

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

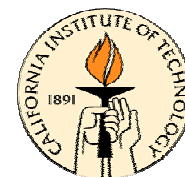
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# Outline

- **Introduction & Background**

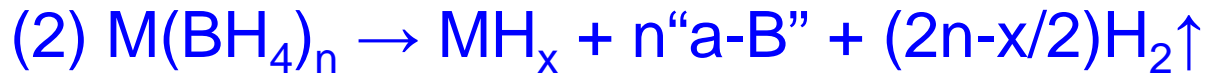
- Desorption behavior of the Borohydrides
- Overview of solid state NMR concepts & methods

- **Examples of NMR Studies Taken from MHCoE Efforts**

- Desorption of  $\text{LiBH}_4$
- Reversible destabilization reactions of  $\text{LiBH}_4\text{-MgH}_2$
- Phase relationship in the Li-Sc-B-H system

- **Summary & Conclusions**

# What Happens when Borohydrides are Heated?



Several studies have indicated various intermediate phases

Hypothetical candidates: “LiBH<sub>3</sub>”, “LiBH<sub>2</sub>”, and “LiBH”

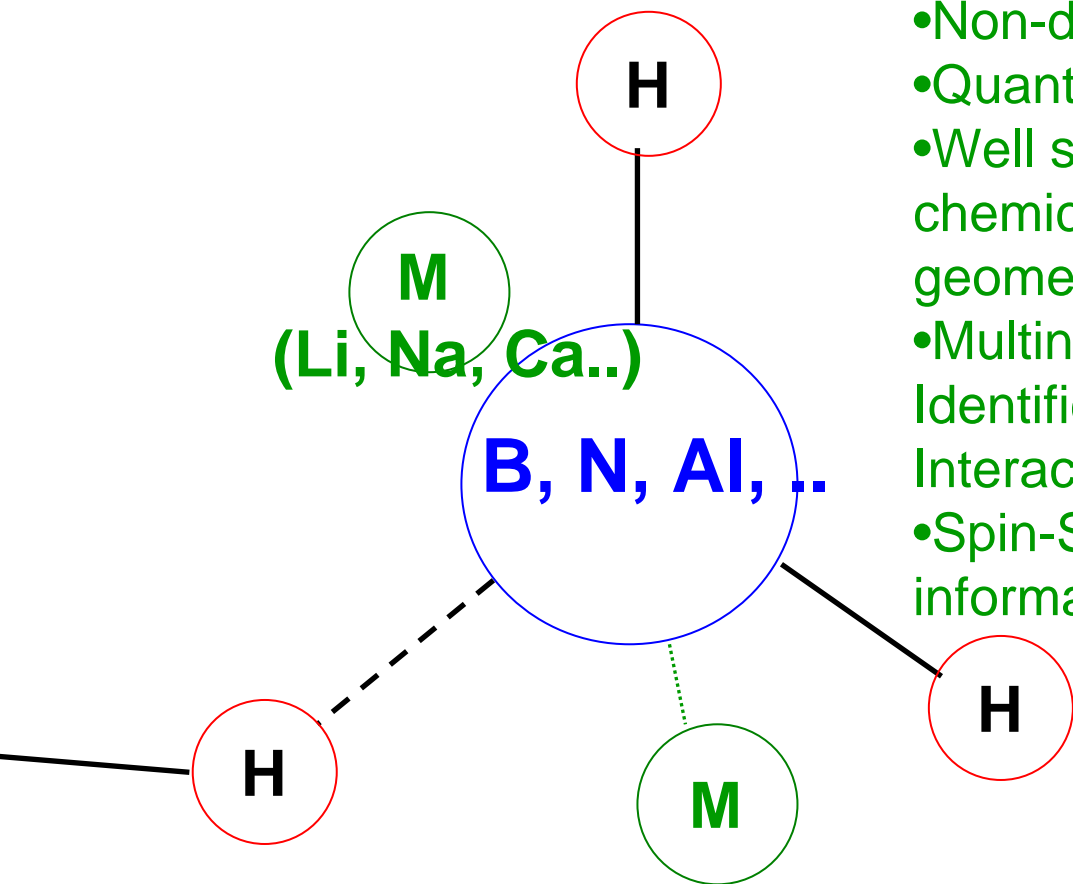
**Boron phases mostly NOT identifiable via XRD/NPD (“Amorphous”)**

**During desorption of LiBH<sub>4</sub>, “polyboranes” were recently suggested [1,2] from First Principles Theory & Raman spectroscopy as actual phases that formed!**



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

$I=1/2$ :  $^1\text{H}$ ,  $^{15}\text{N}$ , ...

$I=1$  :  $^2\text{H}$ ,  $^6\text{Li}$ , ...

$I=3/2$  :  $^{23}\text{Na}$ ,  $^7\text{Li}$ ,  $^{11}\text{B}$ , ...

$I=5/2$  :  $^{27}\text{Al}$ ,  $^{25}\text{Mg}$ , ...

$I=7/2$  :  $^{45}\text{Sc}$ ,  $^{43}\text{Ca}$ , ...

# 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).

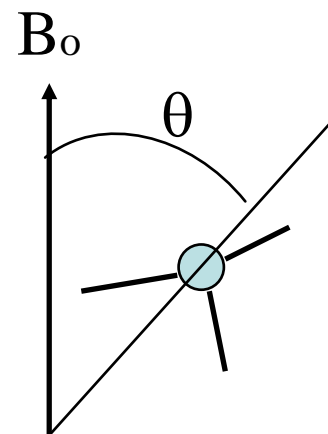
# High Resolution Solid State NMR

## Removing Anisotropic Interactions to Sharpen Spectra

(Pulse manipulations, mechanical rotations)

**MAS**, MQMAS, **CPMAS**

$$\begin{aligned} \mathbf{H} &= \hbar\omega_{\text{I}} \\ &= \mathbf{H}_{\text{z}} + \mathbf{H}_{\text{cs}} + \mathbf{H}_{\text{D}} + \mathbf{H}_{\text{Q}} \\ \omega_{\text{I}} &\sim \omega_{\text{iso}} + \omega_{\text{aniso}} \end{aligned}$$



