# Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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California Institute of Technology
with Metal Hydride Center of Excellence

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Project ID # STP 28

# Overview

## Timeline

- Project start date: October 1, 2004
- Project end date: September 30, 2009

## On board hydrogen storage Barriers and Targets

(B) Weight and volume of on board hydrogen storage systems

(M) Reversibility of high capacity solid state storage materials

(N) Kinetics (fueling/refueling times) associated with current solid state storage materials

## Budget

- Total project funding
  - DOE share $1M (5 yrs)
  - Contractor share $250k (5 yrs)
- Funding for FY06
  - DOE share $250k
  - Contractor share $62.5k
- Funding for FY07
  - DOE share $200k
  - Contractor share $50k

## Partners

Interactions/ collaborations:

HRL Laboratories (John Vajo)
Univ. Illinois (Ian Robertson)
Carnegie Mellon (D. Sholl)
Univ. Pittsburgh (J. Karl Johnson)
Brookhaven Natl Lab (J. Graetz)
NIST (Terry Udovic)

# Objectives

- To understand as to whether thermodynamically tractable reactions based on hydride destabilization, like $Mg_2Si+2H_2 <-> 2MgH_2+Si$ that should be reversible but appear not to be, are kinetically limited.
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through "theoretical screening" by Center partner members.
- To understand issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- To follow up on previously studied reactions with phase identification via x-ray diffraction, NMR and transmission electron microscopy.

## Current Status

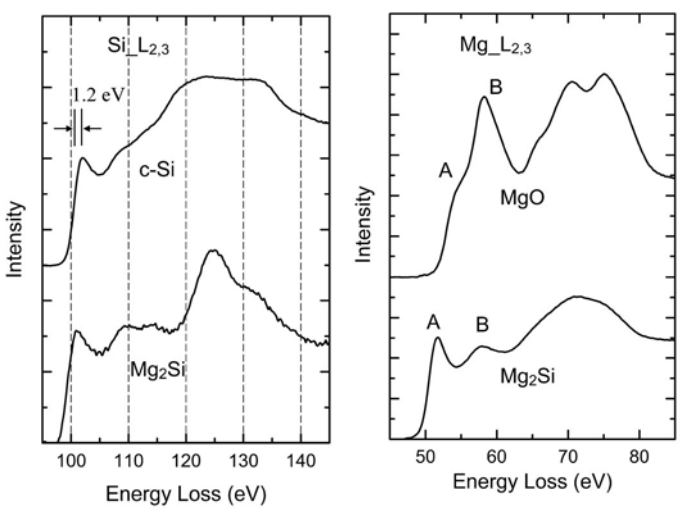
- No Go on $Mg_2Si$, completion of analysis of MgSi bonding in this system.
- Analysis of $ScH_2+2(LiBH_4) \leftrightarrow ScB_2+LiH+4H_2$ (8.8 wt%), predicted to have ZPE corrected $\Delta H$ of ~34 kJ/mole but dehydrogenation occurs at temps >300°C.
- Reverse reaction attempting to hydrogenate $ScB_2$ as of yet shows no absorption.
- $Ca(AlH_4)_2+2LiBH_4$ shows some reversibility on basis of our mechano-synthesis of $Ca(AlH_4)_2$ (~70% yield).
- Recent dehydrogenation using pure $Ca(AlH_4)_2$ from Felderhoff shows slightly higher yield (going from ~6.6 to 7.3wt%).
- NMR analysis critical in identifying bonding in these systems that have little or no long range order.

## Challenges

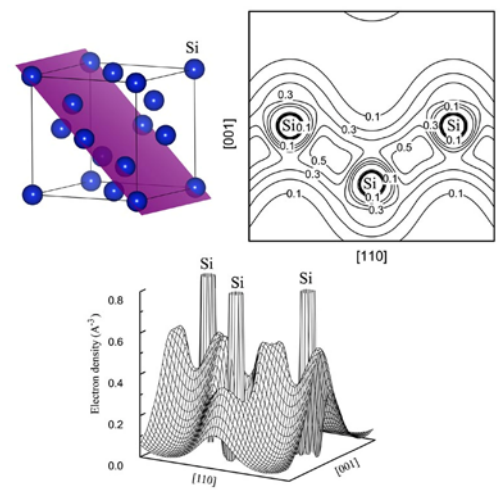
- Reversibility of thermodynamically suitable systems empirically unpredictable on the basis of reaction enthalpies.
- Solid state diffusion of B containing species appears to be a limitation.

