Discovery of a New Species in the Hydrogen Chemistry of $NaAlH_4$ by *In Situ* NMR

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BES016

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$NaAlH_4$ for Reversible Hydrogen Storage

Well known stepwise reaction:

1) $NaAlH_4 \leftrightarrow 1/3\,Na_3AlH_6 + 2/3Al + H_2$ (3.7 wt %)

2) $Na_3AlH_6 \leftrightarrow 3NaH + Al + 3/2H_2$ (1.9 wt %)

Steps 1 and 2 found to be reversible with the introduction of Ti catalyst*. This is especially important for re-hydriding.

- Require mobility of Na and/or Al, not just H. (H/D exchange)

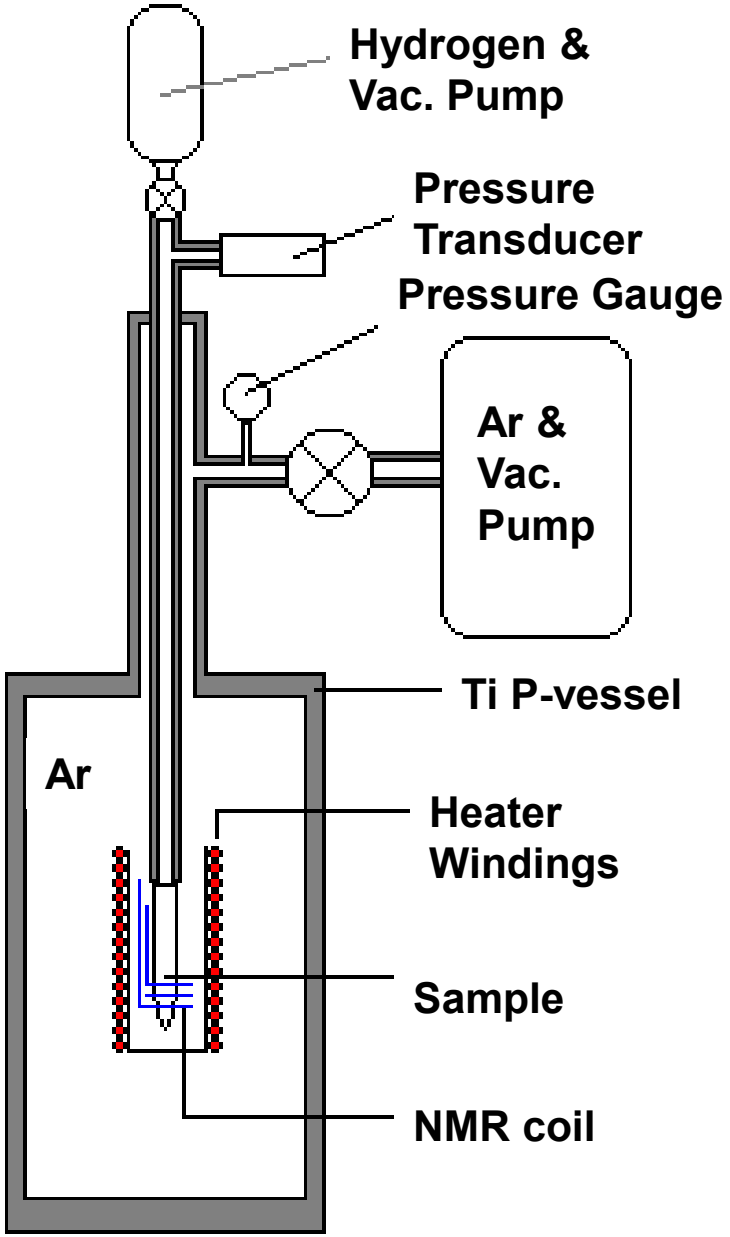
  Note: Na:Al ratio changes from 1:1 to 3:1 to 1:0 as one goes $NaAlH_4$ to Na_3AlH_6 to NaH

- Such mobile Na- or Al-bearing species are likely to be crucial chemical intermediates. While these may provide key understanding of the chemistry, they have yet to be directly detected.

- We report here the discovery of the candidate Al-bearing mobile species.

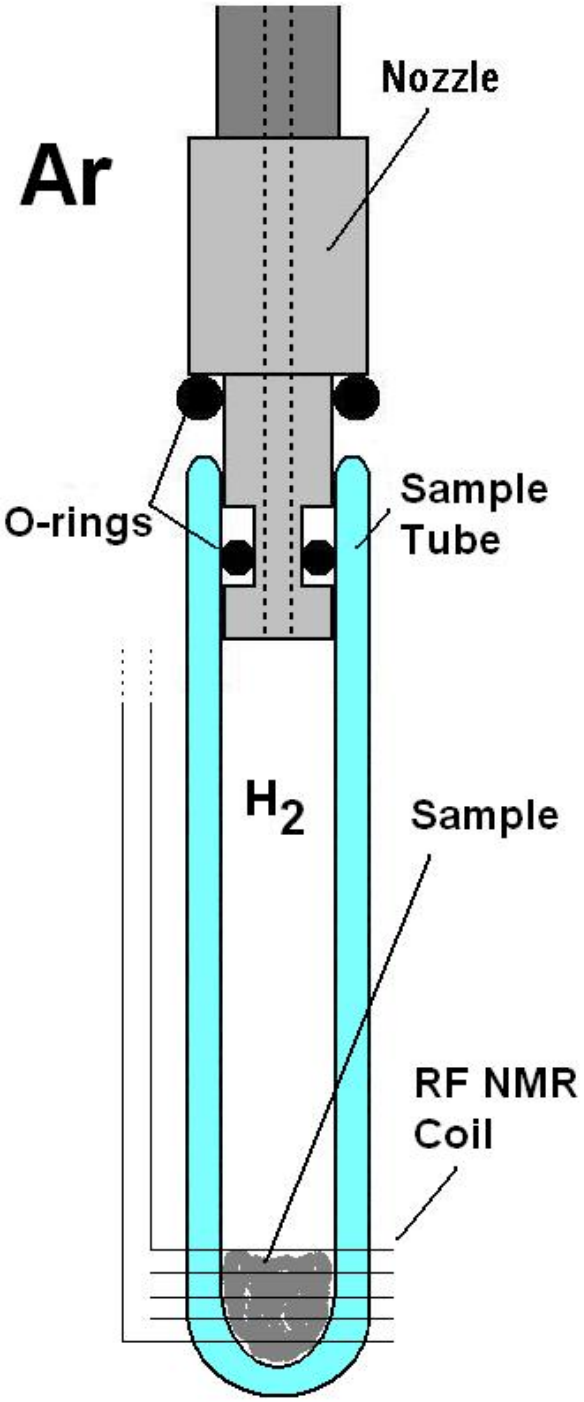
*B. Bogdanovic and M. Schwickardi, J. Alloys Compd. 253, 1 (1997)

High-T, High-P *In Situ* NMR Probe



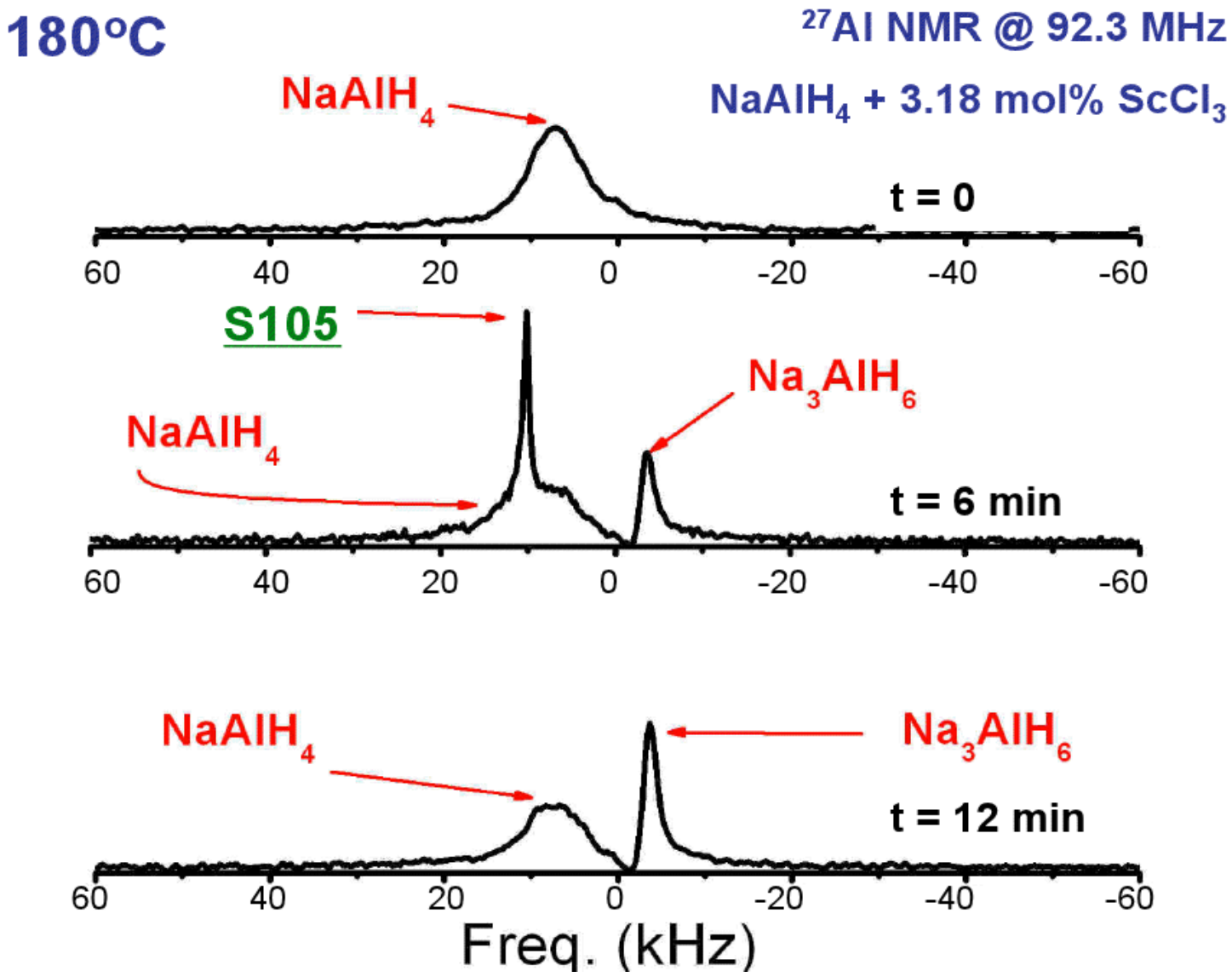
- *In Situ* NMR probe (shown) can presently go to 350°C, 6000 psi Ar (415 bars). 3000 psi H_2 (208 bars).
- Can react $NaAlH_4$ (doped with a few mol% Sc or Ti) in the pressure vessel while doing **^{27}Al NMR**, measuring pressure to monitor the reaction.
- Glass vessel, transparent to RF fields, is weak in tension but strong in compression – so we use high-P argon outside the glass.

