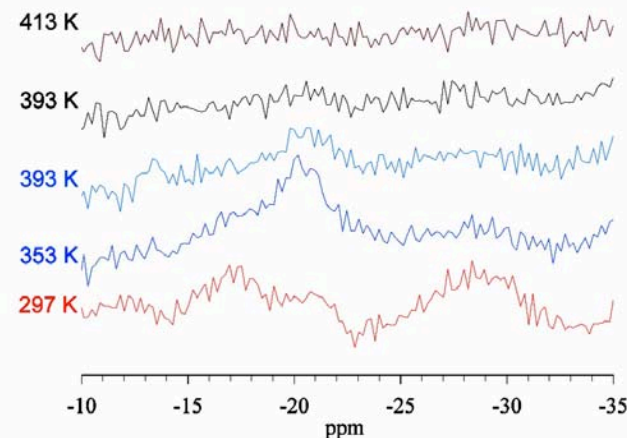


- Enhancement in hydrogen release from  $Mg(BH_4)_2$  was investigated with use of catalysts ( $TiF_3/ScCl_3$ ) (in collaboration with Dr. V. Stavila at SNL).
- Addition of 5 mol% each  $TiF_3$  and  $ScCl_3$  showed remarkable increase in rate of hydrogen desorption compared to the uncatalyzed counterpart.<sup>a</sup>
- Ball milling of  $Mg(BH_4)_2$  resulted in partial phase transition at room T, which is relatively well resolved by peak shift in  $^{11}B$  MAS NMR, and the formation of a few transient species (see peaks near -10 ~ -30 ppm in  $^{11}B$  MAS NMR spectrum) that is nominally due to interaction between the additives and  $Mg(BH_4)_2$ .
- Use of  $TiF_3$  only did not reveal the formation of the transient species although  $^{19}F$  MAS NMR study showed transformation of  $TiF_3$  as a result of ball milling.
- *In Situ* VT  $^{11}B$  NMR showed the disappearance of the transient species relatively low T, before the decomposition of  $Mg(BH_4)_2$ .

<sup>a</sup>Newhouse, R. J et al. *J. Phys. Chem. C*, 2010,114, 5224.

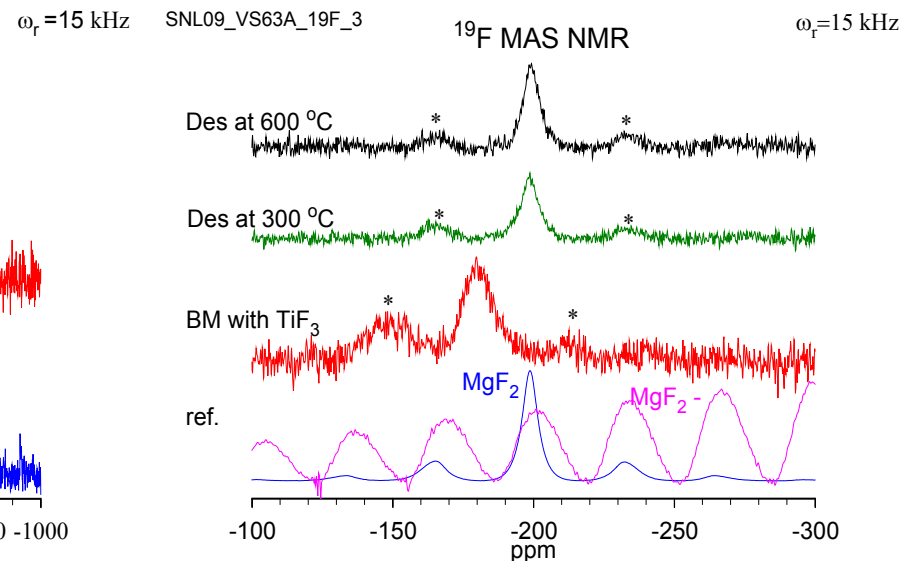
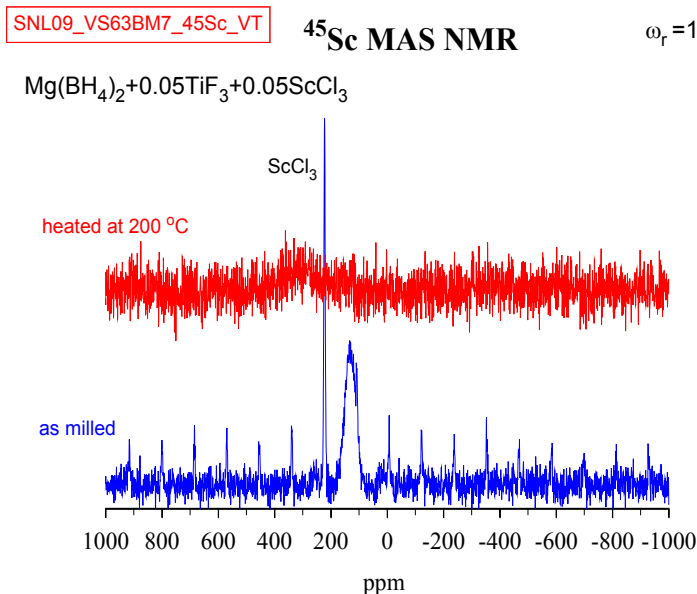