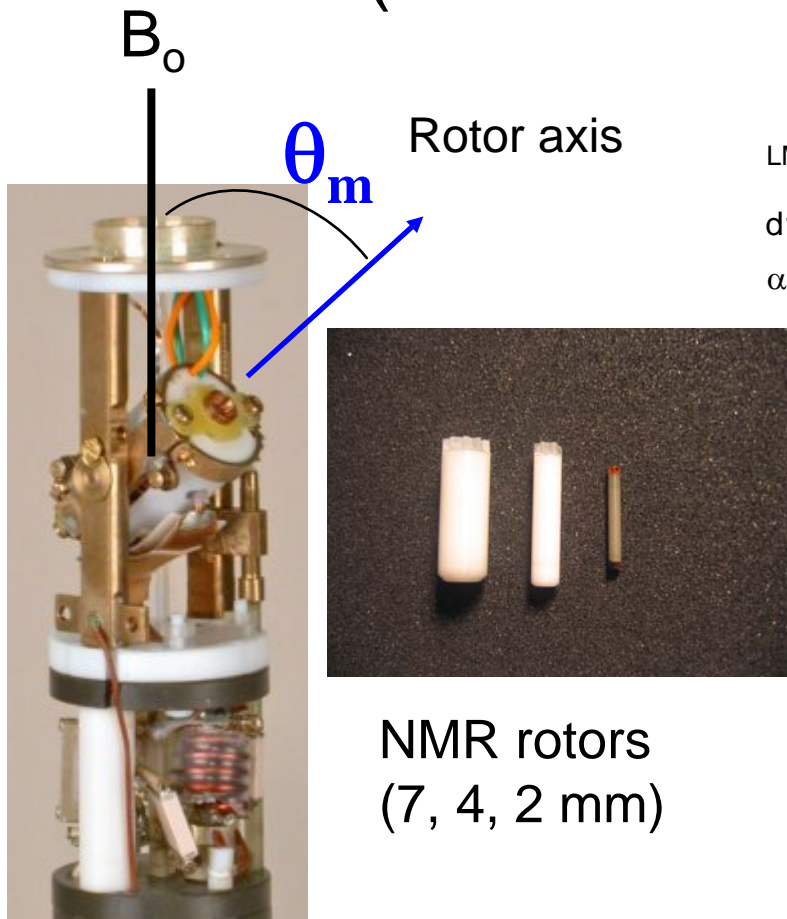
$$\omega_{\text{aniso}} \sim (3\cos^2\theta - 1)$$

Magic Angle:

$\langle 3\cos^2\theta - 1 \rangle = 0$  when  $\theta_{\text{m}} = 54.7^\circ$  ["Magic Angle"]

# Magic Angle Spinning (MAS)

( $^{27}\text{Al}$  @ 130.35 MHz for  $\alpha\text{-AlH}_3$ )



