Evaluations of Formation and Reversibility of Metal Borohydrides via Volumetric and Nuclear Magnetic Resonance Methods

ROBERT C. BOWMAN, JR. AND JOSEPH W. REITER
Jet Propulsion Laboratory, Pasadena, CA 91109-8099, USA

SON-JONG HWANG AND CHUL KIM
Division of Chemistry and Chemical Engineering
California Institute of Technology, Pasadena, CA 91125, USA

HOURIA KABBOUR, JUSTIN PUREWAL, AND C. C. AHN
Division of Engineering and Applied Science
California Institute of Technology, Pasadena, CA 91125, USA

ACS Hydrogen 2008 Meeting, Cocoa Beach, FL

February 25, 2008

Jet Propulsion Laboratory
California Institute of Technology

Outline

- **Introduction & Background**
  - **Desorption behavior of the Borohydrides**
  - **Overview of solid state NMR concepts & methods**
- **Examples of NMR Studies Taken from MHCoE Efforts**
  - **Desorption of $LiBH_4$**
  - **Reversible destabilization reactions of $LiBH_4$-MgH_2**
  - **Phase relationship in the Li-Sc-B-H system**
- **Summary & Conclusions**

What Happens when Borohydrides are Heated?

(1) $LiBH_4 \rightarrow LiH + B\ (amorphous) + 1.5H_2\uparrow$

(2) $M(BH_4)_n \rightarrow MH_x + n$"a-B" $+ (2n\text{-}x/2)H_2\uparrow$

Several studies have indicated various intermediate phases

Hypothetical candidates: "$LiBH_3$", "$LiBH_2$", and "LiBH"

Boron phases mostly NOT identifiable via XRD/NPD ("Amorphous")

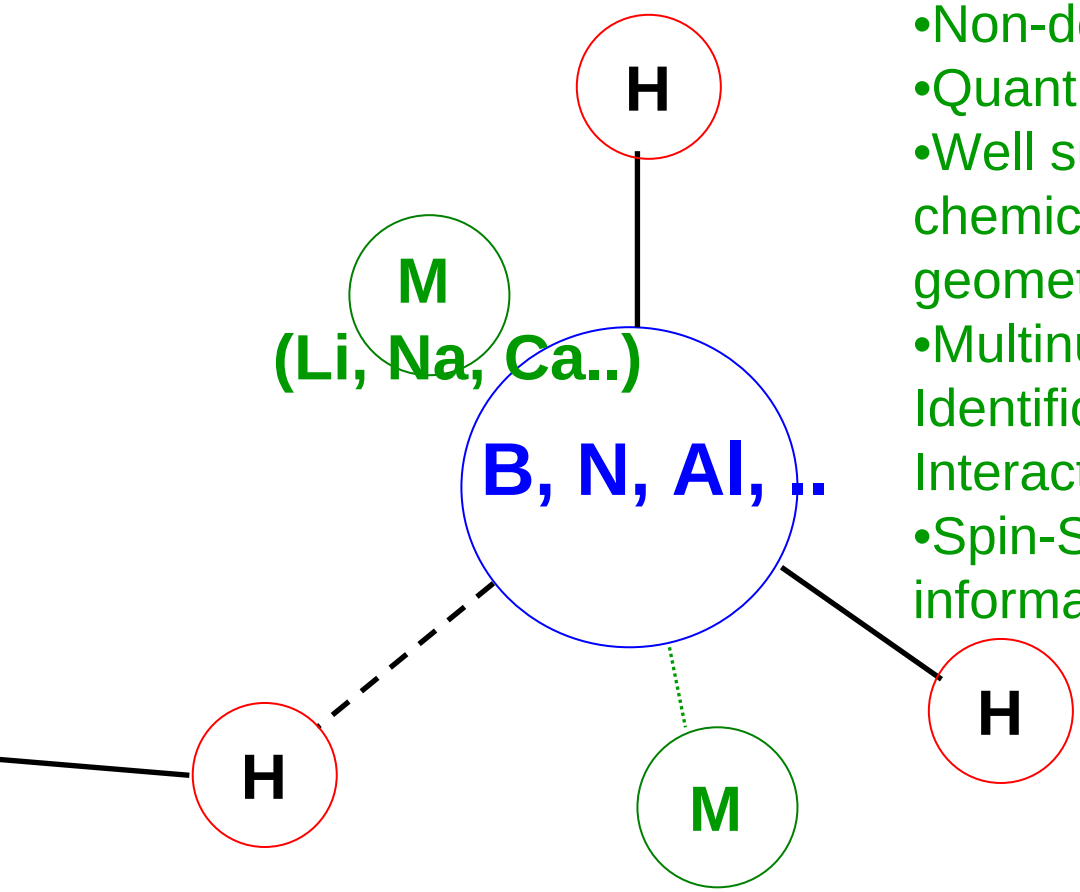
During desorption of $LiBH_4$, "polyboranes" were recently suggested [1,2] from First Principles Theory & Raman spectroscopy as actual phases that formed!

$$LiBH_4 \leftrightarrow \tfrac{1}{12}Li_2B_{12}H_{12} + \tfrac{5}{6}LiH + \tfrac{13}{12}H_2 \qquad (3)$$

$$\leftrightarrow LiH + B + \tfrac{3}{2}H_2. \qquad (4)$$

1. S. Orimo, et al., APL **89** (2006) 021920
2. N. Ohba,et al., PRB **74** (2006) 075110

NMR for Complex Metal Hydrides



- Element specific
- Non-destructive
- Quantitative
- Well suited for short range orders – chemical bonding, coordination geometries,..
- Multinuclear Approach: Phase Identification (CS, Quadrupole Interaction)
- Spin-Spin correlation : Connectivity information (dipole coupling)-CPMAS

I=1/2: ^{1}H, ^{15}N, …
I=1 : ^{2}H, ^{6}Li, …
I=3/2 : ^{23}Na, ^{7}Li, ^{11}B, …
I=5/2 : ^{27}Al,^{25}Mg, …
I=7/2 : ^{45}Sc, ^{43}Ca, …

NMR Studies of M-H Systems

- R.G. Barnes, “ NMR in Metal Hydrogen Systems” Topics in Applied Physics, Vol **73** (1997), pp 93 – 151.
- R. C. Bowman, Jr. and S.-J. Hwang, “Nuclear Magnetic Resonance Studies of Hydrogen Storage Materials”, Mater. Matters **2**(No.2), 29 (2007).

General Review of High Resolution Solid State NMR

- K. J. D. MacKenzie and M. E. Smith, *Multinuclear Solid-State NMR of Inorganic Materials* (Pergamon, Amsterdam, 2002).

