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Applications of Nuclear Magnetic Resonance to Metal Hydrogen Materials

Part II: High Resolution (HR) Solid State NMR

-Demonstrate the utility of HR Solid State NMR for study of Hydrogen storage Materials (HSM).
-Principles & methods of multinuclear spectroscopy (MAS, CP, MQ)
-Examples: HR-NMR Studies of MH_x materials – phase compositions, etc.

Son-Jong Hwang and Robert C. Bowman, Jr.

California Institute of Technology

Pasadena, CA

Summer School Lectures

MH2008

23 June 2008

NMR

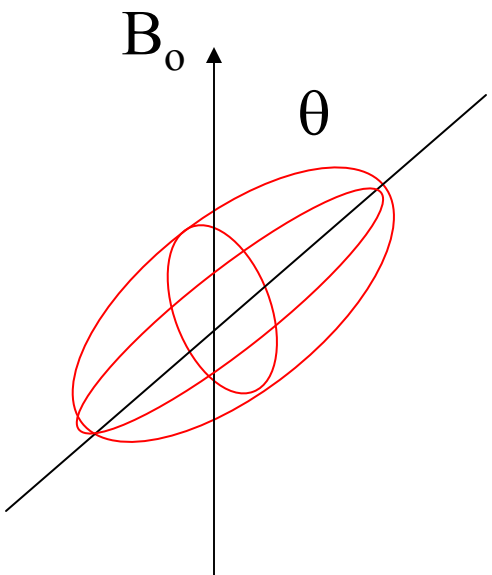
- One of the most powerful tool for studying structures and dynamics for all states.
- Uses RF energy to probe frequencies and amplitudes of a nucleus (NMR active spin, I>0) in the presence of external applied magnetic field (B_o).
- Non-destructive, element specific, quantitative
- Well suited for short range orders – chemical bonding, coordination geometries.
- Wide applicability : organic, inorganic, biological materials, polymers, catalysts, etc.

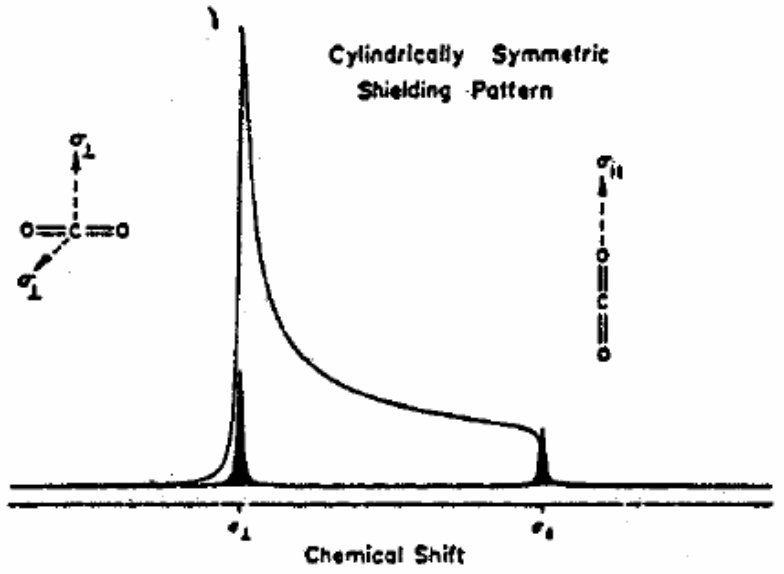
Hamiltonians

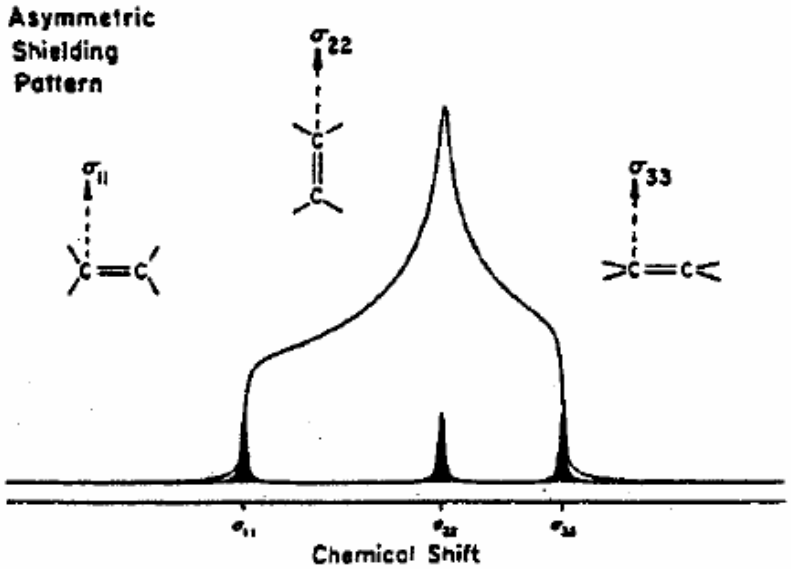
$$\mathbf{H} = \hbar\omega$$
$$= \mathbf{H_z} + \mathbf{H_{cs}} + \mathbf{H_D} + \mathbf{H_Q}$$
$$\omega \sim \omega_{iso} + \omega_{aniso}$$

- H_{CS} : Chemical shielding, local field electrons around nucleus.

$$H_{cs} = \gamma \mathbf{I} \cdot \sigma \cdot B_o$$
$$= \gamma B_o I_z [\delta_{iso} + 1/2 \delta_{CSA}(3\cos^2\theta - 1)]$$







^{13}C Static NMR powder patterns

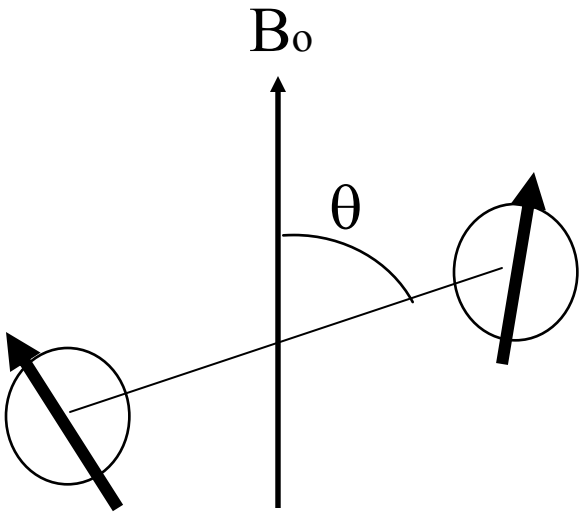
Hamiltonians

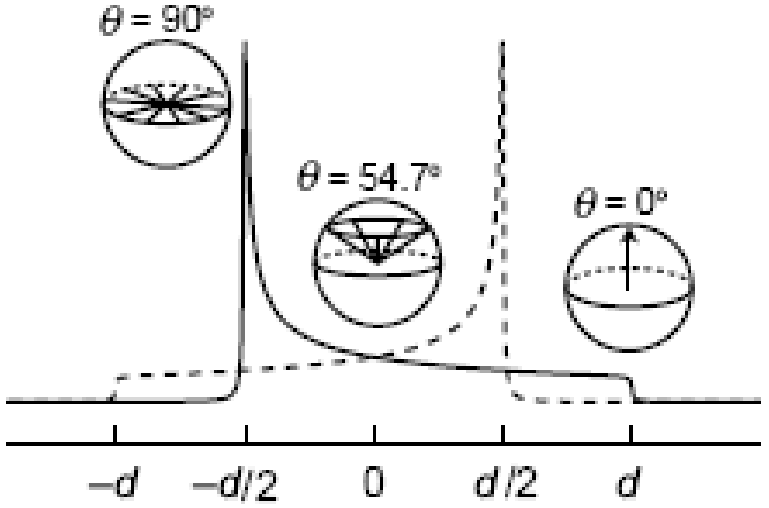
$$\mathbf{H} = \hbar\omega$$
$$= H_z + H_{cs} + \mathbf{H_D} + H_Q$$
$$\omega \sim \omega_{iso} + \omega_{aniso}$$

- H_D : dipolar coupling, through space interaction

$H_D = -2\mathbf{I}\cdot\mathbf{D}\cdot\mathbf{S}$ **(heteronuclear)**

$$= -\left(\frac{u_o}{4\pi}\right)\frac{\hbar\gamma_I\gamma_S}{r_{IS}^3}(3\cos^2\theta - 1)I_zS_z$$





High Resolution NMR in Solids

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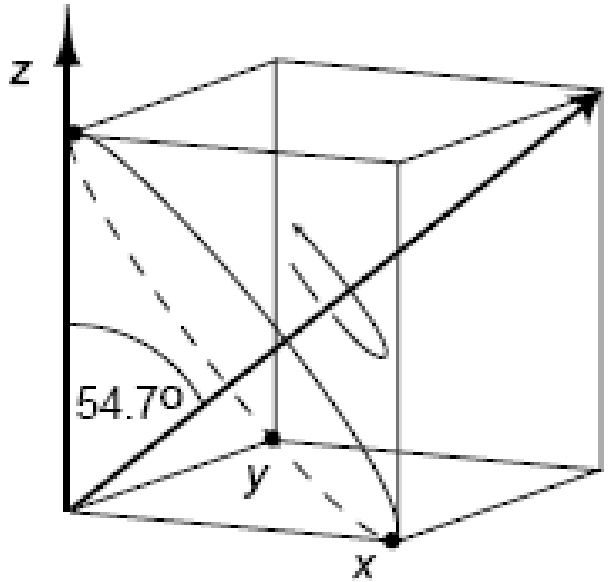
Removing Anisotropic part of Interactions

$\omega_{aniso} \sim (3\cos^2\theta - 1) \Rightarrow 0$



Magic Angle: $P_2(\cos^2\theta_m)=0$

$\langle 3\cos^2\theta - 1 \rangle = 1/2\ (3\cos^2\theta_m - 1)(3\cos^2\beta - 1)$

$= 0$ when $\theta_m = 54.7$

demonstrated by Raymond Andrew (1960)

- Anisotropic components become time dependent (crystallites move around).
- Incomplete averaging ($\omega_{aniso} > \omega_r$) yields spinning sidebands at integer multiples of a spinning speed (ω_r).
- Pulse manipulation works for certain cases at static, and can be combined with MAS.
- Signal strength can be improved by cross polarization (CP) MAS method. Correlation spectroscopy at higher dimensions (2D, 3D)
- Removed anisotropic information under MAS can be recovered (i.e. dipolar recoupling for distance measurement).

High Resolution NMR in Solids

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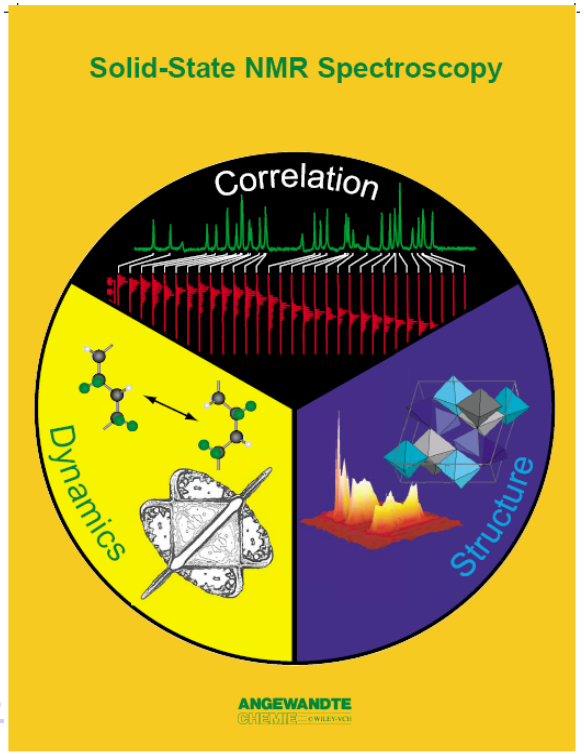
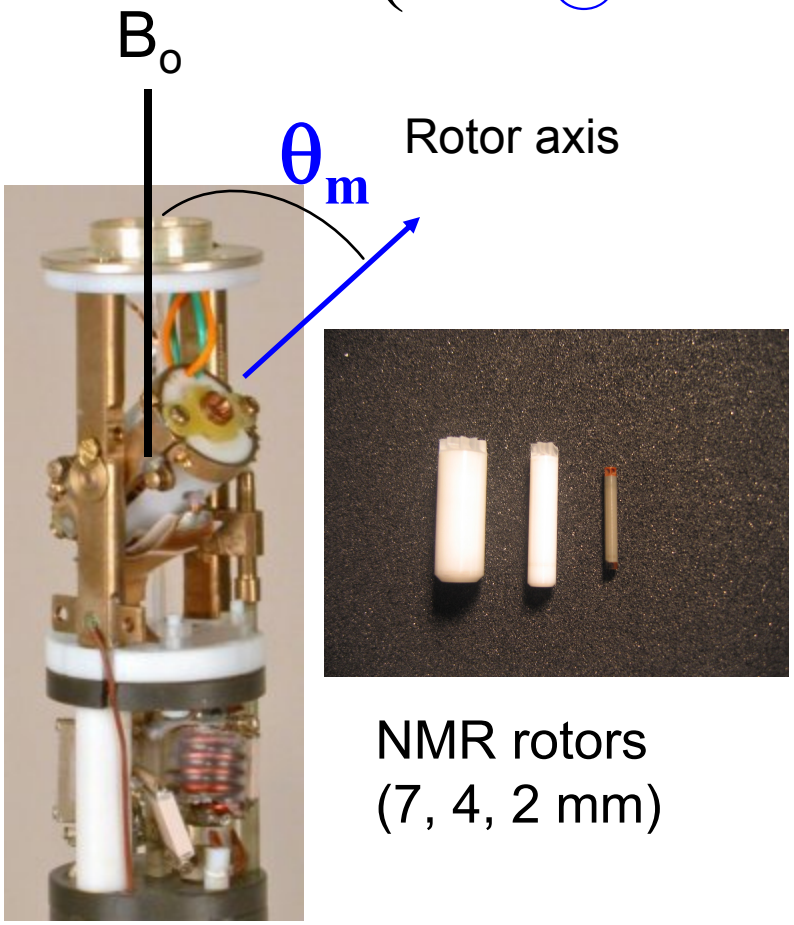
Recommended readings:

