

# Tritium Solid State NMR Spectroscopy at PNNL for Evaluation of Hydrogen Storage Materials

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Hydrogen Storage Lab PI Workshop

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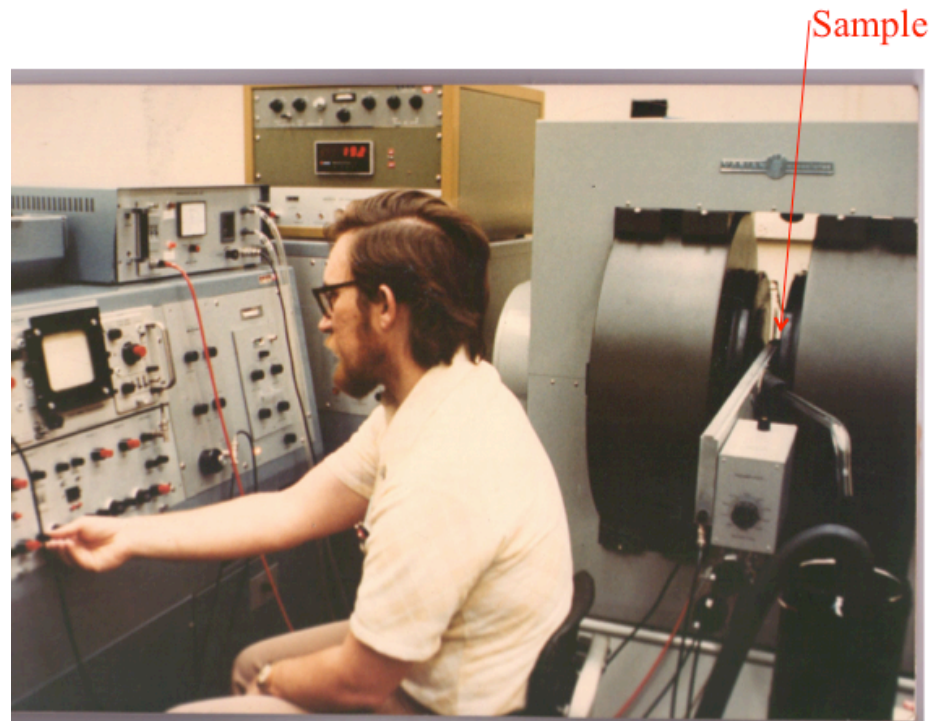
***Revised edition Nov 23, 2015***

# Introduction

**Rational design of new materials to meet DOE performance targets requires greater insights on the diffusion mechanisms and phase transformation processes than are currently available..**

- NMR measurements of *relaxation times* and *spectra* provide direct and unique opportunities to observe the hydrogen isotopes in crystalline & amorphous phases.
- major challenge with  $^1\text{H}$  NMR studies, is the ubiquitous amounts present in most hosts and/or contaminating sources (e.g.,  $\text{H}_2\text{O}$ ) obscuring signals from intermediate or transitory species involved with hydrogen transport and reactions.

**Tritium NMR offers an Novel and Insightful Approach to Gain This Necessary Knowledge!**



Bob at Mound Lab NMR Spectrometer circa 1976

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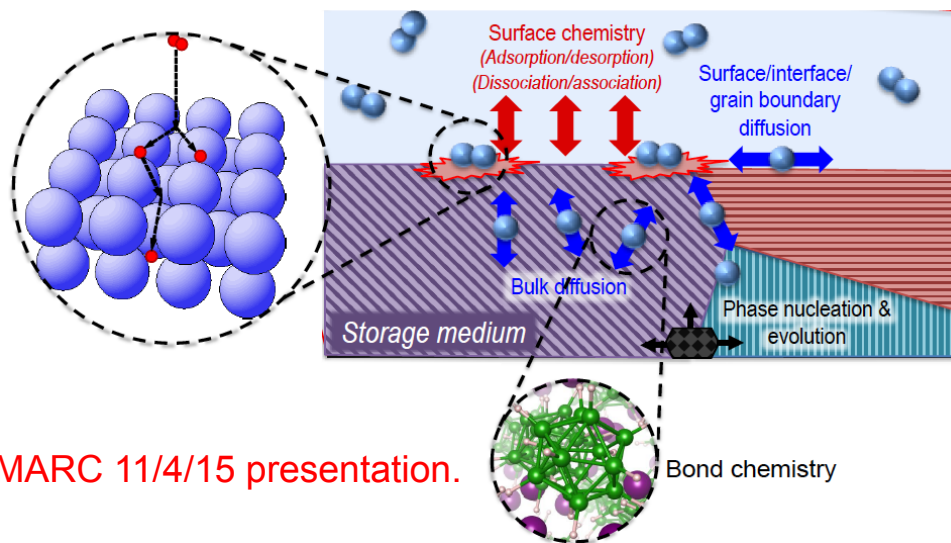
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## NMR (Proton, Deuteron, & Triton) Experiments will Benefit Research Efforts to Understand and Enhance Hydrogen Storage Properties

**Research challenges:** Unraveling the mechanisms of hydrogen uptake & release, in particular the chemical and physical processes that govern

- (i) hydrogen activation,
- (ii) hydrogen diffusion,
- (iii) phase conversion

**We will perform NMR with all three hydrogen isotopes (i.e.,  $^1\text{H}$ ,  $^2\text{H}$ , &  $^3\text{H}$ ) to provide critical tests to predictions from advanced first-principles models and simulations for metals, hydrides, oxides, mixed phases, etc. for chemisorption reactions (e.g.,  $\text{MgH}_2$ , alanates, borohydrides, etc.)**

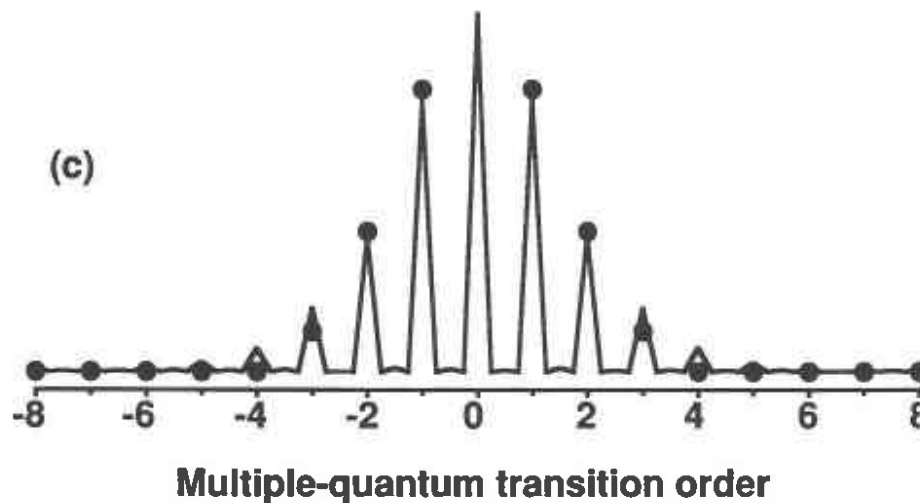
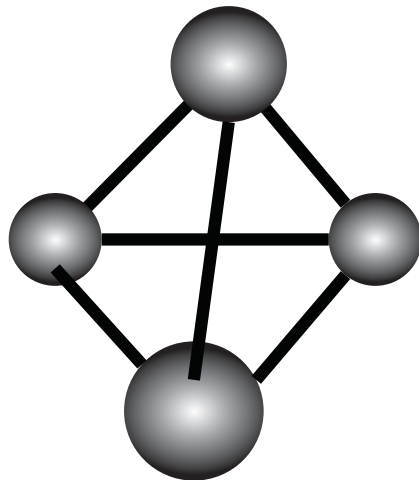


HyMARC 11/4/15 presentation.

**Species from the HyMARC Multi-scale modeling efforts would be identified and their mobilities verified from various NMR parameters.**

One approach to enhance the volumetric capacity of a physisorption sorbent material (e.g., MOF or carbon) is to demonstrate experimentally the sorption of 2 hydrogen molecules on a single metal site. While neutron diffraction is suitable for crystalline samples, NMR will provide alternative approach for amorphous or other disordered materials.

**Nuclear spin cluster (i.e., pair of T<sub>2</sub> molecules) determination by multiple-quantum <sup>3</sup>H NMR**



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# Outline

- 1. We propose two specific examples that will benefit from using  $^3\text{H}$  NMR to probe key issues**
  - **Experiment validation of the number of adsorbed  $\text{H}_2$  ( $\text{T}_2$ ) molecules on a single metal site (NMR should be viable for crystalline or amorphous material (e.g., carbon or non-crystalline MOF).**
  - **Metal Hydrides ( $\text{MgH}_2$  plus tritium-doped catalytic additives).**
- 2. Properties of tritium (NMR & radiographic)**
- 3. Past tritium NMR work (Mound Laboratory & elsewhere)**
- 4. NMR of radioactive materials at PNNL (issues preparing & handling tritium samples)**

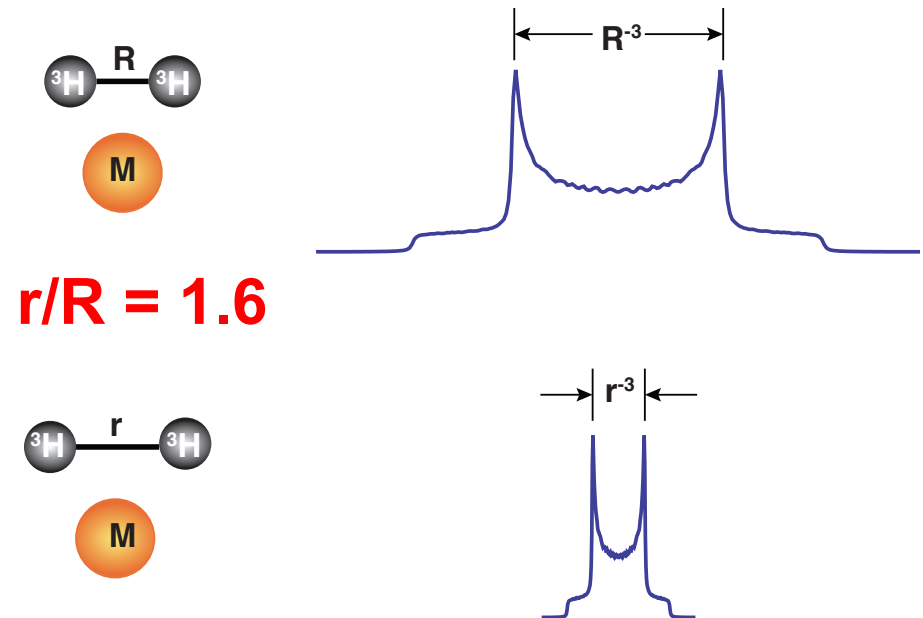


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# Propose $^3\text{H}$ NMR experiments for physisorption. binding multiple $\text{T}_2(\text{H}_2)$ to unsaturated metals