Baker, Conradi, *Rev. Sci. Instrum.* 76, 073906 (2005).



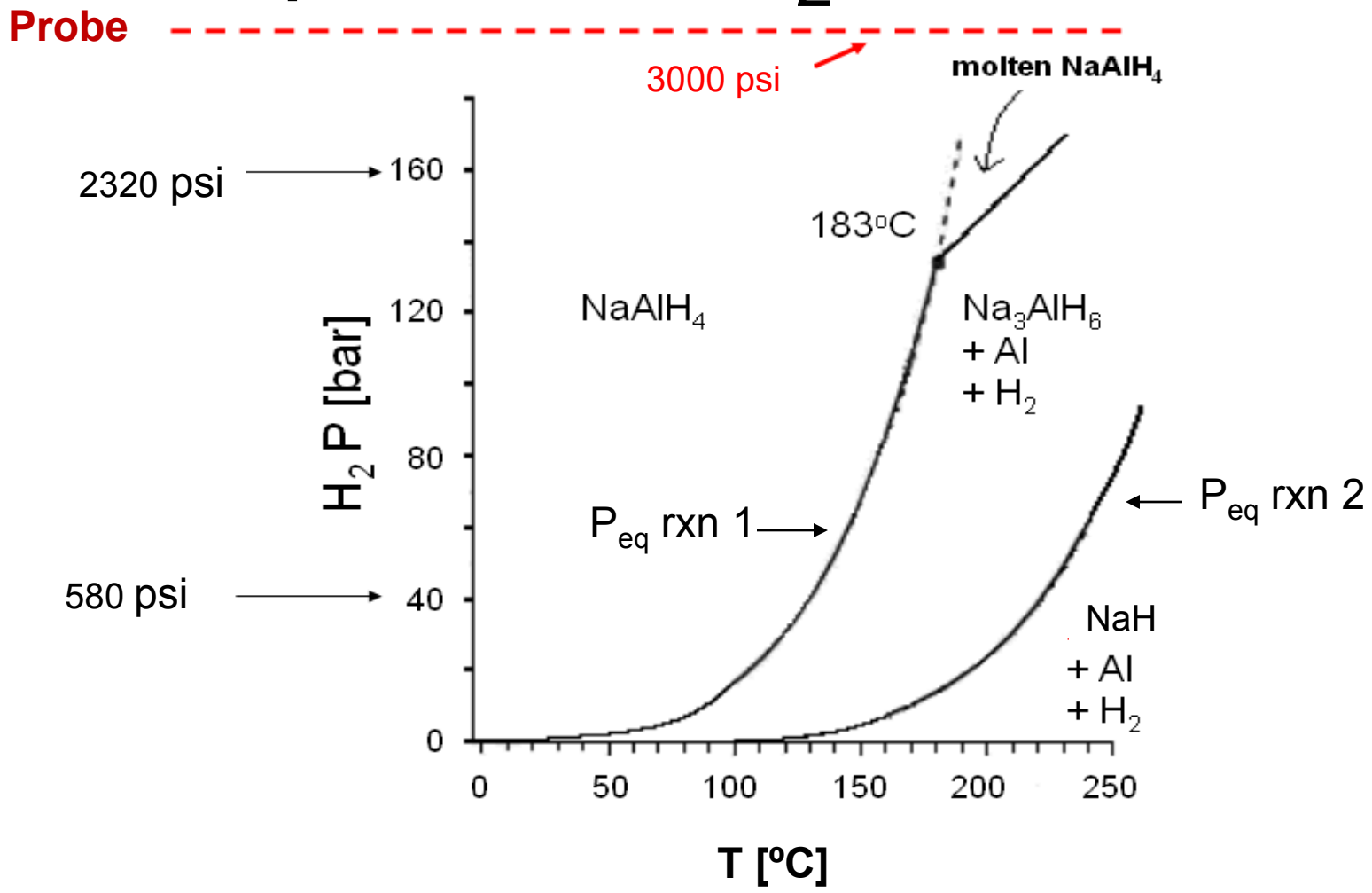
Probe Details

- Internally heated
- Water cooling coils
- Ar over-P surrounds all
- H_2 high-P volume small (less than 12 cc)



S105 is new and had not been seen before. It is narrow (so is very mobile) and Al-bearing. This could be our missing species responsible for metal-atom transport! But, S105 does not stick around and allow us to identify it.

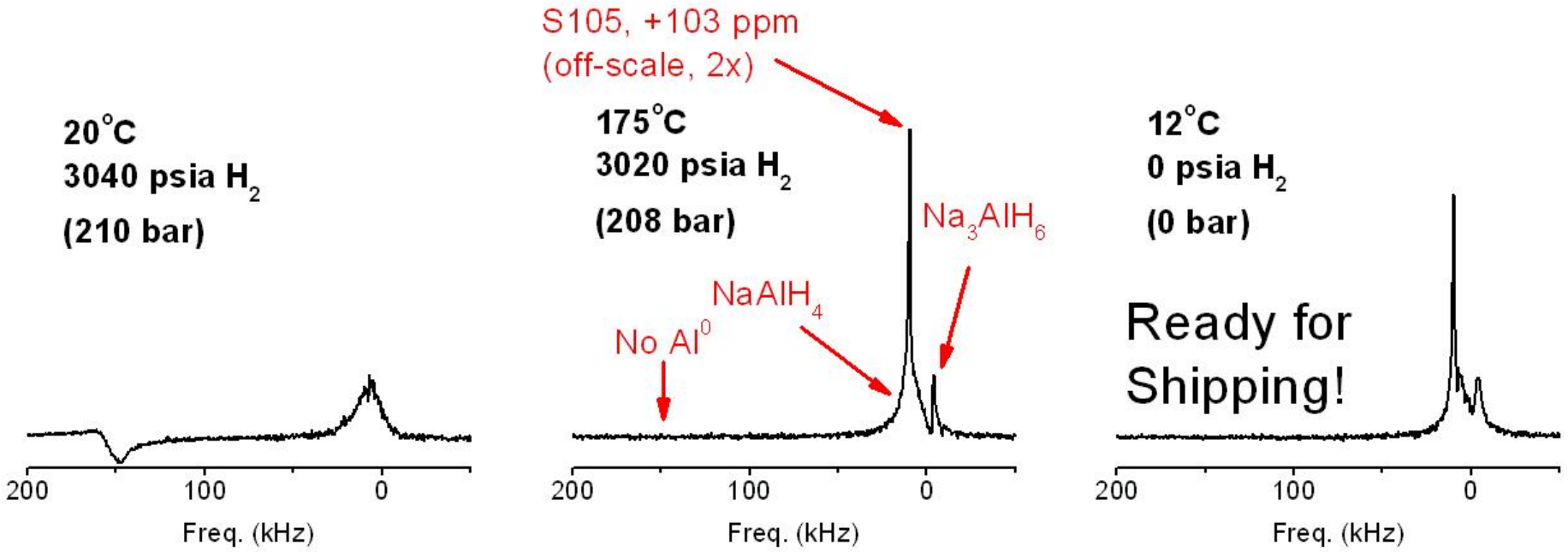
Equilibrium H_2 Pressure



- When P is greater than $P_{eq,}$ reaction is forced to left side.
- So at P=200 bar=3000 psi, we can prevent the sample "dehydriding away".
  But will we still see S105? Try it and find out!