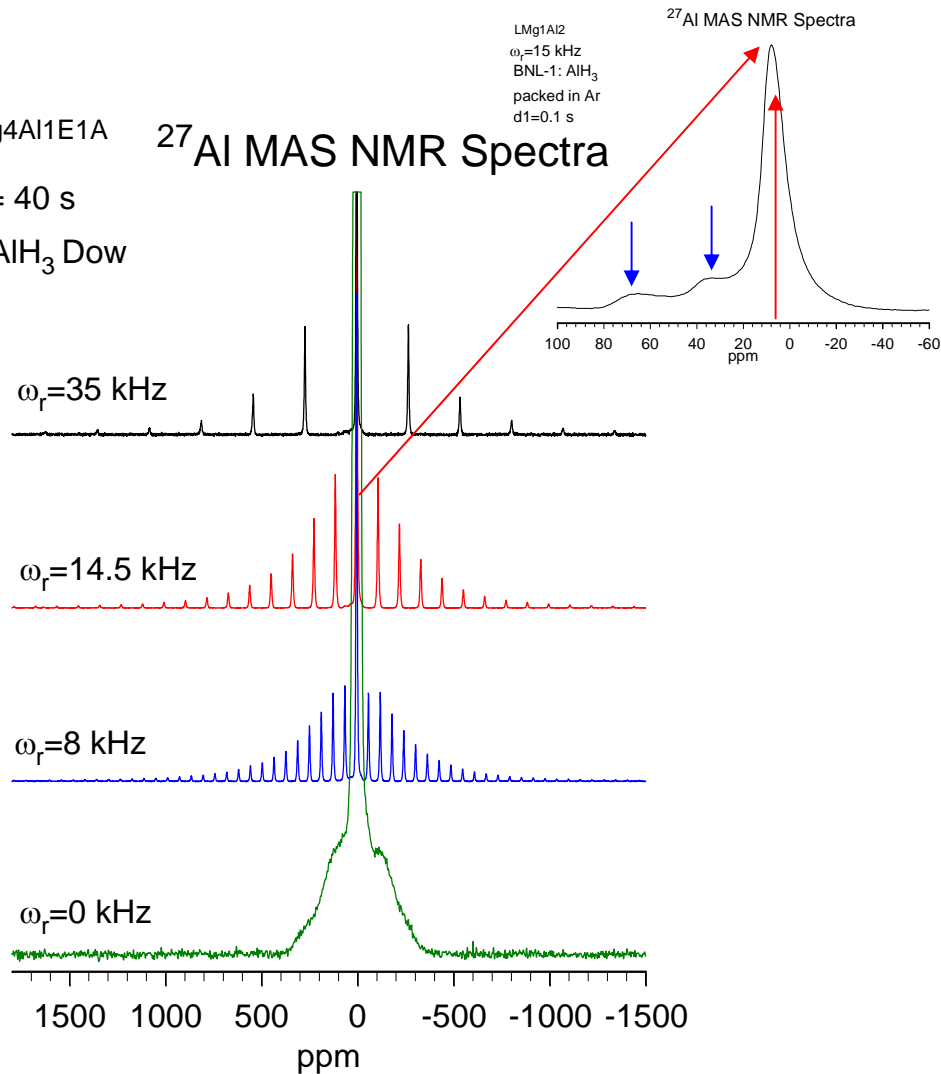
Commercial probe (~1 mm) ~ 70 kHz

LMg4Al1E1A

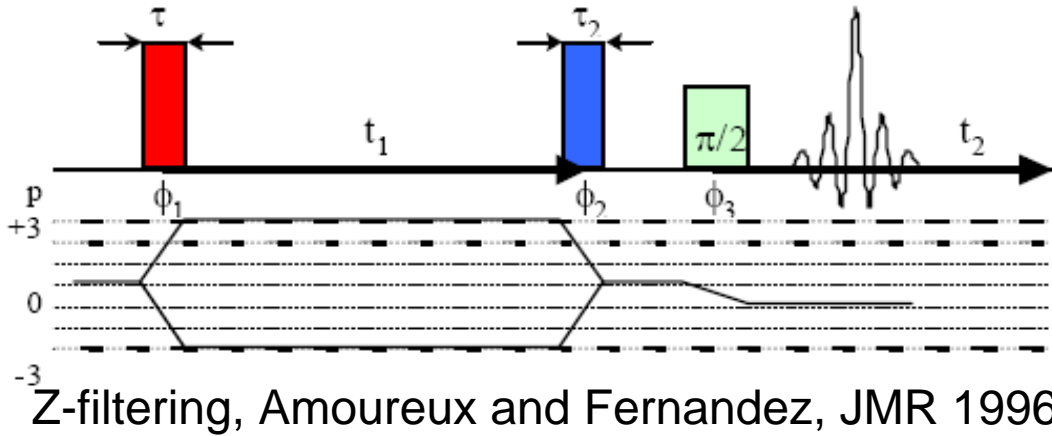
$^{27}\text{Al}$  MAS NMR Spectra

d1= 40 s

$\alpha\text{-AlH}_3$  Dow

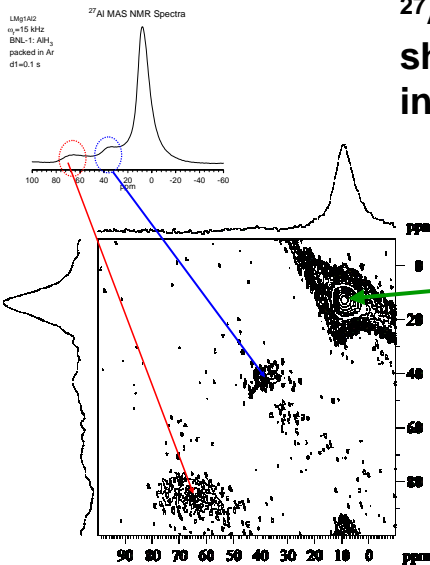


# Multiple Quantum (MQ) NMR Method



$$\mathbf{H} = \mathbf{H}_Z + \mathbf{H}_{CS} + \mathbf{H}_D + \mathbf{H}_Q$$

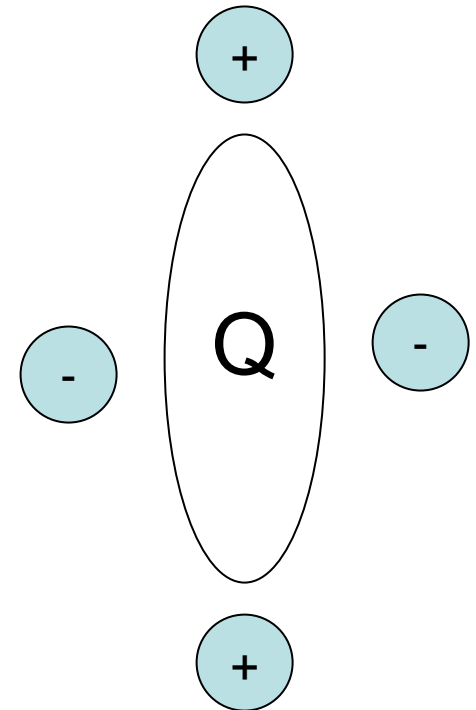
$$\mathbf{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}$$



**27Al Triple Quantum (3Q) MAS spectrum:**  
 showing the presence of 3 distinctive sites  
 in  $\alpha\text{-AlH}_3$  with two oxide impurities.

$\alpha\text{-AlH}_3$

Main peak @ ~6 ppm from  $\alpha\text{-AlH}_3$  with two  
 "Al-O" peaks at ~40 ppm & 65 ppm.