- Computational results predict the binding of multiply  $\text{H}_2$  to unsaturated metal sites in properly designed MOFS. Need experiments to confirm and benchmark calculations.
- NMR is very sensitive (small sample size) but difficult with H background from hydrogen in MOF linkers



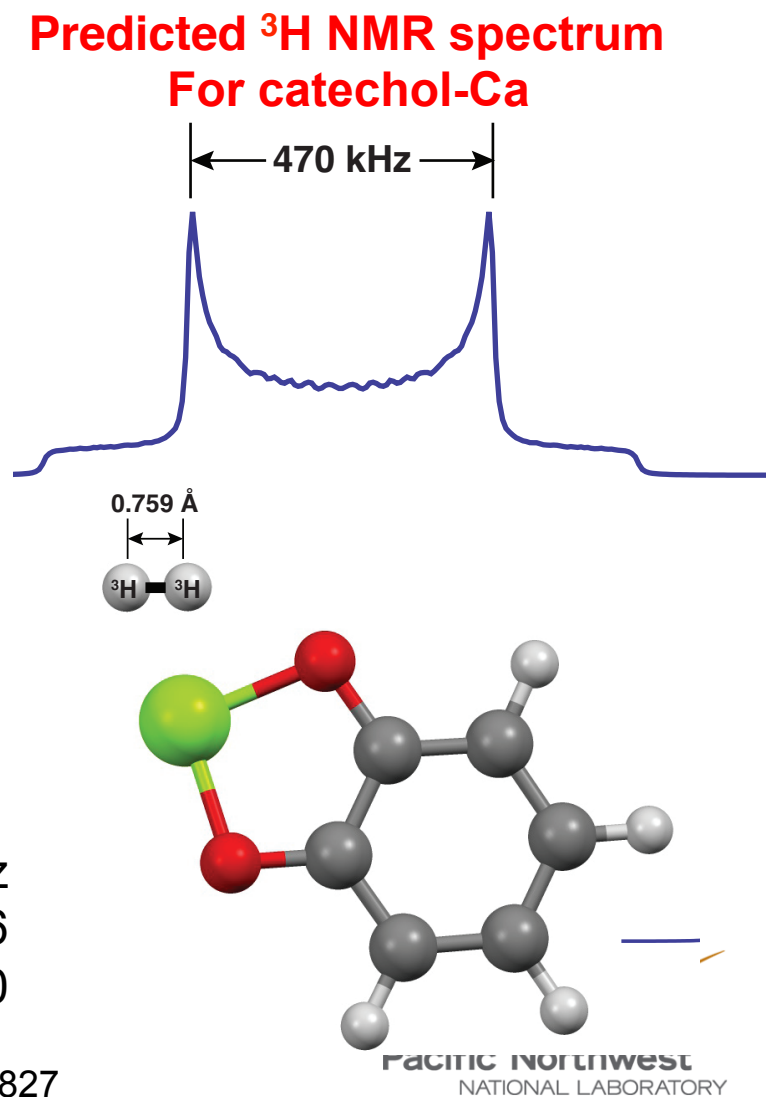
Simulated Tritium NMR spectrum of adsorbed  $^3\text{H}_2$ : illustrating dependence of the splitting's on  $^3\text{H}$ - $^3\text{H}$  distance

# $^3\text{H}$ NMR is unique approach for screening interactions of $\text{H}_2$ to unsaturated metals in non-crystalline materials.

- ‘Pake’ powder pattern (batman wings) shows unique splitting that is correlated with H—H bond distance.
- **Presence of 2  $\text{T}_2$ 's bond to single metal site will provide unique powder pattern.**
- Simulated Tritium NMR spectrum of  $^3\text{H}_2$  molecules adsorbed on catechol-Mg and catechol-Ca:  $1/R_{\text{HH}}^3$  dependence of splitting's.

	$\Delta H_{\text{ads}}$ (kJ/mol)	H—H ( $\text{\AA}$ )	kHz
Cat Mg	-18.6	0.755	476
Cat Ca	-11.1	0.759	470

Tsvion, Long, Head-Gordon JACS **136** (2014) 136, 17827



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# Understanding Effects of Processing (e.g., Ball Milling) and “known to be effective” Catalysts (e.g., Ti, Sc, V, Nb, etc.) on $\text{MgH}_2$ .

## Specific questions to be addressed with $^3\text{H}$ NMR experiments:

- Additives enhance rates of  $\text{H}_2$  uptake and release in  $\text{MgH}_2$  – how does this work? Which additives are better? Why  $\text{Nb}_2\text{O}_5$ ?
- $\text{MgD}_2$  vs  $\text{MgT}_2$ ; What is the chemical nature of the early sites populated (sub-stoichiometric amount of T to Mg, is T located only on surfaces or can hydrogen isotopes diffuse rapidly throughout bulk via defects?)
- NMR chemical shifts ( $^3\text{H}$  spectra) will be used to identify key intermediates & products.  $^3\text{H}$ -NMR relaxation times ( $T_1$ ) will be used to identify dynamics, i.e., mobility & quantify activation barriers for H mobility and transport in presence of additives.

Additives, labeled with T, will provide a quantitative approach to measure relative rates as function of temperature.

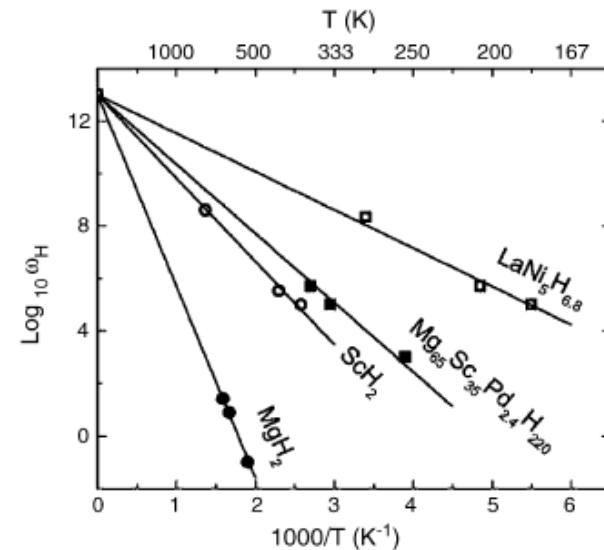


Fig. 3. Relaxation map showing rate  $\omega_{\text{H}}$  of H hopping as a function of reciprocal temperature in  $\text{MgH}_2$ ,  $\text{ScH}_2$ ,  $\text{MgScH}_x$ , and  $\text{LaNi}_5\text{H}_{6.8}$ . The data points correspond to  $T_1$  and  $T_{1p}$  minima and the onset of averaging (increasing  $T_2$  or  $T_2^*$ ); the smallest rates are from  $\omega_{\text{H}} = 1/T_{1D}$ . The approximate activation values  $\Delta E/k$  for the four systems are 16,800, 7300, 6100, and 3400 K, corresponding to  $\Delta E$  of 140, 61, 51, and 28 kJ/mol, respectively.

Conradi, et al., JALCOM  
446-447 (2007) 499

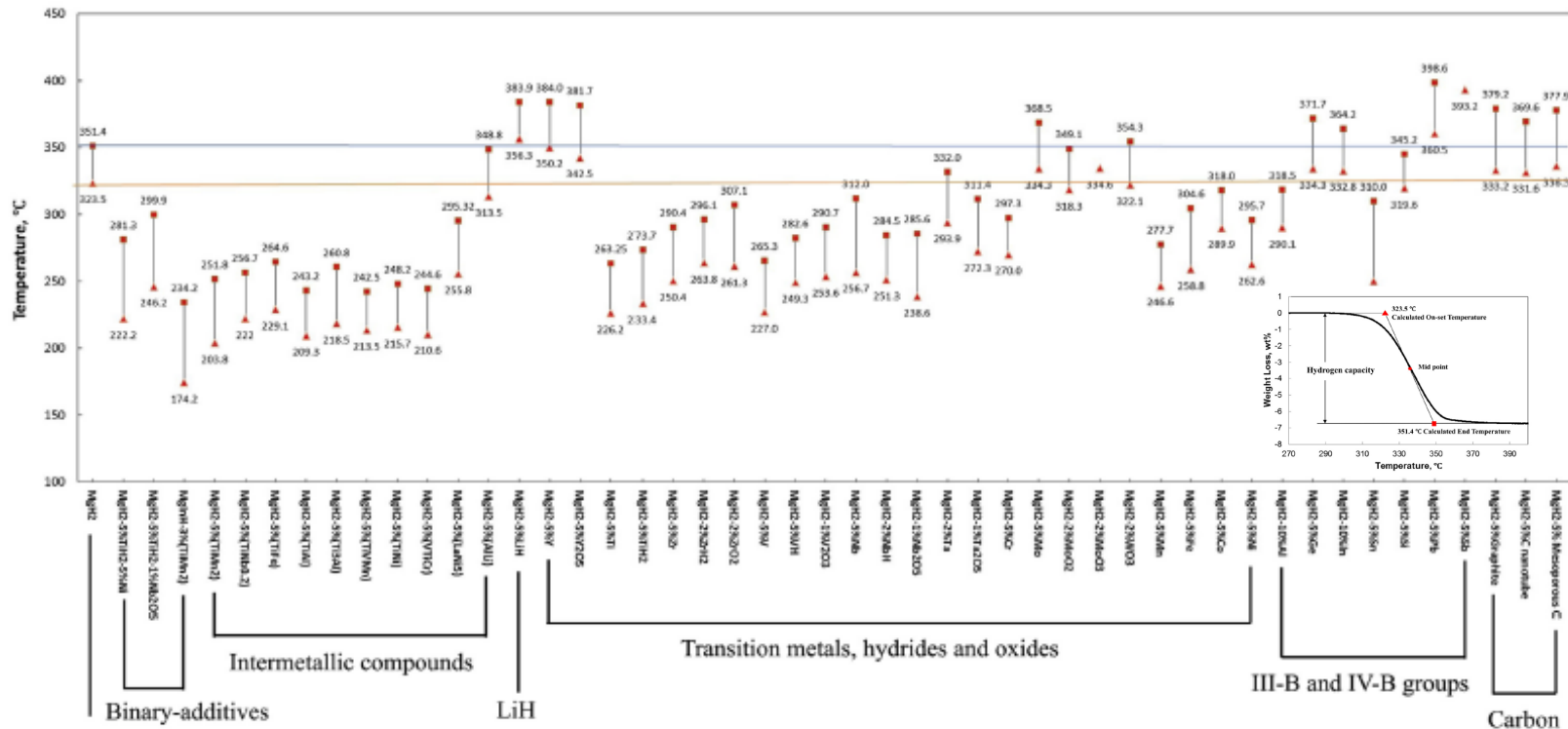
  
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# Effect of Various Additives on Dehydrogenation Temperature of $MgH_2$ . The Percentage of the Additives to $MgH_2$ was in mol%.