B. Bogdanović, R.A. Brand, A. Marjanović, M. Schwickardi, J. Tölle, J. Alloys Compd. 302 (2000) 36–58

How to Generate and Preserve Species-M: Bringing S105 To Ambient

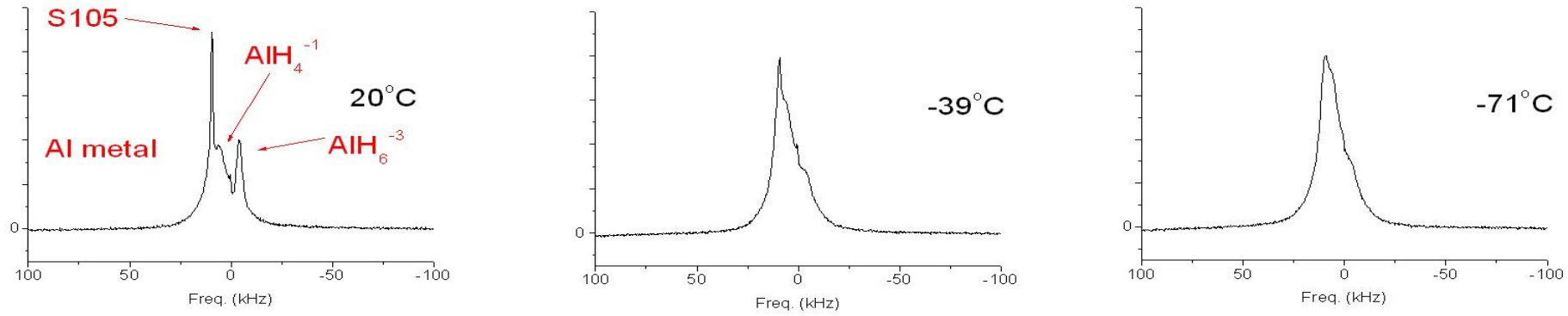


^{27}Al Spectrum, $NaAlH_4$ + 4 mol% $ScCl_3$

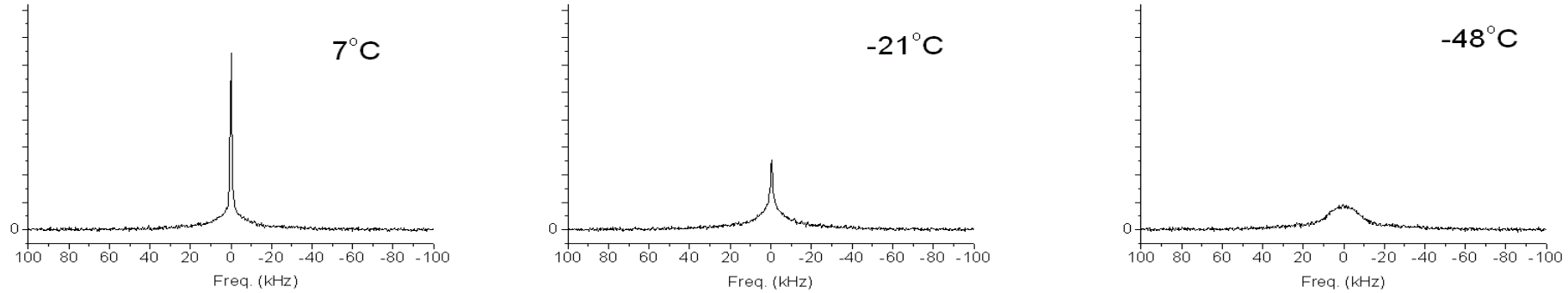
S105 remains at ambient conditions, so it can be studied by magic-angle spinning NMR, x-ray diffraction, etc. S105 can be shipped anywhere, as it is stable.

Note: whenever we see S105, it is accompanied by Na_3AlH_6 (but not Al metal).

S105 is Narrowed by Motional Averaging



^{27}Al Cold Spectra, undoped $NaAlH_4$



^{1}H, Cold Spectra

so <u>not</u> H_2 gas

Material from Aldrich

- S105 is narrow at room-T because of rapid motions.
- Whenever S105 is observed in ^{27}Al, there is also a sharp hydrogen NMR line.
- So this mobile species has Al and H (but no Na – sharp ^{23}Na signal never observed).

Summary

- New species S105 forms under reaction conditions.
  - P,T cycle allows recovery at ambient (doped or bare)
- NMR of S105 says highly mobile, Al_xH_y.
  - Very short ^{27}Al T_1
  - ^{27}Al is motionally narrowed
  - S105 has 15% of ^{27}Al intensity
  - Companion sharp peak in ^{1}H NMR
  - CPMAS at low-T confirms hydrogenated
- ^{27}Al shift very close to $NaAlH_4$.
- Diffraction says highly disordered.

Ivancic, Conradi et al, *J. Phys. Chem. Lett.* 1, 2412 (2010).

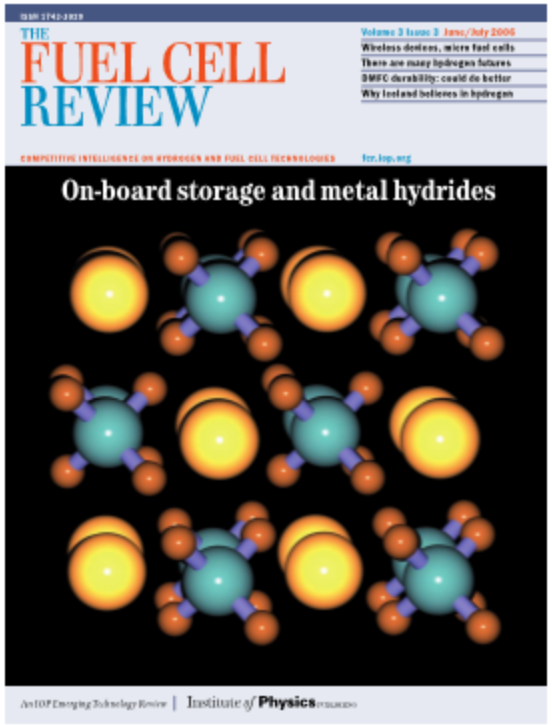
What is Species S105?

- We believe S105 is $NaAlH_4$ with a high vacancy concentration.
- Ozolins *et al*.* proposed:
  - $AlH_3^v \rightarrow H^- + AlH_4^- = AlH_5^{-2}$ complexes (hydrogen rich)
  - $NaH^v \rightarrow AlH_3 + AlH_4^- = Al_2H_7^-$ complexes (hydrogen deficient)
- AlH_3 vacancies would cause rapid diffusion of Al and H in large region.
- Explains naturally:
  - Motional narrowed lines
  - Shift, so similar to $NaAlH_4$
  - Disorder observed in diffraction
  - Large signal from relatively few vacancies
- See Eric Majzoub's new structure, too.

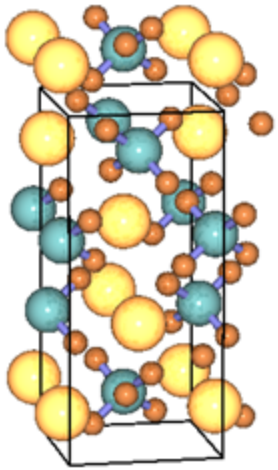
- Questions:
  - Why not 100% of ^{27}Al in S105?
  - Is this relevant to other complex hydrides ($LiBH_4$)?
  - What chemistry creates S105 + Na_3AlH_6?

*Ozolins *et al*., J. Phys. Conf. Ser. 180 (2009) 012076

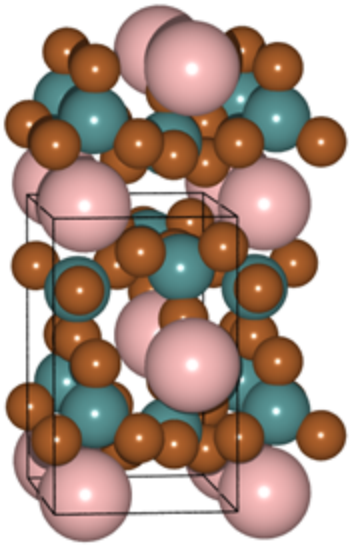
PEGS Method Used to Explore Structural Candidates for S105 Structure



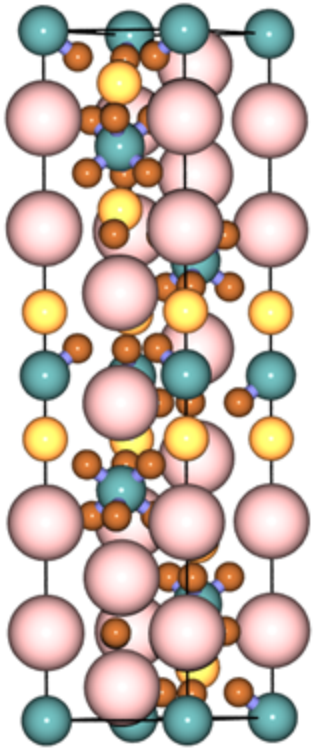
From Eric Majzoub, U Missouri at St. Louis, Physics



$NaAlH_4$



$Ca(BH_4)_2$



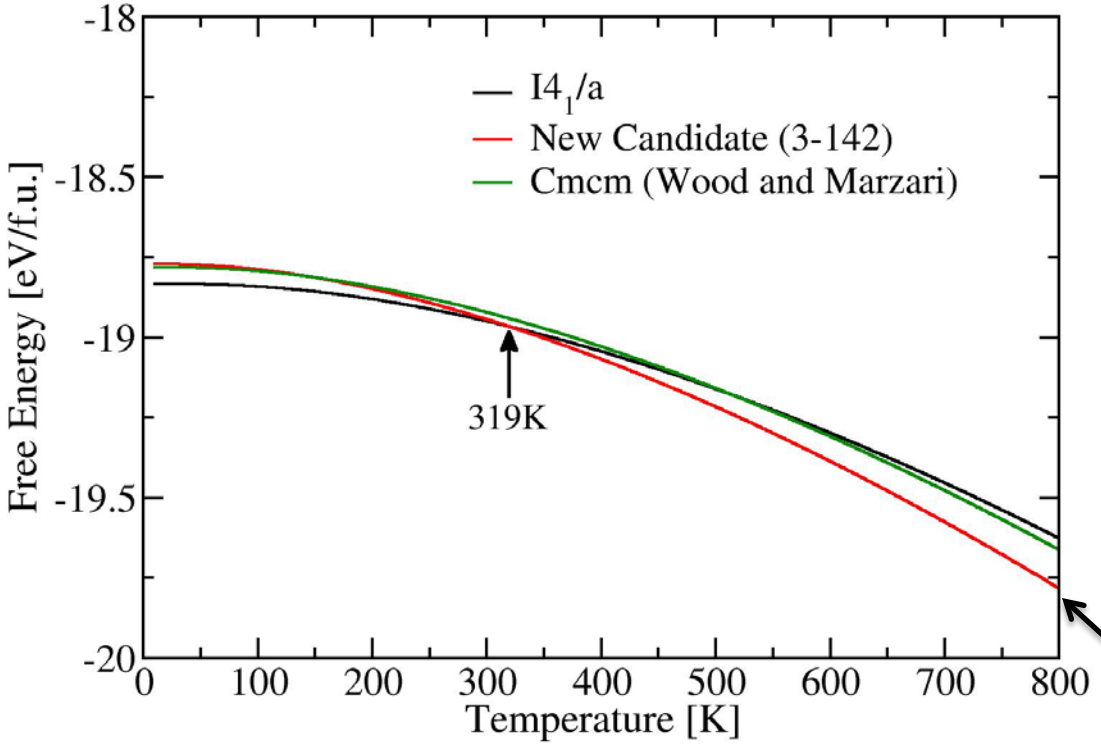
K_2LiAlH_6

First-principles calculated NMR Shifts using VASP in collaboration with G. de Wijs at Radboud University, Netherlands

Radboud Universiteit Nijmegen

- PEGS method - Majzoub & Ozolins, Phys. Rev. B, 77, 104115, (2008)

New High-T Phase Predicted in $NaAlH_4$



- **New PEGS candidate**
- Predicted to be the most stable phase at 320K
- ^{27}Al shift is calculated to agree with S105
- Lower free energy than Cmcm [Wood et al., PRL, **103**, 185901 (2009)]

Heat treated single crystals will be used to look for the S105 phase experimentally.