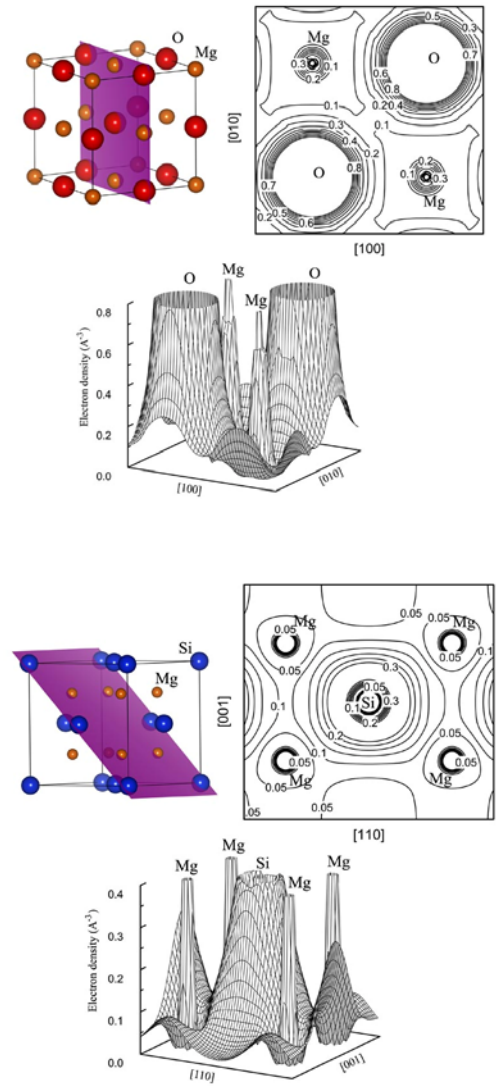
# Technical Accomplishments: Bonding in $Mg_2Si$

- No Go decision on $Mg_2Si$ given challenges in rehydrogenation.
- Final analysis of this system, spectroscopic and computational approaches in explaining the degree of ionicity and covalency in the bonding between Mg and Si.
- Initial XPS results suggested strong covalency but our electron energy loss and WIEN2k calculations indicate 74% ionic component (generally difficult to dissociate).
- Comparisons with MgO and Si standards for validation. Bader analysis indicates charge transfer of 1.48 electron/Mg atom and Mg $L_{23}$ edge analysis shows Mg 3s occupancy.




The Si $L_{2,3}$-edge of c-Si and $Mg_2Si$, respectively on the left. The spectra were normalized with a 30 eV window 50 eV after the edge threshold. The Mg $L_{2,3}$-edge of MgO and $Mg_2Si$, respectively on the right. The spectra were normalized with a window from 80 - 100eV.




The calculated 2-d and 3-d valence electron density of c-Si on {110} type plane shown above, MgO data on {100} shown in upper right and $Mg_2Si$ data on {110} shown at right*.

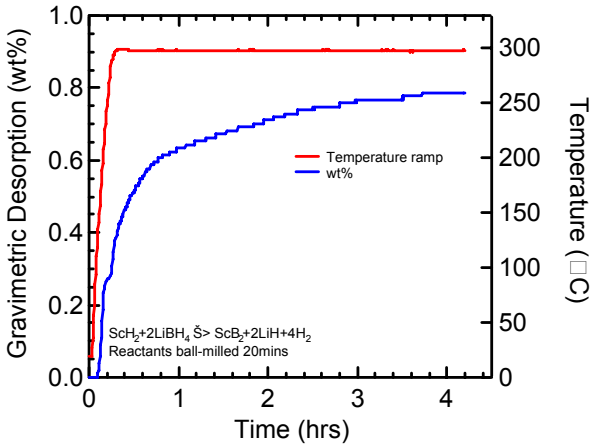
* From S. Miao, PhD, Caltech 2007.