1. Review by Laws et al, Angew. Chem. Int. Ed. 2002, 41, 3096.
2. K. J. D. MacKenzie and M. E. Smith, *Multinuclear Solid-State NMR of Inorganic Materials* (Pergamon, Amsterdam, 2002).
3. See Lecture notes on Web: http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr_schurko.pdf
4) R. C. Bowman, Jr. and S.-J. Hwang, "Nuclear Magnetic Resonance Studies of Hydrogen Storage Materials", Mater. Matters **2**(No.2), 29-31 (2007).



Magic Angle Spinning (MAS)

(^{27}Al @ 130.35 MHz for α-AlH_3)



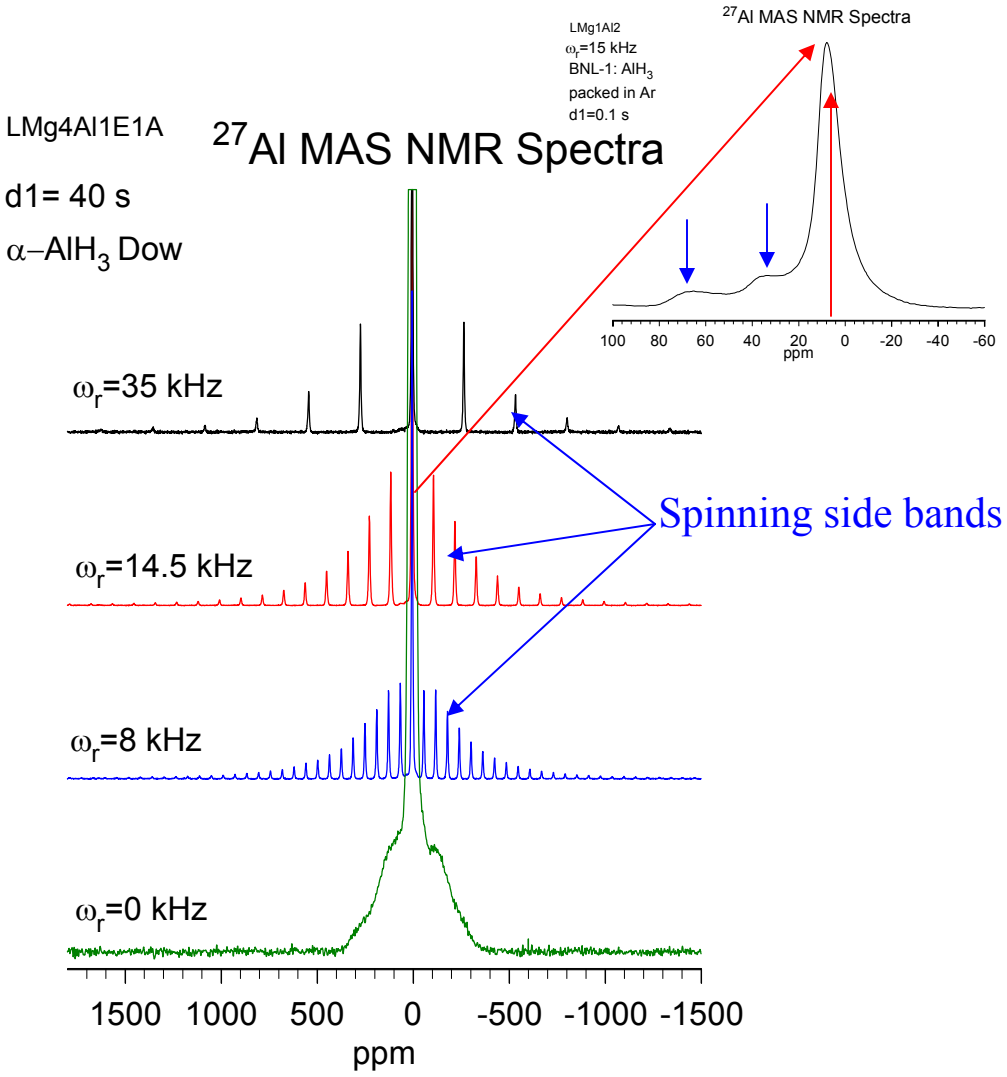
NMR rotors
(7, 4, 2 mm)

Caltech MAS probe in high field superconducting magnet (11.7 T)

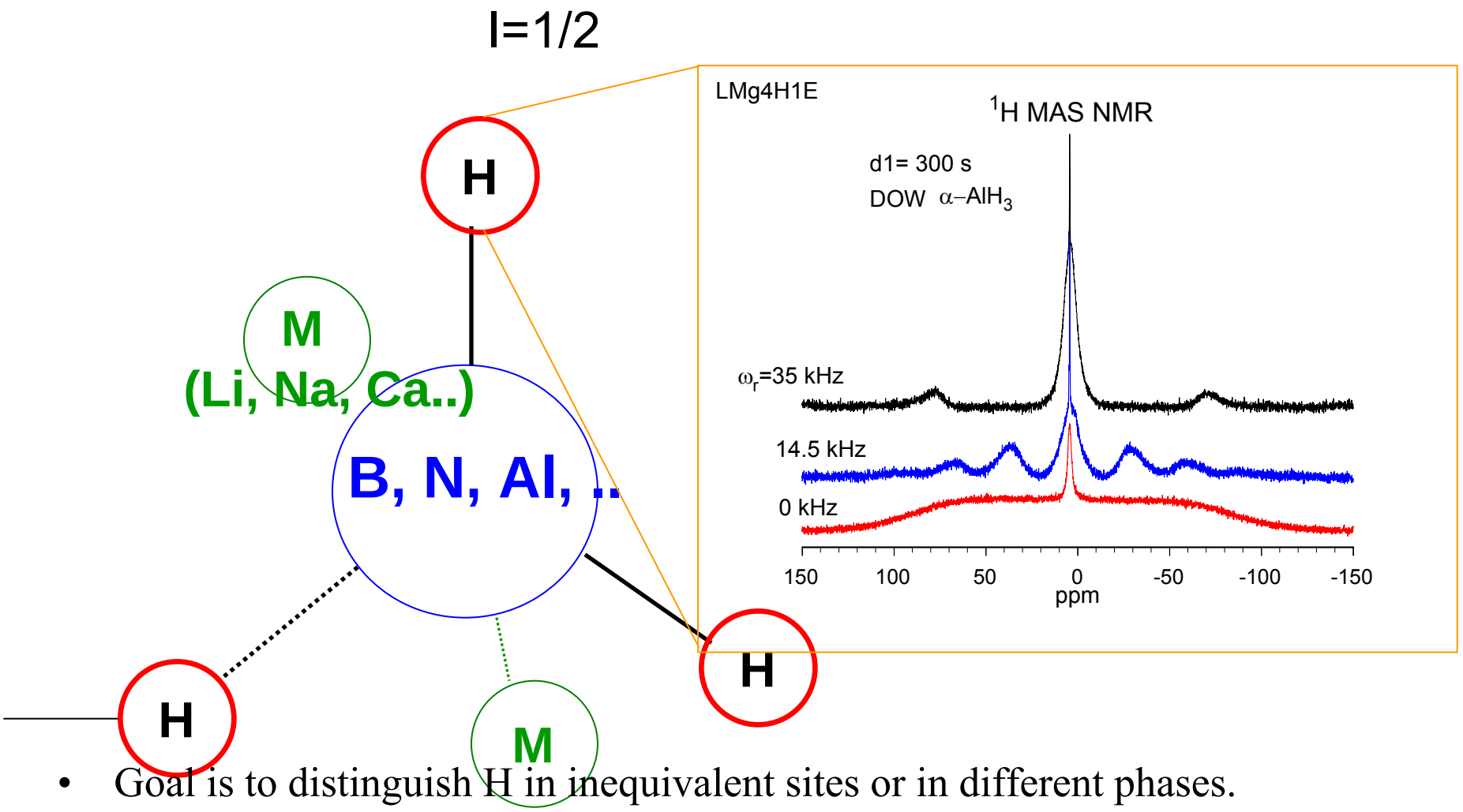
- Samples packed in an Ar filled glove box
- Use of high pressure N_2 gas for spinning

Commercial probe (~1 mm) ~ 70 kHz (exist)

^{27}Al MAS NMR of AlH_3

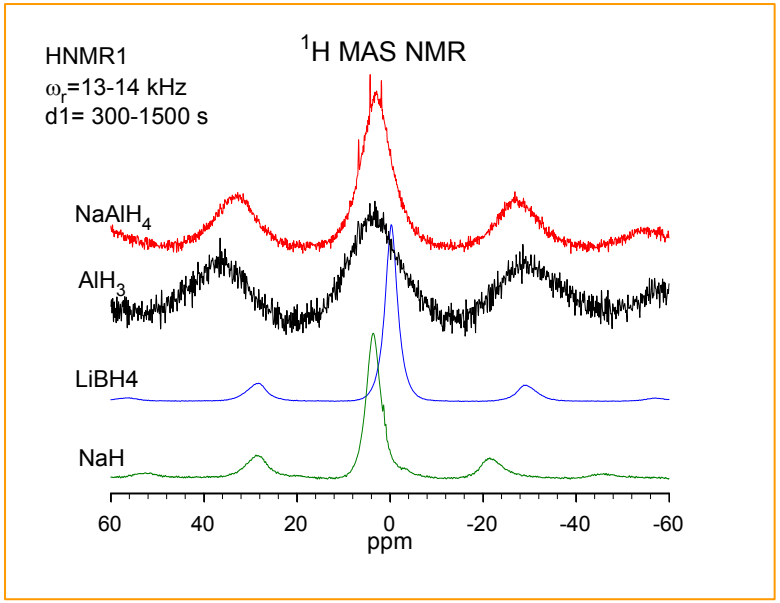


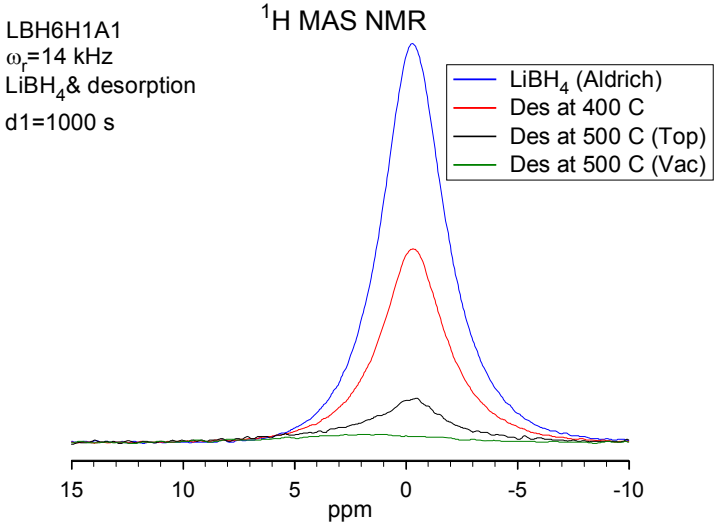
High-Resolution ^{1}H NMR in Metal Hydrides