SNL09\_VS63BM7\_11B\_VT\_1  $^{11}B$  VT MAS NMR





- More than 60% of  $\text{ScCl}_3$  transforms to render a broad signal (133.2 ppm) in  $^{45}\text{Sc}$  MAS NMR and its structure is yet to be identified. In conjunction with  $^{11}\text{B}$  NMR, the formation of  $\text{ScCl}_x(\text{BH}_4)_y$  type of species can be speculated.



Phase changes associated with the additives ( $\text{TiF}_3$  and  $\text{ScCl}_3$ ) were monitored by  $^{19}\text{F}$  and  $^{45}\text{Sc}$  MAS NMR Exp as the desorption proceeds. Reference spectra ( $\text{TiF}_3$ -Aldrich,  $\text{ScCl}_3$ -Alfa) for  $^{19}\text{F}$  NMR are provided. Note that  $\text{TiF}_3$  shows a number of spinning sidebands with its center band peak at  $\sim -234$  ppm.

- Variable T NMR experiments revealed that disappearance of  $^{45}\text{Sc}$  signal after heating, indicating formation of species with invisible broad signal (only 5 mol%) or paramagnetic.
- $^{45}\text{Sc}$  NMR confirmed no formation of  $\text{ScF}_3$  (-52ppm)<sup>a</sup>,  $\text{ScB}_2$  ( $\sim 760$  ppm) or  $\text{ScH}_2$  ( $> 600$  ppm).

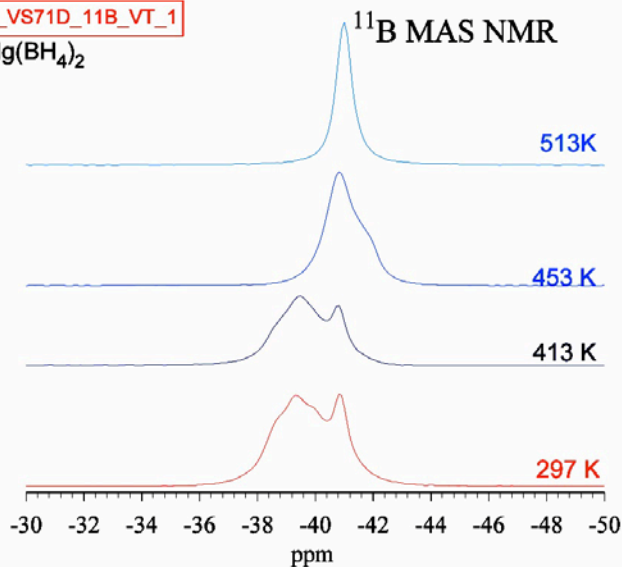
<sup>a</sup>Lo, A. Y. H. et al. *J. Am. Chem. Soc.* 2007, 129, 4687.