High Resolution Solid State NMR

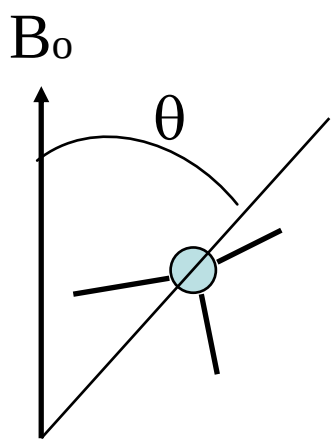
Removing Anisotropic Interactions to Sharpen Spectra

(Pulse manipulations, mechanical rotations)

MAS, MQMAS, CPMAS

$$H = \hbar\omega_I = H_z + H_{cs} + H_D + H_Q$$

$$\omega_I \sim \omega_{iso} + \omega_{aniso}$$



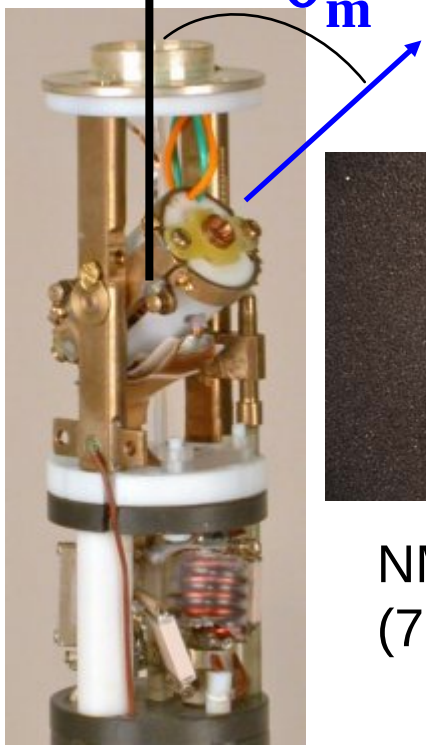
$$\omega_{aniso} \sim (3\cos^2\theta - 1)$$

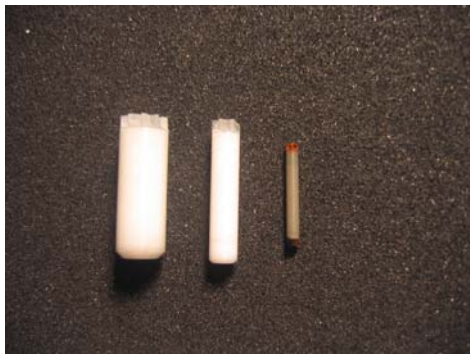
Magic Angle:

$\langle 3\cos^2\theta - 1 \rangle = 0$ when $\theta_m = 54.7^\circ$ ["Magic Angle"]

Magic Angle Spinning (MAS)

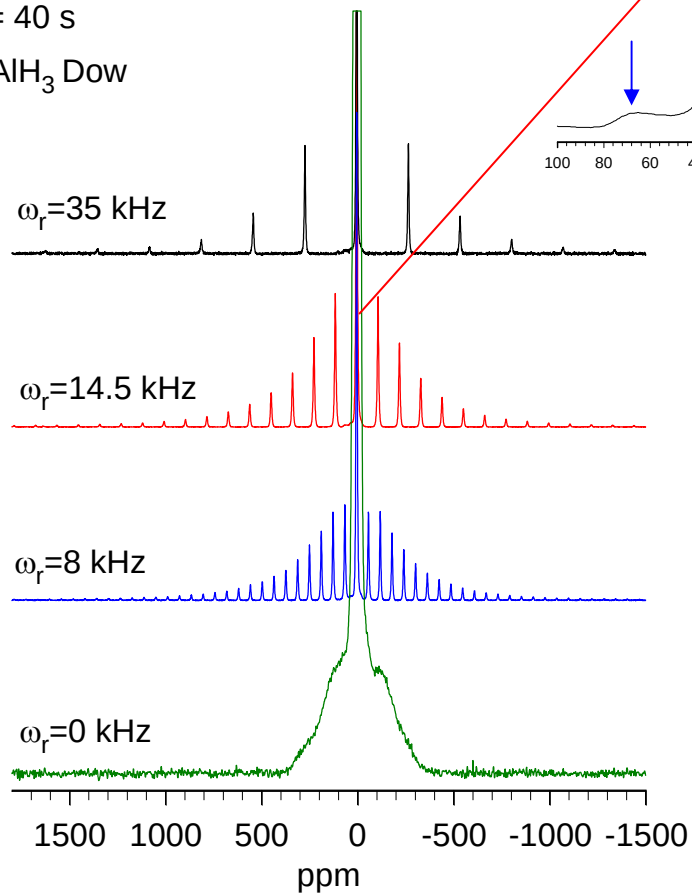
(^{27}Al @ 130.35 MHz for α-AlH_3)

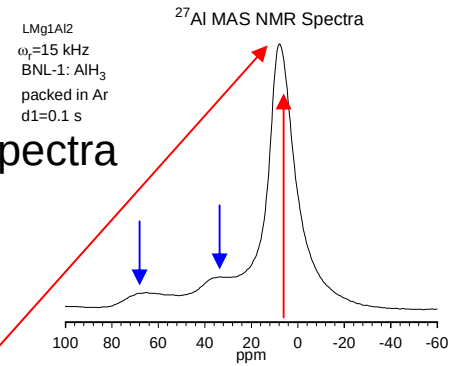




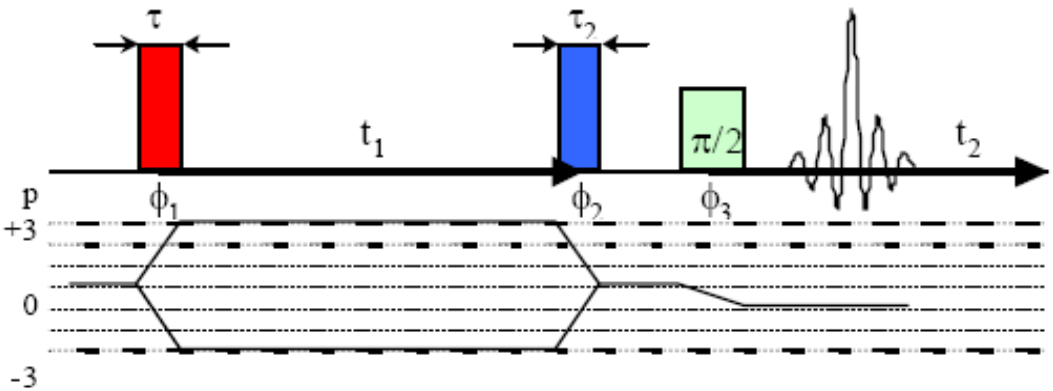
NMR rotors
(7, 4, 2 mm)