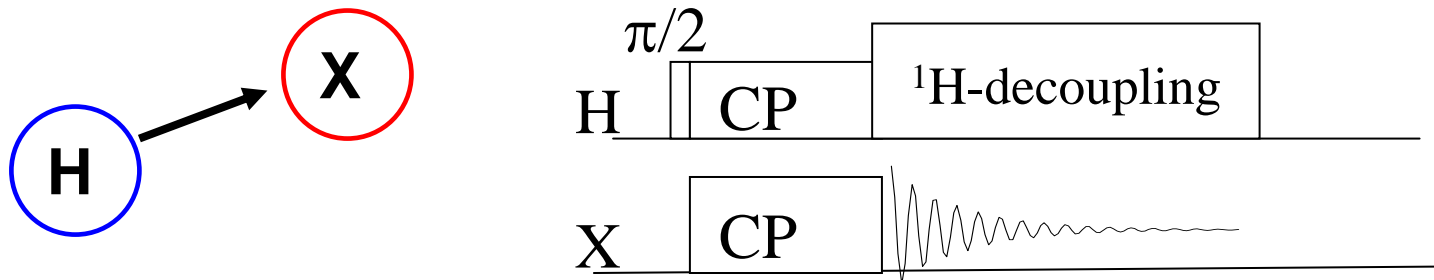


Electrostatic gradients



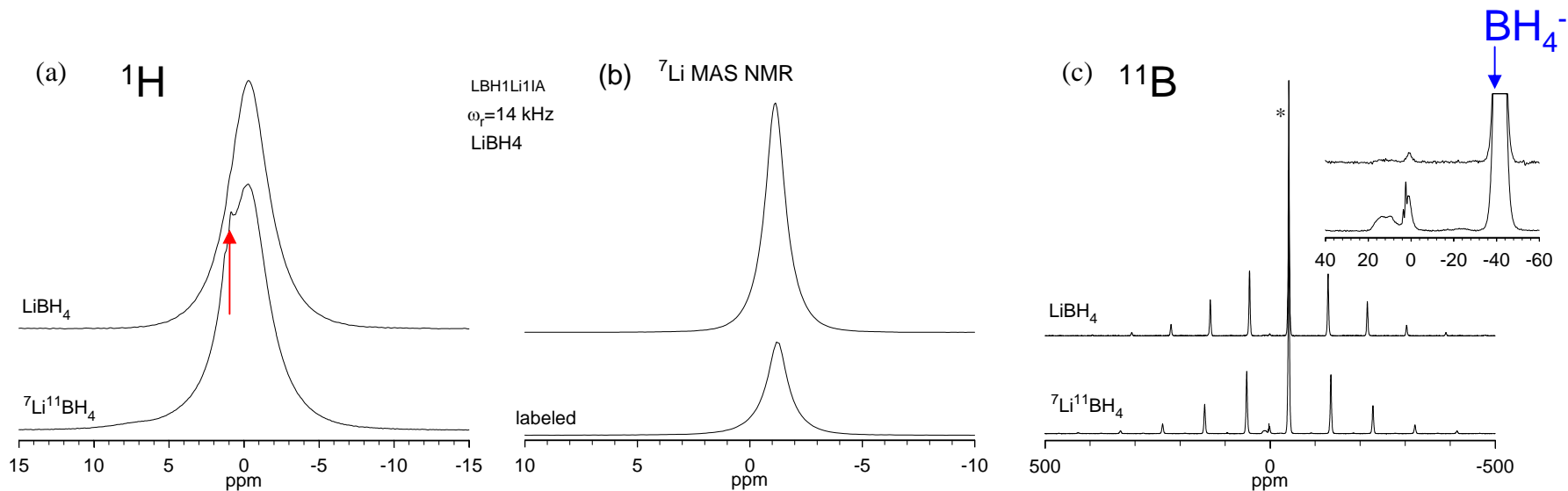
# Cross-Polarization (CP) MAS Spectra With **Protons**

- 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  $^1\text{H}$  neighbors  $\Rightarrow$  No CP signal from X**

# MAS-NMR Spectra for As-Prepared $\text{LiBH}_4$

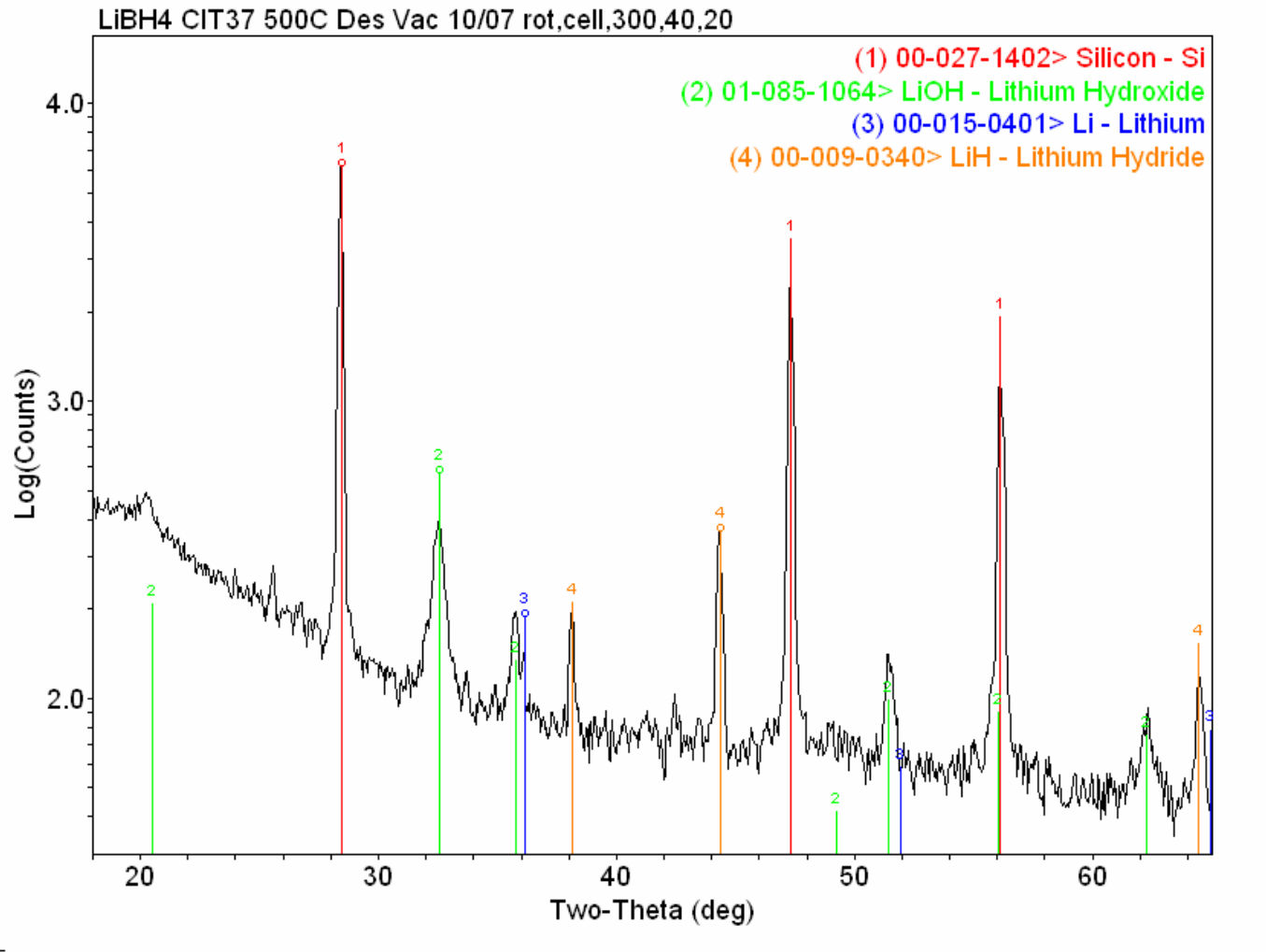


NIST synthesized  $^7\text{Li}^{11}\text{B}$  sample compared to natural isotope abundant  $\text{LiBH}_4$  from Alfa-Aesar.