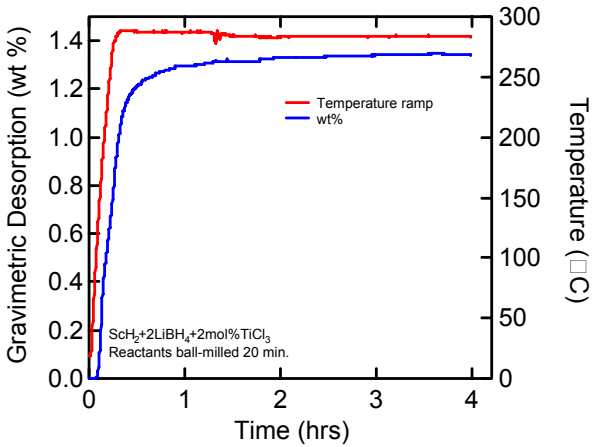
# Technical Accomplishments: $ScH_2$+2$LiBH_4$ study, a low reaction enthalpy system

- Reaction enthalpies of < 40kJ/mole a priority in order to obviate high exothermic hydrogenation heat.
- While ultimately too costly for engineering applications,

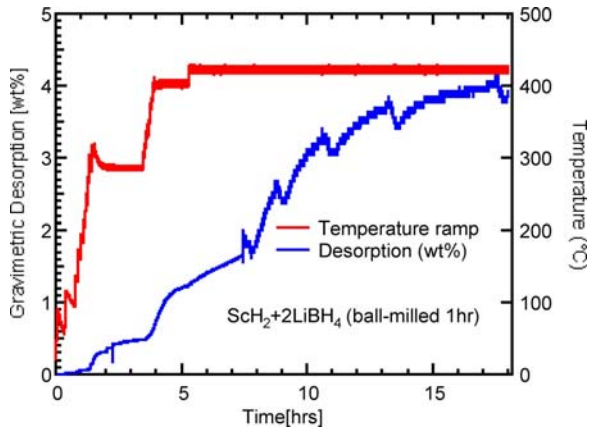
  $ScH_2$+2$LiBH_4$ <–> $ScB_2$+2LiH+4$H_2$ (8.9wt%) identified by Center partners D. Sholl and J.K. Johnson as thermodynamically suitable candidates with $\Delta H$ of 34 kJ/mole after zero point energy corrections, an important system to evaluate empirically in order to better address role of computational effort.
- Our kinetic analysis (next slide) shows < 1wt% gravimetric $H_2$ release at 300°C (upper left trace), and ~ 4wt% after 17 hrs at 400°C for these reactants (center trace). X-ray analysis of product phase (lower right) shows substantial background, due presumably to large amorphous component and remnant $ScH_2$. No formation of $ScB_2$ discernable during dehydrogenation. Reaction paths for this system of uncertainty and equilibrium not reached.
- Work with catalyst and better initial mixture improves kinetics. However, attempts at hydrogenating an initial $ScB_2$+2LiH mixture have not as yet been successful.

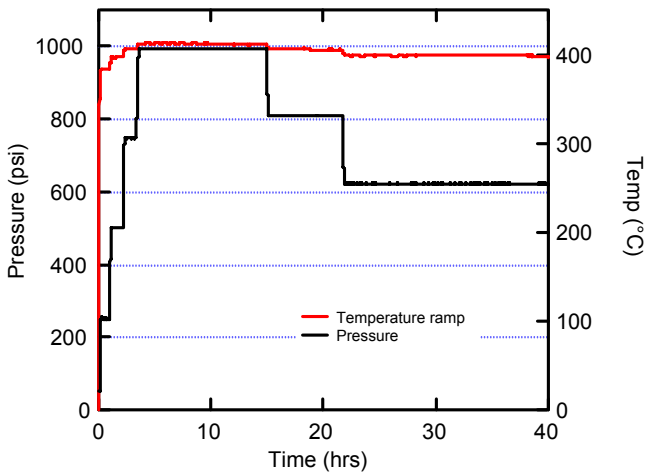
# Technical Accomplishments: $ScH_2$+2$LiBH_4$ study, a low reaction enthalpy system cont'd:



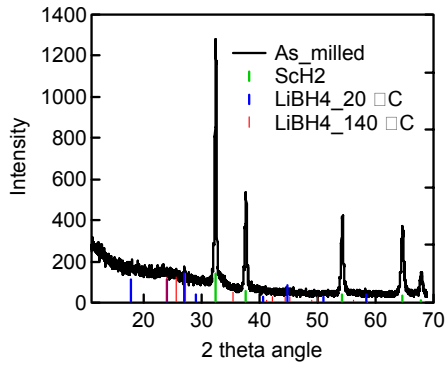



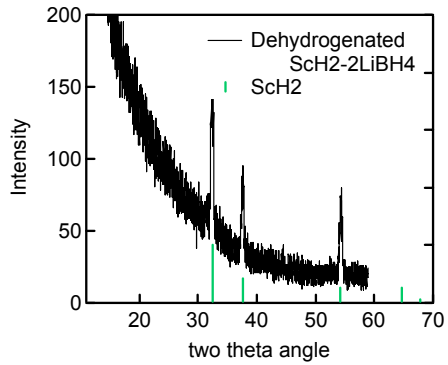

Upper figure shows kinetic trace to 300°C. Dehydrogenation < 1wt%. Lower figure shows desorption improvement due to $TiCl_3$ catalyst incorporation.




Desorption limits ~4 wt% at 400°C shown in upper plot. Theoretical limit for gravimetric desorption is 8.9 wt%. Lower plot shows absorption attempt with initial $ScB_2$+2LiH starting mixture. No absorption seen. Pressure behavior indicates gas law dependence only.

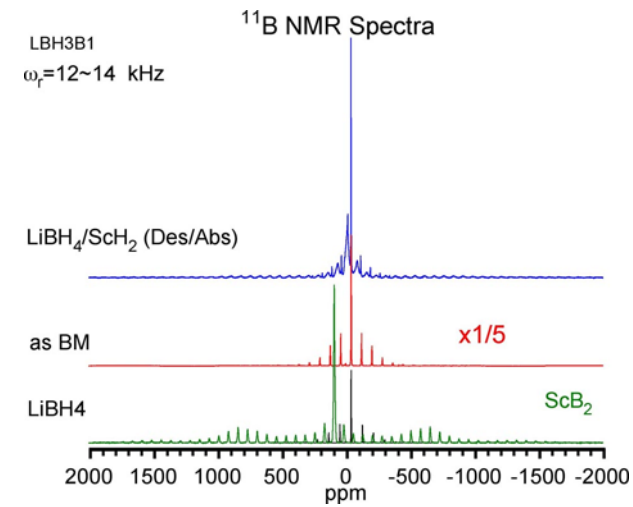


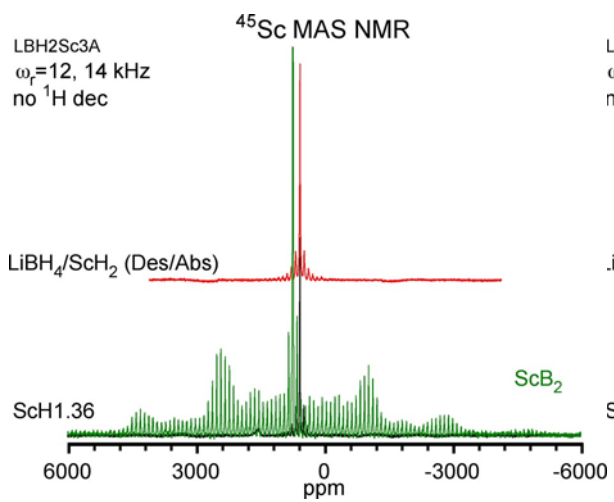



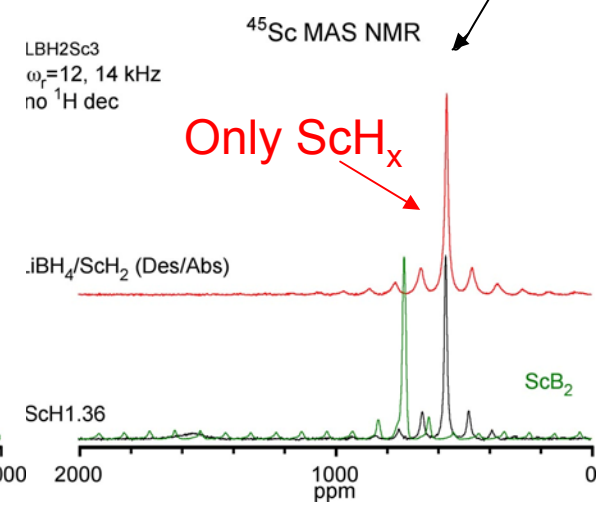

X-ray data of reaction product from 400°C desorption in lower plot shows remnant $ScH_2$. Kinetics in this system are either slow or the reaction pathways to equilibrium are more complex than assumed.