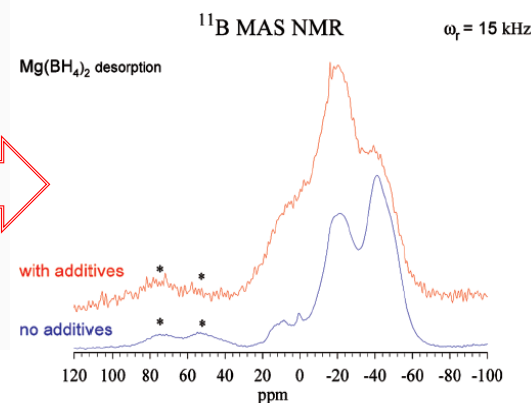
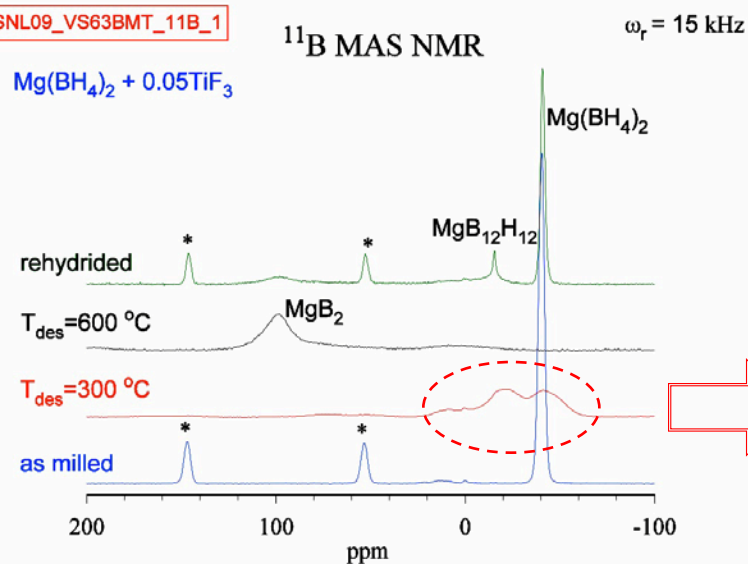
SNL10\_VS71D\_11B\_VT\_1

$\alpha$ - $\text{Mg}(\text{BH}_4)_2$



SNL09\_VS63BMT\_11B\_1

$\text{Mg}(\text{BH}_4)_2 + 0.05\text{TlF}_3$



$^{11}\text{B}$  MAS NMR spectra acquired for  $\text{Mg}(\text{BH}_4)_2$  after reactions showed

- phase transition ( $\alpha$  to  $\beta$ ) takes place near at 413 K with additives, which is about 40 degree below that without additives: Improved kinetics.
- Partition of numerous intermediates (analyzed from peak decomposition, see Table I) were found to be different depending on the presence of additives.
- Mostly  $\text{MgB}_2$  were formed when heated up to 600 °C.
- Rehydrogenation (90 Mpa  $\text{H}_2$  at 392 °C for 72 h) from the decomposition product to  $\text{Mg}(\text{BH}_4)_2$  as well as intermediates such as  $\text{MgB}_{12}\text{H}_{12}$ .

**TABLE 1: Proposed Boron Species from the Deconvolution Analysis of  $^{11}\text{B}$  MAS NMR Spectra of  $\text{Mg}(\text{BH}_4)_2$  with Additives and without after Desorption at 300 °C**

	chemical shift (ppm)	relative quantity	
		no additives	with additives
$\text{B}_2\text{O}_3$ or B-OH type oxide contaminant	20-0	0.03	0.04
amorphous	2.2	0.06	0.23
$\text{MgB}_{12}\text{H}_{12}$	-16.8	0.01	<0.002
early stage intermediates	-21.8	0.43	0.5
$\text{Mg}(\text{BH}_4)_2$ -I	-39.4	0.06	0.03
$\text{Mg}(\text{BH}_4)_2$ -II	-45.4	0.41	0.2