C. Zhou, et al., J. Power Sources **278** (2015) 38.



Baseline

$T(\text{des}) = 600 \text{ K}$  for  $MgH_2$  ball milled without additives

$T(\text{des}) < 400 \text{ K}$  with intermetallics additives

$400 \text{ K} < T(\text{des}) < 430 \text{ K}$  with metals, hydrides, oxides of Ti, V, & Nb



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# Proton NMR of MgH<sub>2</sub> with Additives

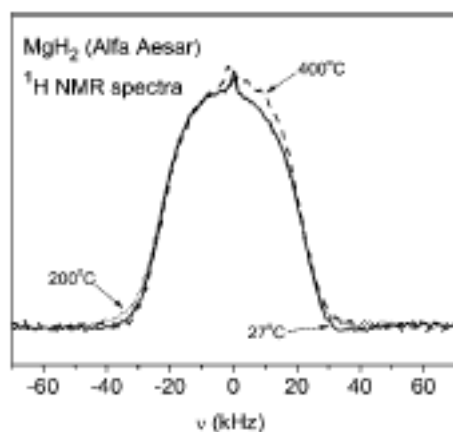


Figure 1. Hydrogen NMR spectra of coarse-grain MgH<sub>2</sub> from Alfa at three temperatures. No motional narrowing is evident. Short rf pulses of 1 μs were used. A small narrow signal from trapped H

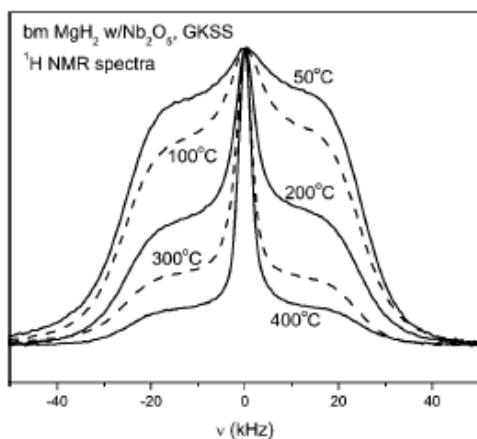


Figure 3. H NMR spectra of ball-milled MgH<sub>2</sub> with Nb<sub>2</sub>O<sub>5</sub> additive. The spectra are superpositions of broad and narrow components. The broad components have somewhat box-like shapes (compare to Figure 1) because of use of long (π/2) rf pulses here.

Corey, et al. JPC-C 112 (2008) 19874

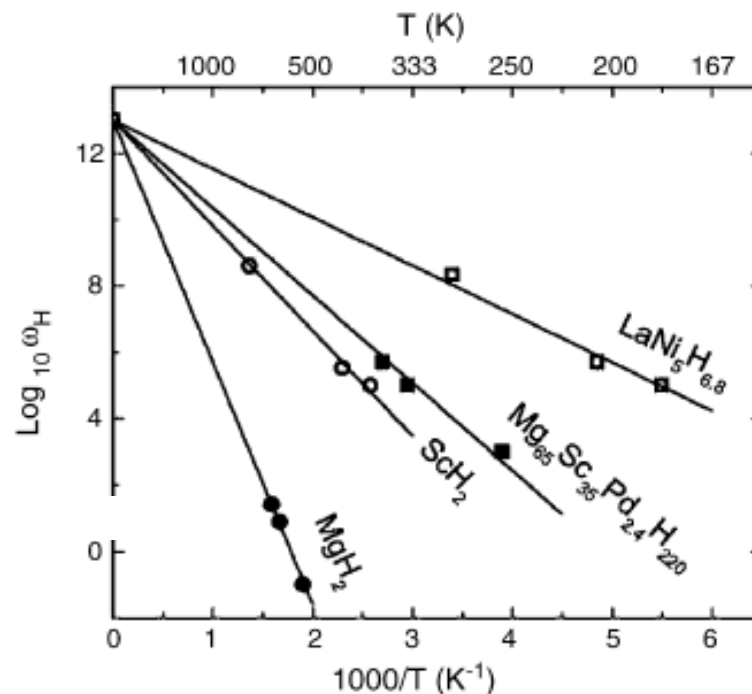


Fig. 3. Relaxation map showing rate  $\omega_H$  of H hopping as a function of reciprocal temperature in MgH<sub>2</sub>, ScH<sub>2</sub>, MgScH<sub>x</sub>, and LaNi<sub>5</sub>H<sub>6.8</sub>. The data points correspond to  $T_1$  and  $T_{1\rho}$  minima and the onset of averaging (increasing  $T_2$  or  $T_2^*$ ); the smallest rates are from  $\omega_H = 1/T_{1D}$ . The approximate activation values  $\Delta E/k$  for the four systems are 16,800, 7300, 6100, and 3400 K, corresponding to  $\Delta E$  of 140, 61, 51, and 28 kJ/mol, respectively.

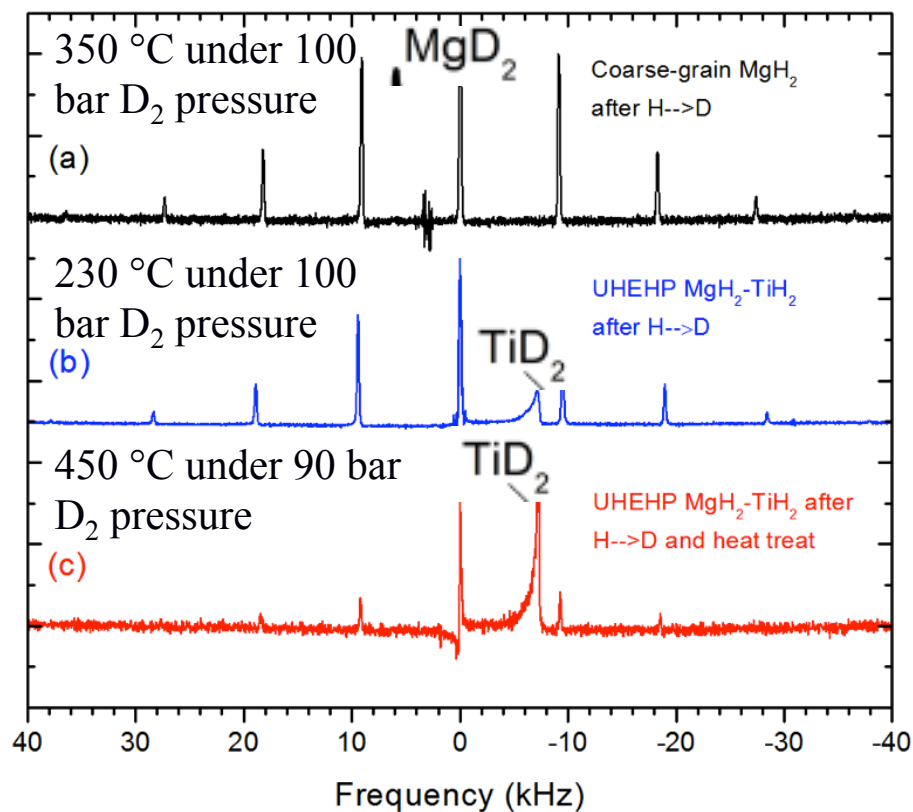
Conradi, et al., JALCOM 446-447 (2007) 499



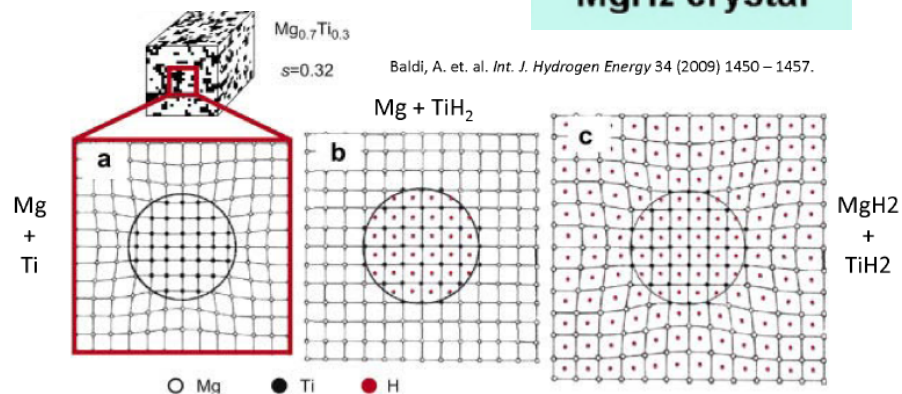
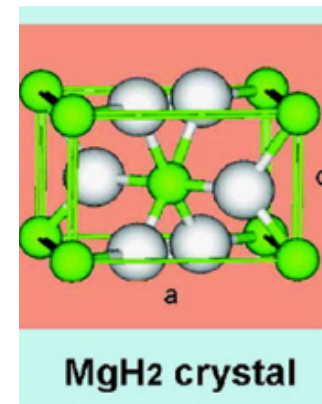
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# $^2\text{D}$ MAS ( $\nu = 46$ MHz, $f_s = 9$ kHz) Room Temperature Spectra of $\text{MgD}_2/\text{TiD}_2$



The D nuclei have non-cubic symmetry in the Rutile ( $\text{TiO}_2$ ) Structure



heat-treated  $\text{MgD}_2 / \text{TiD}_2$  has been shown to have cubic  $\text{MgD}_2$ , with nearly complete Mg / Ti segregation from  $^2\text{D}$  MAS-NMR, where spinning sideband amplitudes show strength of electric field gradients (EFG)

S. Emery, et al., *J. Phys. Chem. C* **119** (2015) 7656–7661

# Strategy for Incorporating Tritium NMR at PNNL Radiological Spectroscopy Laboratories into Hydrogen Storage Materials Research

1. Fabricate appropriate  $^3\text{H}$  sample probes & verify safe operation for proposed NMR experiments.
2. Demonstrate feasibility of  $^3\text{H}$  NMR experiments to study key reaction processes & mechanisms
  - Processed tritiated  $\text{MgH}_2/\text{MgD}_2$  with/without “catalytic” additives).
  - Demonstrate experimentally whether sorption of two  $\text{H}_2(\text{T}_2)$  molecules occur on a single metal site with NMR for crystalline or amorphous MOF candidates.