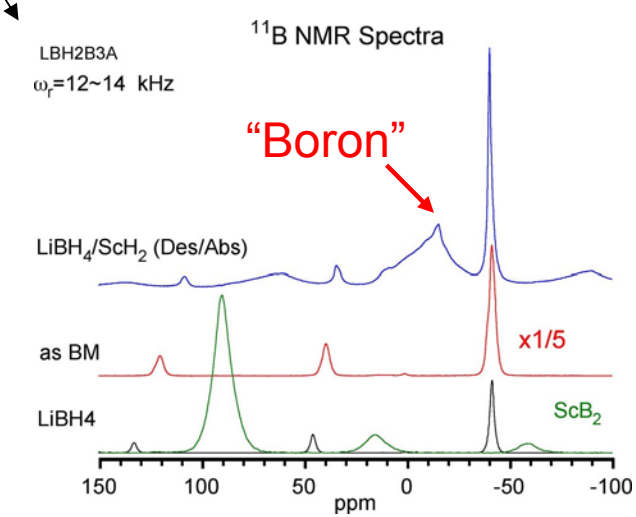
# Technical Accomplishments: NMR of $ScH_2$+2$LiBH_4$ System

- Lack of crystallographic data from x-ray diffraction => spectroscopic analysis via NMR virtually the only way to identify bonding in product phases from previous kinetic reactions.
- Upper plot in lower right spectra show presence of elemental Boron. Boron in diboride structures in hexagonal layered form between metal but non-hexagonal formation usually irreversible.
- Upper plot of lower center spectra indicate presence of $ScH_x$ verifying $ScH_2$ presence as noted in x-ray diffraction data.
- Identification of reactants that cannot be rehydrogenated of value in ultimately determining reaction pathways not predicted from thermodynamics.



# Technical Accomplishments: $Ca(AlH4)_2$+2$LiBH_4$

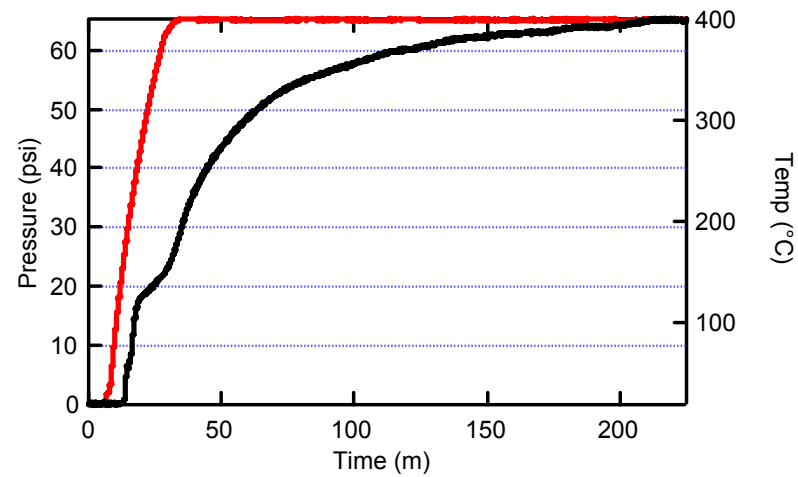
- $Ca(AlH4)_2$ not viable as stand-alone hydride: $\Delta H$ = +12.5 kJ/mol* so no reversibility expected**.
- But possible destabilization reaction with $LiBH_4$ as noted by Center partner J.K. Johnson.