Commercial probe (~1 mm) ~ 70 kHz





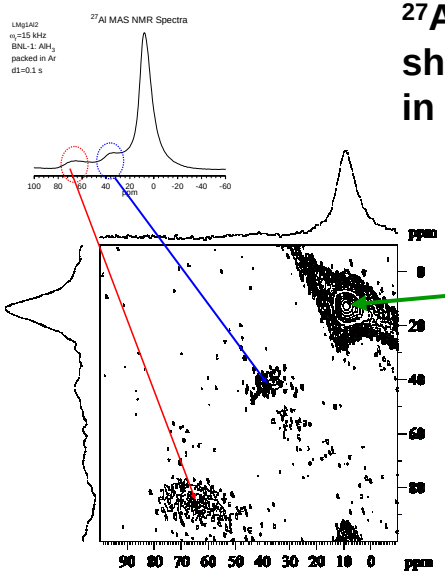
Multiple Quantum (MQ) NMR Method



Z-filtering, Amoureux and Fernandez, JMR 1996

$$\mathbf{H}=\mathbf{H_z}+\mathbf{H_{CS}}+\mathbf{H_D}+\mathbf{H_Q}$$

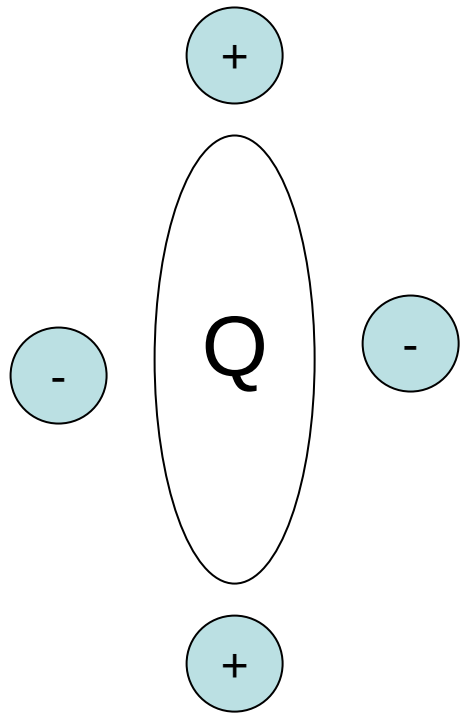
$$H_Q=\frac{eQ}{2I(2I-1)\hbar}I\cdot V\cdot I$$



^{27}Al Triple Quantum (3Q) MAS spectrum: showing the presence of 3 distinctive sites in α-phase AlH_3 with two oxide impurities.

α-AlH_3

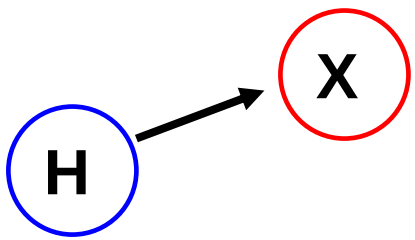
Main peak @ ~6 ppm from α-AlH_3 with two "Al-O" peaks at ~40 ppm & 65 ppm.

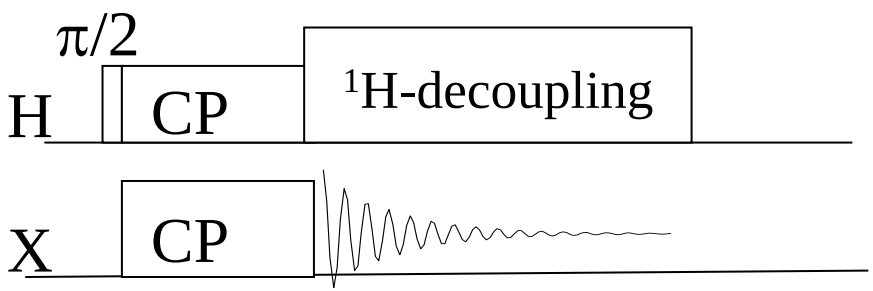


Electrostatic gradients

Cross-Polarization (CP) MAS Spectra With Protons

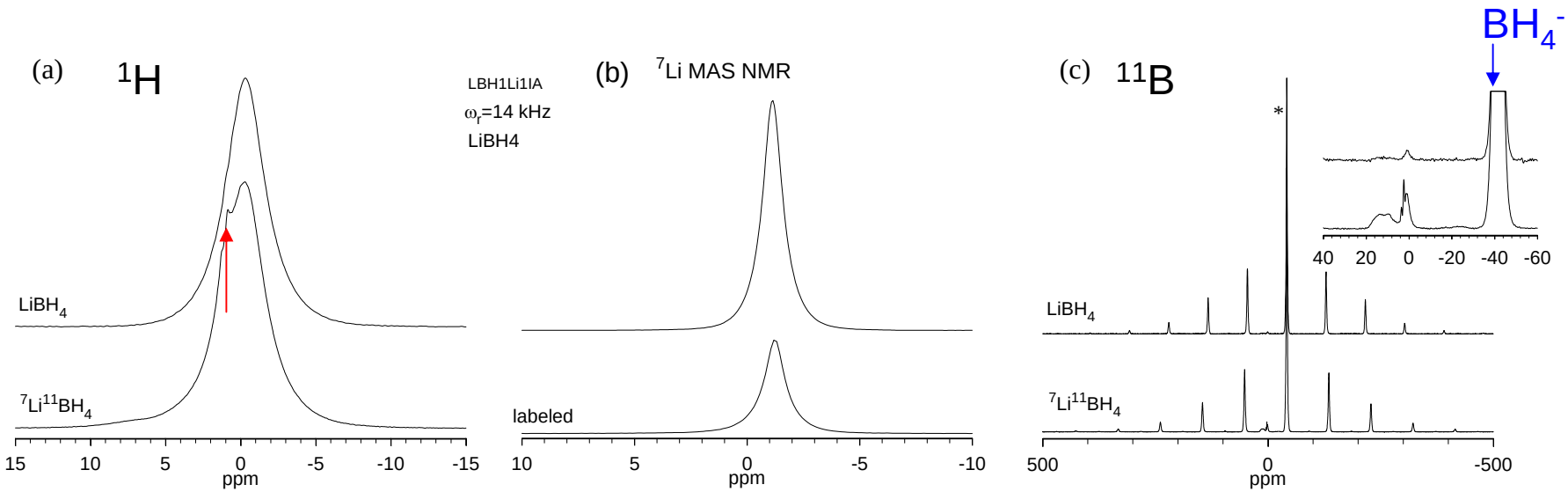
- To assist in observing dilute spins
  - (Pines, et al., J.Chem. Phys. 1973, Stejskal, et al., J. Magn. Reson. 1977.)
- To obtain information on spins that are close in space.
- One of the most widely used techniques in solid-state NMR (However, rarely applied to MH_x until the last few years).