**Solicit & investigate samples from DOE researchers for reaction or isotope exchange with  $\text{T}_2$  gas.**

# NMR spectroscopy of hydrogen isotopes

Isotope	Ground state nuclear spin $I$	Half life (y)	Quadrupolar moment ( $\times 10^{-24}$ cm <sup>2</sup> )	Gyromagnetic ratio ( $2\pi$ Hz/G)	Larmor frequency in 11.74 T field (MHz)
<sup>1</sup> H (H)	1/2	stable	0	4257.8	500.0
<sup>2</sup> H (D)	1	stable	0.00282	653.6	76.8
<sup>3</sup> H (T)	1/2	12.4	0	4541.5	533.3

**Tritium is Radioactive (Beta Decay):**



**Energy of Beta Particles:**

**Average Energy 5.7 KeV; Max = 18.1 KeV**

## Why $^3\text{H}$ NMR spectroscopy is attractive for studies of hydrogen storage materials

- 🚫 Highest NMR sensitivity of all magnetic nuclei (5 ppm m/m) - (i.e., T/H signal ratio is 1.2 at fixed magnetic field)
- 🚫 Spectral resolution equivalent to  $^1\text{H}$
- 🚫 Spin =  $\frac{1}{2}$  just like protons (hence, no quadrupolar complications as with deuterons)
- 🚫 No background signals from H-bearing hosts or environmental contaminants (e.g., moisture, residual solvents, etc.)
- 🚫 Site-selective detection through isotope labeling
- 🚫 Many attractive candidates can form hydride (tritide) phases directly from gas – straightforward synthesis or T can be added via isotope exchange with hydride or deuteride solids
- 🚫 Probe of reaction dynamics and energetics through measurement of isotope effects



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## Technical Issue & Challenges for $^3\text{H}$ NMR Experiments

- ☢ Radioactive (low energy beta-particles) imposes safety and containment issues for potential volatile radioisotopes in liquid and MAS sample vessels (fabrication of robust & pricey components along with development of adequate safety protocols)
- ☢ Synthesis of  $^3\text{H}$ -labeled materials (PNNL has equipment & expertise to react materials with  $\text{T}_2$  gas up to circa 10 bar)
- ☢ Development of NMR probes with adequate  $^1\text{H}$ -decoupling capability as the close magnetic moments of H & T may impact spin decoupling methods, but difference is about same as with H & F spins, which have been done previously (can also avoid by using mixed D and T samples)
- ☢ Safety protocols & constraints on pressure and temperature ranges for T-spins will restrict some *in-situ* NMR experiments, but *ex-situ* measurements following processing & treatment would be possible in many circumstances.



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## Mound Laboratory was Heavily Involved with Metal Tritides

In-house processing, weapons surveillance & material synthesis (1955 until facility closure circa 1992) done at this AEC/DOE site in Miamisburg OH

- **Uranium tritide ( $UT_3$ ) reactors & storage systems (“U-beds”)**
- **Palladium (Pd) separation & purification systems**
- **Li(D,T) was made and fabricated into components for numerous nuclear weapons tests.**

R&D Projects for the Design Labs (Sandia, LANL, LLNL)

- **Mechanisms & mitigation of self-radiolysis effects in Li(D,T)**
- **$^3\text{He}$  retention and release by aging metal tritides (i.e., accumulating from tritium decay)**

Tritium storage & shipping containers (adapted U-beds) for fusion & commercial applications.

Fundamental studies of hydrides as alternative energy candidates was supported by DOE/BES between 1975 and ~1987.



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# Developed & Utilized Unique Spectrometer for T & <sup>3</sup>He NMR Experiments



Bob at Mound Lab NMR Spectrometer circa 1976



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**Typical metal hydride (tritide) NMR samples were sealed in glass tubes initially under vacuum (however,  $^3\text{He}$  gas accumulated over time).**



**The tritide samples were in the range of 100 - 1000 Ci. Most were stored in ovens or freezers for time periods up to several years and periodically taken to spectrometer for the NMR measurements.**

Note: These specific NMR tubes contain powders of non-radioactive metal hydrides

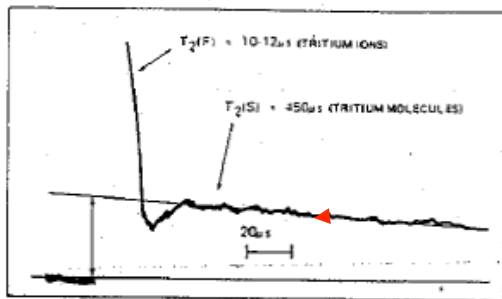
**Solid State NMR measurements of metal tritides/hydrides started at Mound in 1973 and continued for nearly 20 years.**

  
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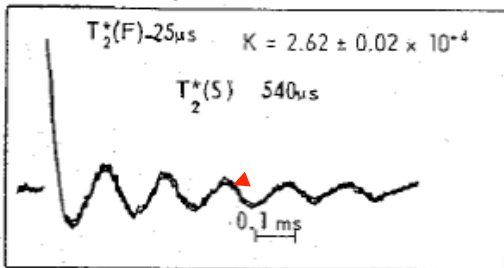
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# LiT Radiation Damage Characterized by Pulsed Nuclear Magnetic Resonance Methods @ Mound Lab

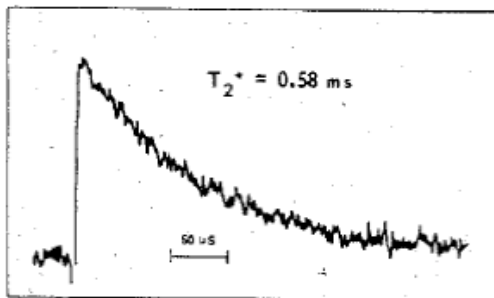
- Identified (H,D,T)<sub>2</sub> & Li metal
- Concentration from spin counts



TRITIUM NMR SIGNAL



LITHIUM NMR SIGNAL



<sup>3</sup>He NMR SIGNAL

-T<sub>2</sub> Gas

-Li metal

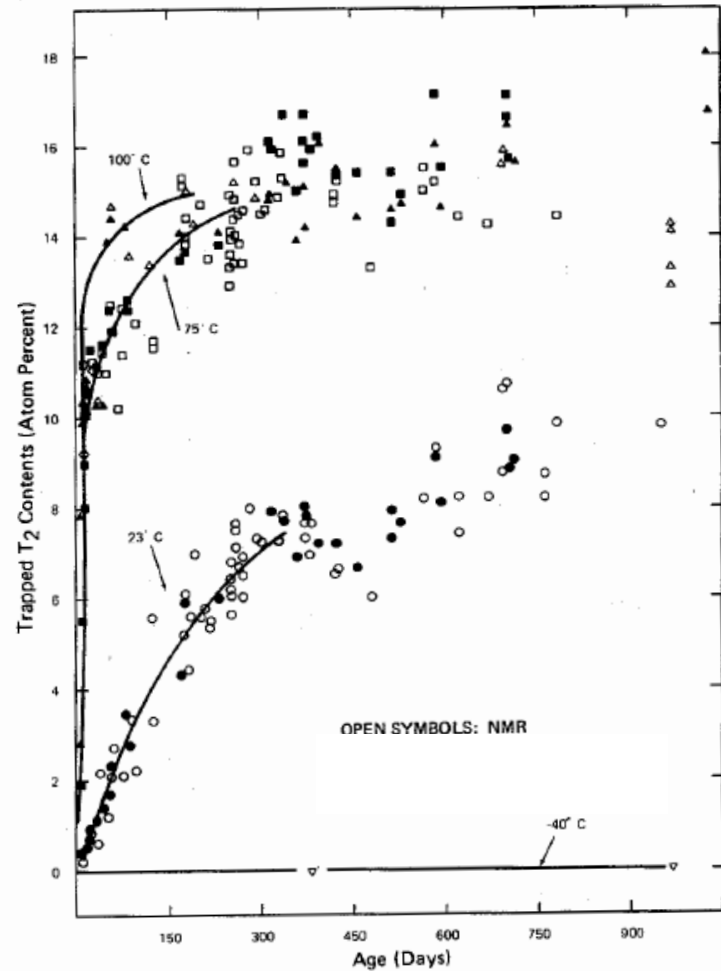


FIGURE 3 - Trapped T<sub>2</sub> contents in LiT samples aged at -40°C, 23°C, 75°C, and 100°C.

*Mound Lab Operated by Battelle Since 1963*

## Summary of Li(H, D, T) Behavior Derived from NMR

- **Swelling due to radiolytical decomposition: Molecular hydrogen & lithium metal**
- **$T_2$  and  $^3\text{He}$  are trapped in microscopic gas bubbles ( $d < 100 \text{ nm}$ )**
- **Bubble size increase with temperature (larger) and radiation dose/age**
- **Helium outgassing is mainly due to bursting bubbles**
- **Li metal formation lags formation of gas bubbles at all temperatures [Not covered in this presentation]**
- **Complex synergistic relation between swelling & bubble formation**

More information & references can be found:

1. P. C. Souers, et al., *J. Nuclear Materials* 154 (1988) 308-317.
2. R. Bowman, et al., *J. Nuclear Materials* 154 (1988) 318-331.

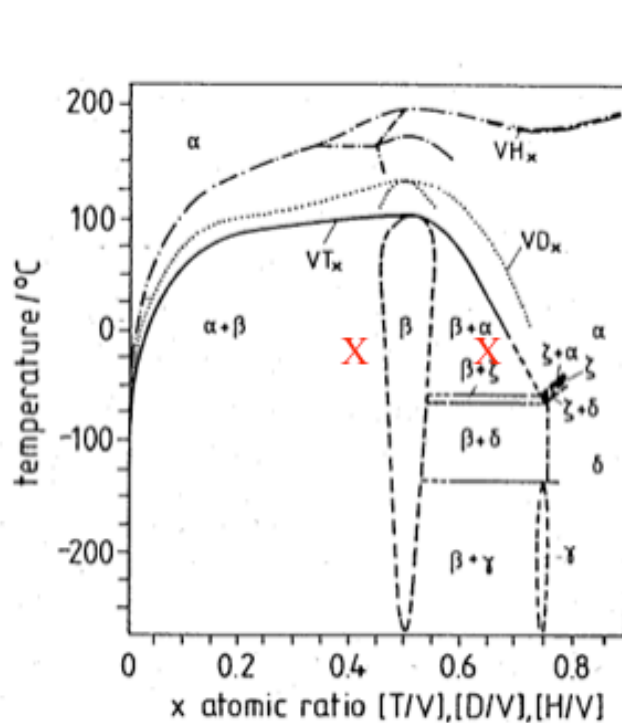


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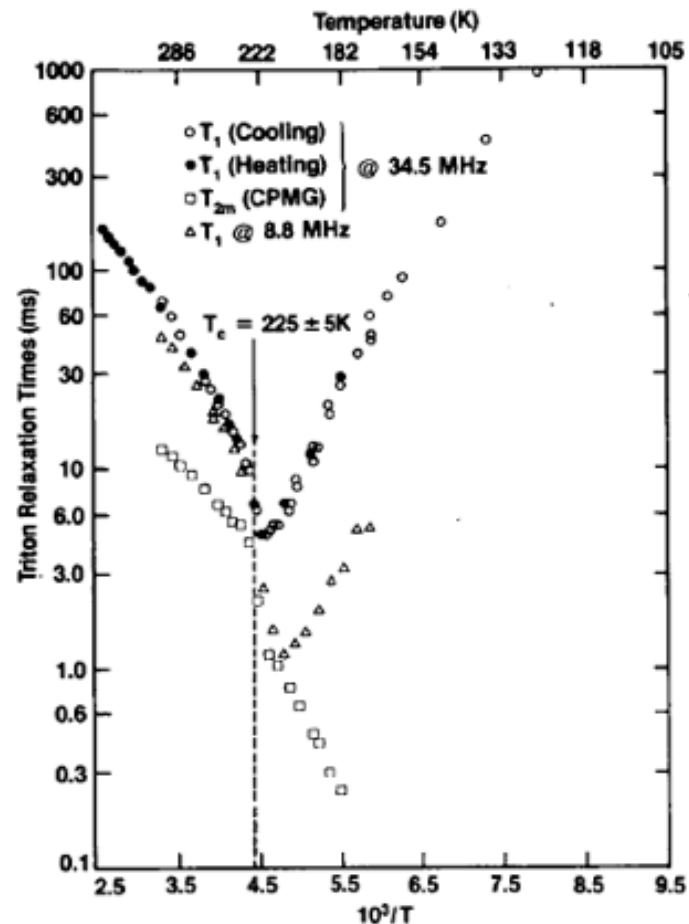
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# Isotope Effects of Phase Transitions & $^3\text{H}$ Relaxation times in the $\text{VT}_x$ Phases