New PEGS predicted phase has lower free energy above 320K

Hydrogen NMR of Palladium-Hydride: Measuring the Hydride-Gas Exchange Rate

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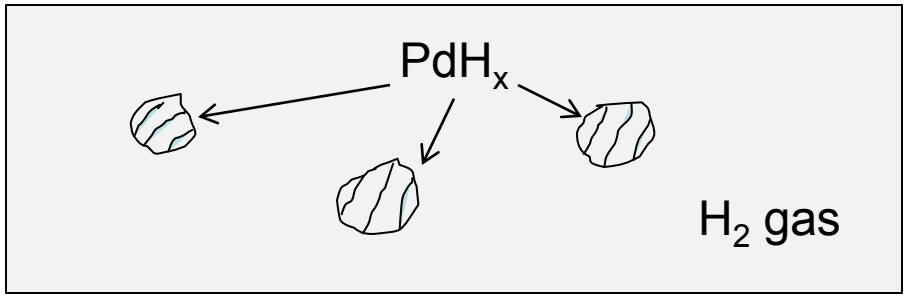
Introduction: PdH_x and Hydride-Gas Exchange



Dynamic equilibrium:
$Pd + (x/2)H_2 \leftrightarrow PdHx$

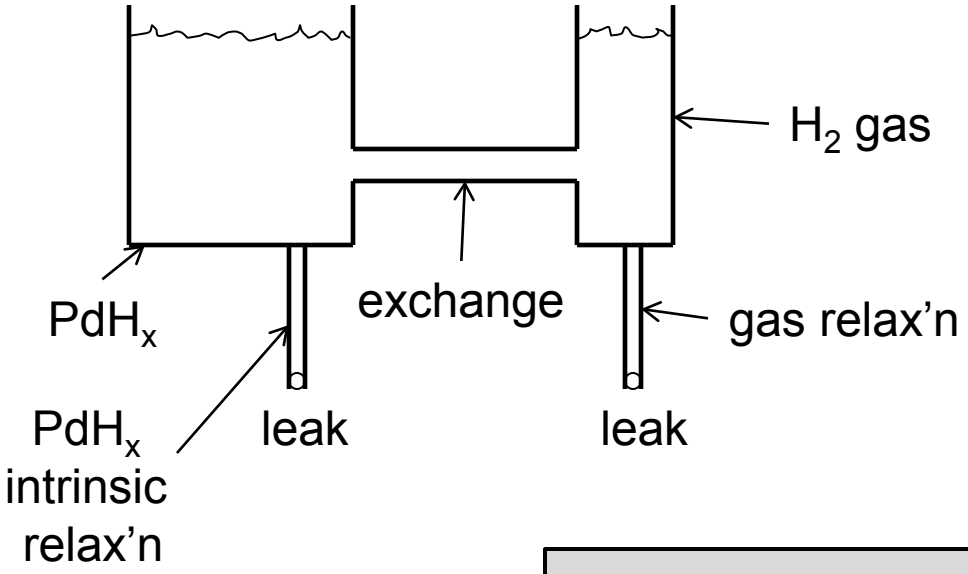
T_1 relaxation:

- T_1 in H_2 gas is short (~ms), because of short H-H bond and favorable τ_C
- Intrinsic T_1 of H in PdH_x ~200 ms. Comes from Korringa and BPP

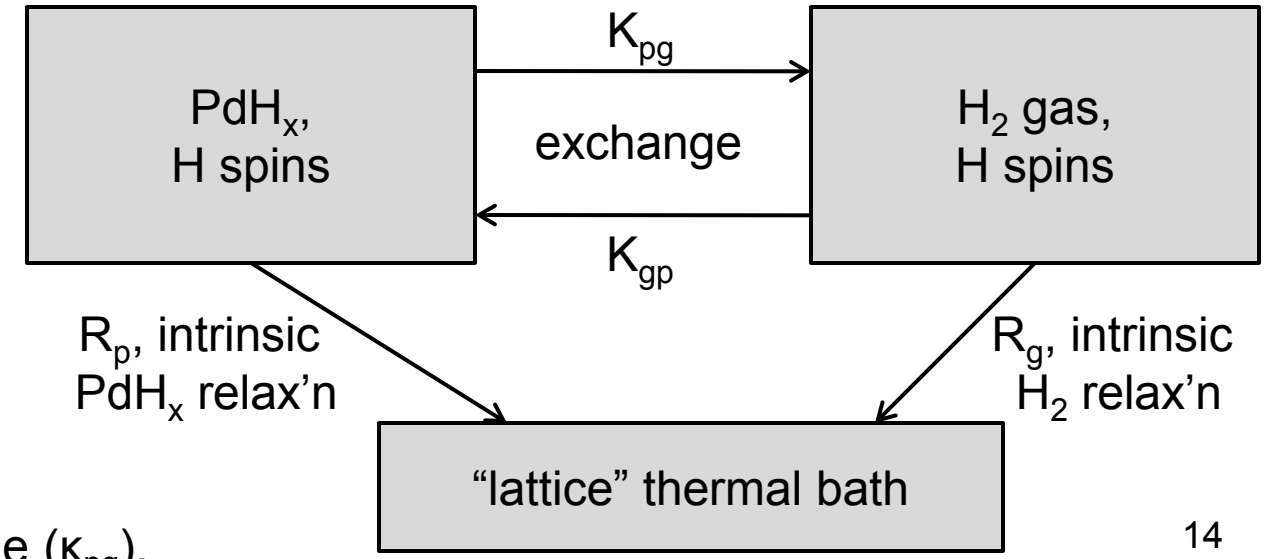
Idea: If exchange were rapid enough, <u>apparent</u> T_1 of hydride would be reduced. Could <u>measure</u> the exchange rate from apparent hydride T_1.

Simple case, limit: If $T_1^{gas}=0$, gas spins always at equilibrium. An H going from PdH_x to gas phase will be replaced by a fully relaxed H from the gas.

2 bucket analogy



H nuclear spins in PdH_x can relax via:
- intrinsic relaxation mechanism, or
- by <u>exchanging</u> with (very rapidly relaxing) gas phase.



- Can use this relaxation to measure rate of palladium-gas exchange (κ_{pg}).

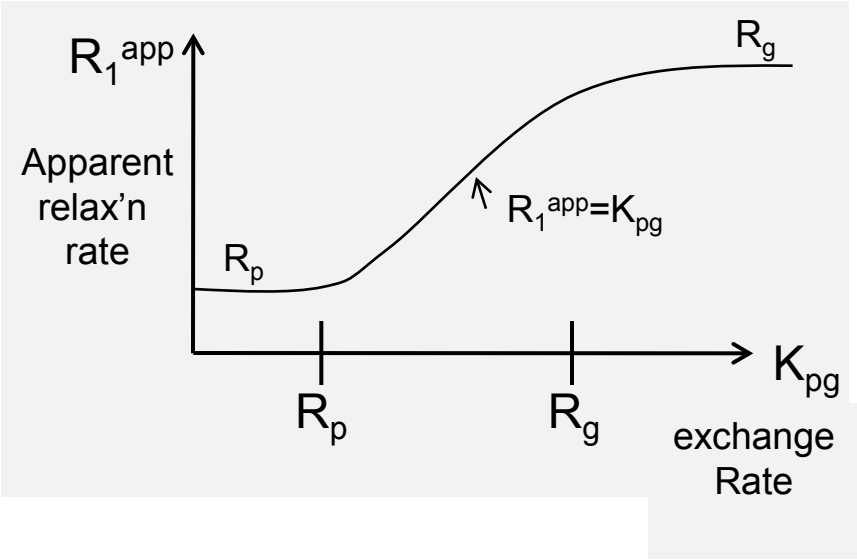
Summary of all the equations

1. For maximum impact of exchange on hydride phase apparent T_1, want $N_g \gtrsim N_p$. (Need lots of gas around PdH_x powder particles)
2. $\left(\frac{1}{T_1}\right)^{app} = \boxed{R_1^{app} \; is \; \cong K_{pg}}$, exchange rate, provided

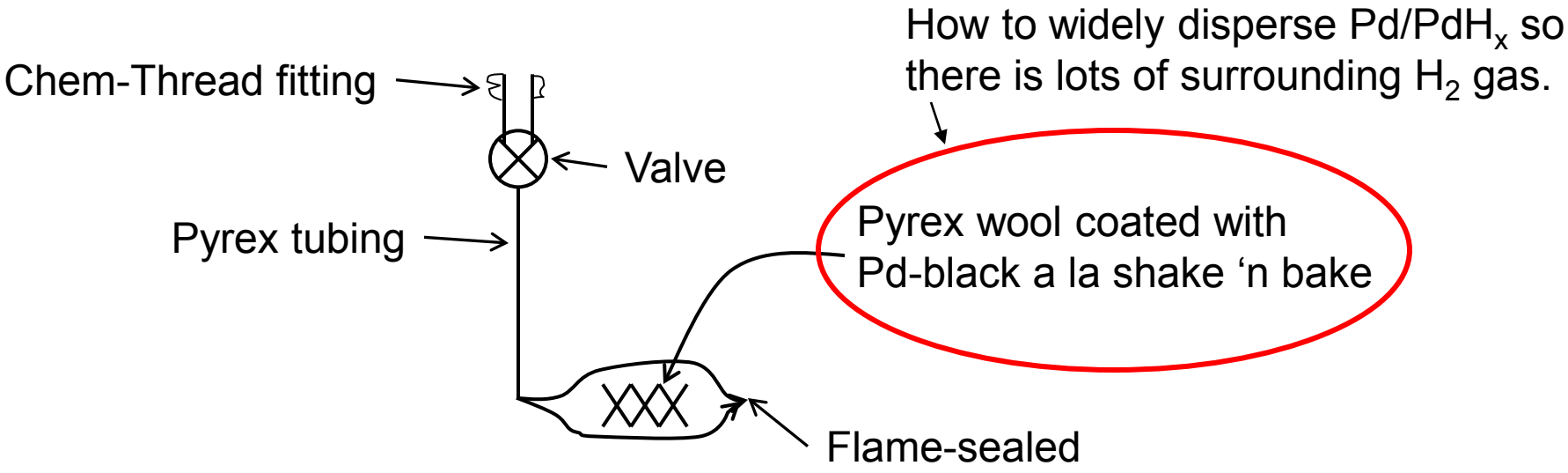
$$R_p \lesssim K_{pg} \lesssim R_g\left(\frac{N_g}{N_g+N_p}\right)$$