- Goal is to distinguish H in inequivalent sites or in different phases.
- ^{1}H NMR is mainly broadened by strong homonulcear dipolar coupling (> 50 kHz), not much resolution gain even under MAS unless addition motional narrowing is associated (i.e.H_2 gas, or rotating BH_4 groups)

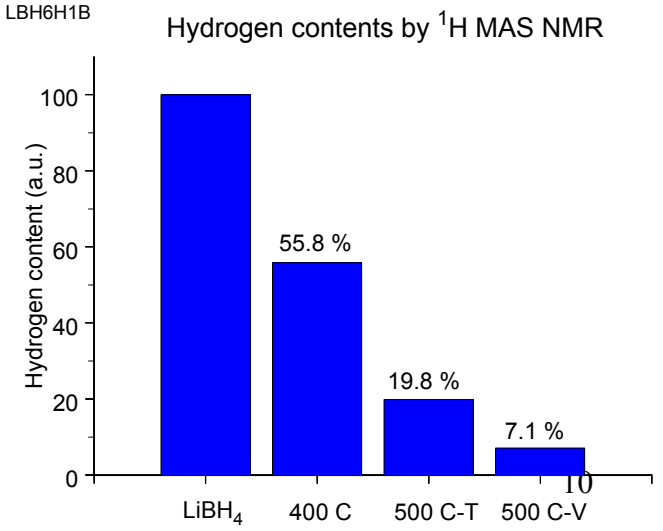
^{1}H NMR in Metal Hydrides





LiBH$_4$ -> decomposes

- ^{1}H relaxation times are very long for most complex metal hydrides: need to use 1000s of seconds. This becomes a problem for CPMAS methods.
- Provides a quantitative measure of H content, which can be correlated with TGA data. Rehydrogenation can be readily examined.
- Rather rigorous decoupling methods need to be tried (i.e. CRAMPS, DUMBO)

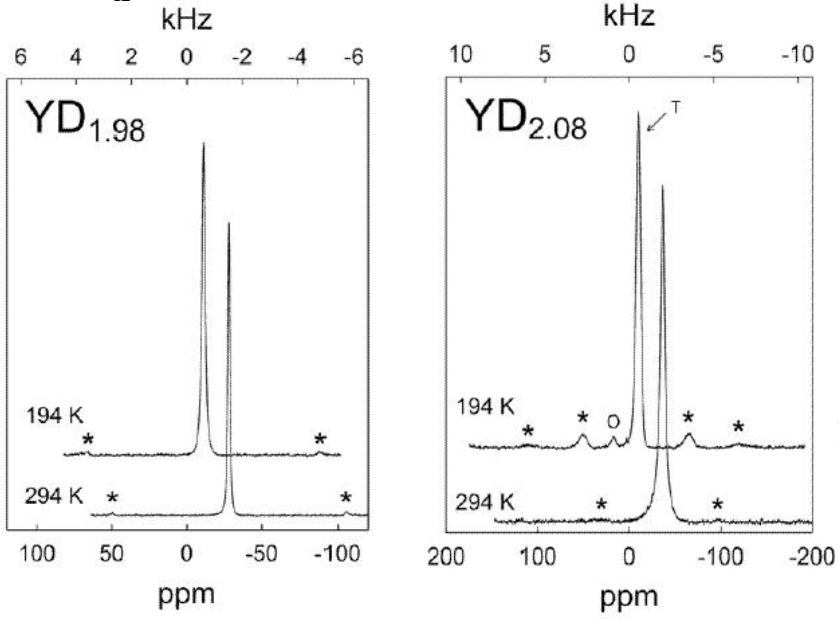


MAS Deuterium NMR

- **^{2}D-^{2}D dipole width ≅ 1 kHz ⇒ can fully narrow with 4-8 kHz MAS.**
- **^{2}D is spin-1 so has quadrupole interaction, but MAS averages to 0.**
- **Magnetic susceptibility of powder sample distorts dc field, B_o. But MAS also averages this to 0.**

Conclusion – MAS deuterium NMR is easy and works well in metal-deuterides. Under-appreciated by the metal hydride NMR community!

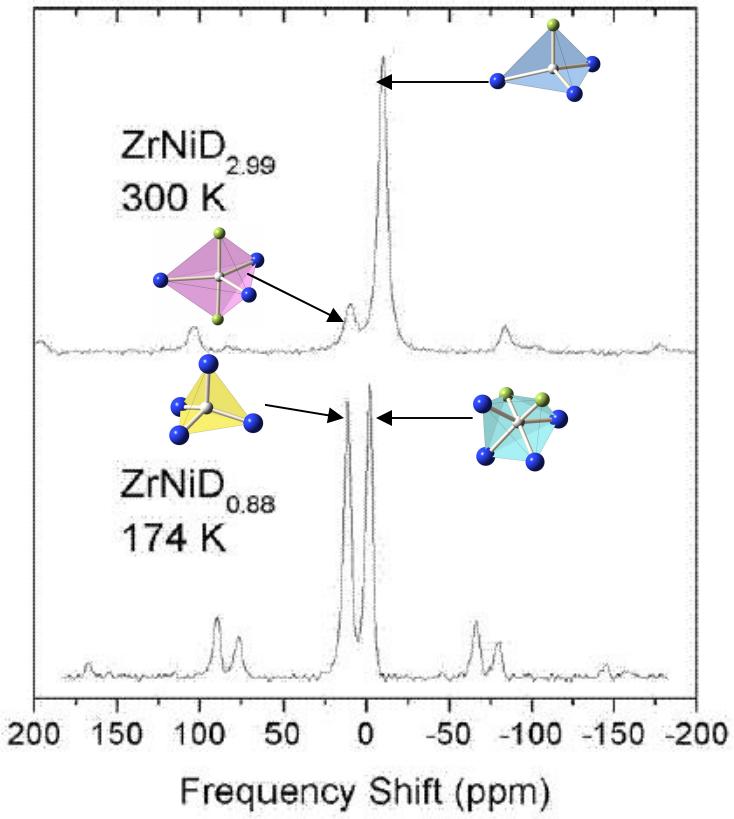
YD_x for x ≅ 2: T-sites and O-sites



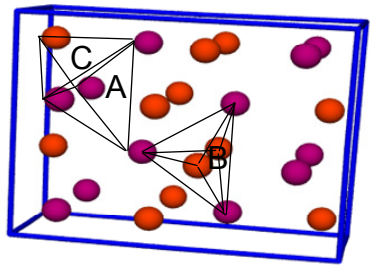
- YD_2 structure is fluorite (cubic), with two T and one O per metal.
- Simple Picture is T-sites fill first up to x = 2; additional H,D beyond x = 2 go to O-sites.
- There were neutron diffraction and NMR reports saying otherwise.
- MAS deuterium NMR says simple picture is correct, quantitatively.

N.L. Adolphi, et al., Phys. Rev. B**53** (1996) 15054–15062.

Second Example: Deuterium Sites in $ZrNiD_x$ Phases



$ZrNiH_x$ orthorhombic structure



Site	type
A	Zr_4
B	Zr_3Ni_2
C	Zr_3Ni

x = 2.99 is γ phase.

- There are Zr_3Ni_2 and Zr_3Ni sites (1:2).

x = 0.88 is β phase.

- Previously accepted structure has all equivalent D atoms ⇒ incorrect!
- MAS-NMR shows two distinct sites (1:1) that have Zr_4Ni_2 and Zr_4 coordination from NPD.

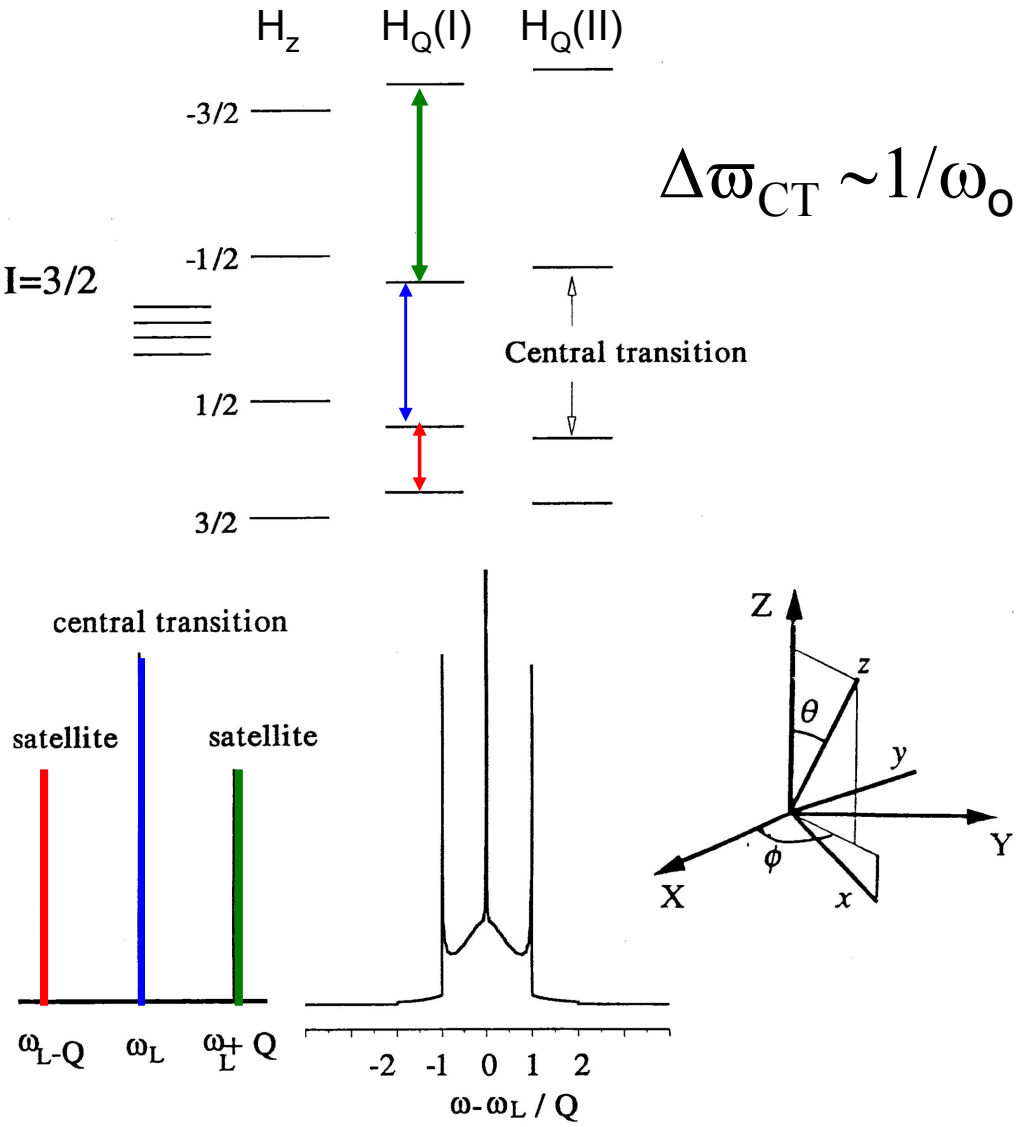
New neutron vibration spectra and neutron powder diffraction at NIST confirms existence of these two inequivalent D-atom sites in β-$ZrNiH_x$ phase.

•R. C. Bowman, Jr., et al., Phys. Rev. B **74** (2006) 184109.

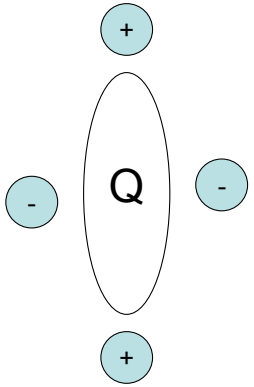
•H. Wu, et al., Phys. Rev. B **75** (2007) 064105.