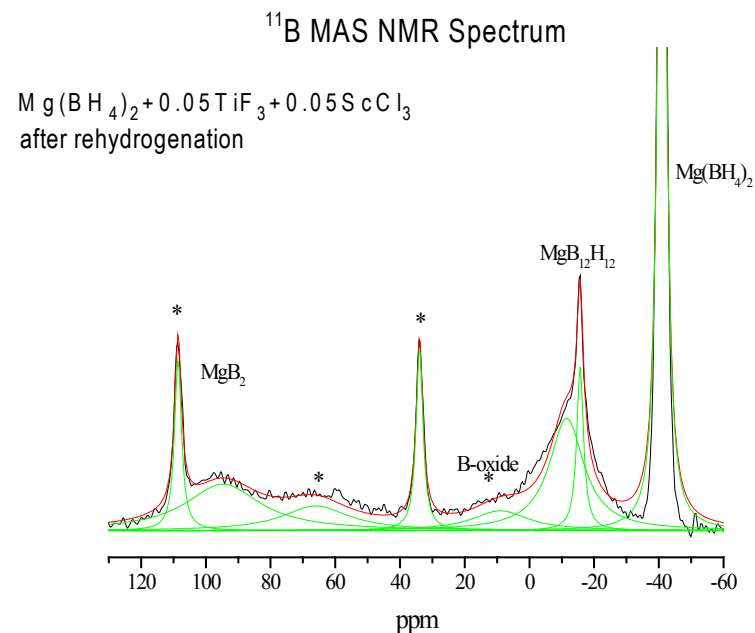




**Table II. Proposed boron species based on deconvolutions of  $^{11}\text{B}$  MAS NMR spectra of samples after the rehydrogenation reaction.**

	Chemical shift (ppm)	Relative quantity	
		no additives	with additives
$\text{MgB}_2$	97.3	0.25	0.21
Amorphous*	-11	0.04	0.23
$\text{MgB}_{12}\text{H}_{12}$	-15.5	0.05	0.07
$\text{Mg}(\text{BH}_4)_2$	-40.95	0.66	0.49

\*Amorphous phase in this system means nearly  $[\text{B}_{12}\text{H}_{12}]^{2-}$  related species.



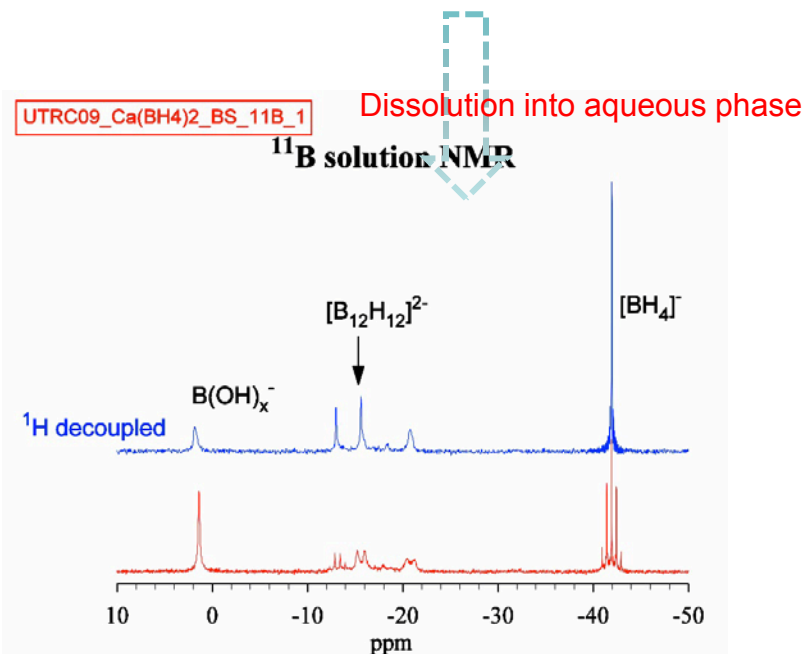
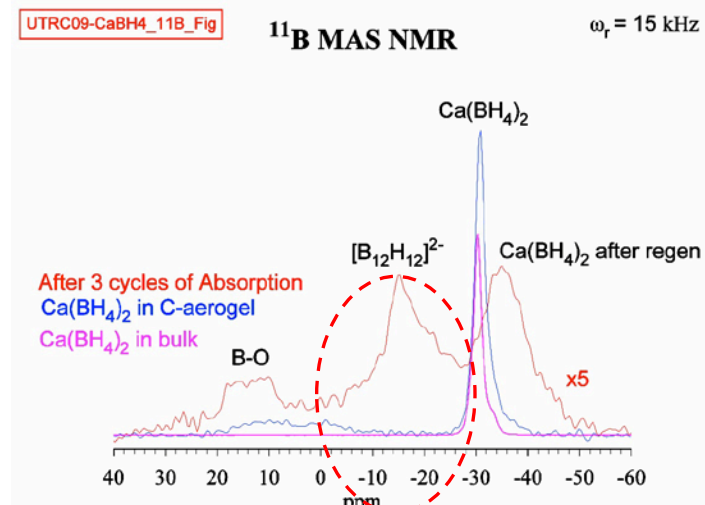
# Technical accomplishments:

## NMR Analysis of $\text{Ca}(\text{BH}_4)_2$ in C-aerogel system (UTRC)

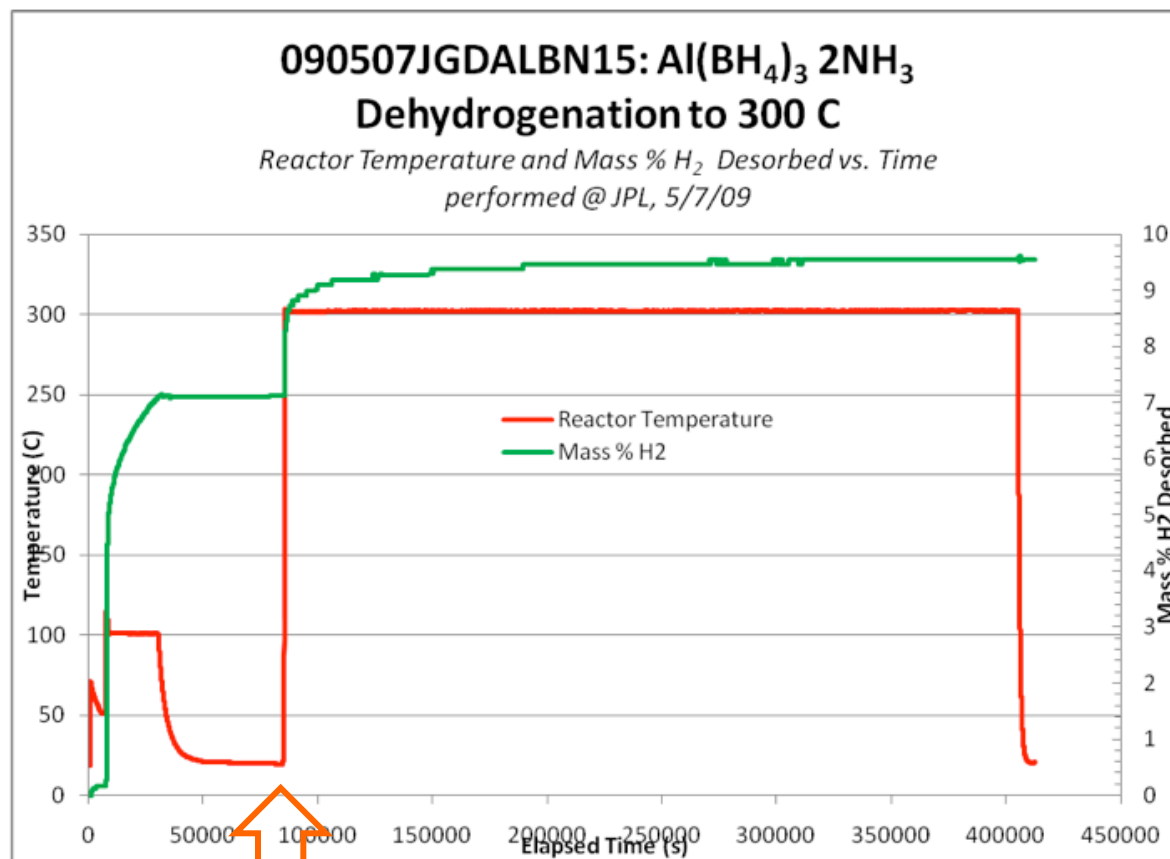
**Table III. Phase distribution after cycles of Des/Absorption for a system of  $\text{Ca}(\text{BH}_4)_2$  incorporated into C-aerogel**