V-T Phase Diagram compared to V-H and V-D Systems (Lasser & Schober - 1987)

**BCC  $\alpha$ -Phase:** T = Tetrahedral sites  
**Monoclinic (BCT)  $\beta$ -Phase:**  
 T = Octahedral sites

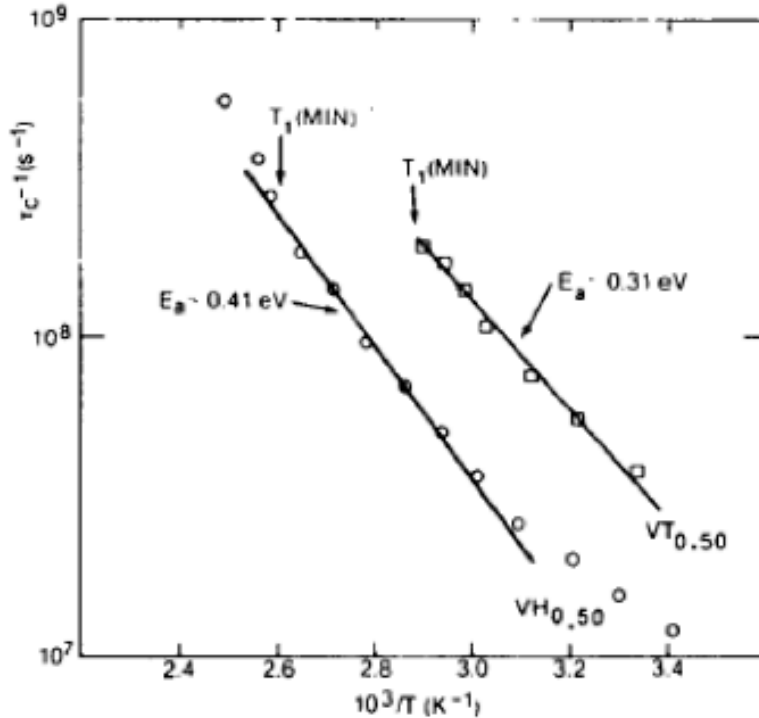


Tritium  $T_1$  &  $T_{2m}$  relaxation times for  $\text{VT}_{0.75}$  during heating & cooling cycles

Bowman, et al. *Scr. Met.* 16 (1982) 933



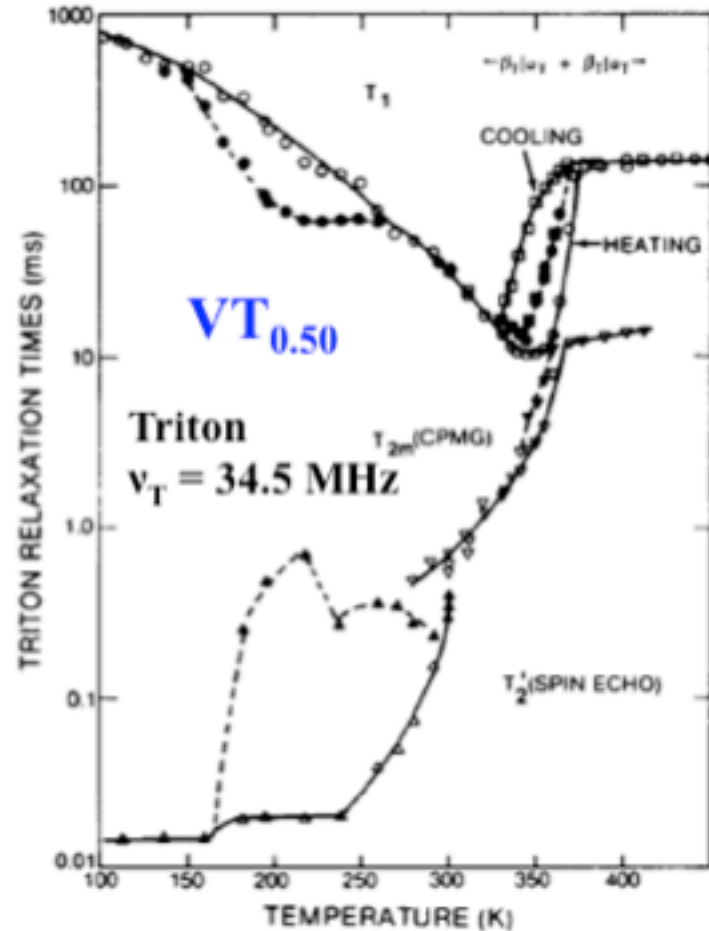
# T Atoms in $\beta$ -VT<sub>0.50</sub> Diffuses Faster than H Atoms in $\beta$ -VH<sub>0.50</sub> with Lower Activation Energy ( $E_a$ )



**Diffusion correlation times ( $\tau_c$ ) derived from  $T_1$  data**

Bowman, et al. *Scr. Met.* **17** (1983) 937

Bowman, et al. *Fusion Tech.* **8** (1985) 2366.



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## Metal Tritides Studied Using NMR @ Mound Laboratory

Metal Tritide	Host Crystal Structure	Typical NMR Samples		T ( <sup>1</sup> H) Relaxation Times (ms)			Special Comments, Etc.
		Mass (grams)	Initial T-content (10 <sup>20</sup> atoms)	T <sub>2</sub> <sup>*</sup>	T <sub>2m</sub>	T <sub>1</sub>	
LiT	FCC (NaCl)	0.28	169	0.011/0.45	-/2.6	~2000/380	Ionic salt, rigid lattice, self-radiolysis giving ~ 9% T <sub>2</sub> gas in bubbles & Li metal
TiT <sub>1.88</sub>	FCC (CaF <sub>2</sub> )	~1.0	~200	0.011	-	231	Metallic, non-stoichiometric, rigid lattice, tetrahedral T-sites
VT <sub>0.50</sub>	Monoclinic	2.72	155	0.065	0.13	22.6	Metallic, non-stoichiometric, octahedral T-sites, mobile
VT <sub>0.75</sub>	BCC	1.79	151	0.039	0.78	22.8	Metallic, non-stoichiometric, tetrahedral T-sites, very mobile
Mg <sub>2</sub> NiT <sub>3.96</sub>	Monoclinic	0.68	135	0.017	-	510	Semiconducting, NiH <sub>4</sub> <sup>+</sup> ions, stoichiometric, no T <sub>2</sub> gas seen up to 1285 days @ 300 K
PdT <sub>0.65</sub>	FCC (NaCl)	2.42	87	0.114 <sup>a</sup>	1.4 <sup>a</sup>	76 <sup>a</sup>	Metallic, ductile, very mobile tritium
ZrNiT <sub>2.93</sub>	Orthorhombic	1.84	204	0.007/0.036	-/0.06	235	Metallic, non-stoichiometric, both rigid & mobile tritium in two sites
BaT <sub>1.93</sub>	Orthorhombic	1.61	131	0.021	-	3380	Ionic, stoichiometric, no T <sub>2</sub> gas seen up to 858 days @ 300 K
UT <sub>3.0</sub>	FCC (β-W)	~3.0	~220	0.009	-	~4	Metallic, rigid lattice, paramagnetic [ferromagnetic T <sub>c</sub> @ 183 K]