Quadrupolar Interactions in NMR for I > ½

- I=2/3: ^{7}Li, ^{23}Na, ^{11}B,…
- I=5/2: ^{27}Al, …
- I=7/2: ^{45}Sc, …



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



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

- Non spherical charge distribution!
- Nucleus electric quadrupole moment couples to electric field gradients (EFG)
- Huge anisotropic broadening
- 2nd order term not averaged by MAS

$$\omega_Q^{(2)} \sim P_2(\cos\theta) + P_4(\cos\theta)$$

Comparing Static versus MAS ^{27}Al Spectra for α-AlH_3

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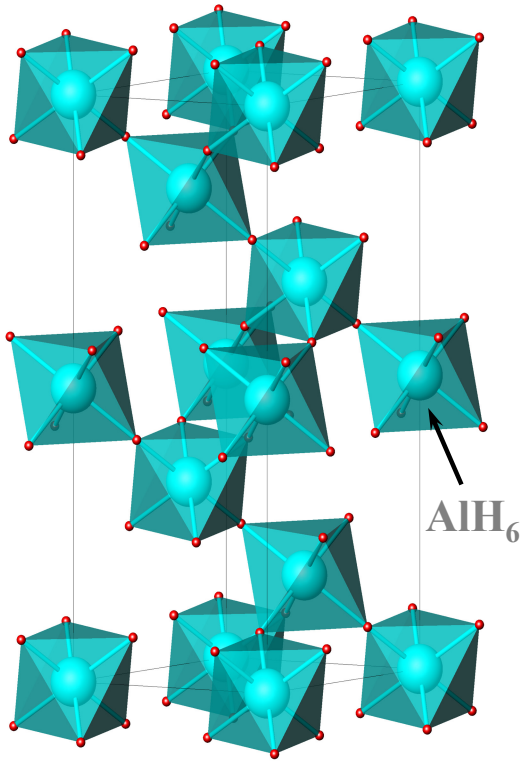
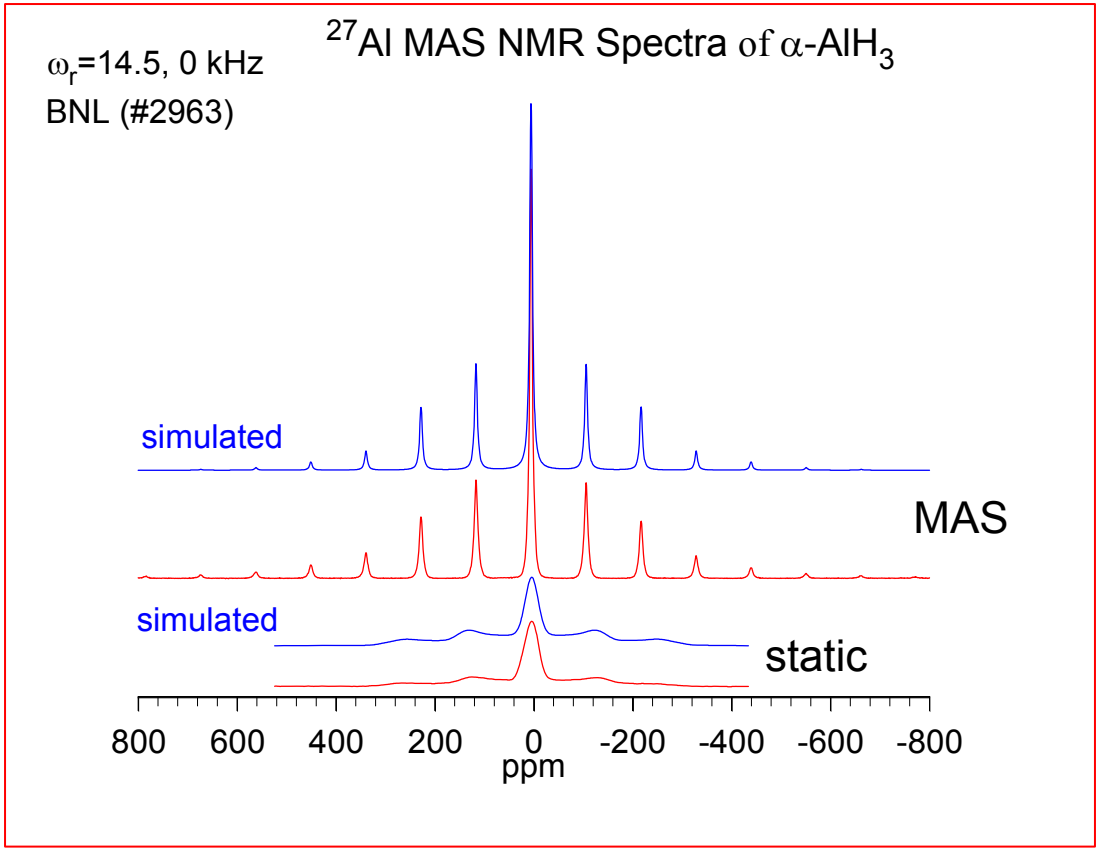
α-AlH_3



Al–Al=3.237 Å
Al-H=1.725 Å
Al-H-Al ∠ 141 °



δ_{iso} (ppm)	C_Q (MHz)	η
5.8	0.25	0.1

S. Hwang, et al. *Mater. Res. Soc. Symp. Proc*. **2006**, **Vol 927E**, pp 0927-EE03-03.

MAS-NMR of γ-Phase AlH_3

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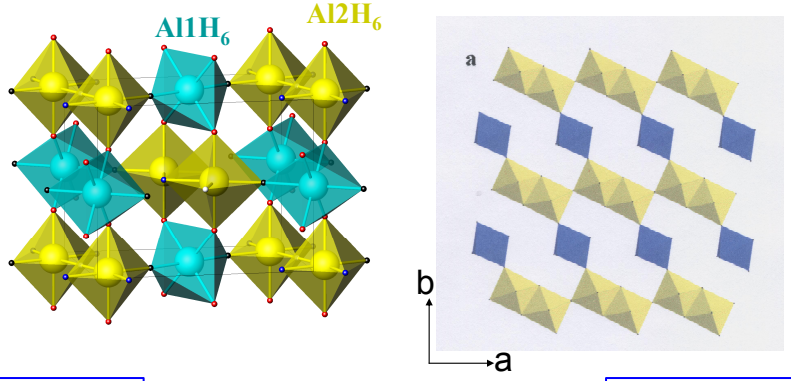
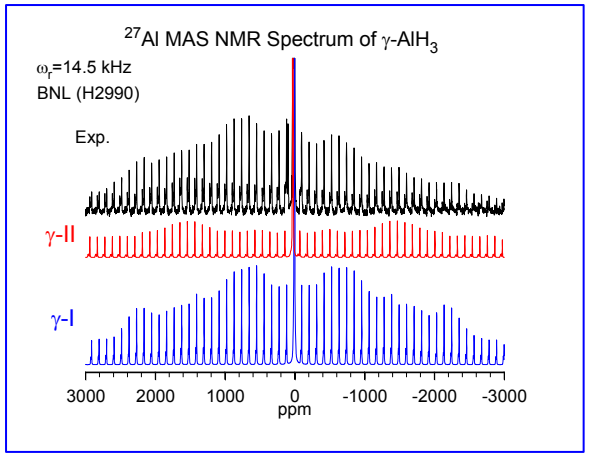
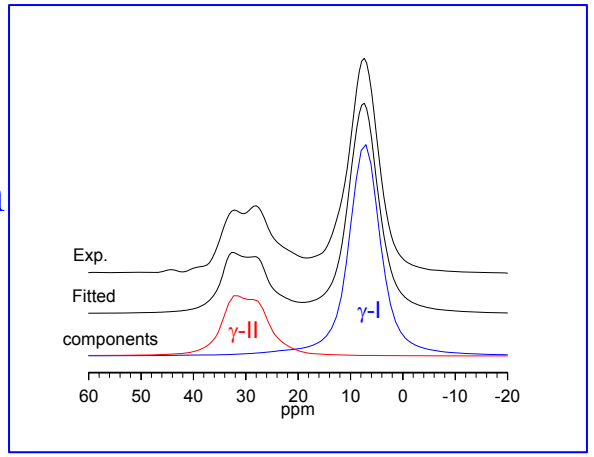




The 2 distinct AlH_6 sites are clearly seen in NMR spectra



Sample	δ_{iso} (ppm)	C_Q (MHz)	η	Ratio
γ-AlH_3	γ-I: 10.9	2.9	0.55	0.48 (Al1H6)
	γ-II:36.0	4.2	0.3	1.0 (Al2H6)

S.-J. Hwang, et al., J. Alloys Compounds **446–447** (2007) 290–295.

^{27}Al MAS-NMR Study of γ-AlH_3 Stability

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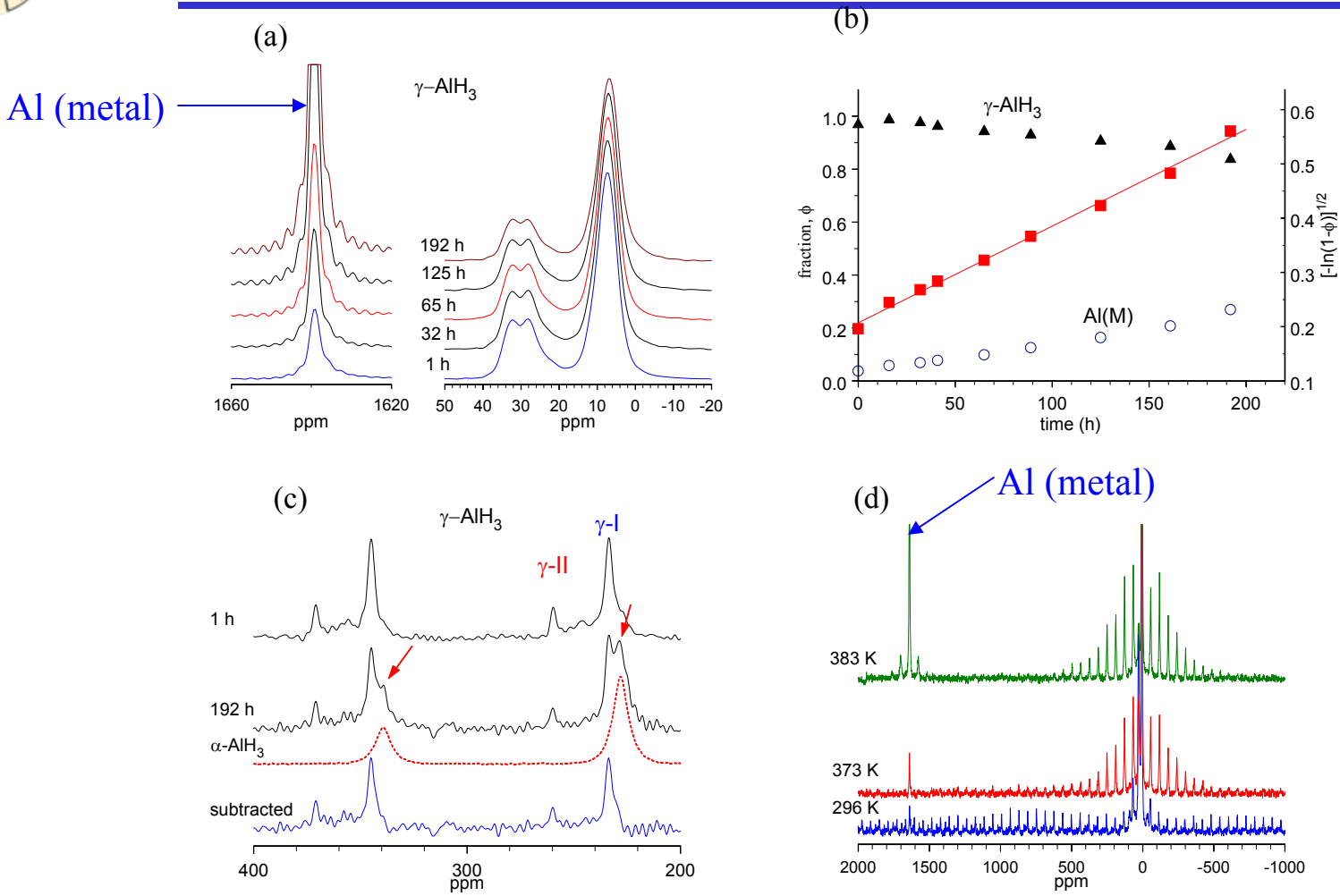

Room Temperature γ-AlH_3 material (BNL H-3013) is unstable

- Conversion Rate = 4.95×10^{-7} s^{-1} which is about a tenth slower than at 60 ºC.
- Simultaneously γ-AlH_3 converts to α-AlH_3 & decomposes to form Al metal

S.-J. Hwang, et al., J. Alloys Compounds **446–447** (2007) 290–295.