or, for $N_g \gg N_p$,

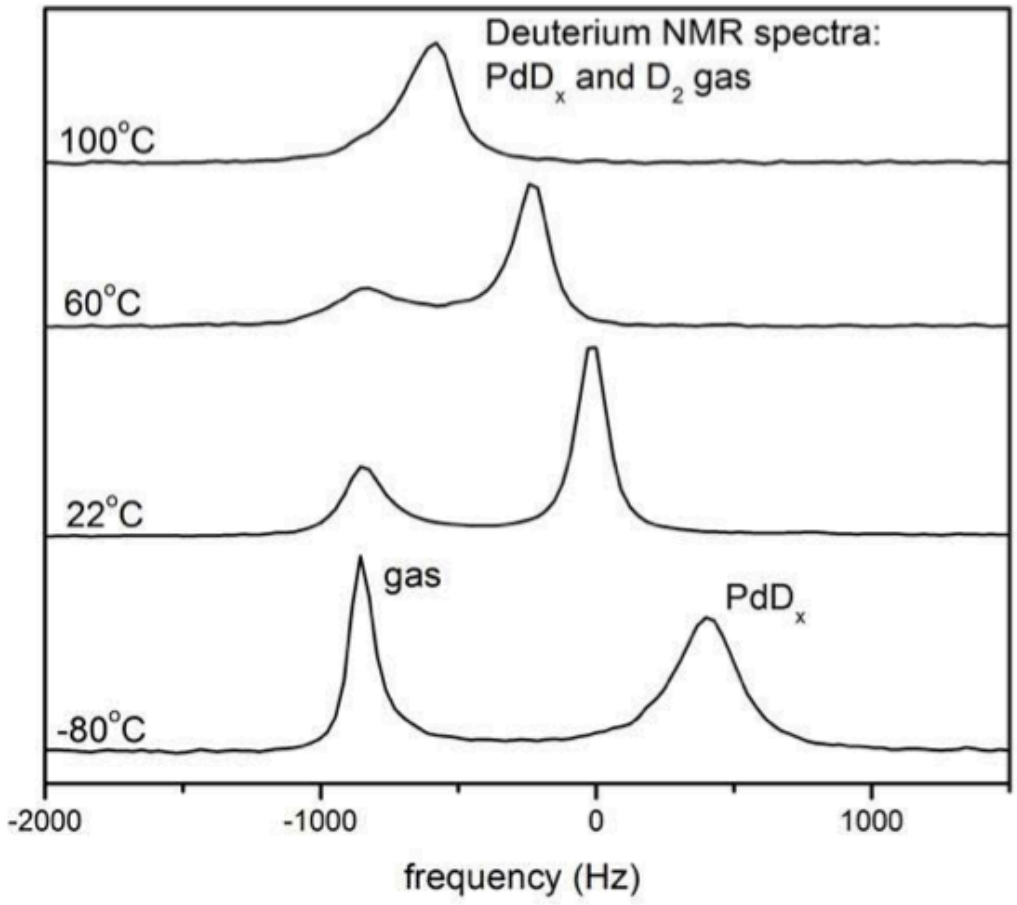
$$\boxed{R_p \lesssim K_{pg} \lesssim R_g}$$



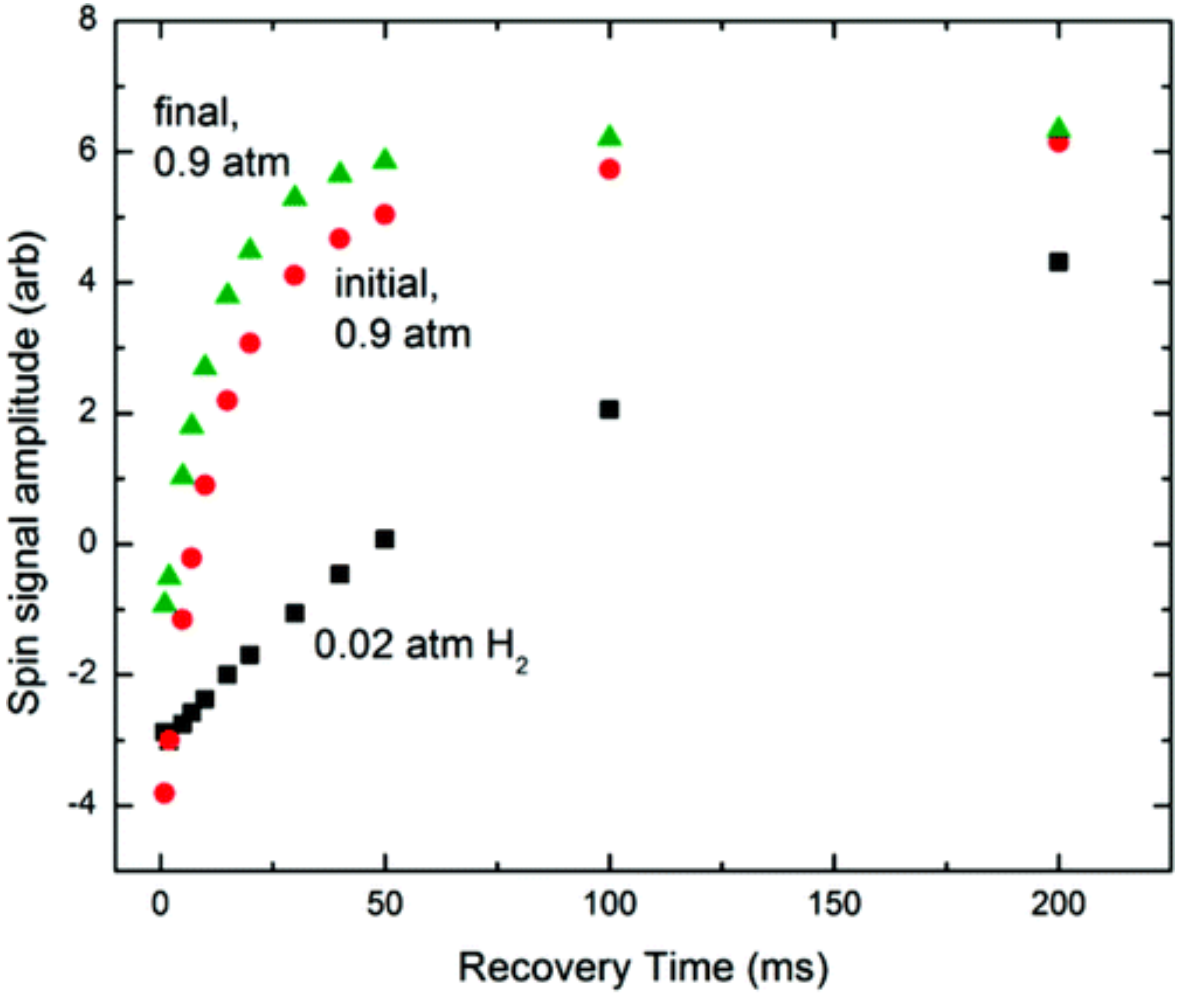
Sample Preparation



- Evacuate at 150ºC overnight
- At 100ºC, add 5 Torr H_2 and evacuate; 8 times
- At room-T, hydride to 0.9 bar and evacuate
- At room-T, hydride to 0.9 bar (and seal).