No ^{1}H neighbors => No CP signal from X

MAS-NMR Spectra for As-Prepared $LiBH_4$



NIST synthesized $^{7}Li^{11}BH_4$ sample compared to natural isotope abundant $LiBH_4$ from Alfa-Aesar.

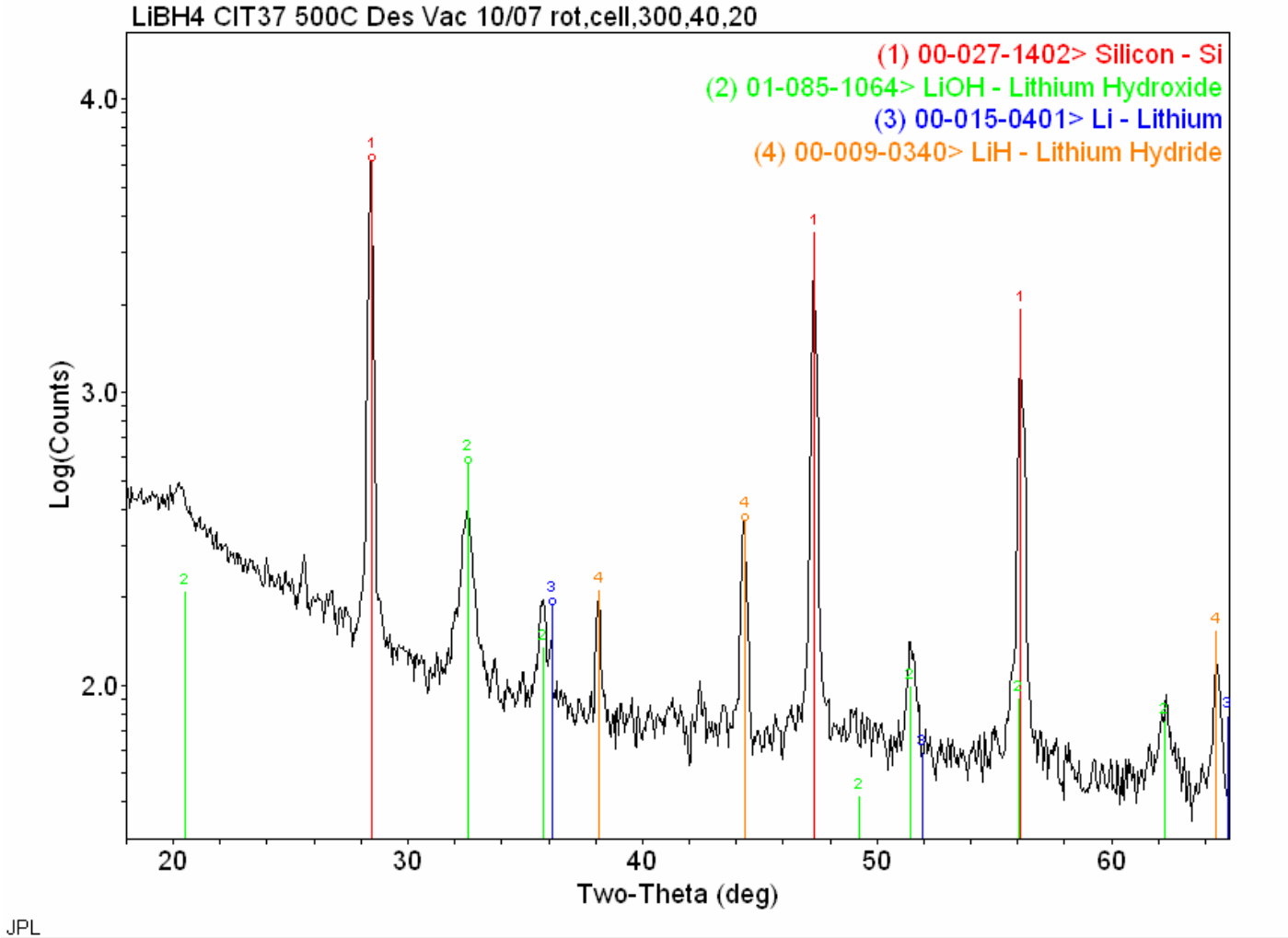
(a) ^{1}H MAS NMR has $LiBH_4$ peak at -0.3 ppm with shoulder at ~1 ppm in $^{7}Li^{11}BH_4$ from $B(OH)_3$ impurities

(b) ^{7}Li MAS NMR Spectra where $LiBH_4$ peak is at -1.2 ppm.

(c) ^{11}B MAS NMR spectra. The expanded view shows low level peaks from impurities (i.e., $B(OH)_3$ and B_2O_3). The main peaks for BH_4^- species occur at -41.3 ppm for the central transition (-1/2↔1/2) of ^{11}B (I=3/2), with spinning sidebands over about 800 ppm range from the satellite transitions.

M. R. Hartman, et al., *J. Solid State Chem.* **180** (2007) 1298-1305.

XRD of $LiBH_4$ (Aldrich) Vacuum Desorbed to 500 ºC @ JPL



Comments: (1) no boron phases detected, (2) LiH seen, (3) LiOH may be from air leaks into XRD cell, (4) Li metal seems unlikely but possibly Li_2O. (Internal Si reference)

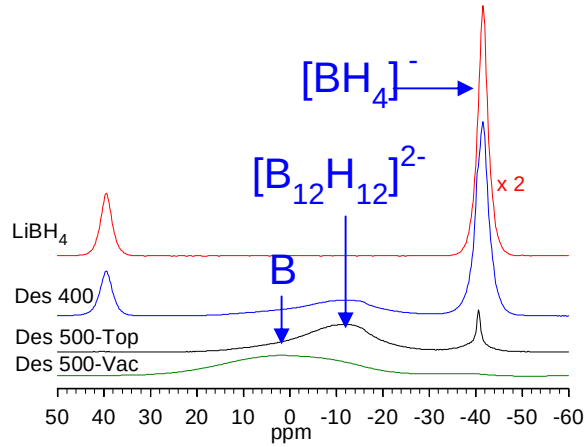
NMR Spectra of Desorbed $LiBH_4$ Samples

- 400 °C : CIT-24
- 500 °C-Top: CIT-29 Top
- 500 °C-Vac: CIT-37; Vacuum to 500 °C