2nd order Quadrupole coupling

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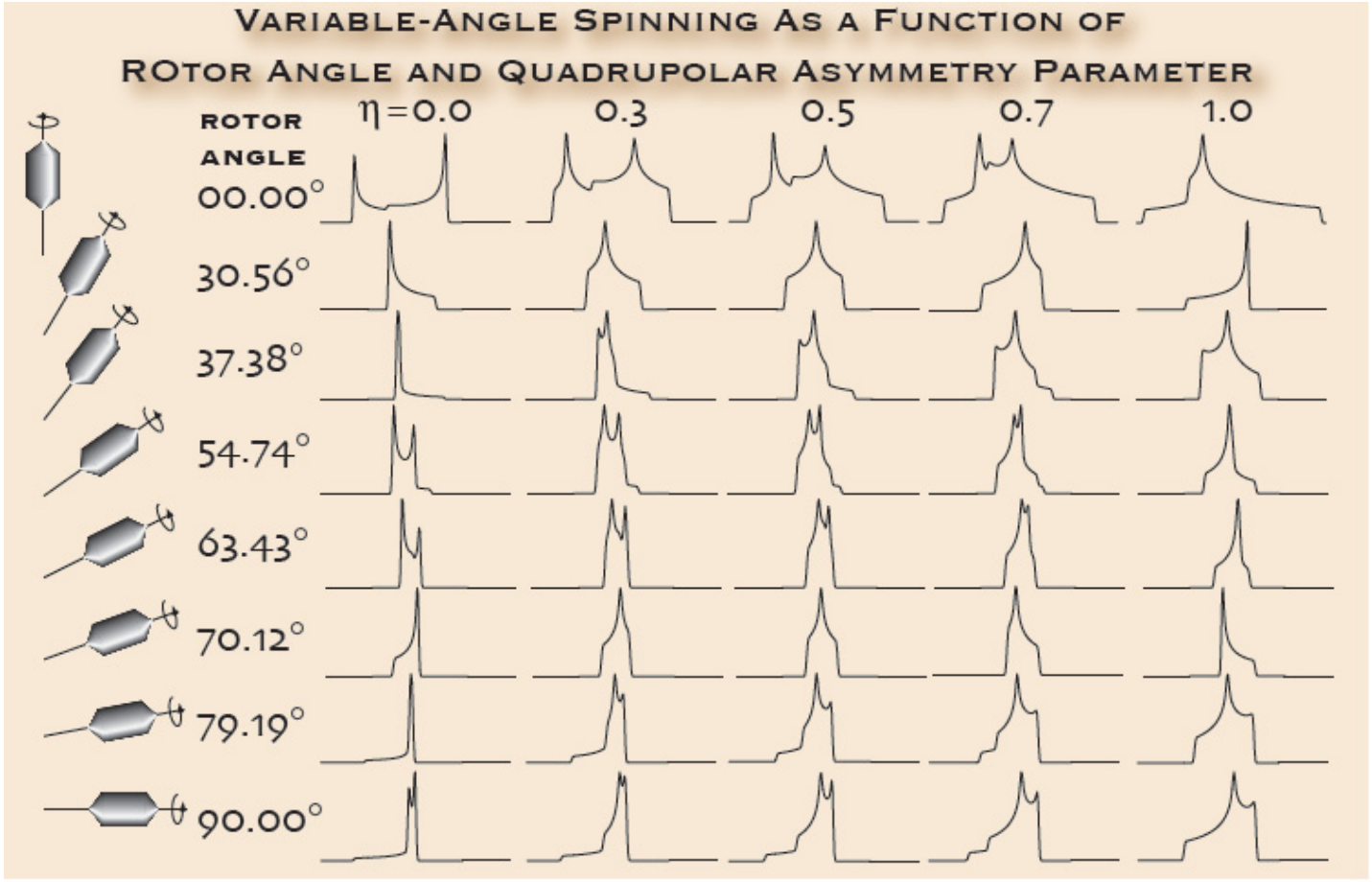
$\omega_Q^{(2)}(CT) \sim \omega_Q^{(2)}{}_{iso} + P_2(\cos\theta) + P_4(\cos\theta)$ $\quad P_4(\cos\theta)=0$ at $\theta=30.56$ or 70.12°



Ganapathy, Schramm, and Oldfield, *J. Chem. Phys.*,1982, 77, 4360

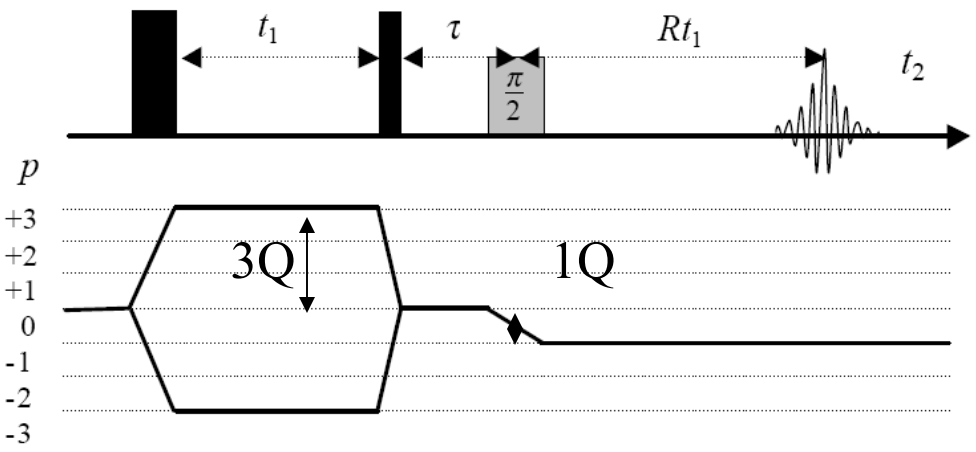
Great deal of methodology development since 1990,

Few solutions
- DOR
- DAS
- MQMAS
- STMAS

check Encyclopedia of NMR

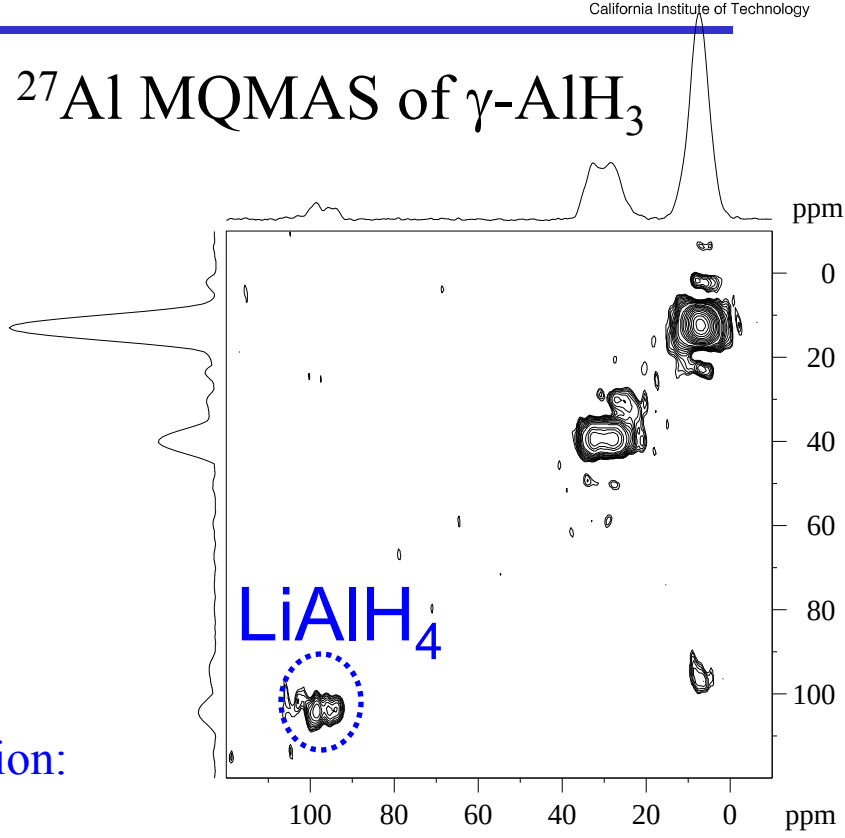
http://www.grandinetti.org/index.html

Multiple Quantum (MQ) MAS NMR



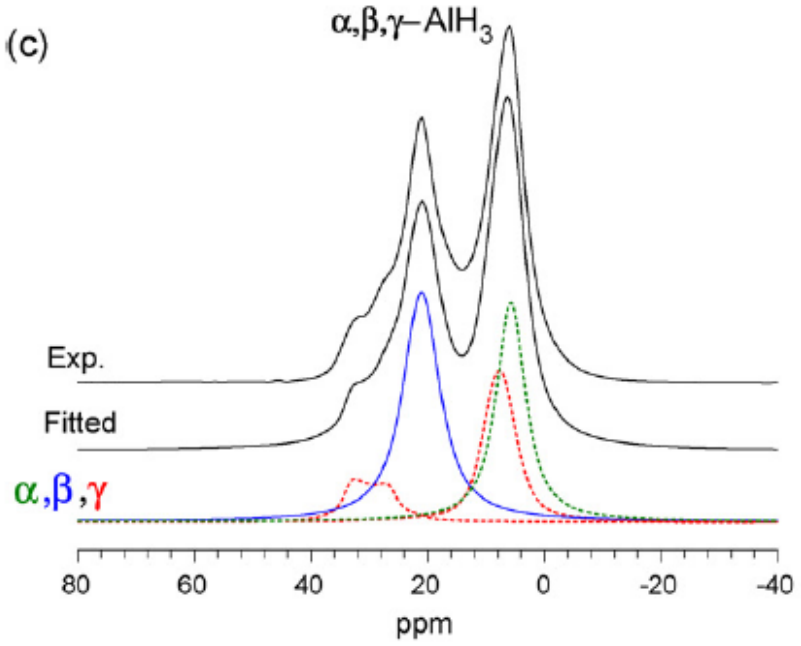
Z-filtering, Amoureux and Fernandez, JMR 1996

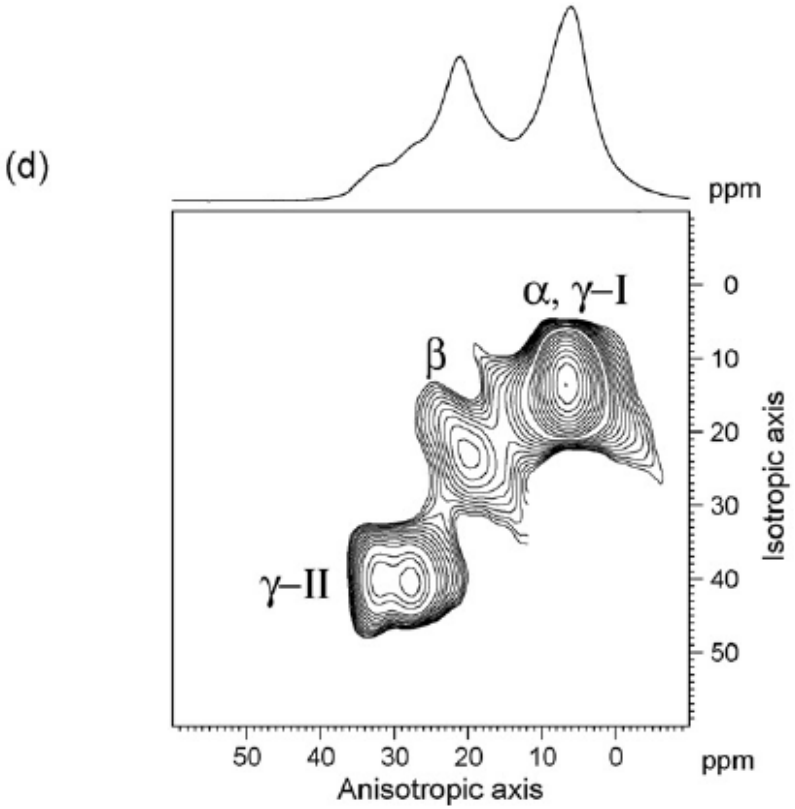
^{27}Al MQMAS of γ-AlH_3



- Correlates MQ and 1Q transitions under MAS condition: anisotropic vs isotropic in 2D spectrum.
- Pioneered by Lucio Frydman et al *(J. Am. Chem. Soc.*, 117, 5367 (1995)
- Well developed, becomes a routine technique. (see review by Amoureux and Pruski, "Advances in MQMQS NMR, in Encyclopedia of NMR, Vol 9, 226)
- Robust, use of regular MAS probe.
- Need shearing transformation (R is a function of multiple quantum order P, R=7/9 for 3Q)
- Limited applications in MH area: some ^{11}B and ^{27}Al MQMAS NMR reported (i.e. Wiench et al, J. Solid State Chem. 177 (2004), 648)