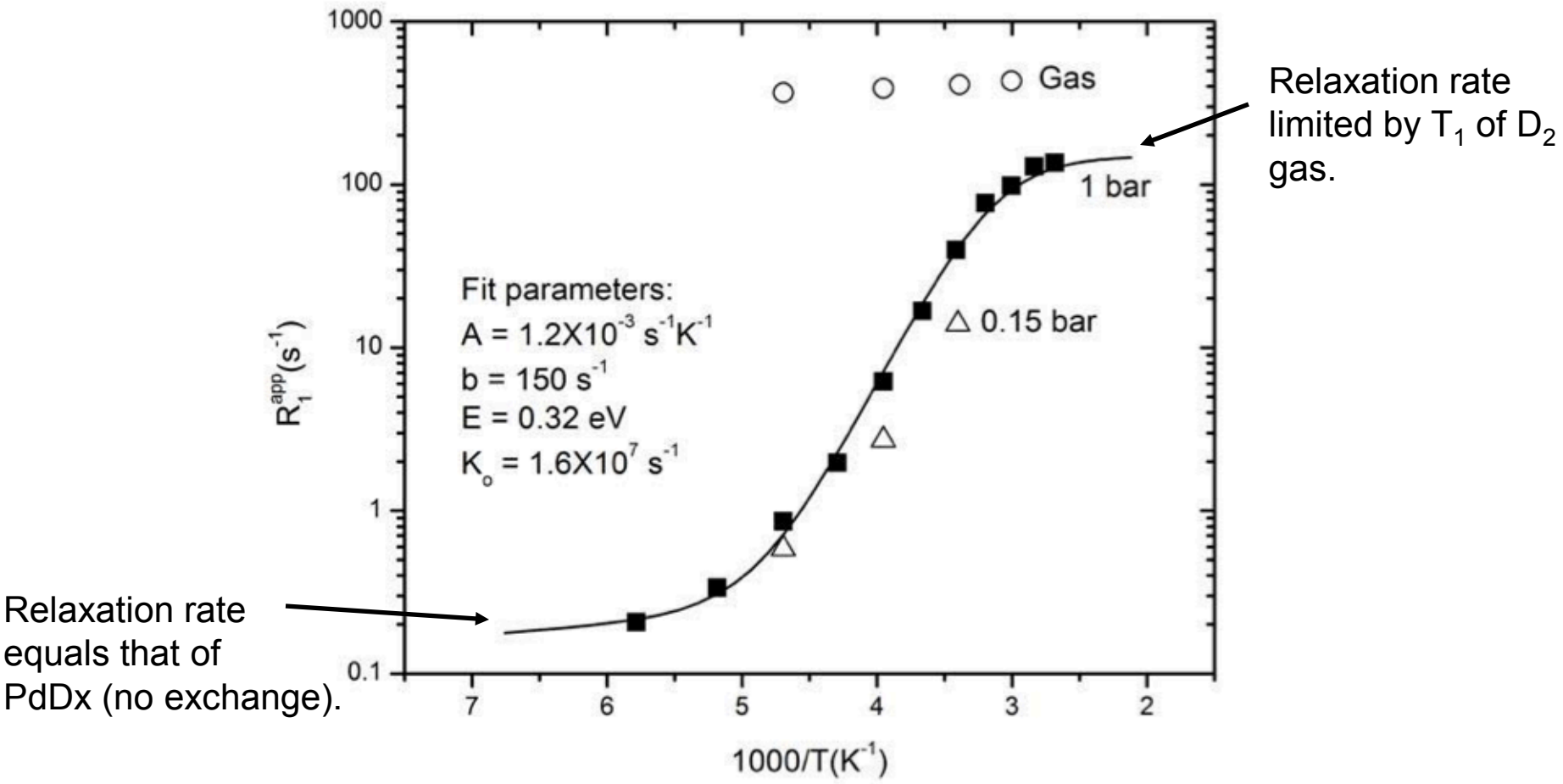


Deuterium NMR spectra of PdD_x and the surrounding D_2 gas at several temperatures. The 22°C spectrum shows that there are about half as many D nuclear spins in the gas as in the deuteride. At -80°C, PdD_x broadens due to the slowing of the internal motions. At 60°C, the gas resonance is broadened by gas-deuteride exchange; by 100°C, the resonances are partially merged.



Faster relaxation of green and red shows effect of PdH_x exchanging with H_2 gas.

Magnetization recoveries as functions of time following spin inversion. Palladium black well-dispersed on glass wool; with 0.9 atm H_2 (circles), 0.02 atm (squares), and after return to 0.9 atm (triangles). At low pressure, the exchange effect is blocked, decreasing the overall apparent rate of relaxation.



Nuclear spin-lattice relaxation rates R_1 for D_2 gas and for the deuteride resonance, for both 1.0 bar and 0.15 bar of surrounding D_2 gas. With less gas, the exchange enhancement of R_1^{app} is reduced. At 1.0 bar, R_1^{app} of the deuteride is limited at low temperatures by the intrinsic relaxation in the deuteride solid and at high temperatures by the gas phase relaxation, according to eqn. (3). In between, R_1^{app} is approximately equal to the exchange rate K_{pg}. The solid curve is a fit of eqns. (5) and (6) to the data.

Conclusions

- Can measure rate of hydride-gas exchange, to characterize surface quality.
- Exchange is measured at equilibrium.
- Compared to H/D isotope exchange, very fast exchange can be measured with our method.
- Exchange rate and activation energy very similar for PdH_x/H_2 and PdD_x/D_2 (0.32 eV).
- Will now study other, non-Pd systems.

NMR investigation of nanoporous γ-$Mg(BH_4)_2$

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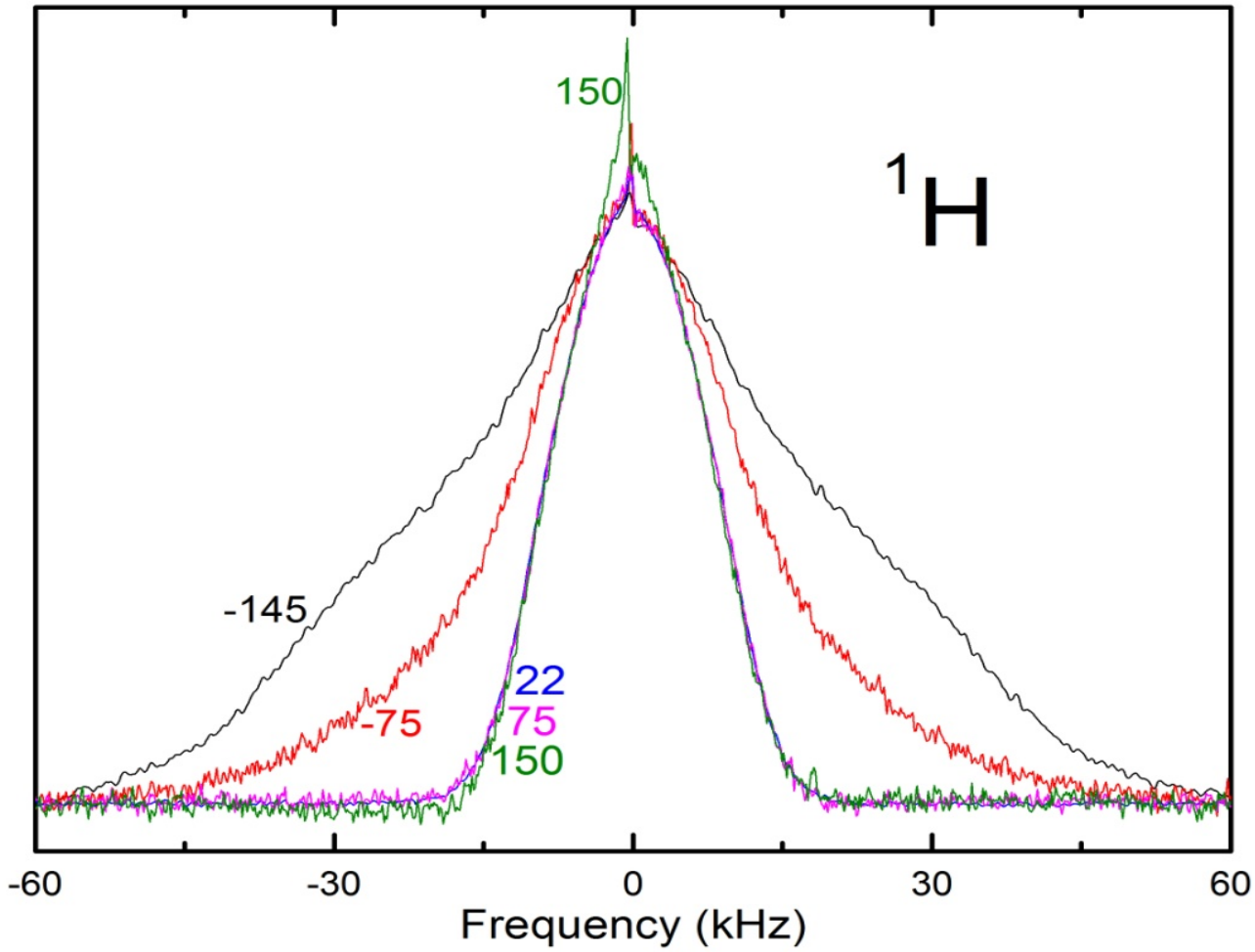
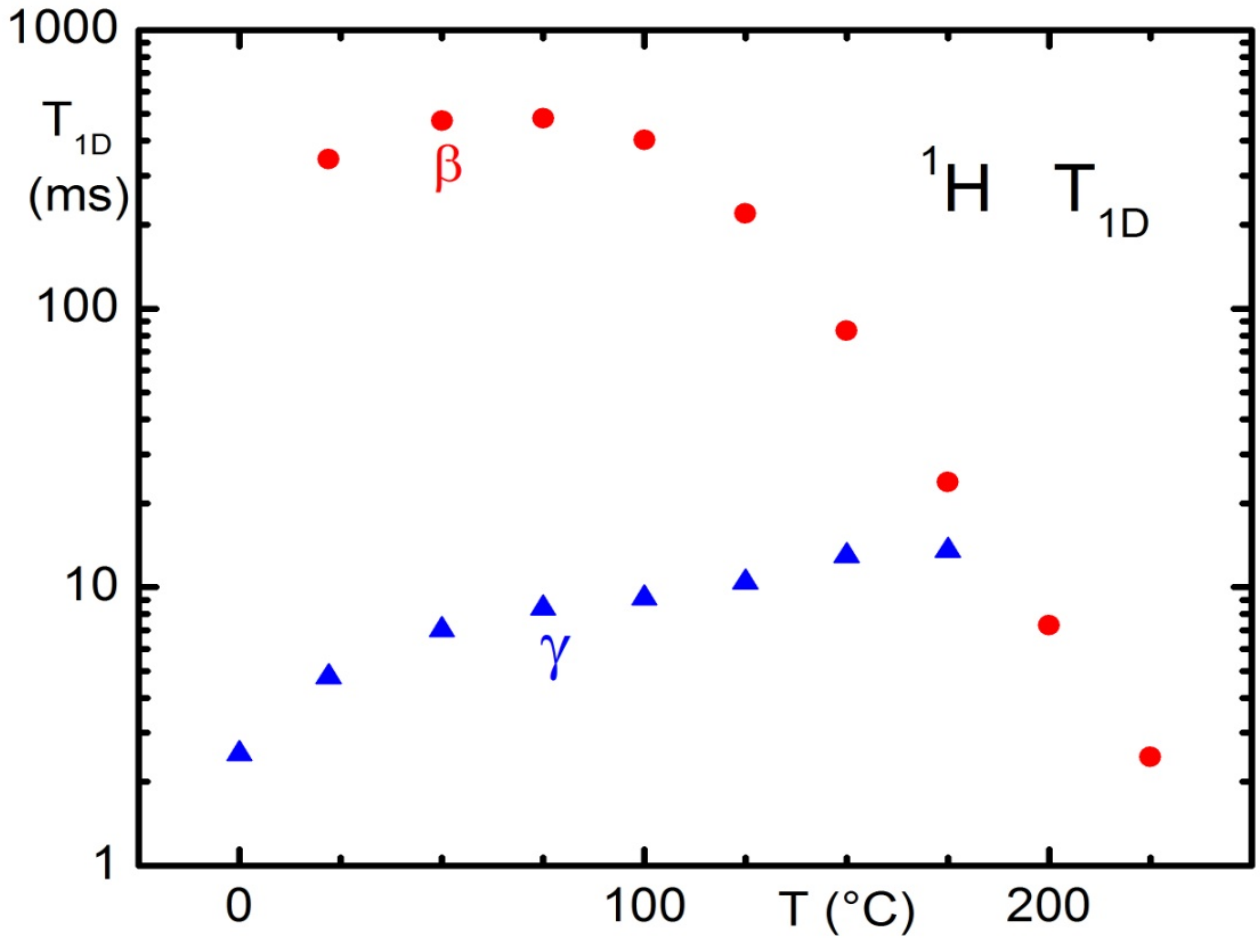
γ-$Mg(BH_4)_2$ has 33% open volume (!), so we may expect enhanced rate of diffusion (of BH_4^-, for example). Diffusion of these species is crucial to dehydriding and rehydriding reactions.