- (a)  $^1\text{H}$  MAS NMR has  $\text{LiBH}_4$  peak at -0.3 ppm with shoulder at ~1 ppm in  $^7\text{Li}^{11}\text{B}$  from  $\text{B}(\text{OH})_3$  impurities
- (b)  $^7\text{Li}$  MAS NMR Spectra where  $\text{LiBH}_4$  peak is at -1.2 ppm.
- (c)  $^{11}\text{B}$  MAS NMR spectra. The expanded view shows low level peaks from impurities (i.e.,  $\text{B}(\text{OH})_3$  and  $\text{B}_2\text{O}_3$ ). The main peaks for  $\text{BH}_4^-$  species occur at -41.3 ppm for the central transition ( $-1/2 \leftrightarrow 1/2$ ) of  $^{11}\text{B}$  ( $I=3/2$ ), 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 $\text{LiBH}_4$ (Aldrich) Vacuum Desorbed to 500 °C @ 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  $\text{Li}_2\text{O}$ . (Internal Si reference)

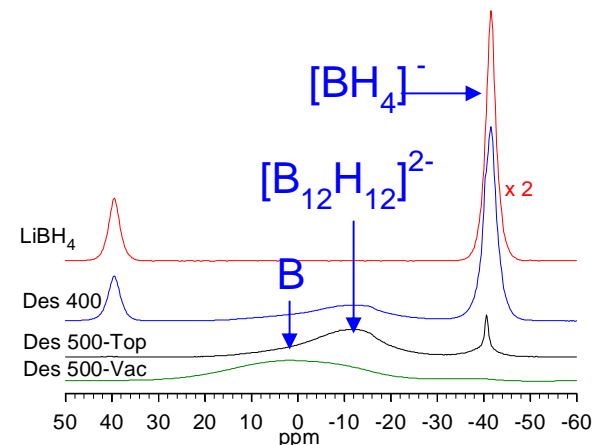
# NMR Spectra of Desorbed LiBH<sub>4</sub> Samples

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

LBH6B1A1

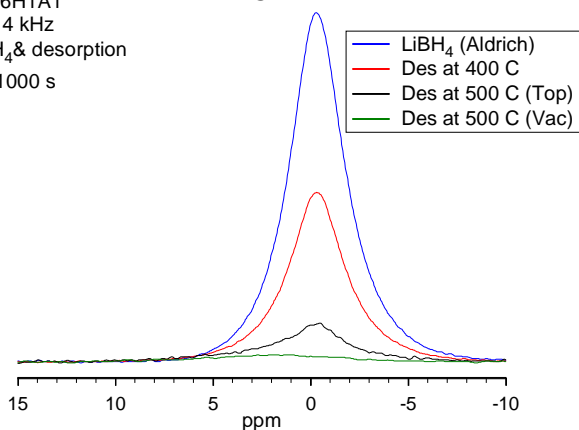
## Solid MAS

<sup>11</sup>B NMR Spectra



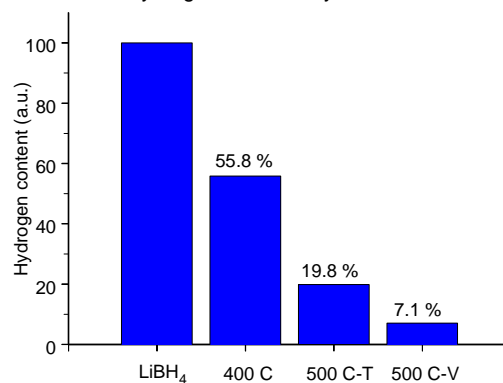
LBH6H1A1  
ω<sub>r</sub>=14 kHz  
LiBH<sub>4</sub>& desorption  
d1=1000 s