<sup>a</sup>Measured on a PdT<sub>0.10</sub> sample aged for 8-years

# Update & Status of Metal Tritide & $^3\text{H}$ NMR Efforts

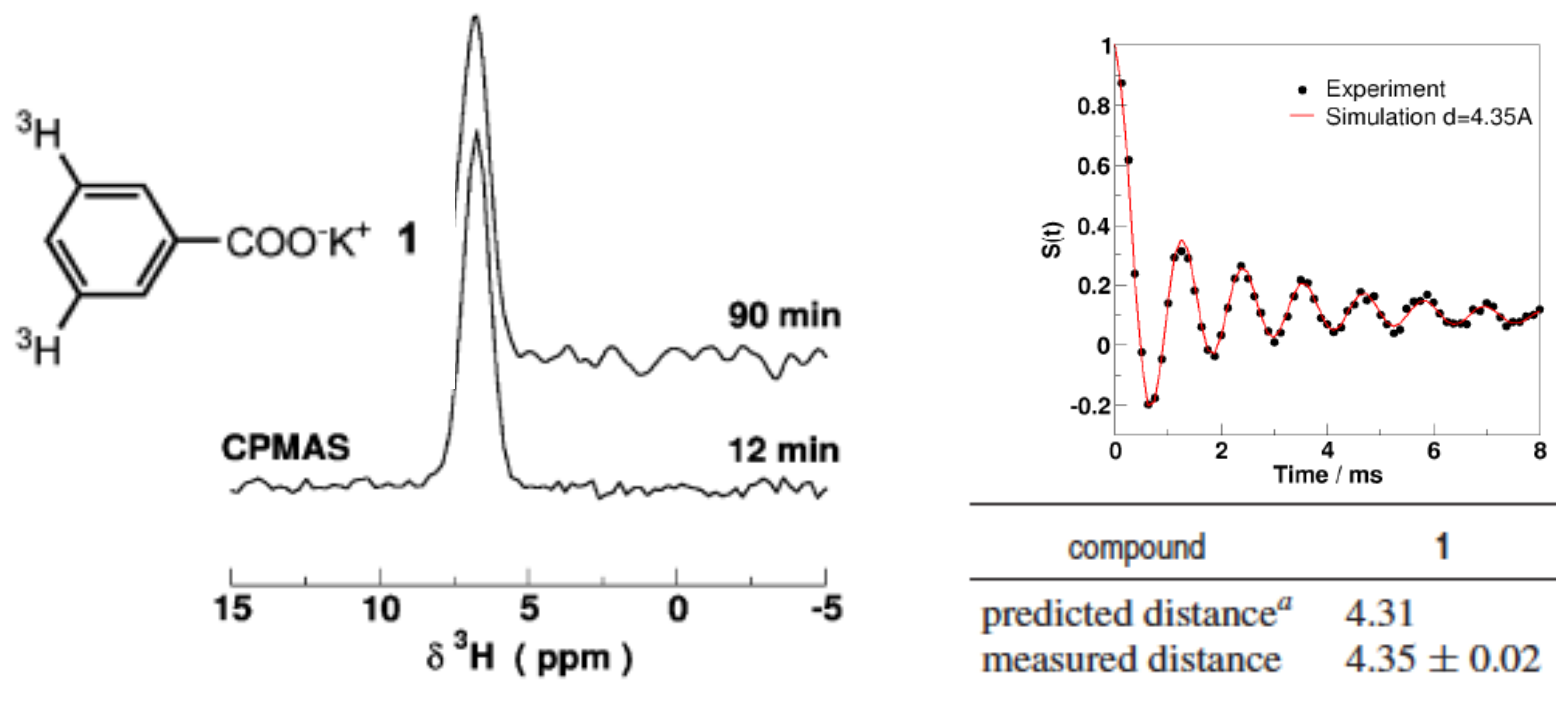
- Metal tritides are still being used in the DOE weapons complex (i.e., SRNL, LANL, etc.) & Energy & Environmental R&D (i.e., PNNL)
- Research continues in USA, France, China, Japan, etc. on properties and helium retention in metal tritides relating to fusion as well as other nuclear and commercial technologies.
- However, there appears to have been only one group (France @ MH2014) to use NMR to study  $^3\text{He}$  behavior in any metal tritide (e.g.,  $\text{PdT}_x$ ) during past 25 years. **(At Mound Laboratory we had developed & implemented a truly unique NMR methodology to investigate these materials!)**
- Over the past 25+ years, novel & highly sophisticated NMR methods on  $^1\text{H}$  and  $^2\text{H}$  are currently being used to evaluate and assess high performance hydrogen storage materials to meet the very demanding requirements specified by DOE for hydrogen fuel cell powered vehicles.

**It is possible to do similar NMR experiments with T-spins.**





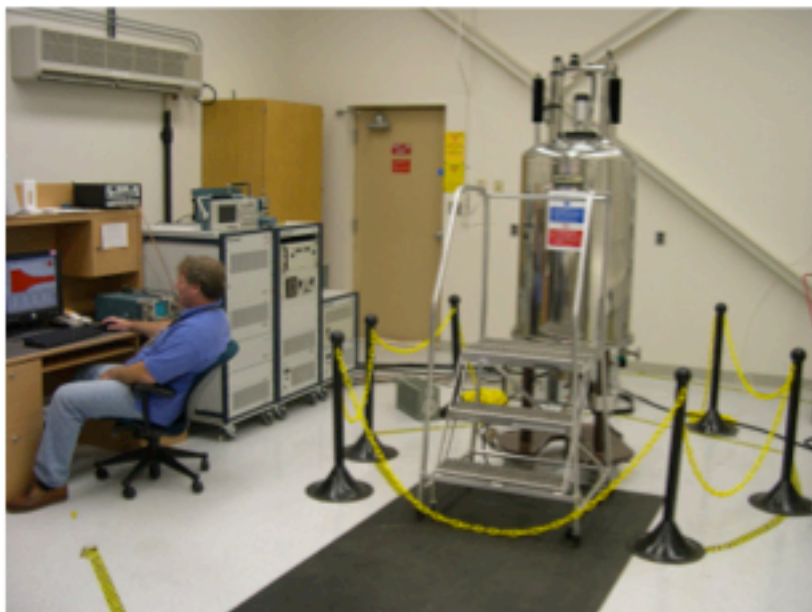
# Measurement of Long-Range Interatomic Distances by Solid-State Tritium-NMR Spectroscopy



**Figure 2.** Comparison between  $^3\text{H}$  spectra of compound **1** obtained by direct acquisition (top) and  $^1\text{H}$ - $^3\text{H}$  cross-polarization (bottom) in eight scans. Total experiment times are indicated on the right; MAS = magic angle spinning; CP = cross-polarization.

A. K. L. Yuen, et al., J. Am. Chem. Soc. 132 (2010) 1734  
(French Researchers)

## Radiological NMR spectroscopy at the Pacific Northwest National Laboratory



- ✚ NMR laboratory in the RPL (late 2002)

- ✚ 300 MHz wide bore magnet with solid state and high-resolution solution state capabilities

- ✚ **Laboratory space permanently classified as a Radiation Buffer Area**

- ✚ New EMSL radiological NMR laboratory (2013)

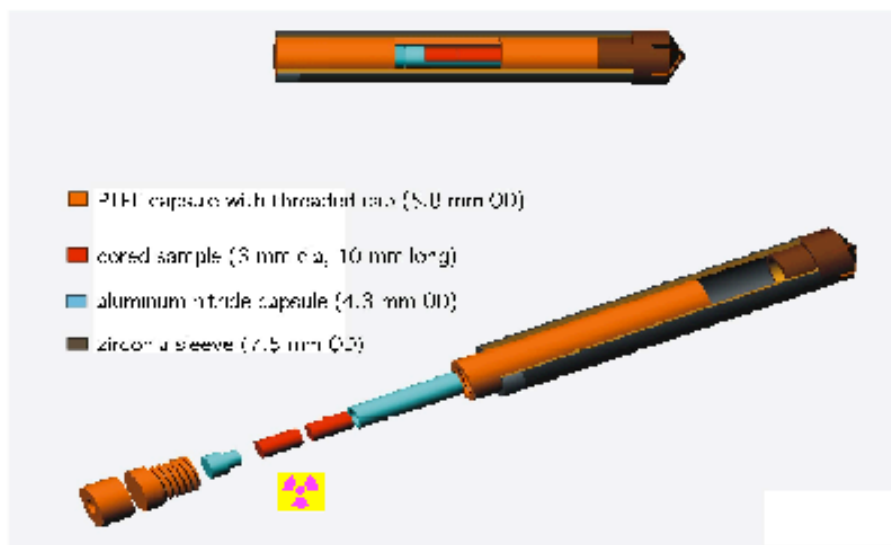
- ✚ Category 3 nuclear facility

- ✚ 100 and 750 MHz instruments with solid state and high-resolution solution state capabilities

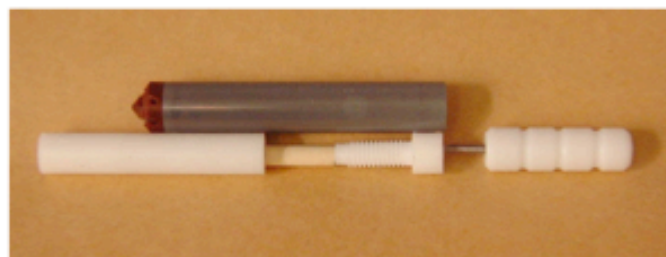
- ✚ **Laboratory space permanently classified as a Radiation Buffer Area**



## Triple containment rotor for radiological MAS-NMR spectroscopy



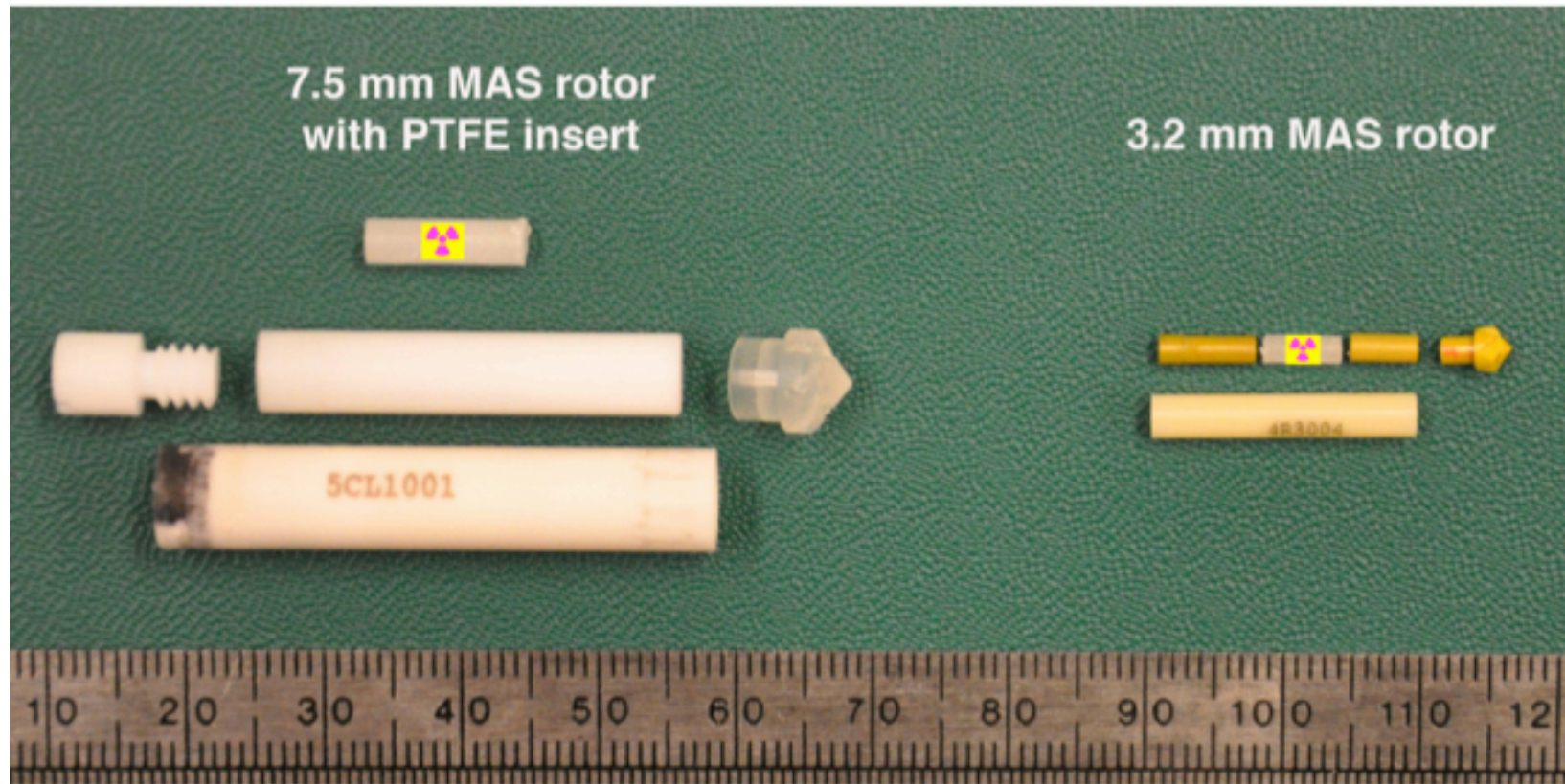
All three exterior surfaces free of radioactive contamination