Solid MAS

LBH6B1A1

^{11}B NMR Spectra



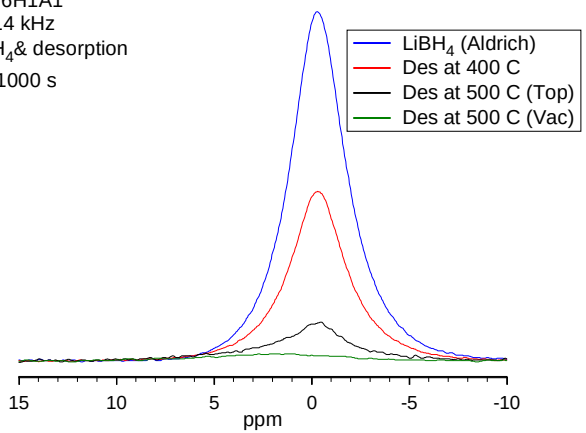
LBH6H1A1

ω_r=14 kHz

$LiBH_4$& desorption

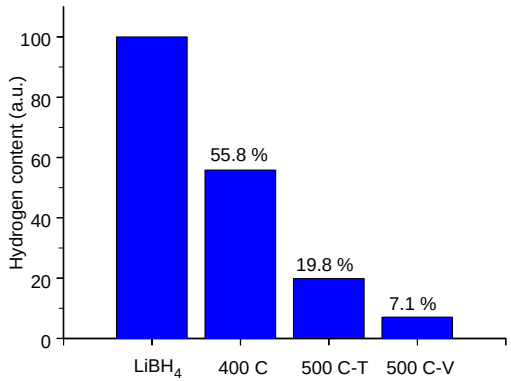
d1=1000 s

^{1}H MAS NMR



LBH6H1B

Hydrogen contents by ^{1}H MAS NMR

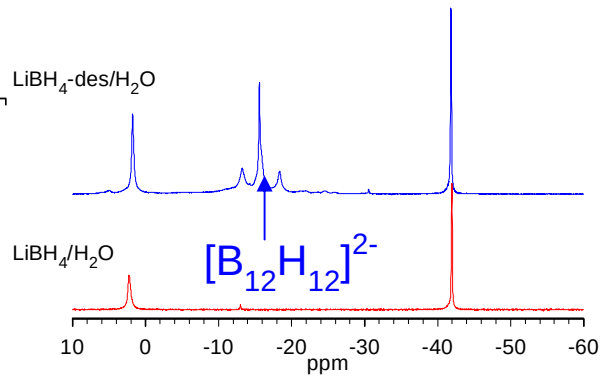


HR-NMR Liquid Solution

LBH5B2C

^{11}B NMR Spectra

CIT-24: des-$LiBH_4/H_2O$



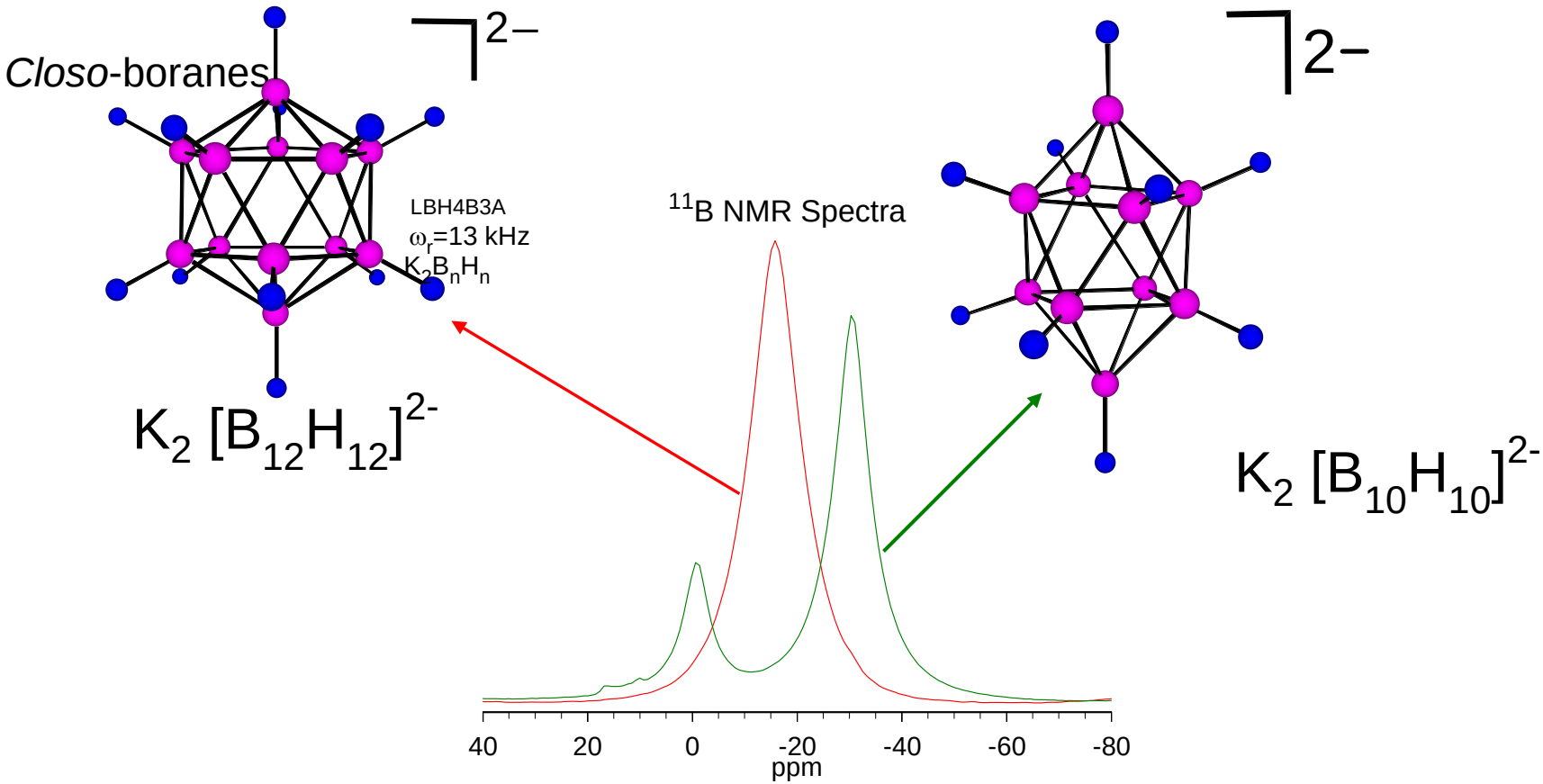
In the case of intermediate ($[B_{12}H_{12}]^{2-}$ anion) formation

$12LiBH_4 \rightarrow Li_2B_{12}H_{12} + 10\ LiH + 13H_2 \uparrow$: 54.2% H loss

$\rightarrow 12B + 12LiH + 5H_2 \uparrow$: 20.8% H loss – total 75% of H

$\rightarrow 12B + 12Li + 6\ H_2$: 25 % H loss – total 100% of H

NMR: Formation of B_nH_n type complexes?