## <sup>1</sup>H MAS NMR



LBH6H1B

## Hydrogen contents by <sup>1</sup>H MAS NMR

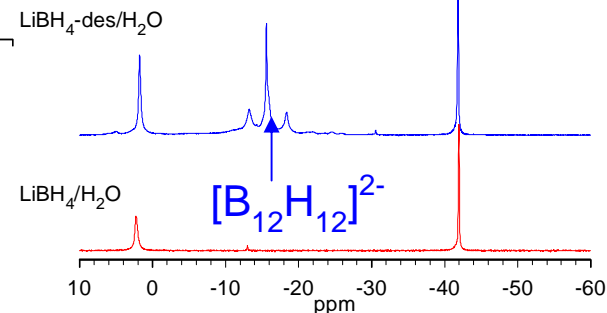


## HR-NMR Liquid Solution

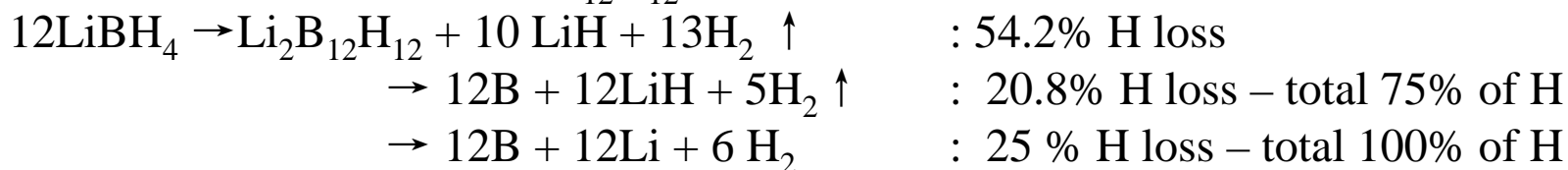
LBH5B2C

<sup>11</sup>B NMR Spectra

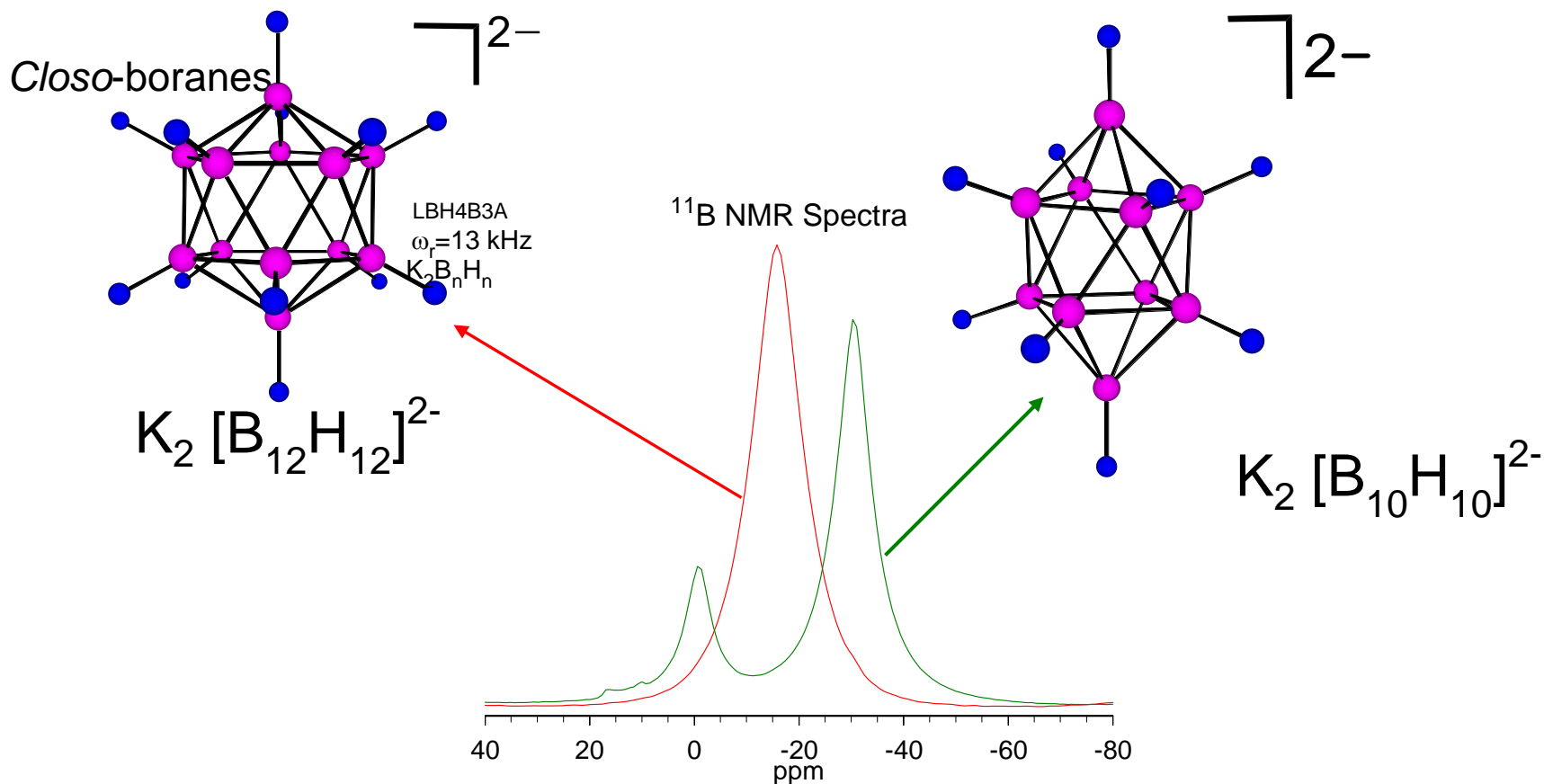
CIT-24: des-LiBH<sub>4</sub>/H<sub>2</sub>O



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



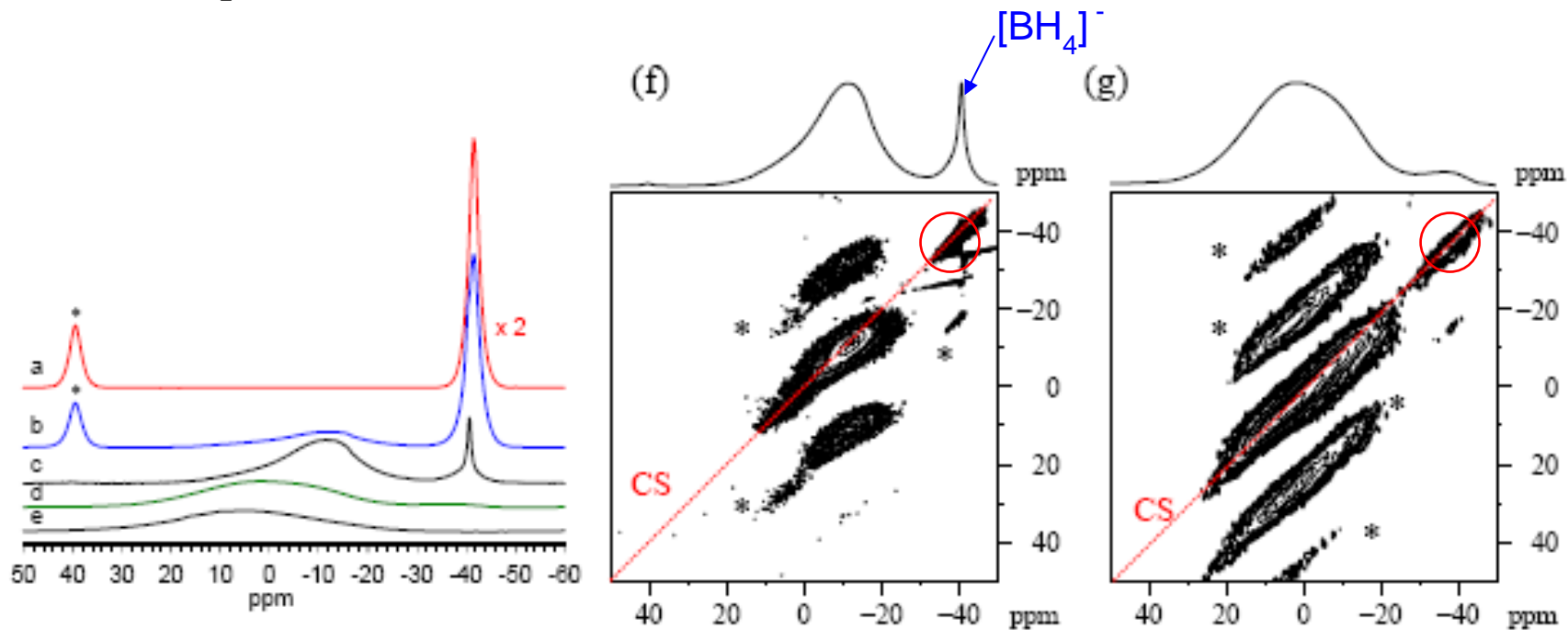
# NMR: Formation of $B_nH_n$ type complexes?