Farnan, Cho, Weber, Scheele, Johnson, Kozelisky, *Rev. Sci. Instr.* **75**, 5232 (2004)

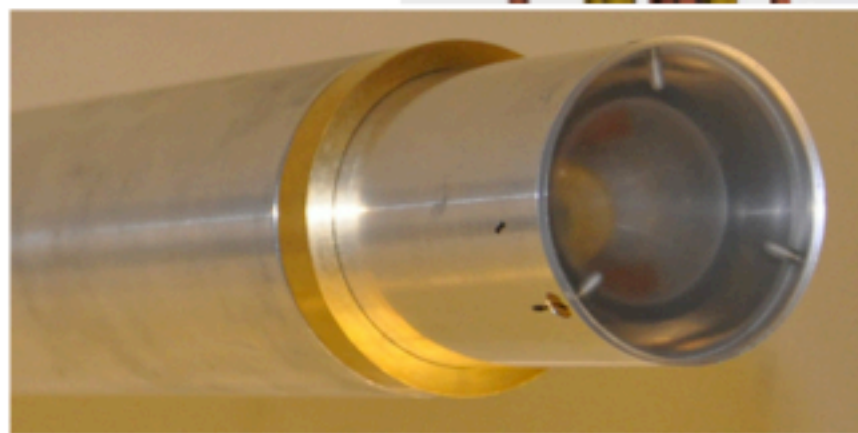
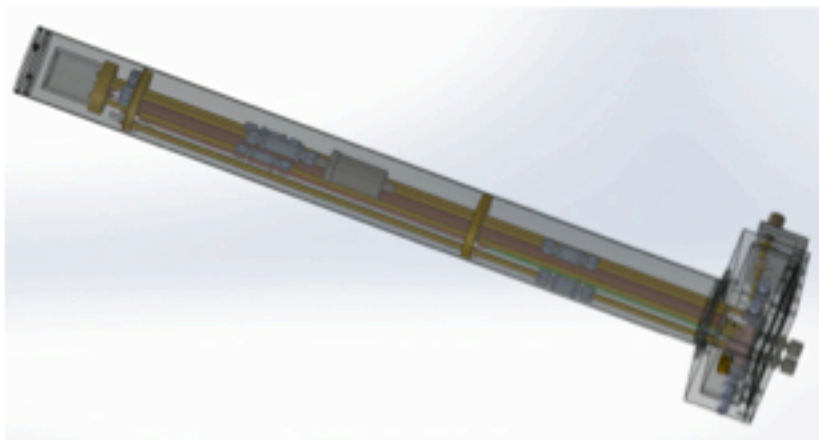
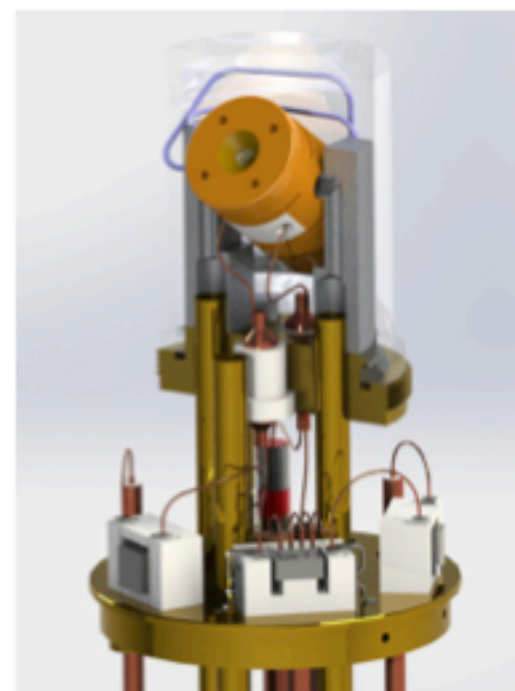
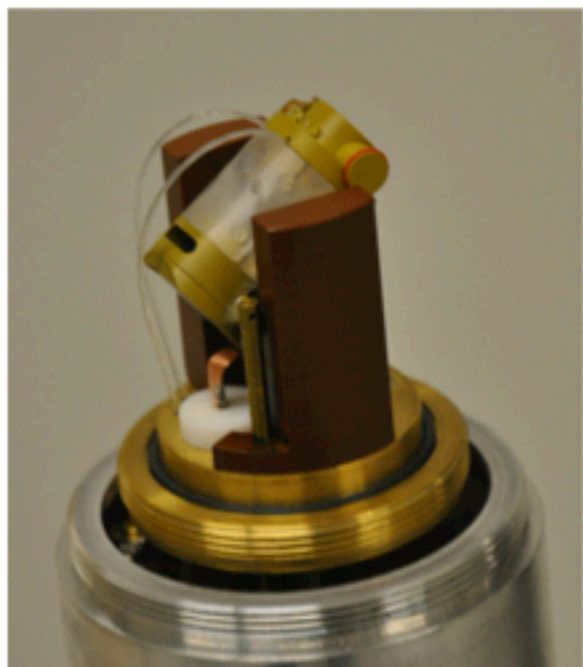
5

## Sample pellets made from molds



- ☒ Easier sample loading
- ☒ Even mass distribution for more stable spinning
- ☒ Reduced dispersibility

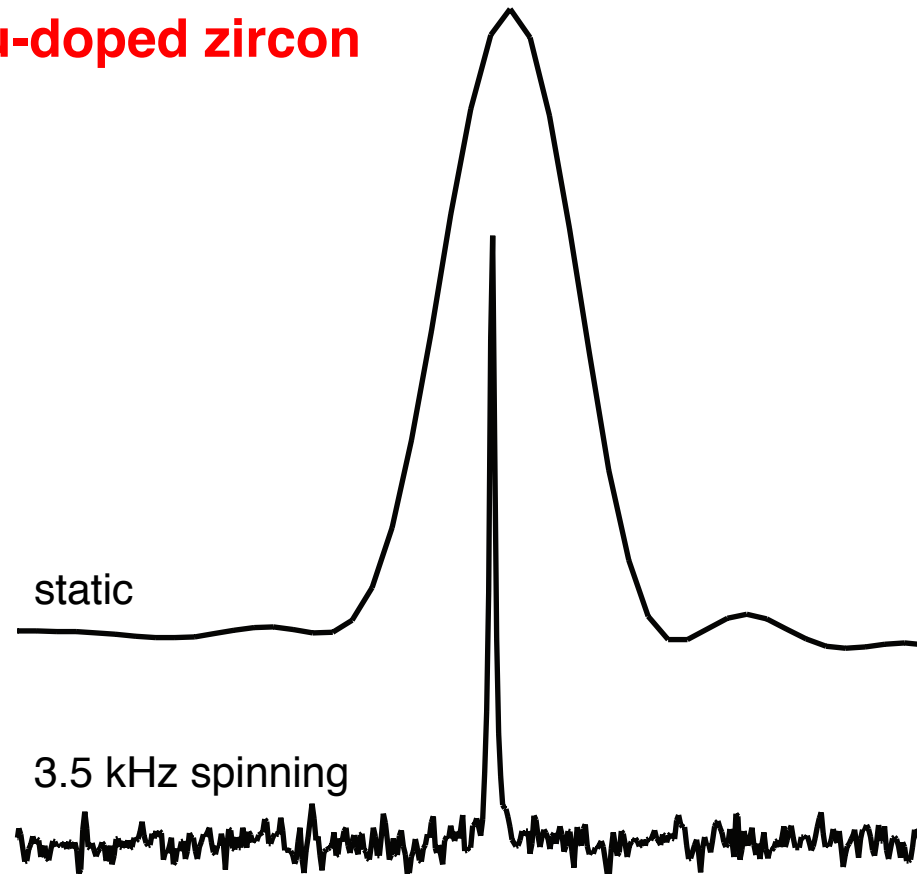
# Sealed radiological magical angle spinning NMR probe (750 MHz)



# Magic-Angle-Spinning (MAS) provides Substantial Improvement in Resolution from Solid Samples

$^{29}\text{Si}$  MAS NMR spectroscopy

10 wt%  $^{239}\text{Pu}$ -doped zircon



Farnan, Cho, and Weber, *Nature* **445**, 190 (2007).

# Appendix

Additional information not covered during the presentation along with a collection of open literature references on NMR studies of tritium behavior and  $^3\text{He}$  retention and distribution in metal tritides. A bibliography of tritium NMR publications on other materials is also included.

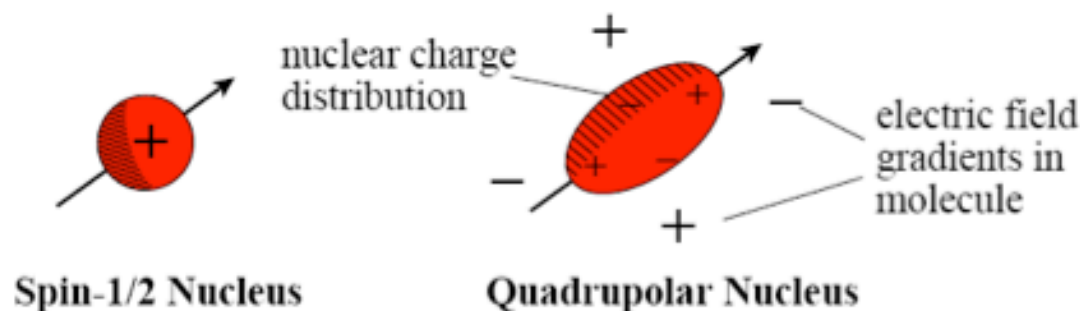


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# Types & Properties of NMR Active Nuclei

No NMR for  $I = 0$  nuclei (i.e.,  $^4\text{He}$ ,  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{28}\text{Si}$ , etc.)



*Most abundant isotopes in the periodic table*

H																	He	
Li	Be	<b>SPIN-1/2</b>										B	C	N	O	F	Ne	
Na	Mg	<b>INTEGER SPINS</b>										Al	Si	P	S	Cl	Ar	
		<b>HALF-INTEGER QUADRUPOLEAR SPINS</b>																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

## NMR active nuclei for M-H Studies

$I = 1/2$ :  $^1\text{H}$ ,  $^3\text{H}^*$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{29}\text{Si}$ , etc.