$$Ca(AlH_4)_2 + 2LiBH_4$$

Activated using ball-milling, 1 hour at 400 rpm

Desorption up to 400°C
6.6–7.3 wt%

Reabsorption up to ~65 bar




| Cycle | 1 | 2 | 3 |
|---|---|---|---|
| Desorption (mass loss, wt.%) | 6.64 | 2.65 | 2.74 |
| Reabsorption (mass gain, wt.%) | 1.65 | 4.56 | 3.06 |

As milled

Sample reground

**but as a stand-alone hydride, hydrogen would be released via following 3 decomposition steps:
(from Mal'tseva et al, Russ. J. Inorg. Chem., 46, 1793 (2001))

$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 1.5H_2$ _____ T=200°C

___ $CaAlH_5 \rightarrow CaH_2 + Al + 1.5H_2$ _____ T=260–550°C

___ $CaH_2 \rightarrow Ca + H_2$ _____ T=600–700°C

2 first steps would yield ~ 5.9 wt. % $H_2$

While endothermic heat and stable end-products were determined for this system theoretically, kinetic pathways are not always predictable and the ability to rehydrogenate this system suggests that further study and phase identification warranted.

*O. M. Lovvik, *Physical Review B* 71, 144111 (2005)

# Technical Accomplishments: $Ca(AlH4)_2$+2$LiBH_4$ cont'd

Initial work on this system required $Ca(AlH4)_2$ initial product.
Ball milling or THF processing with salt by-product typical as with:

$4CaH_2+2AlCl_3 \rightarrow Ca(AlH_4)_2+3CaCl_2$ (W. Shwab et al., *Naturforsch* (1953), 8b, 690) or

$2NaAlH_4+CaCl_2 \rightarrow Ca(AlH_4)_2+2NaCl$ (D.N. Dymova et al., *Russ. J. Inorgan. Chem.*, (1970), 15(9), 1201) or

$2LiAlH_4+CaCl_2 \rightarrow Ca(AlH4)_2+2LiCl$ (M. Mamatha et al., *J. Alloys Compounds*, (2006), Vol. 407, 78.)

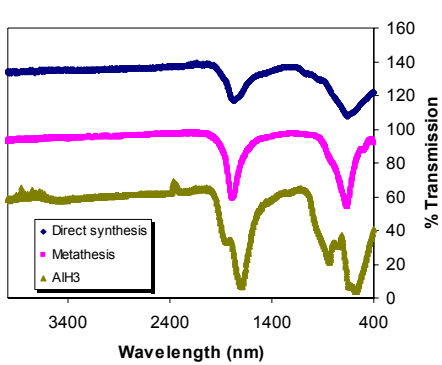
but salt by-products require further processing to remove.

Our approach <u>used for 1st time</u> is direct mechano-synthesis using ball mill

$2AlH_3 + CaH_2 \rightarrow Ca(AlH4)_2$ ($AlH_3$ provided by Center partner, J. Graetz of BNL.)

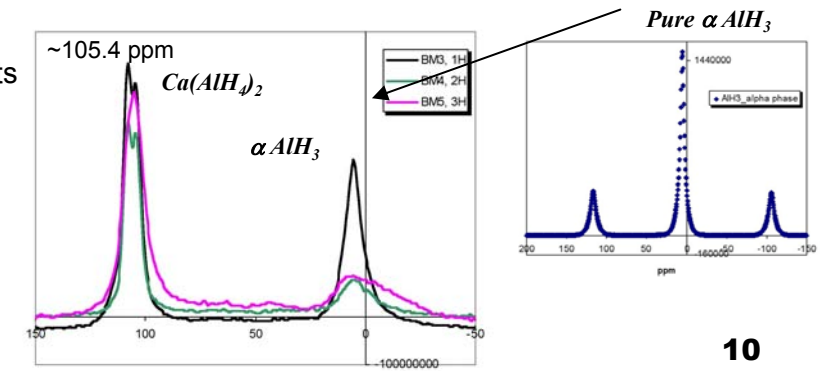
Sample preparation conditions as noted in Table below. >70% yield as determined by Al NMR.

| Speed (rpm) | 500 | 500 | 500 | 200 | 500 |
|---|---|---|---|---|---|
| Time (hours) | 1 | 2 | 3 | 10 | 6 |
| Ratio via Al NMR | 57.5/42/0.5 | 72.2/26.7/1.1 | 71.6/26.3/2.1 | No reaction | decomposes |




FTIR results at left show overlap of $AlH_3$ and $(CaAlH_4)_2$ bonds but NMR data at right show reaction products clearly identified.