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

# $^{11}\text{B}$ NMR spectra after hydrogen desorption reactions of $\text{LiBH}_4$ :

- a)  $\text{LiBH}_4$  (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)  $^{11}\text{B}$  MQMAS spectrum of sample c),  
g)  $^{11}\text{B}$  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  $\text{LiBH}_4$

MQMAS a-B Phase

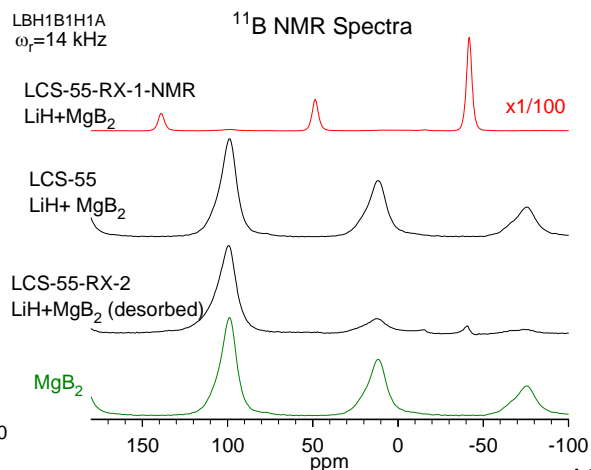
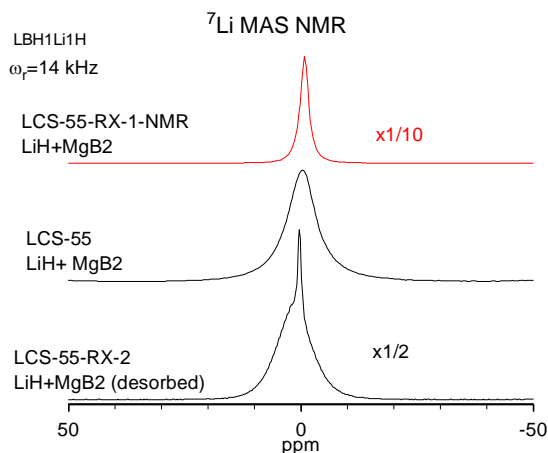
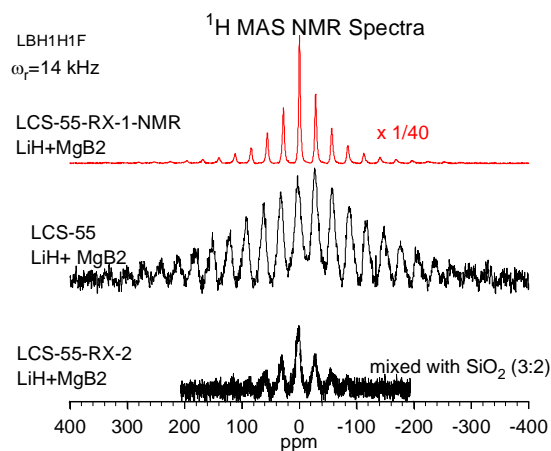
MAS-NMR determined phase formation and reversibility in Destabilized  $\text{LiBH}_4/\text{MgH}_2$ :



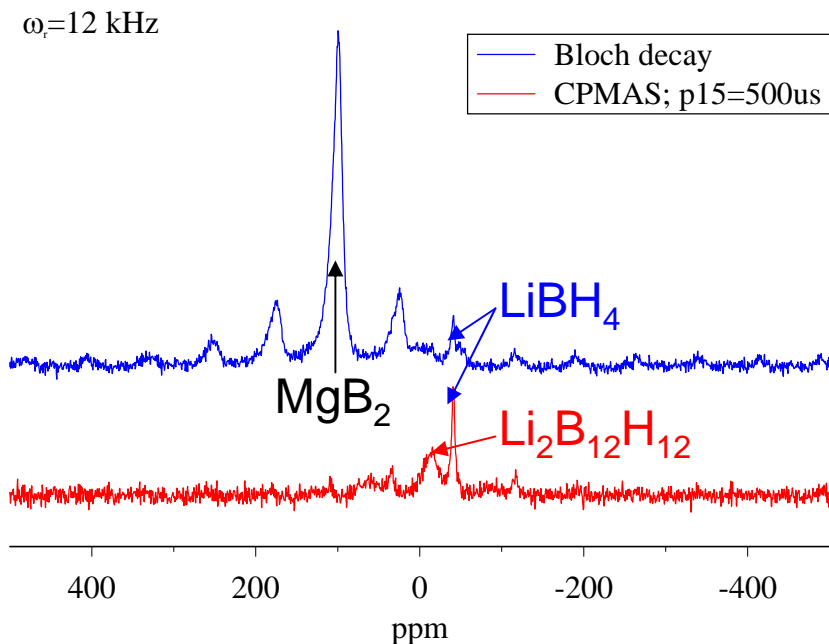
(J. J. Vajo, et al., J. Phys. Chem. B **109** (2005) 3719)

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

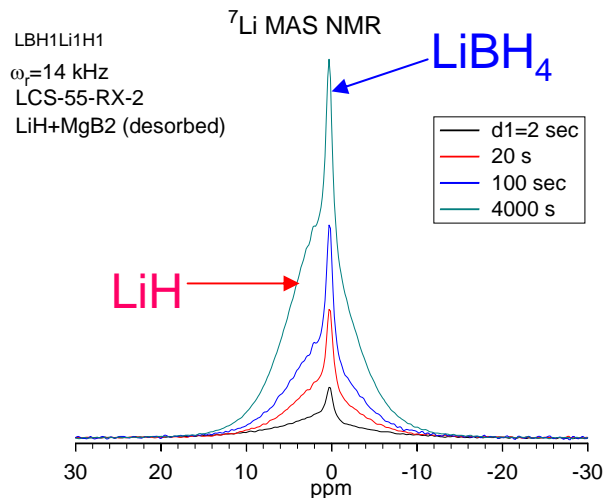
Samples	Code	Treatment	Comments
$\text{LiH} + \text{MgB}_2$	LCS-55	As ball milled	From J. Vajo [HRL]
$\text{LiBH}_x + \text{MgH}_2$	LCS-55: RX-1	Absorbed $\text{H}_2$	Saturated hydrides
$\text{MgB}_2 + \text{LiH} + \text{LiBH}_x$	LCS-55: RX-2 + $\text{SiO}_2$ Powder	Desorbed $\text{H}_2$ : diluted for better MAS-NMR	Incomplete desorb reaction noted