Sample	Description	[H] (a.u)	$\text{Ca}(\text{BH}_4)_2$	Intermediate (-6 ~ -26 ppm)	B-O (> 0 ppm)
UTRC-09-06	$\text{Ca}(\text{BH}_4)_2$ in C-aerogel	100	100		27.4
UTRC-09-06-1	After 3 cycled of hydrogenation	42.9	40.2	44.8	20.0

- As made: 38 wt% of  $\text{Ca}(\text{BH}_4)_2$  was loaded into C-aerogel.
- $^{11}\text{B}$  MAS NMR showed no noticeable broadening of  $\text{Ca}(\text{BH}_4)_2$ , indicating no particular interaction of the borohydride with the surface of C-aerogel.
- The rehydrogenated  $\text{Ca}(\text{BH}_4)_2$  reveals significant peak shift (from -30 ppm to -35 ppm) and broadening, and this result is noticeably different from that of bulk reaction case.
- Accumulation of the intermediate (mostly  $\text{CaB}_{12}\text{H}_{12}$ ) was also observed for this system like the case of bulk samples.
- Dissolution of the reaction intermediate into aqueous phase again confirmed the formation of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  via  $^{11}\text{B}$  solution NMR.



- $\text{Al}(\text{BH}_4)_3$  was enriched with  $^{15}\text{N}$ -labeled  $\text{NH}_3$  for the purpose of enhancing NMR activity
- Desorption occurred @JPL in two steps, with samples removed at 7% mass loss for NMR screening
- Total desorption shows net ~7% @  $250^\circ\text{C}$ , >9% @  $330^\circ\text{C}$



Partial sample removed from reactor; desorption continues (mass% results adjusted accordingly)

- NMR investigations of the products of these reactions are still underway!



For additional detail, see Brown et. al., poster ST068



- **All Projects**
  - [FY10] Complete active project investigations and archive extant data for transmission to MHCoe Leadership; provide feedback as required to support upselect of promising storage materials for use in the ongoing Engineering Center effort.
    - Prepare to close-out MHCoe effort, Oct-Dec 2010

- **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, including C60 scaffolded architectures
  - 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, NIST, SRNL, & UTRC
- **Future directions**
  - Continue aggressive investigations of destabilization routes in the Al-B-N-H system
  - Utilize NMR methods within  $^{15}\text{N}$ -enriched systems

# Back-up Slides (Not Presented)

- Equipped with three solid sample NMR spectrometers.
- A number of solution and solid sample NMR probes available.
- Capability of in-situ variable temperatures (-100 °C ~ +150 °C)
- Dr. Son-Jong Hwang is CSNF manager and lead NMR spectroscopist.



**Bruker DSX 500 spectrometer (11.7 T)**

Used for majority of MHCoE samples, including both those direct from JPL and those acquired in collaborative work with partners



**Bruker AM 300 spectrometer (7.0 T)**

Also in use; spectrometer console was updated in 2008 via DOE/EERE support for doing more routine MAS-NMR measurements (i.e., variable temperatures, etc.)