MAS-NMR Spectra for Samples: Dr. S. S. Jalisatgi (U. Missouri-Columbia)

^{11}B NMR spectra after hydrogen desorption reactions of $LiBH_4$:

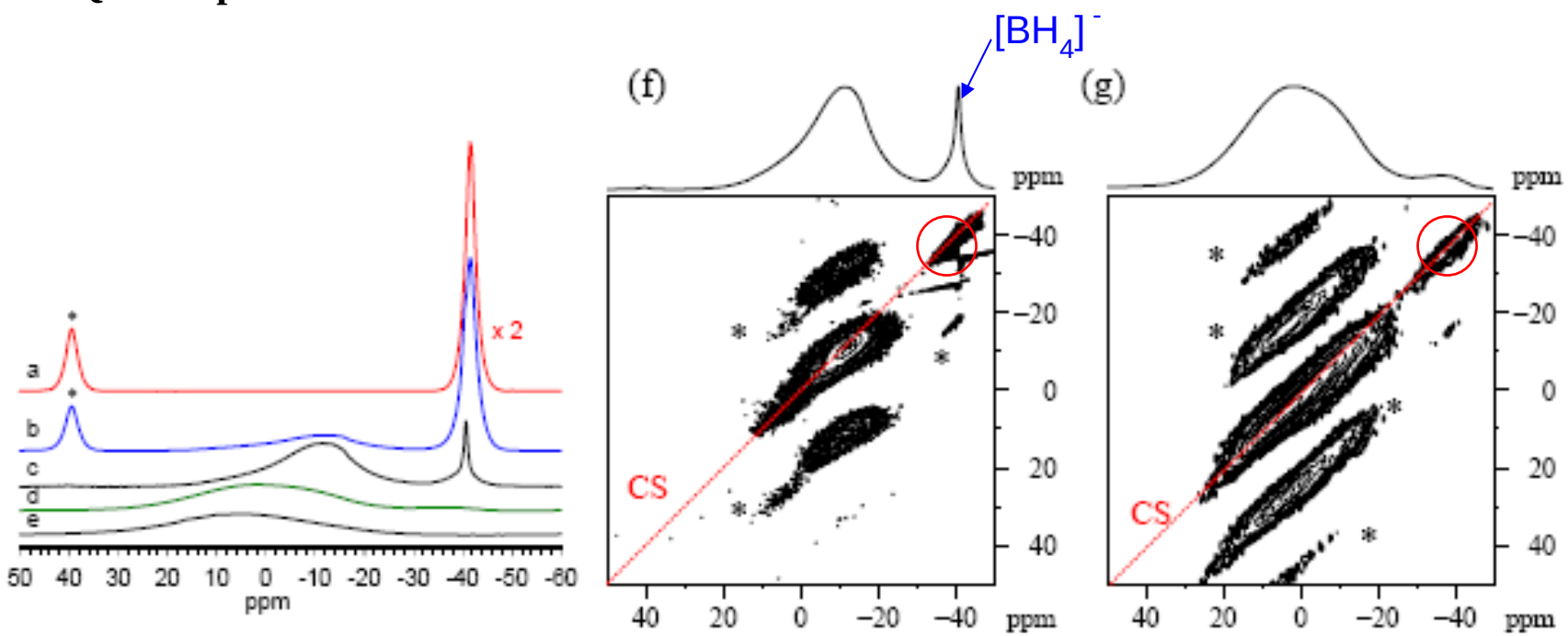
a) $LiBH_4$ (as received, Sigma-Aldrich), b) desorbed at 400 °C,

c) desorbed at 500 °C, d) desorbed at 500 °C under vacuum,

e) elemental boron in amorphous phase (Sigma-Aldrich),

f) ^{11}B MQMAS spectrum of sample c),

g) ^{11}B MQMAS spectrum of sample d). Spinning side bands are marked with *. The dashed line in 2D MQMAS spectra is the chemical shift axis.



MQMAS 500°C Desorbed $LiBH_4$

MQMAS a-B Phase

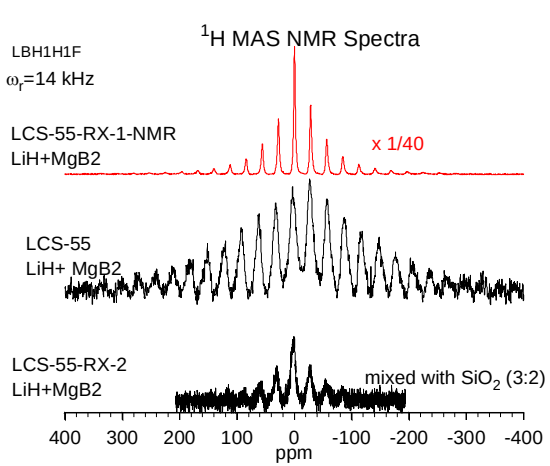
MAS-NMR determined phase formation and reversibility in Destabilized $LiBH_4/MgH_2$:

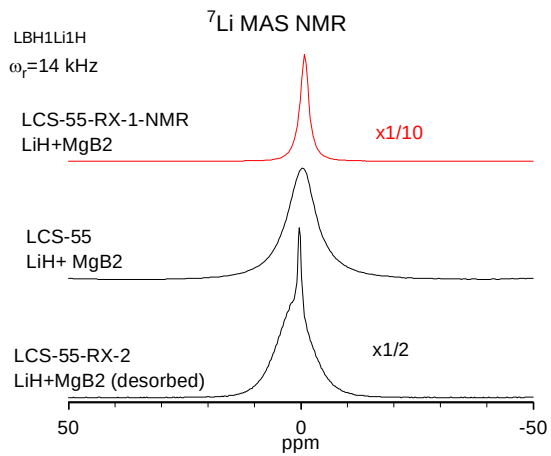
"$MgH_2 + 2LiBH_4 = 2LiH + MgB_2 + 4H_2$"