No line narrowing up to 150ÁC, so no sign of enhanced BH_4^- diffusion.

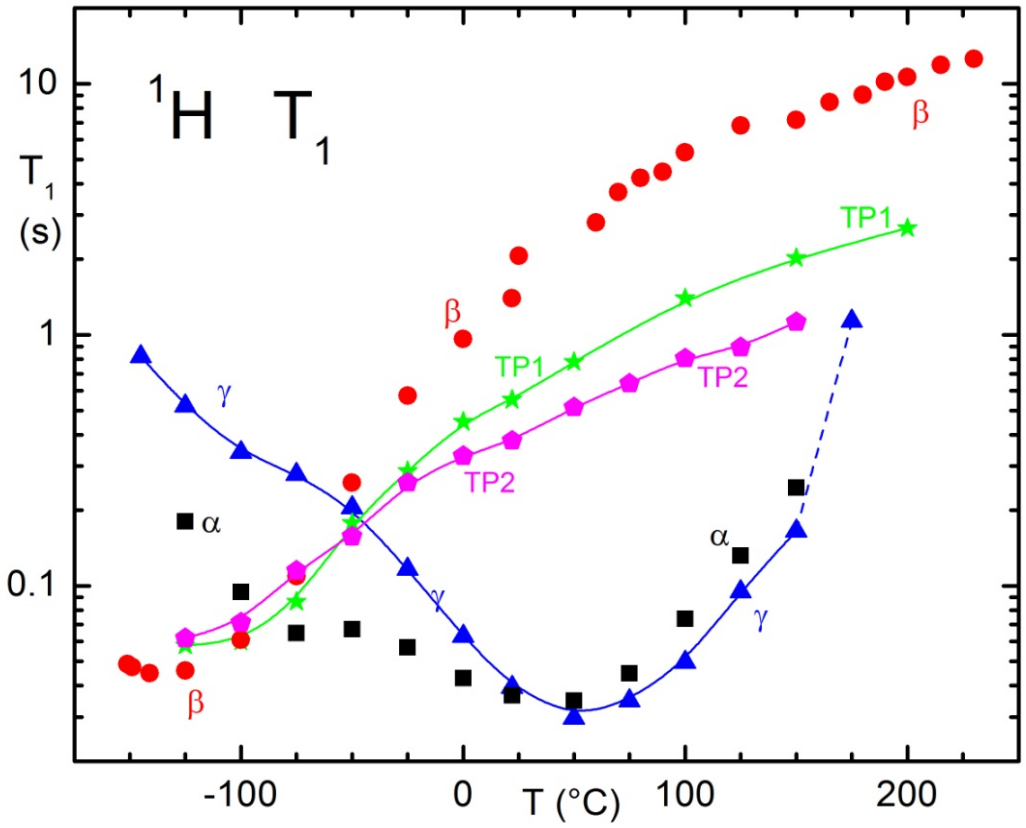
Hydrogen NMR spectra of γ-$Mg(BH_4)_2$ at several temperatures. At -75 and -145°C, pronounced broadening is due to slowing of the BH_4 reorientations. At and above 22°C, no further narrowing of the main resonance occurs, ruling out rapid BH_4 translational diffusion. At the highest temperature, a narrow component appears, reflecting a small fraction of mobile spins, probably from residual solvent.



T_{1D} is sensitive to hopping motion too slow to narrow the NMR line.

But again we see no evidence of BH_4^- diffusion.

Hydrogen NMR measurements of T_{1D} in γ-$Mg(BH_4)_2$, together with β-phase data from reference Q for comparison. In γ-phase, there is no sharp decrease in T_{1D} at elevated temperatures that would signal thermally activated diffusive hopping with rates 10^2 s^{-1} or faster. Again, no sign of BH_4^- diffusion.



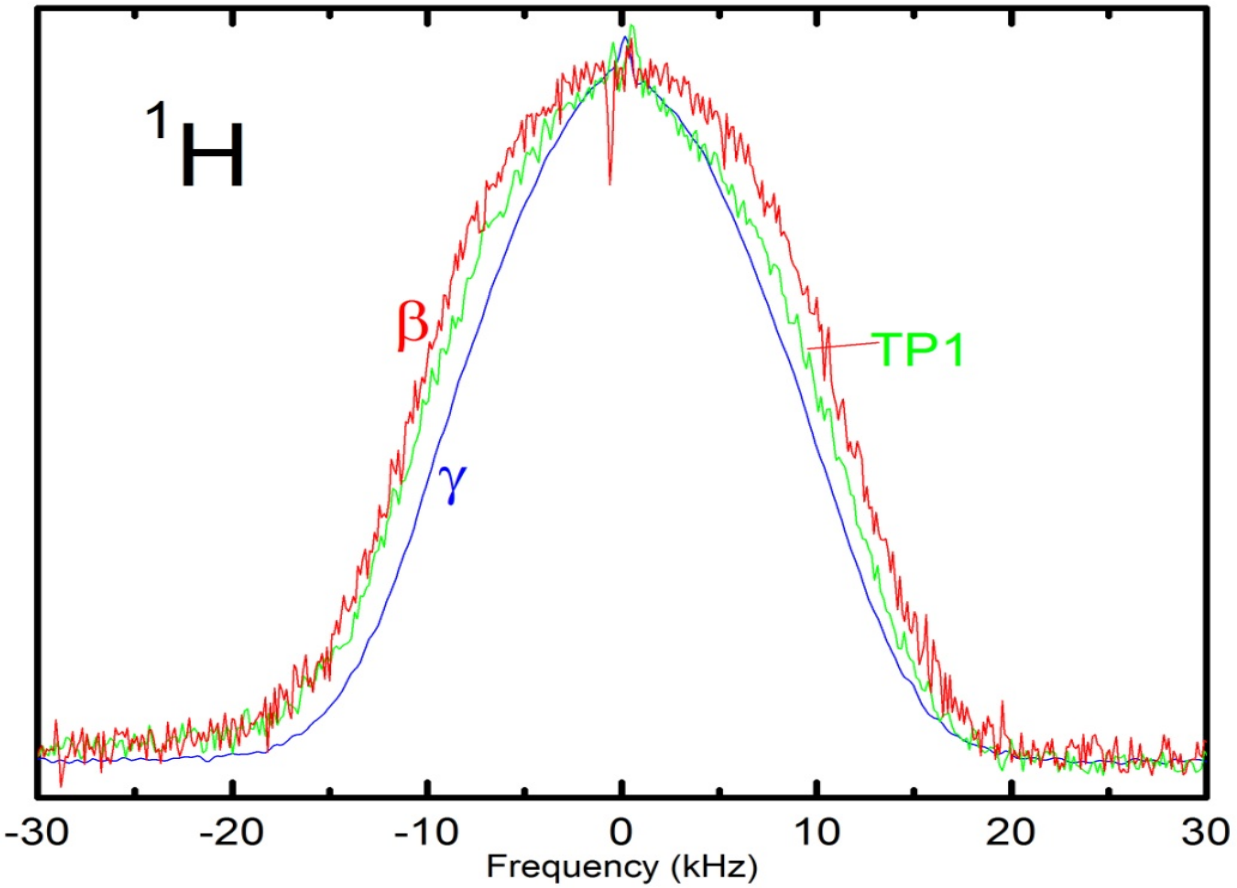
T_1 is controlled fully by BH_4^- reorientations.

In γ, the activation energy is high, as in α.

In β, the activation energy is low.

TP1=result of γ transforming at 175-200°C

Hydrogen NMR T_1 of $Mg(BH_4)_2$. Results are shown (triangles) for γ-phase material from -150 to 175°C; the sharp increase above 150°C (dashed line) shows the transformation to a new structure, TP1. The transformation was completed at 225°C; T_1 of the transformation product TP1 down to -125°C appears (stars). A second sample was transformed to yield TP2 (pentagons). See text for description of temperature cycling histories. For comparison, T_1 of α-phase (squares) and β-phase (circles) is shown.



Hydrogen NMR spectra, all at 22°C. Data are presented for γ-phase and β-phase materials, as well as the transformation product TP1, formed from γ by heating to 225°C.

Linewidths: γ < TP1 < β

Linewidth reflects density because dipole interactions vary as $1/r^3$.

Conclusions

- Despite the large 33% of vacant space in γ-$Mg(BH_4)_2$, there is no sign of BH_4^- diffusion up to 150°C.
- Neither line narrowing nor short T_{1D} is found.
- BH_4^- reorientations have high barrier, like α- and unlike β-phase.
- At approximately 175-200°C, gamma transforms to a denser structure similar to β (from its T_1 behavior and from x-ray diffraction).