$I = 1$ :  $^2\text{H}$ ,  $^6\text{Li}$ ,  $^{14}\text{N}$

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

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

$I = 7/2$ :  $^{45}\text{Sc}$ ,  $^{51}\text{V}$ , etc.

Figures from Rob Schurko's Introductory Solid State NMR Notes

([http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr\\_schurko.pdf](http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr_schurko.pdf))



# Tritium is the Most Sensitive Nuclei for NMR Measurements

## A (conservative) estimate for the detection threshold of T<sub>2</sub> by NMR:

Minimum detectable number of T nuclei by NMR  $\sim 1 \times 10^{16}$  nuclei

Molecules of T<sub>2</sub> in minimum detectable amount  $\sim 5 \times 10^{15}$  molecules

Moles of T<sub>2</sub> in minimum detectable amount  $\sim 8.3 \times 10^{-9}$  moles

Volume of minimum detectable T<sub>2</sub> at STP = **0.00019 mL(STP) of T<sub>2</sub> gas**

Mass of tritium = 0.05  $\mu\text{g}$  = 4.8 mCi



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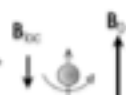
# High Resolution NMR in Solids - Overview

High resolutions,  $\sigma_{iso}$

Cartesian tensor.

$$\mathcal{H}_{cs} = \gamma \mathbf{I} \cdot \bar{\sigma} \cdot \mathbf{B}_0$$

chemical shielding



$$\mathcal{H}_{D} = \sum_{\alpha\beta} h_{\alpha\beta} \gamma_{\alpha} \gamma_{\beta} \left( \mathbf{I}_{\alpha} \cdot \mathbf{I}_{\beta} - \frac{3(\mathbf{I}_{\alpha} \cdot \mathbf{r}_{\alpha\beta})(\mathbf{I}_{\beta} \cdot \mathbf{r}_{\alpha\beta})}{r_{\alpha\beta}^3} \right)$$

dipolar interaction



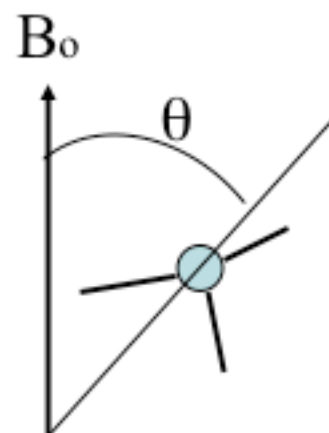
$$D_{\alpha\beta} = h_{\alpha\beta} \gamma_{\alpha} \gamma_{\beta} (\delta_{\alpha\beta} - 3e_{\alpha} e_{\beta})$$

$\alpha, \beta = x, y, z$ ;  $e_{\alpha}$ :  $\alpha$ -component of unit vector along  $r_{\alpha\beta}$

Removing Anisotropic Interactions  
(Pulse manipulations, mechanical rotations)

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

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

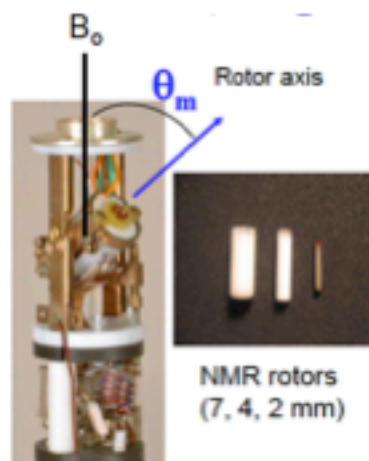


Full use of  
Anisotropy

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

Molecular geometry

- Distance measurements
- MQ spin counting



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

# NMR Relaxation Times & Diffusion (Very General - Focus on Hydrogen Isotopes)

## Pulsed NMR Sequences:

- $T_1$  **Spin-Lattice**: from  $180^\circ$ - $\tau$ - $90^\circ$  and  $(90^\circ$ - $t$ )<sub>n</sub>- $\tau$ - $90^\circ$
- $T_2$  **Spin-Spin**: from free induction decays ( $T_2^*$ ), 2-pulse echoes ( $T_2'$ ), and Carr-Purcell-Meiboom-Gill (CPMG) echo trains ( $T_{2m}$ ).
- $T_{1\rho}$  **Rotating-Frame**: from CW (not chopped) spin-locking.
- $T_{1D}$  **Dipolar**: ( $T_1$  of dipolar-ordered state, essentially  $T_1$  in zero field)

- **Correlation time,  $\tau_c$ :**

$$1/T_2 = K * M_2 * \tau_c$$

- $T_1, T_2$  depend on  $\tau_c$  and  $M_2$   
( $M_2$  = mean-squared dipolar interaction)

- **Mean residence time,  $\tau = 1/\omega_H$ :**

$$\tau_c = \tau / 2$$

- **Diffusion Coefficient:**

$$D(T) = f \langle l^2 \rangle / (6 \tau)$$

- **Activation energy (Arrhenius),  $E_A$ :**

$$1/\tau = (1/\tau_0) \exp(-E_A/kT)$$

$$\tau_0^{-1} = \text{attempt frequency}$$



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## Reviews on Mostly Conventional Solid State NMR Studies of Metal Hydrides

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R. Hempelmann and A. Skripov, “Hydrogen Motion in Metals” in *Hydrogen-Transfer Reactions*, edited by R. L. Schowen, J. P. Klinmann, J. T. Hynes, and H. H. Limbach (Wiley-VCH, Weinheim, 2007) pp. 787-829.



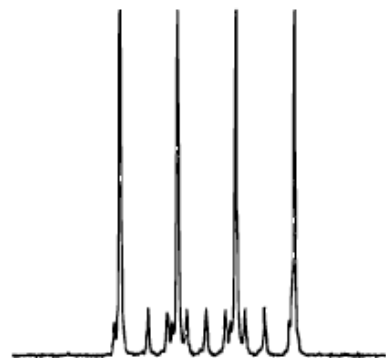
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# T(<sup>3</sup>H) NMR Spectra of LiBT<sub>4</sub> & NaBT<sub>4</sub> Solutions (1996)

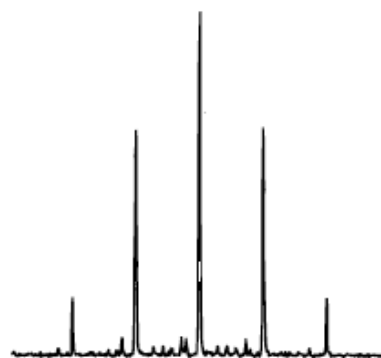
8772 *J. Org. Chem.*, Vol. 61, No. 25, 1996

Species	Multiplicity
NaBH <sub>3</sub> T = 3.3%	1:3:3:1
NaBH <sub>2</sub> T <sub>2</sub> = 17.4%	1:2:1
NaBHT <sub>3</sub> = 41.8%	1:1
NaBT <sub>4</sub> = 37.5%	1

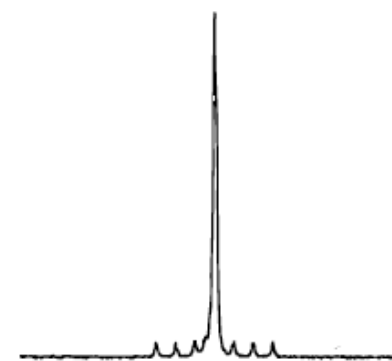
(a) <sup>3</sup>H Spectrum



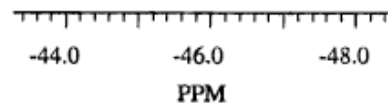
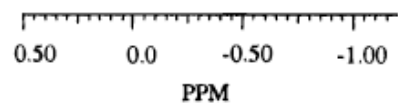
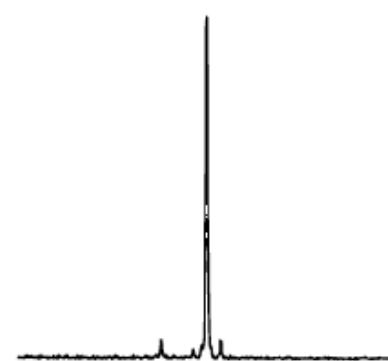
(c) <sup>11</sup>B Spectrum



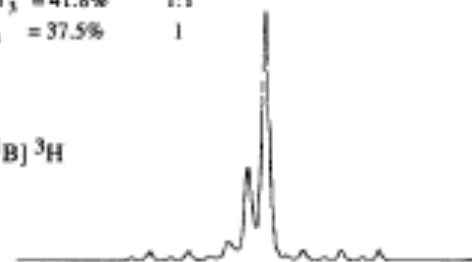
(b) [<sup>11</sup>B] <sup>3</sup>H Spectrum



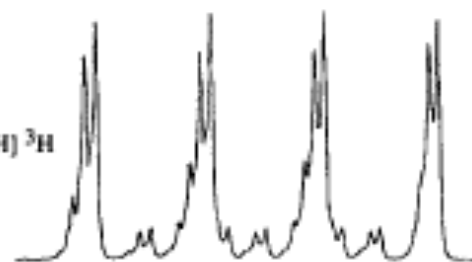
(d) [<sup>3</sup>H] <sup>11</sup>B Spectrum



(g) [<sup>11</sup>B] <sup>3</sup>H



(h) [<sup>1</sup>H] <sup>3</sup>H



(i) <sup>3</sup>H

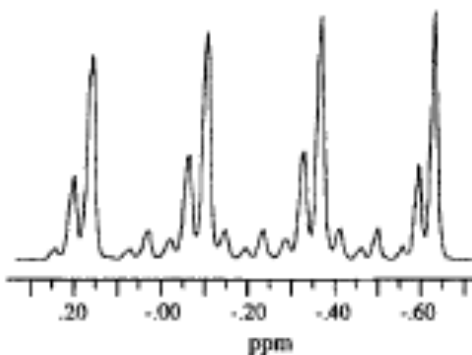


Figure 1. NMR spectra of LiB<sup>3</sup>H<sub>4</sub> in NaOH/CD<sub>3</sub>OD (a–d): (a)

D. Tritium Content = 78%.

NMR Spectra of NaBH<sub>4</sub> / T<sub>2</sub> Gas Exchange Product in 1M NaOH/CD<sub>3</sub>OD. ORY



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- R. C. Bowman, Jr., “Distribution of Helium in Metal Tritides,” *Nature* **271**, 531-33 (1978) [LiT, TiT<sub>x</sub>, UT<sub>3</sub>]
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- R. C. Bowman, Jr., A. Attalla, and B. D. Craft, “Isotope Effects and Helium Retention Behavior in Vanadium Tritide,” *Fusion Technol.* **8**, 2366-2372 (1985).
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- A. K. L. Yuen, et al. “Measurement of Long-Range Interatomic Distances by Solid-State Tritium-NMR Spectroscopy” *J. Am. Chem. Soc.* **132** (2010) 1734. (MAS & CPMAS <sup>3</sup>H NMR experiments).



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