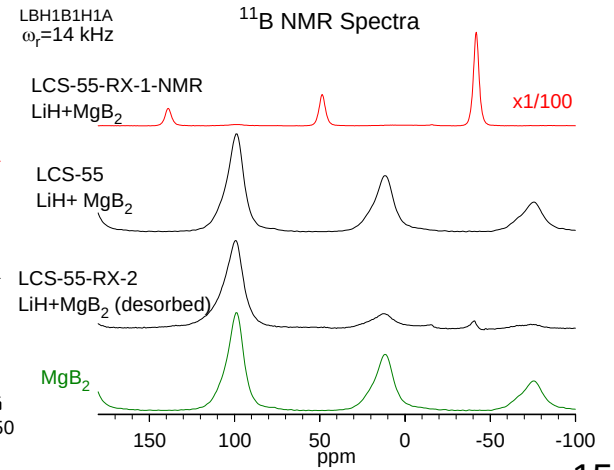
(J. J. Vajo, et al., J. Phys. Chem. B **109** (2005) 3719)

^7Li, ^{11}B and ^1H MAS-NMR gave expected phases with variation in hydrogen contents

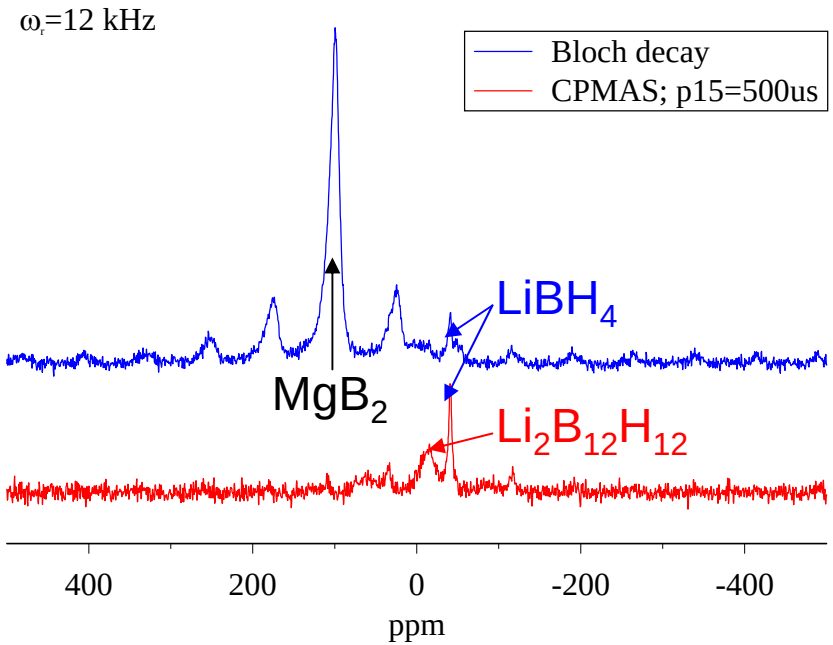
Samples	Code	Treatment	Comments
$LiH+MgB_2$	LCS-55	As ball milled	From J. Vajo [HRL]
$LiBH_x+MgH_2$	LCS-55: RX-1	Absorbed H_2	Saturated hydrides
MgB_2 + LiH + $LiBH_x$	LCS-55: RX-2 + SiO_2 Powder	Desorbed H_2: diluted for better MAS-NMR	Incomplete desorb reaction noted



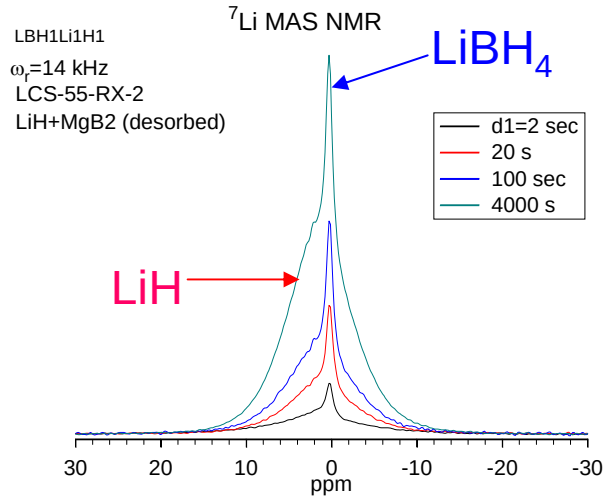




^{11}B MAS & CPMAS of Desorbed LCS-55 RX-2



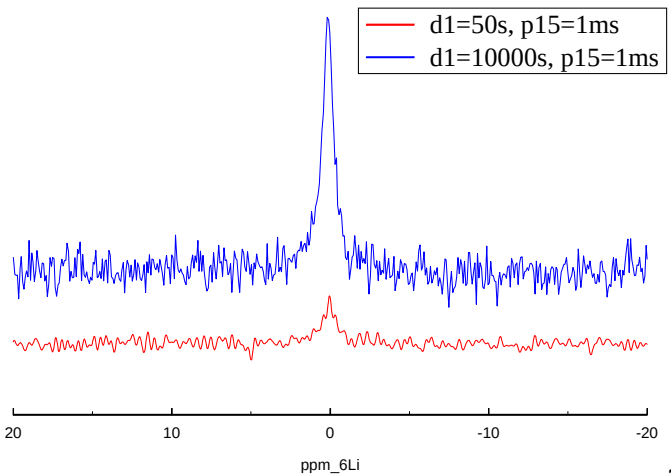
^{7}Li MAS NMR spectra of LCS-55 RX-2.



•LCS-55-RX-2 shows two components, sharp and broad, both showing very slow relaxation rate.

^{6}Li CPMAS NMR spectra of LCS-55 RX-2.

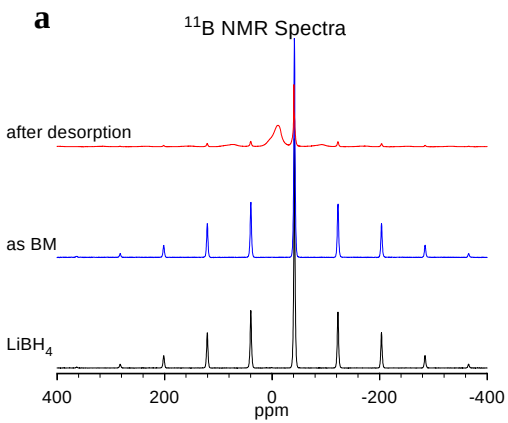
The signal at ~ 0 ppm is a signature of LiH. The longer delay time (10,000 s) improved the signal intensity dramatically, indicating the long T_1 relaxation behavior of LiH - as expected.