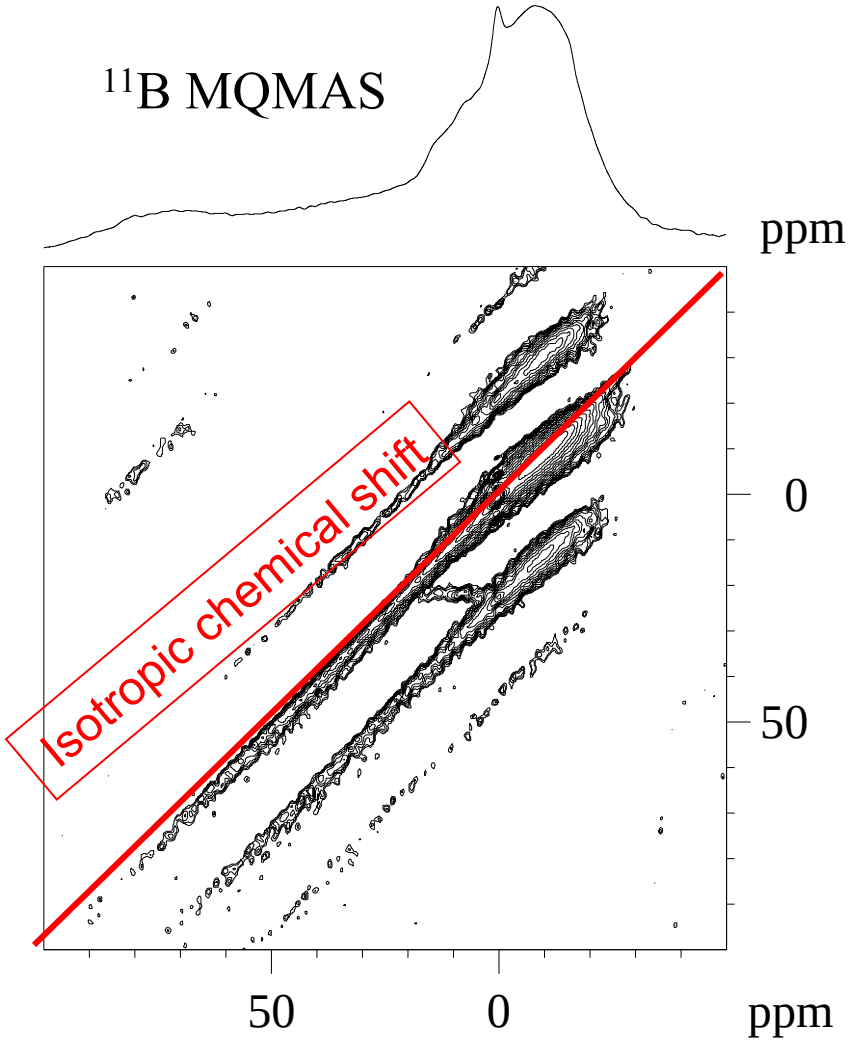
^{27}Al MQMAS Assessment of Mixed AlH_3 Phases





S.-J. Hwang, et al., J. Alloys Compounds **446–447** (2007) 290–295.

MQ MAS NMR of amorphous phases



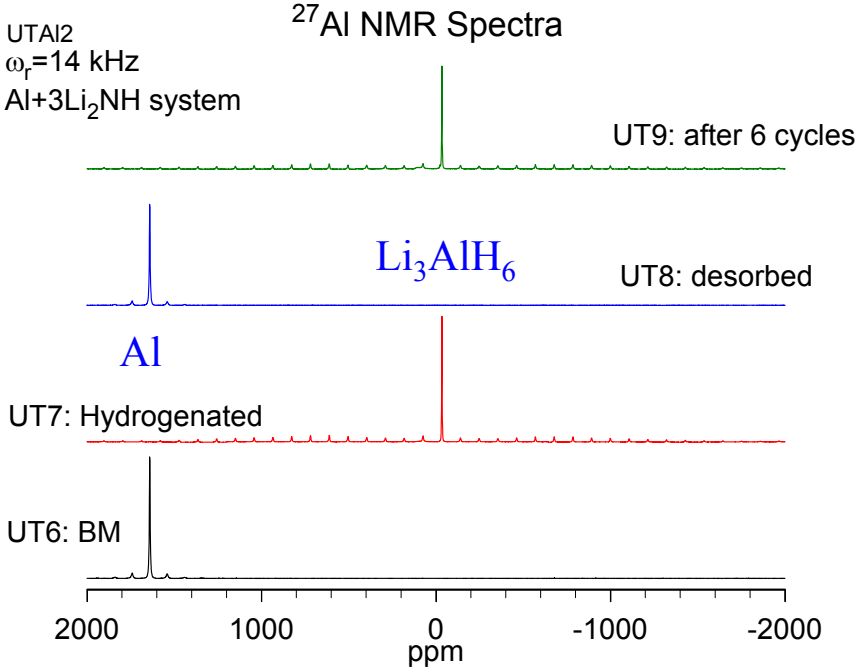
sample: $M(BH_4)_n$ after desoprtion

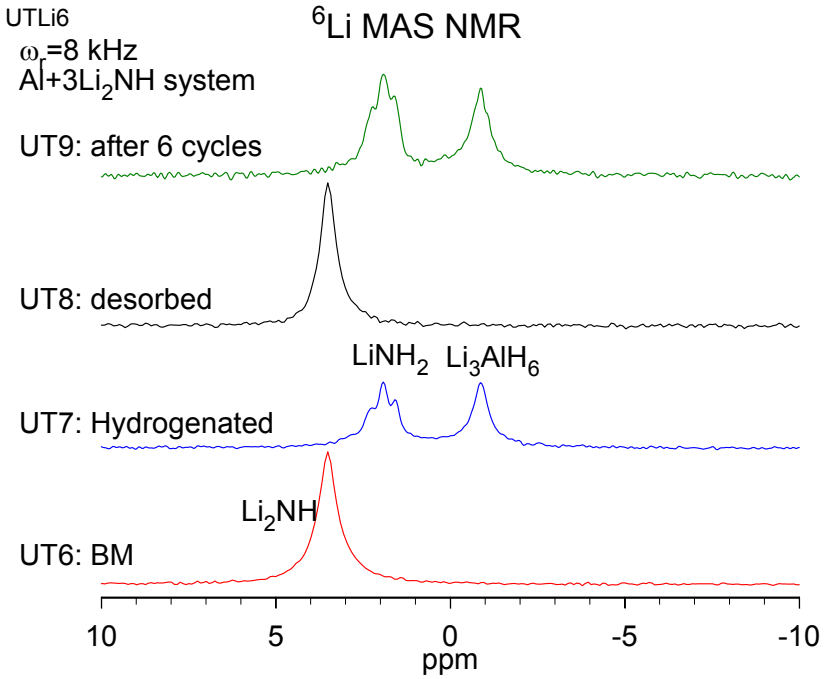
- Signal distributed along the isotropic chemical axis: demonstrates the presence of amorphous phase.
- Not very effective in resolving peaks.
- Needs be combined with chemical shift calculation to get meaningful insights : NMR frequencey is sensitive to geometry changes. (demostrated with Si-O-Si bonds: Clark, Grandinetti, Florian, Stebbins, *Phys. Rev. B*, **70**, 064202 (2004).

Multinuclear MAS NMR Assessing Reactions

$$Al + 3Li_2NH + 9/2H_2 = Li_3AlH_6 + 3LiNH_2$$

Samples from U. Utah: UT6 (ball milled Al & Li_2NH), UT7 (reacted with H_2). UT8 (H_2 desorbed), and UT9 (6 absorb/desorb cycles)





Both ^{27}Al and ^{6}Li MAS NMR spectra confirm conversion of phases according to reaction equation.

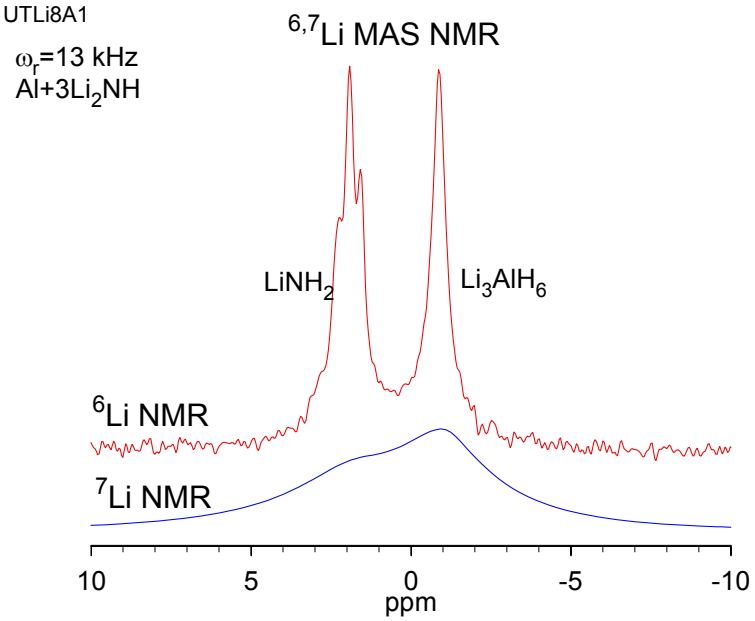
^{6}Li vs ^{7}Li MAS NMR

- **^{6}Li (I=1, 7.42%), ^{7}Li (I=3/2, 92.58%), $\gamma(^7Li)/\gamma(^6Li)=2.6$**
- **Remarkable Resolution improvement! - lower dipole and quadrupole coupling**
- **Penalties: ^{6}Li has less sensitivity & longer T_1**

Table II. Linewidths, resolution improvement factors (R), and ^{6}Li NMR chemical shifts (±0.05 ppm vs LiCl) in various inorganic compounds.

Compound	$\Delta\nu_{1/2}$[Hz] (^{7}Li)	$\Delta\nu_{1/2}$[Hz] (^{6}Li)	R	δ_{iso}[ppm] (^{6}Li)
LiF	no narrowing	640		0.5
LiCl	500	32	5.9	0.00
LiBr	480	31	5.9	-0.68
LiI	450	36	4.7	-3.44
$Li_2B_4O_7$	520	19	10.4	0.31
$LiBO_2$	1180	34	13.1	1.40
Li_2MoO_4	620	22	10.7	1.19
Li_2CO_3	960	26	14.0	1.16
Li_2SiO_3	980	44	8.4	1.58
Li_2SiS_3	320	70	1.7	2.35
Li_4SiS_4	860	30	10.9	2.15
Li_2S	750	58	4.9	3.3

Eckert, et al MRS symp Proc. V 135, 259 (1989)
Grey & Dupre, Chem. Rev. 104, 4493 (2004)



Efficient H-decoupling helps

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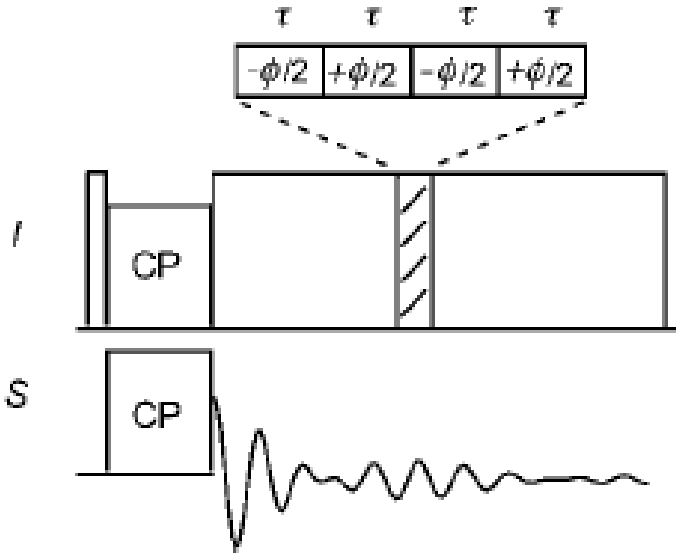
TPPM: two-pulse phase modulation



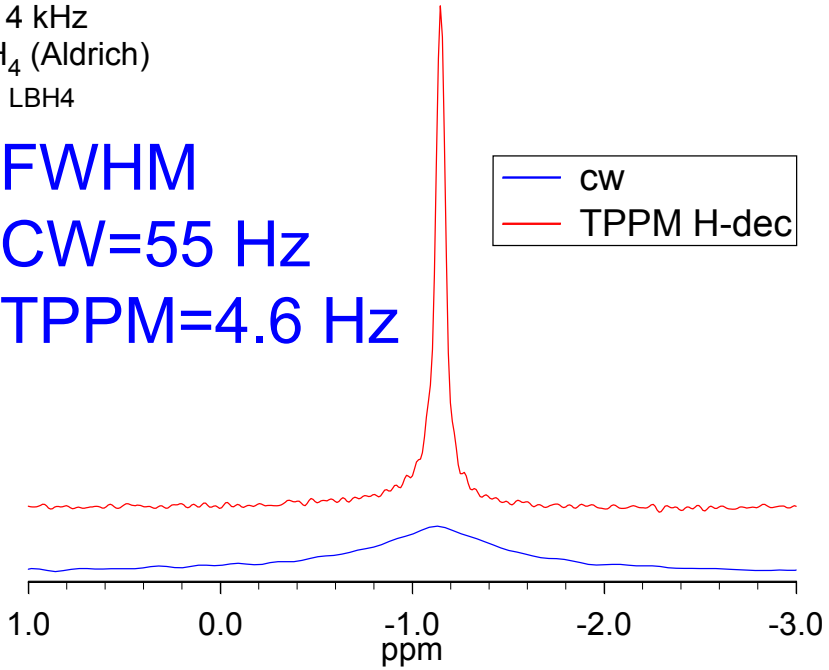
Bennett, A. et al J Chem Phys 103, 6951 (1995)