# $^{11}\text{B}$ MAS & CPMAS of Desorbed LCS-55 RX-2



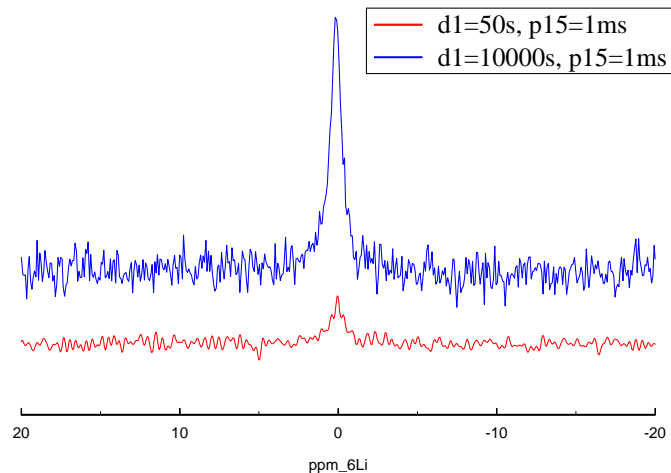
# $^7\text{Li}$ MAS NMR spectra of LCS-55 RX-2.



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

# $^6\text{Li}$ CPMAS NMR spectra of LCS-55 RX-2.

The signal at  $\sim 0$  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.

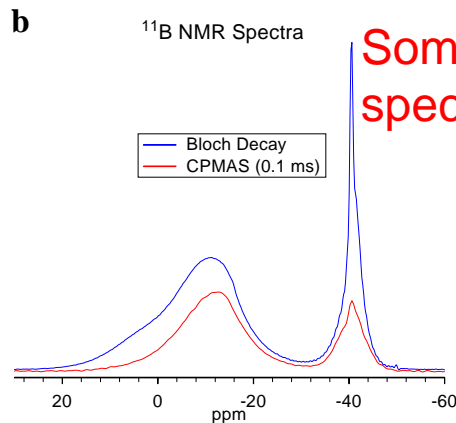
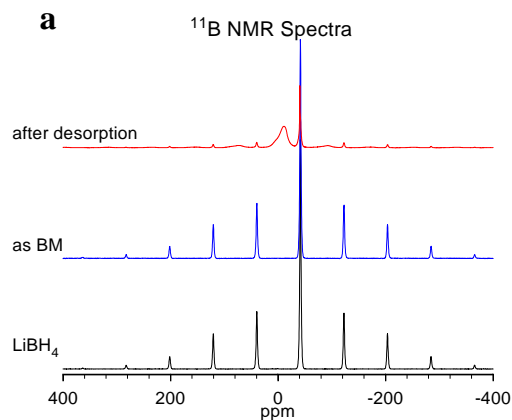




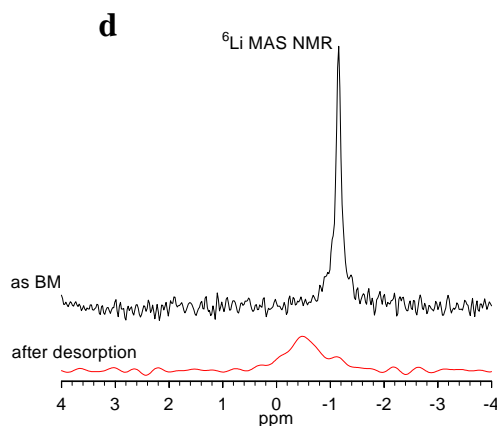
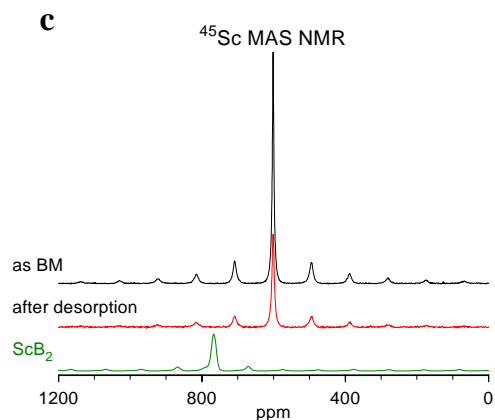
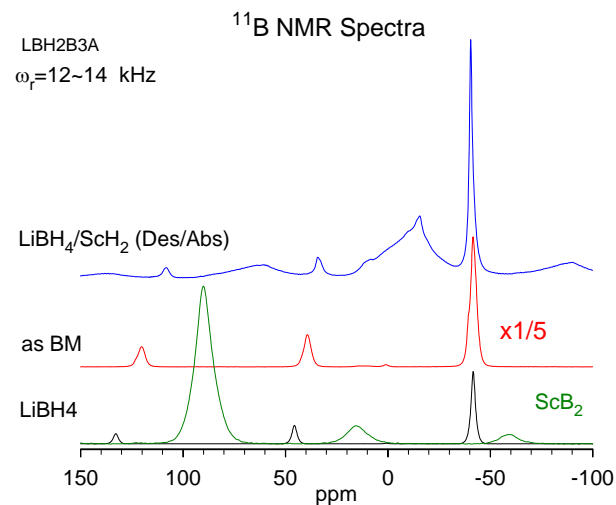
# Investigation of the “ $\text{ScH}_2 + 2\text{LiBH}_4 = 2\text{LiH} + \text{ScB}_2 + 4\text{H}_2$ ”

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

## MAS-NMR Spectra: As Milled & Reacted



Some  $\text{LiBH}_4$  has converted into “ $\text{B}_{12}\text{H}_{12}$ ” species and “elemental boron”



(No predicted  $\text{ScB}_2$  Phase seen!)

Detected only  $\text{ScH}_2$

**Summary:** Desorption did **Not** follow the destabilized process of forming  $\text{ScB}_2$ . Had only partial decomposition of  $\text{LiBH}_4$  into  $\text{LiH} +$  “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.