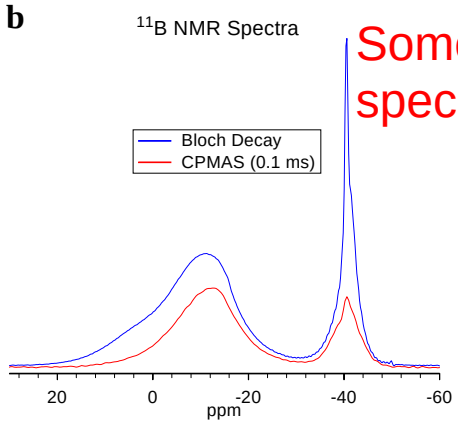


Investigation of the "$ScH_2 + 2LiBH_4 = 2LiH + ScB_2 + 4H_2$"

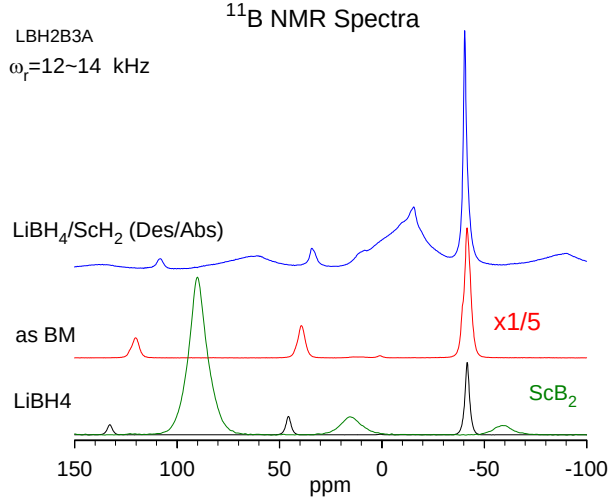
Destabilization Reaction predicted by Alapati, JALCOM **446-447** (2007) 23

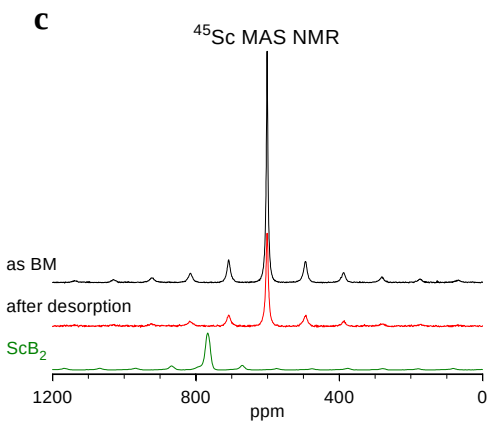
MAS-NMR Spectra: As Milled & Reacted

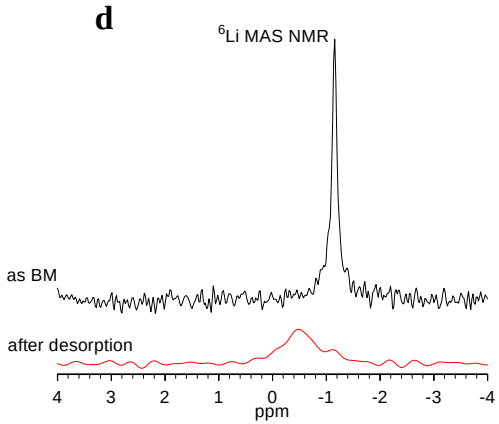




Some $LiBH_4$ has converted into "$B_{12}H_{12}$" species and "elemental boron"







(No predicted ScB_2 Phase seen!)

Detected only ScH_2

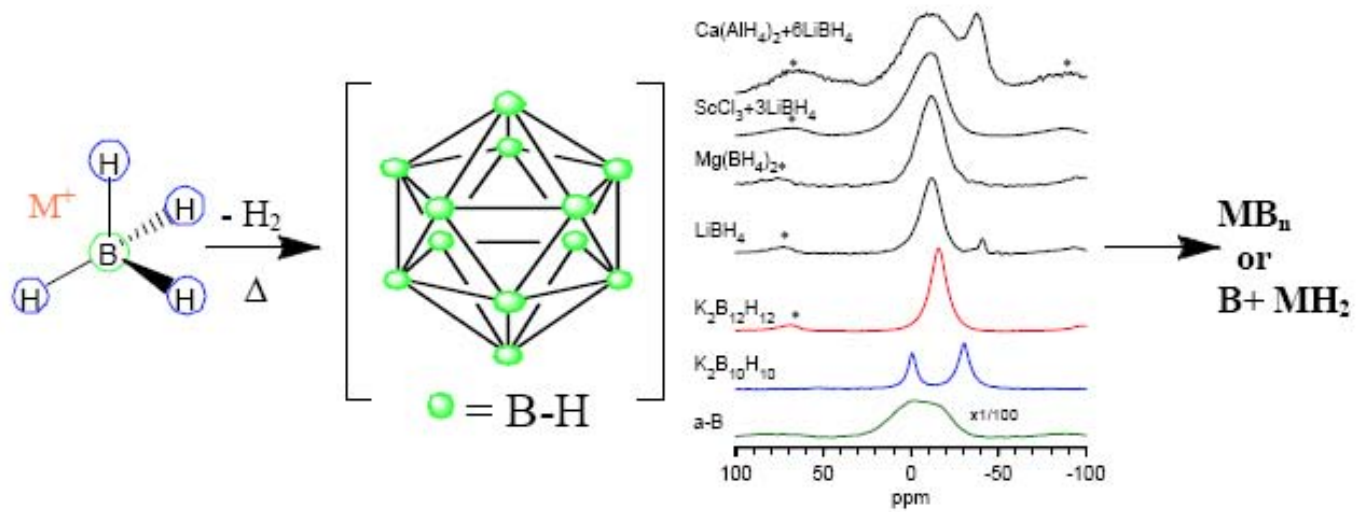
<u>Summary</u>: Desorption did **Not** follow the destabilized process of forming ScB_2. Had only partial decomposition of $LiBH_4$ into LiH + "B" phases with little reversibility indicated following attempted absorption reactions.

Summary & Conclusions

Solid State NMR is a powerful & versatile method to assess properties of hydrogen storage materials – especially the complex metal hydrides.

This talk illustrated usefulness of multi-nuclear MAS, MQMAS, and CPMAS spectra of protons and host nuclei in borohydrides.

- Monitor phase compositions and reactions for both hydrogen desorption and absorption reactions.
- Identified & characterized "$B_{12}H_{12}$ species" as being the dominant intermediate formed during H_2 desorption from several borohydrides.



Hwang, et al., *J. Phys. Chem. C.* 112 (2008) Web Release Date: 13-Feb-2008; **(Letter)** DOI: 10.1021/jp710894t