$^{27}$Al NMR measurements

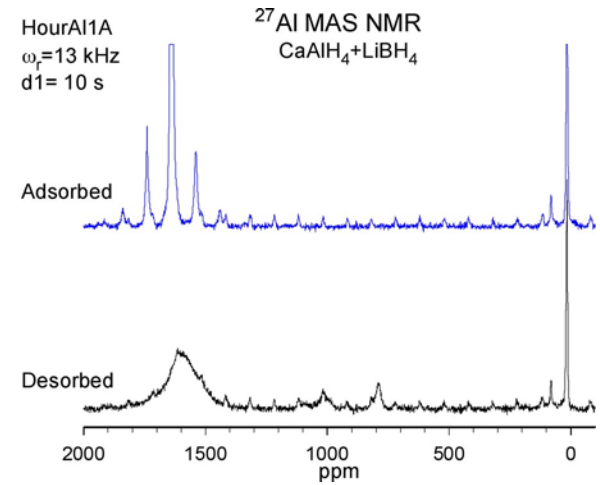


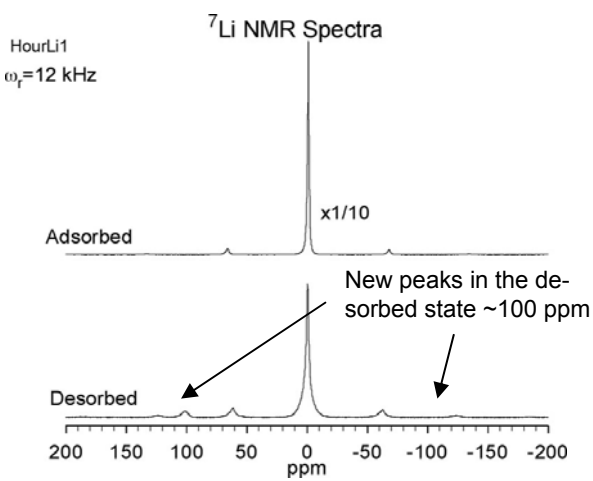
# Technical Accomplishments: NMR of $Ca(AlH4)_2$ +$2LiBH_4$

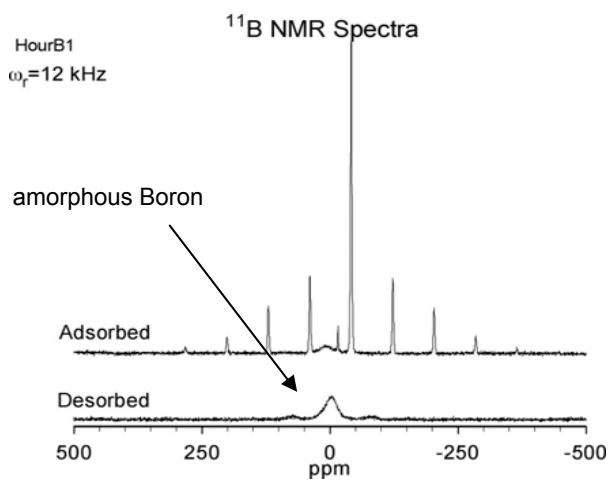
## Absorption/Desorption of a $Ca(AlH_4)_2$ + $2LiBH_4$ ball milled mixture

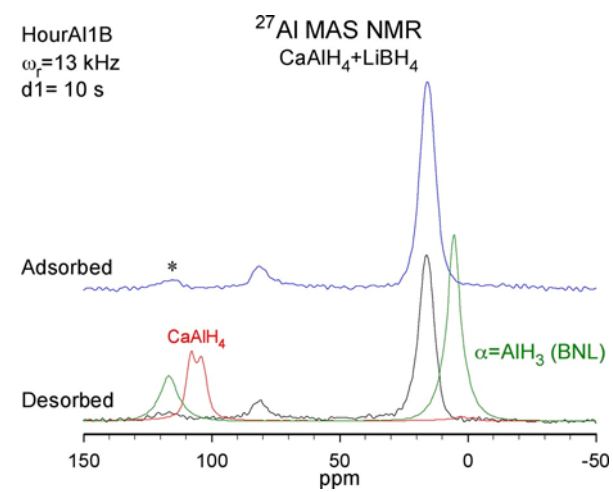
As with ScH-$LiBH_4$ system, no discernable x-ray crystalline peaks after 1st desorption, reliance on NMR data necessary to understand bonding over short spatial scales.