LBH4Li4A1

^{6}Li CPMAS NMR

ω_r=14 kHz
$LiBH_4$ (Aldrich)
Data: LBH4

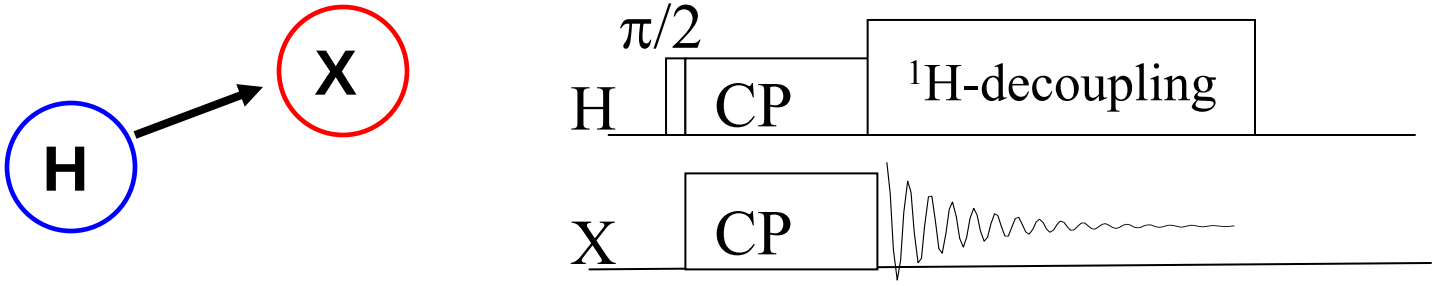
FWHM
CW=55 Hz
TPPM=4.6 Hz



- Need to be optimized before use.
- ϕ=0, 15˚, τ ~ 160 pulse

Cross-Polarization (CP) MAS Spectra

- **To assist in observing dilute spins in presence of protons**
  - (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

Details of Cross Polarization (CP) with Protons

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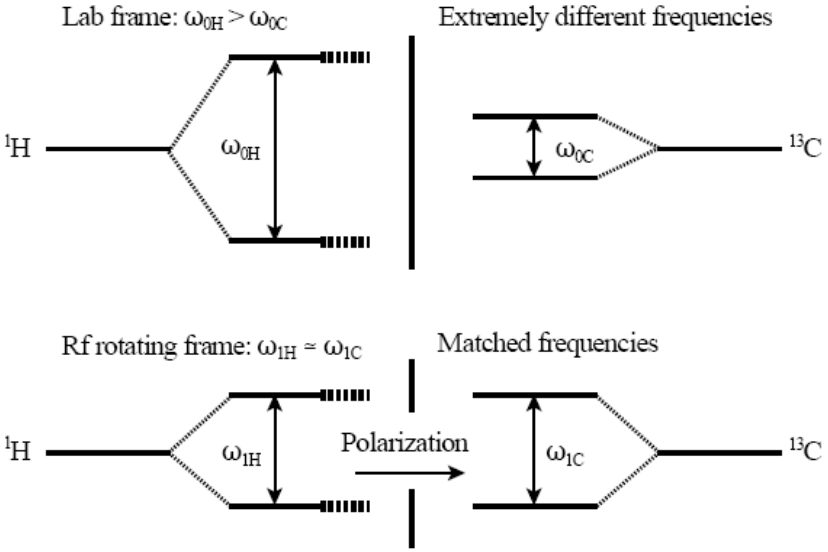
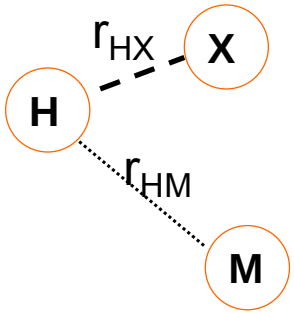
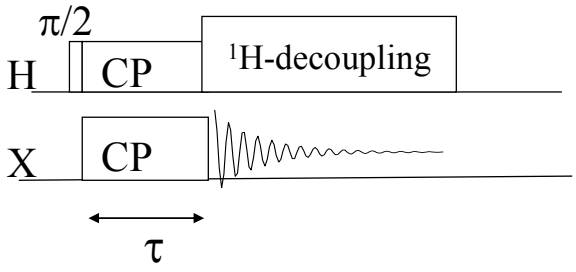
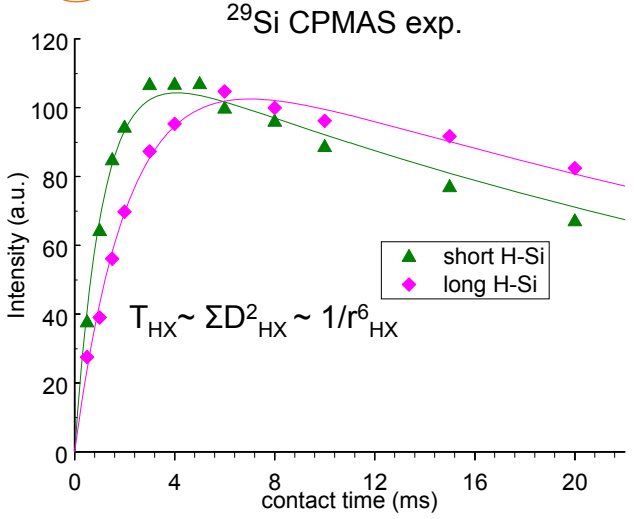
CP requires that nuclei are dipolar coupled to one another and it even works while samples are being spun rapidly at the magic angle but not if the spinning rate is greater than the anisotropic interaction. Hence the acronym CPMAS (Cross Polarization Magic-Angle Spinning)









CP @ Hartmann-Hahn Match

$\gamma_X B_X = \gamma_{H-1} B_{H-1}$ (i.e.: X = ^{29}Si)

^{11}B CPMAS NMR in Borohydrides

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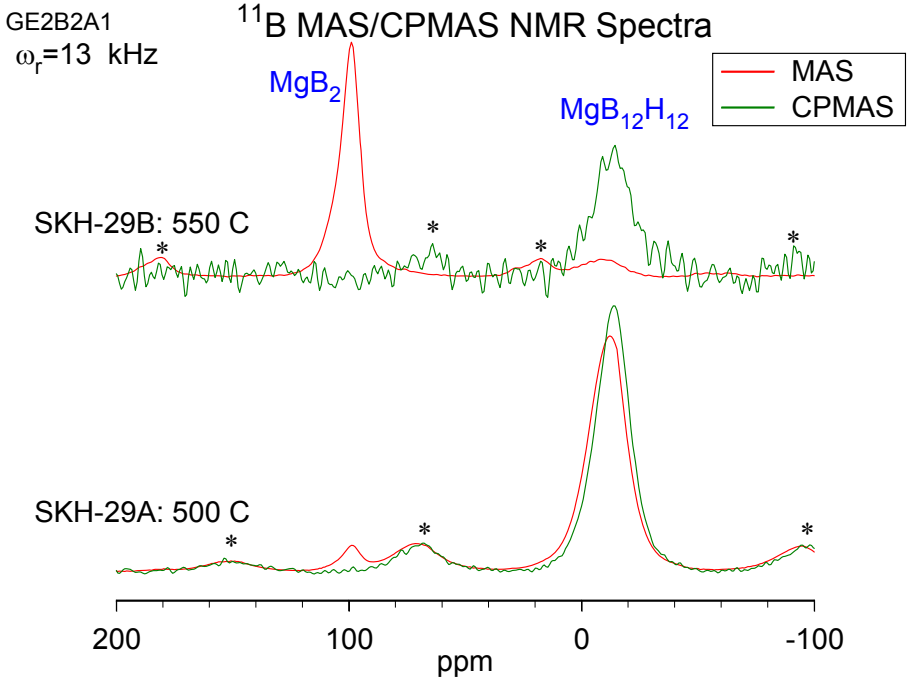
CPMAS Exp of ^{1}H→ X (I>1/2) is not that simple : 2nd order quadrupole copulings cause problems during spin-locking (contact pulse)- distortion of spectral line shap.

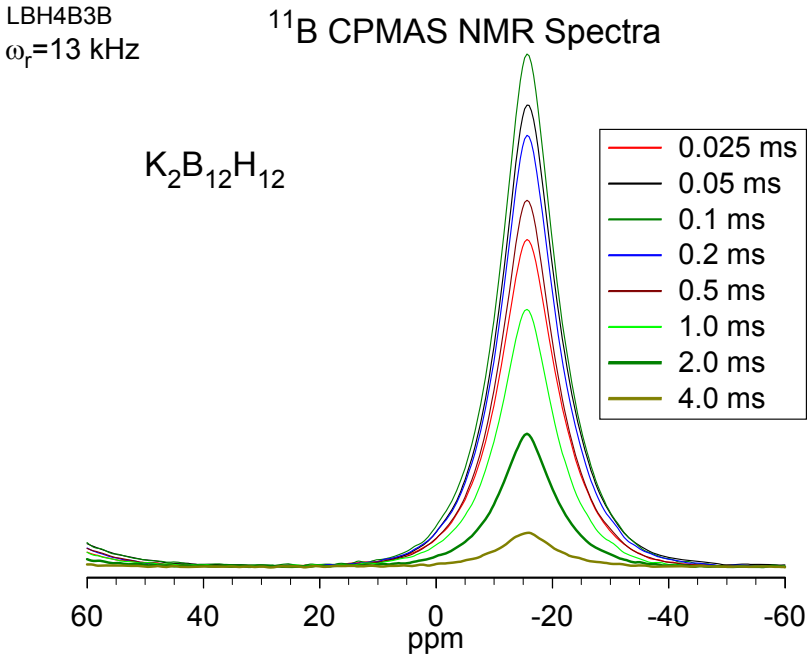
(Amoureux and Pruski, Mol. Phys. 100 (2002), 1595

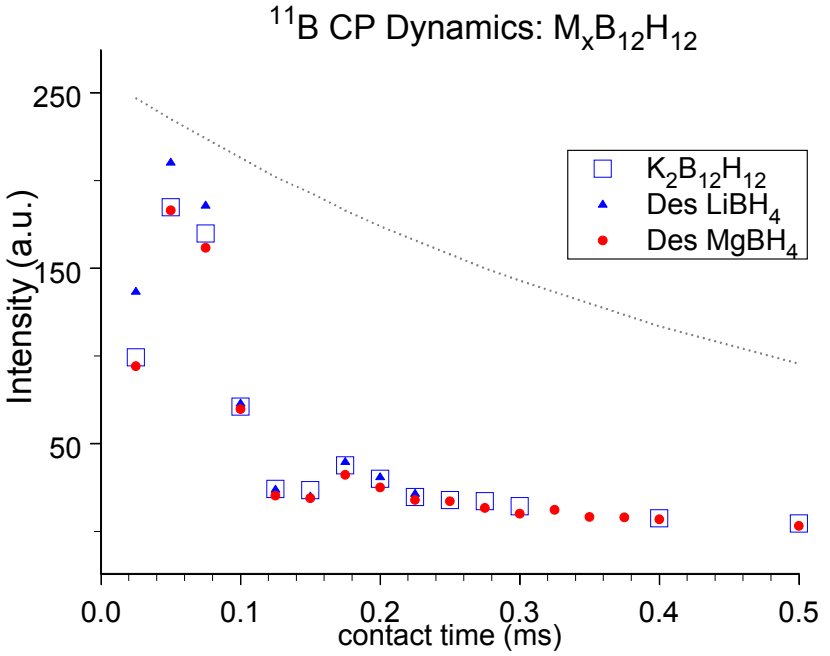
- Rule of thumb: use low power, high spinning

Examples on MH samples
- Demonstrates selective detection of B-H vs B with no H around.