NaH – a simple ionic hydride

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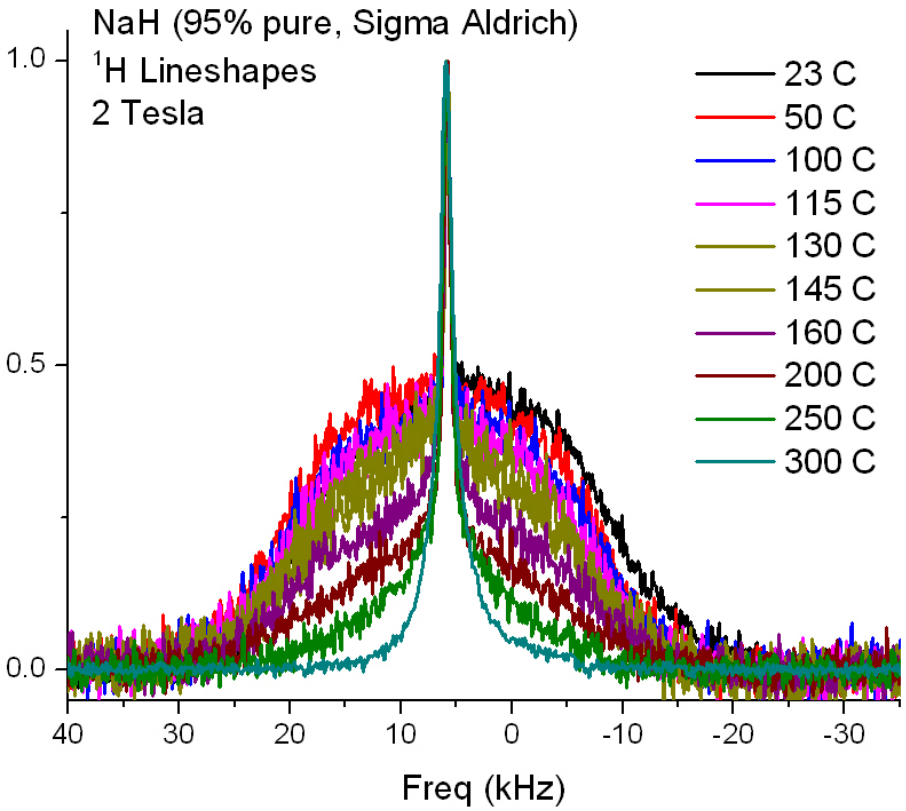
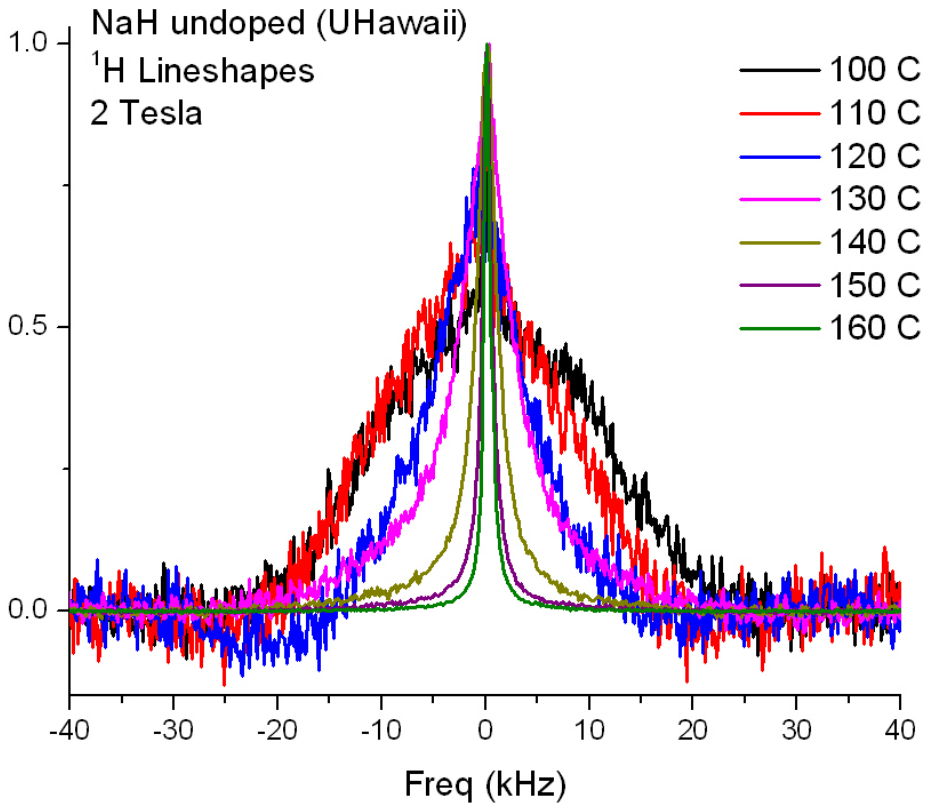
Mark S. Conradi	*Washington U. Physics Dept.*

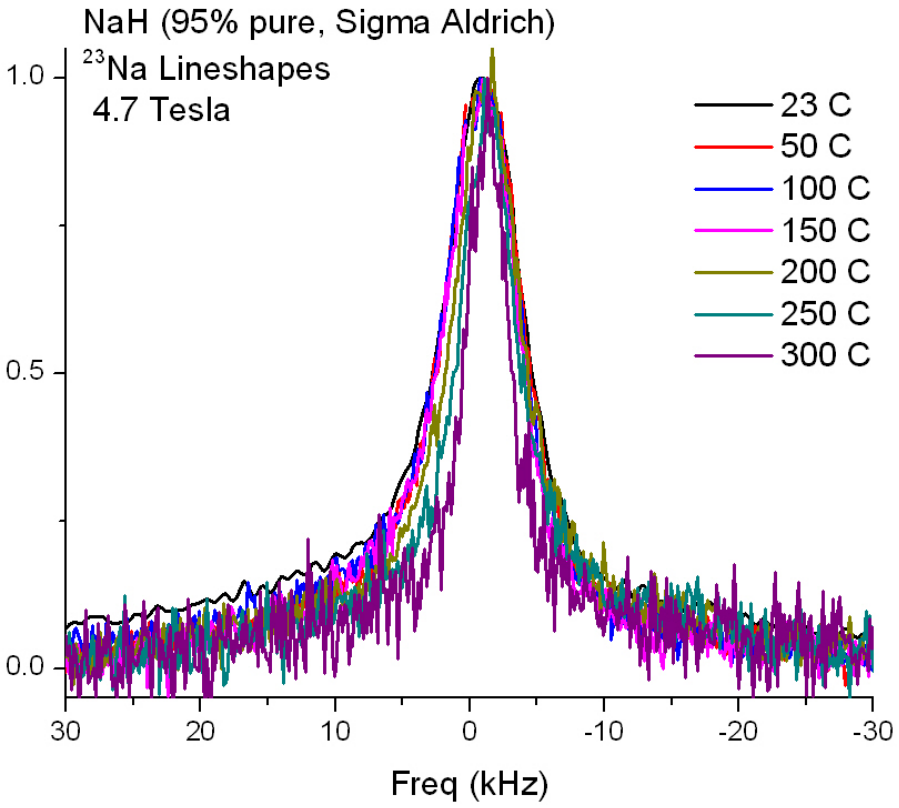
NaH is an archetype of ionic hydrides. This study of NaH continues our program (in past, MgH_2 and $NaMgH_3$).

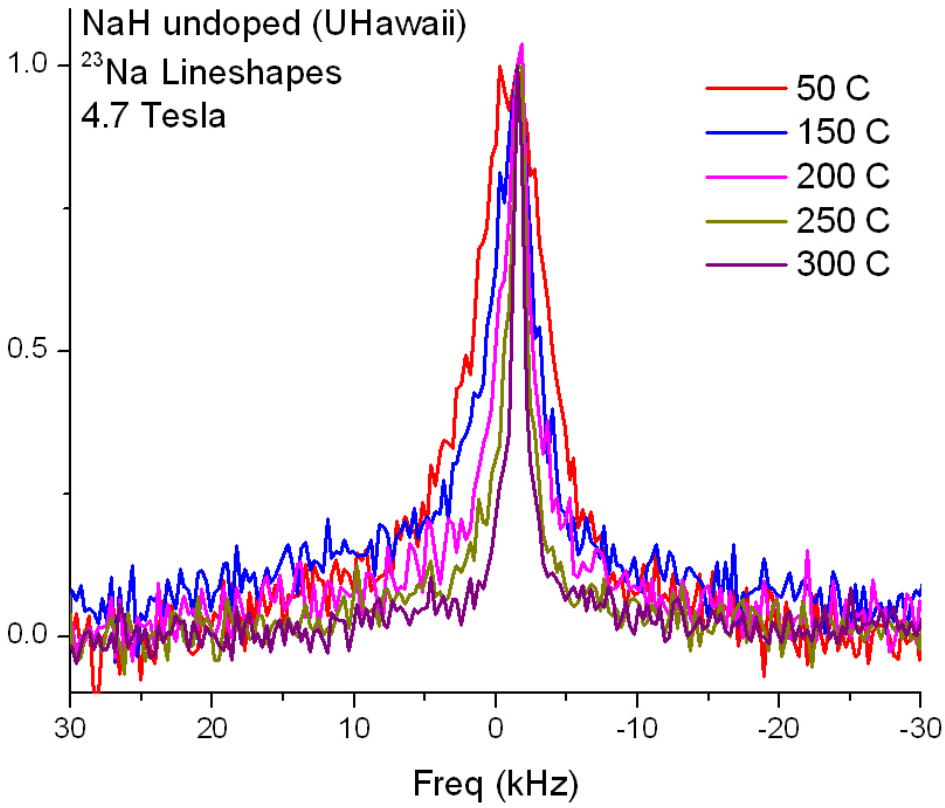




As T increases, the fraction of H that is mobile (line narrowed) grows.
Fraction of immobile H decreases.
In other ionic hydrides, we identified mobile H as those near defects (grain boundaries, for example).
Immobile H are in crystallite interiors.
Above 250°C, the remaining broad component motionally narrows.

In this ball-milled NaH from Craig Jensen at U. Hawaii, we see only a narrowed component by 160°C





Even at 300°C, the 23Na line has narrowed by only a factor of 2.
This shows: H^- hopping averages to zero H-H and H-Na dipole interactions, but not the Na-Na terms. So Na^+ is not diffusing by 300°C.

In UHawaii ball-milled NaH, Na^+ diffusion is rapid by about 300°C, as seen by narrow ^{23}Na line.

Conclusions

- Coarse-grain Aldrich NaH shows a narrow (mobile) fraction of H that grows with temperature, in common with MgH_2 and $NaMgH_3$.

- The ball-milled UHawaii NaH is completely narrowed by 160°C, indicating that defects from ball milling increase H mobility.

- Sodium motion does not occur in coarse Aldrich NaH up to 300°C. But Na diffusion is evident in ball-milled UHawaii NaH.