$^7$Li & $^{27}$Al NMR spectra indicate other phases in addition to LiBH4 and LiH as reaction products – we are presently trying to identify these (eg., $CaAlH_5$, etc.)



# FY 2007-2008 plans

## FY 07 plans:

- Milling time and catalyst dependent studies of $ScH_2$ : $2LiBH_4$ system.
- Reaction path investigation in $Ca(AlH_4)_2$ : $2LiBH_4$ system to understand reversibility mechanism.
- $NaAlH_4$ wetting and aerogel pore size enthalpy dependent studies.
- Continued NMR studies to identify reaction species that lack definitive crystallographic features
- Enthalpy studies in micropore sized aerogels.
  - Our initial work on nanoparticle synthesis had difficulties in addressing subsequent grain/particle growth under hydrogenation/dehydrogenation conditions. These are obviated to extent by the use of scaffolds that "contain" hydrides and limit diffusion during cycling.
  - Recent studies indicate that surface oxidized carbon substrates upon which nanoscaled $NaAlH_4$ is deposited has cyclable properties w/out need for catalyst[1].
  - Moreover, improvements in encapsulated (aerogel) vs bulk behavior shows improvements in capacity for $NaAlH_4$.[2]
  - Recent reports that 1-2 nm sized Mg incorporated into aerogels have reaction enthalpy to 45 kJ/mole (down from 76 kJ/mole in bulk)[3]

# FY 2007-2008 plans cont'd

- Coordination with T. Baumann (LLNL) in synthesis of aerogels with pore size range down to 1 to 2 nm. Surface/interface effects will play a dominant role in reaction enthalpy behavior at these size dimensions.
- Wetting behavior analysis of $NaAlH_4$ (as an already thermodynamically well-understood model system) and Mg to determine contact angle dependence on carbon surface treatment, necessary to understand minimum size constraints in aerogel pores.
- Use of surface treatments/additives to enhance wetting of hydrides in aerogel pores.
- Confirmation of lowered enthalpies and diffusion paths in $NaAlH_4$ and Mg encapsulated within aerogel pores.


1 C.P. Bald, B.P.C. Hereijgers, J.H. Bitter, and K.P. de Jong, "Facilitated Hydrogen Storage in $NaAlH_4$ Supported on Carbon Nanofibers" Angew. Chem. Int. Ed. 2006, 45, 3501–3503.

2 International Patent Application WO 2005/014469 A1, F. Schuth, B. Bogdanovic, A. Taguchi. "Materials encapsulated in porous matrices for the reversible storage of hydrogen"

3 R. W. Wagemans, T. M. Eggenhuisen, K. P. de Jong, P. E. de Jongh, "Magnesium-Carbon Nanocomposites for Hydrogen Storage?," at MH2006 International Symposium on Metal-Hydrogen Systems, Maui, Oct 2006.

# Summary:

- Approach: Synthesis of destabilized hydride systems and kinetic analysis of dehydrogenation/hydrogenation reactions in “theoretically screened” systems of interest.

- Technical accomplishments and progress:
  - $ScH_2$:2$LiBH_4$ of particular interest as a 34kJ/mole system. Dehydrogenation temperature of up to 400°C still not high enough to completely extract theoretical value of hydrogenation. Predicted reaction products not discernable via x-ray or NMR. Reverse reaction does not appear to hydrogenate.
  - $Ca(AlH_4)_2$:2$LiBH_4$ system of interest in dehydrogenation/hydrogenation reactions but reaction pathways also not well understood.
- NMR analysis of value at this point in identifying near neighbor species that are not distinguishable via x-ray diffraction.

- Collaborations: HRL, JPL, U. ILL, Carnegie Mellon, U. Pittsburgh, NIST