CPMAS NMR : Bond distance measurement





B-H distance: 1.2 Å
~ XRD

Phase Formation and Reversibility in Destabilized $LiBH_4/MgH_2$:

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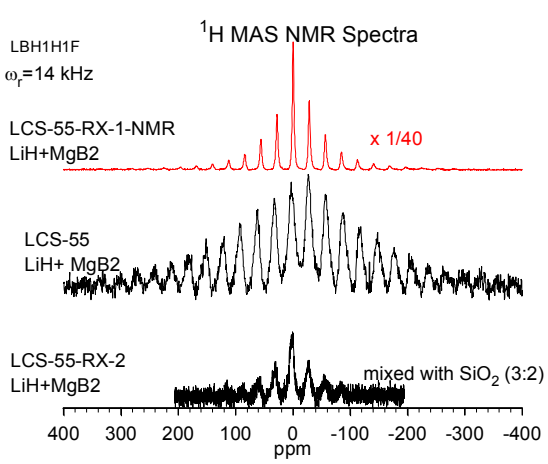
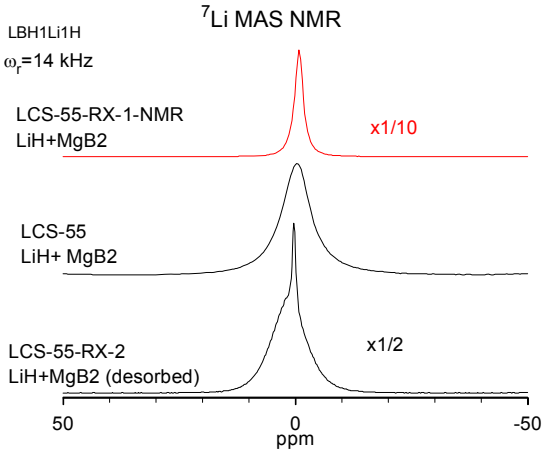
"$MgH_2 + 2LiBH_4 = 2LiH + MgB_2 + 4H_2$"

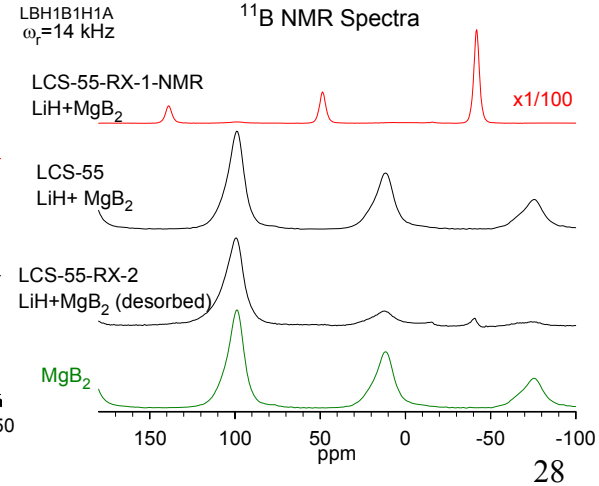
(J. J. Vajo, et al., J. Phys. Chem. B **109** (2005) 3719)

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

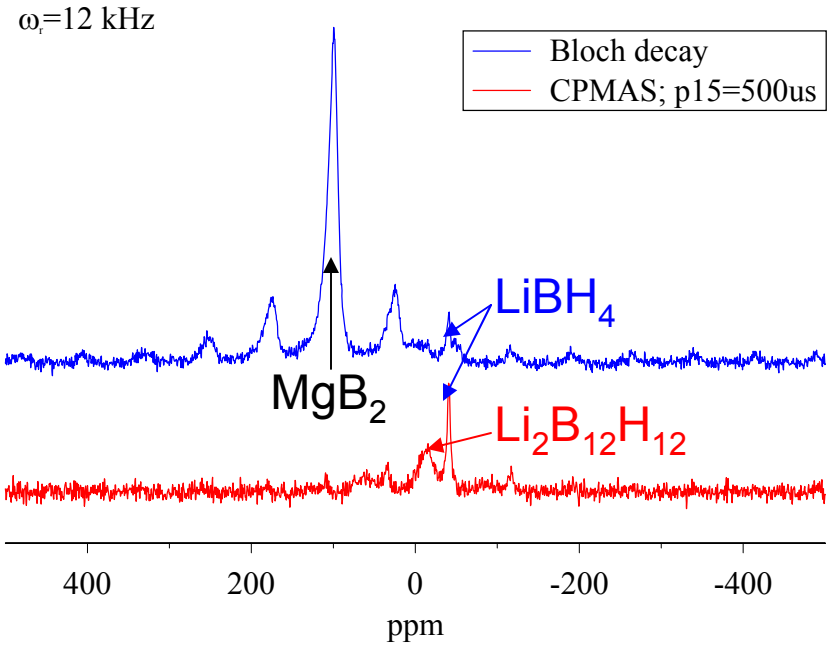
Samples	Code	Treatment	Comments
$LiH+MgB_2$	LCS-55	As ball milled	From J. Vajo [HRL]
$LiBH_x+MgH_2$	LCS-55: RX-1	Absorbed H_2	Saturated hydrides
MgB_2 + LiH + $LiBH_x$	LCS-55: RX-2 + SiO_2 Powder	Desorbed H_2: diluted for better MAS-NMR	Incomplete desorb reaction noted





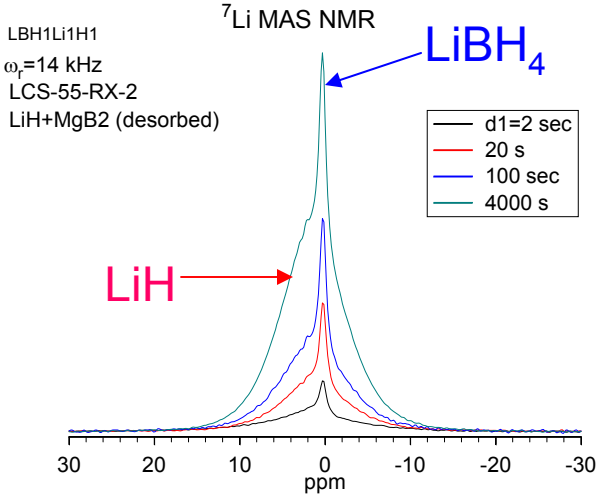


CPMAS Spectra Confirms Phase Identifications



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

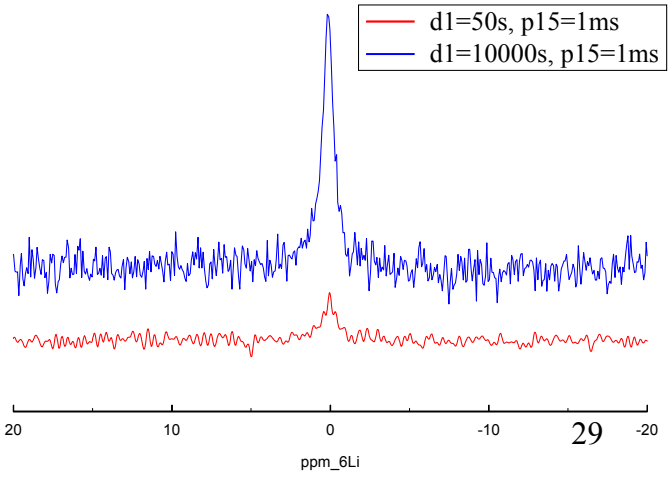
^{7}Li MAS NMR spectra of LCS-55 RX-2.



- 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.



$M_n(BH_4)_{n/2}$ => decomposition

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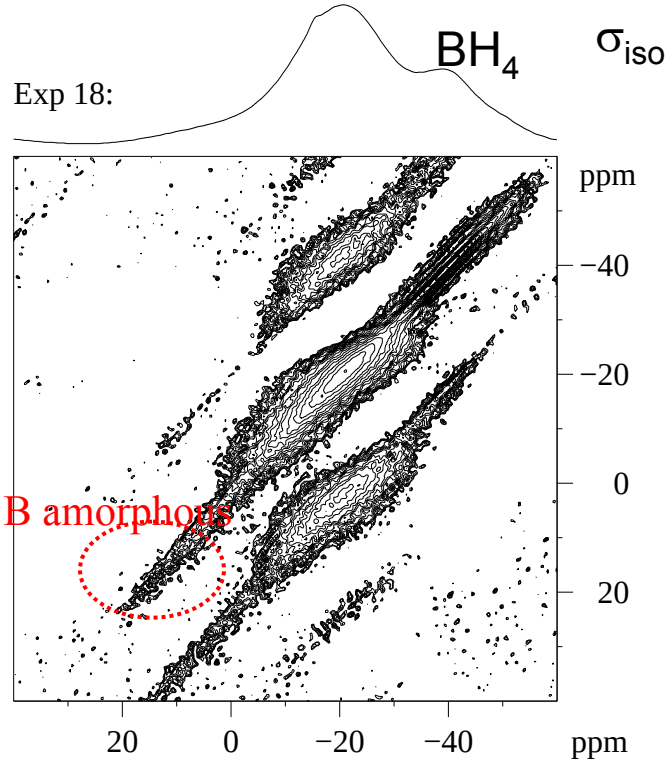
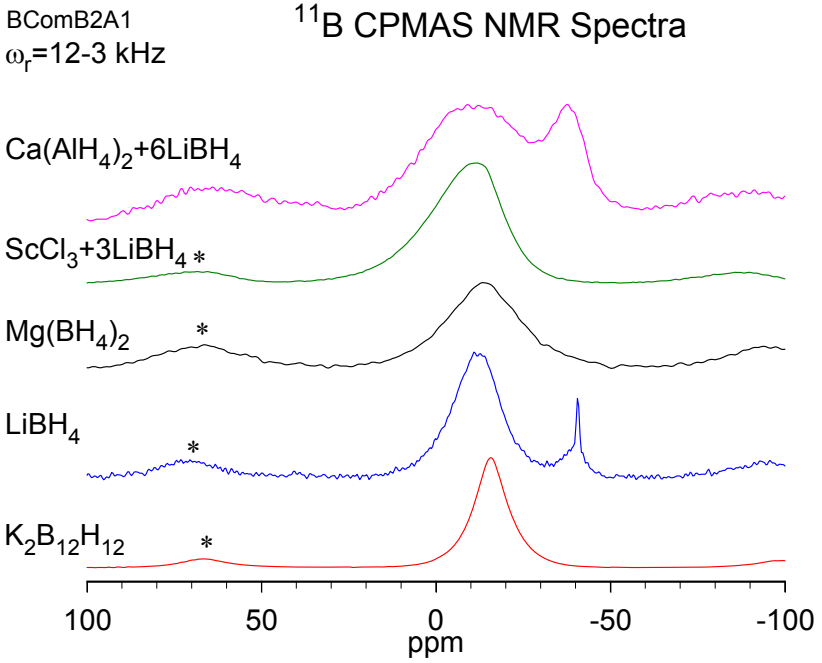
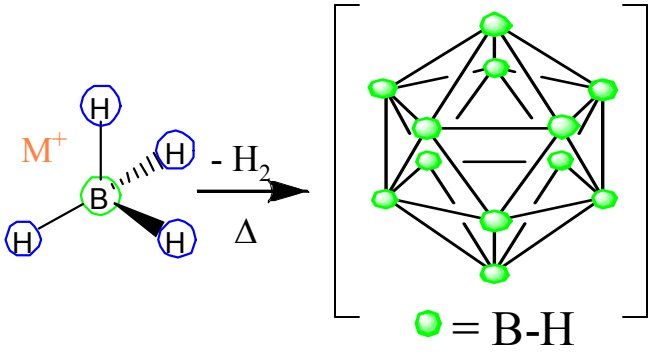
^{11}B MQMAS



Wide distribution of ^{11}B δ_{iso}
Amorphous B complex





Hwang, et al., *J. Phys. Chem. C.* Lett. 2008, 112, 3164.

Summary & Conclusions

Solid State NMR is a powerful & versatile method to assess numerous properties of hydrogen storage materials

Multi-nuclear spectroscopy (hydrogen isotopes & host species)

- Monitor phase compositions and reactions for both hydrogen absorption and adsorption systems
- Usefulness of MAS, MQMAS and CPMAS methods has been shown for various complex metal hydrides
- Identified & characterized "$B_{12}H_{12}$ species" as being the dominant intermediate formed during H_2 desorption from several borohydrides.
- Local structure & site occupancy (i.e, ^2D MAS-NMR spectra)

Diffusion behavior over large dynamic range

- Direct measurement ($D > 10^{-12}$ m^2/s) via Pulsed Field Gradients
- Several types of relaxation times are available to cover wide range of rates; however, quantitative analyses are difficult for complex materials with multiple diffusion processes.