

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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NaAlH₄ for Reversible Hydrogen Storage

Well known stepwise reaction:



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

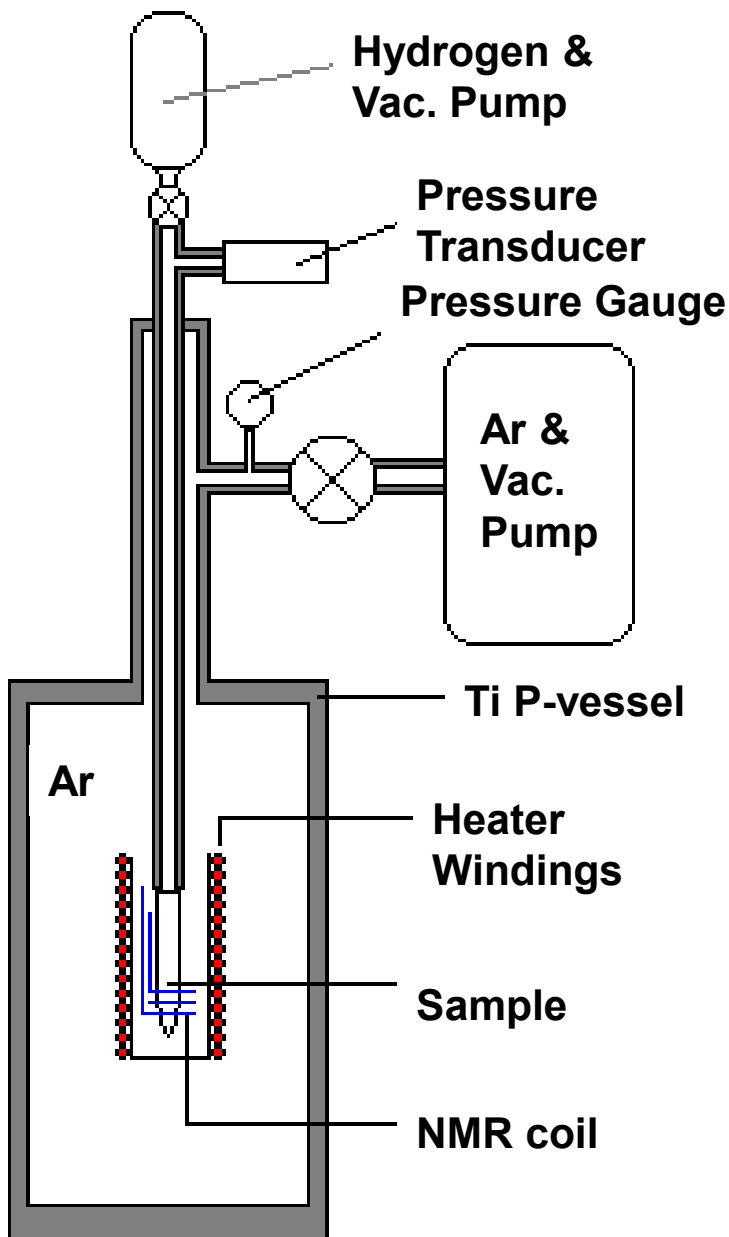
- Require mobility of Na and/or Al, not just H. (H/D exchange)

Note: Na:Al ratio changes from 1:1 to 3:1 to 1:0 as one goes
NaAlH₄ to Na₃AlH₆ 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.

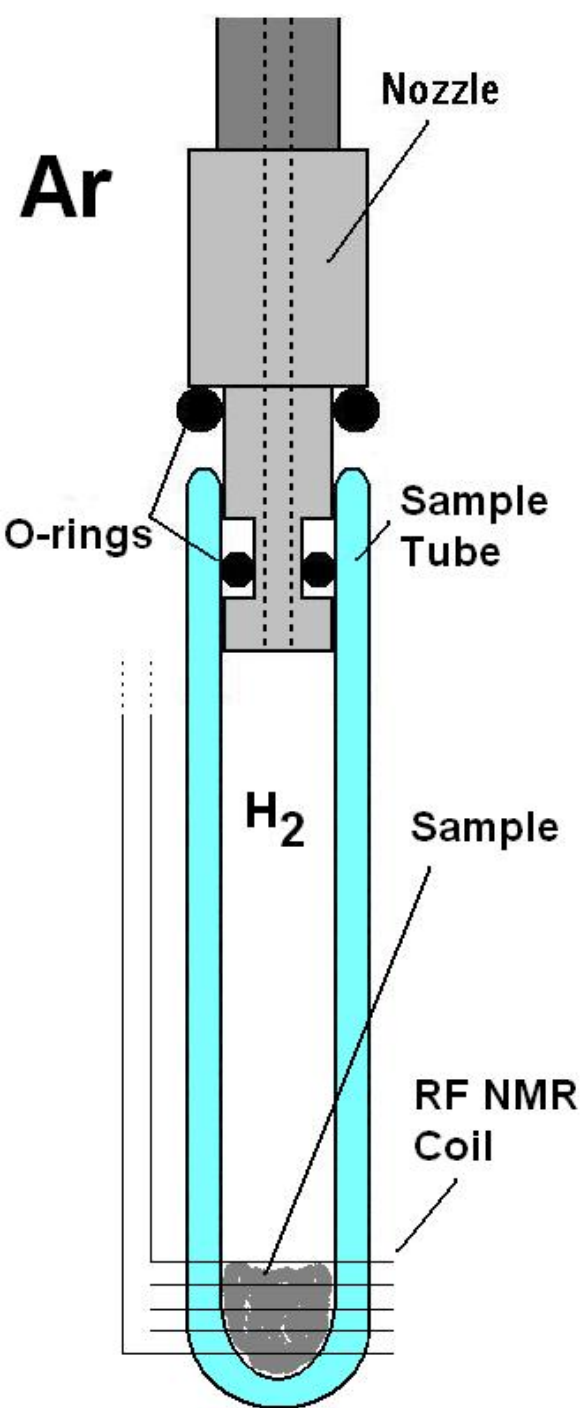
*B. Bogdanovic and M. Schwickardi, J. Alloys Compd. 253, 1 (1997)

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 H₂ (208 bars).
- Can react NaAlH₄ (doped with a few mol% Sc or Ti) in the pressure vessel while doing ²⁷Al 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.

Probe Details

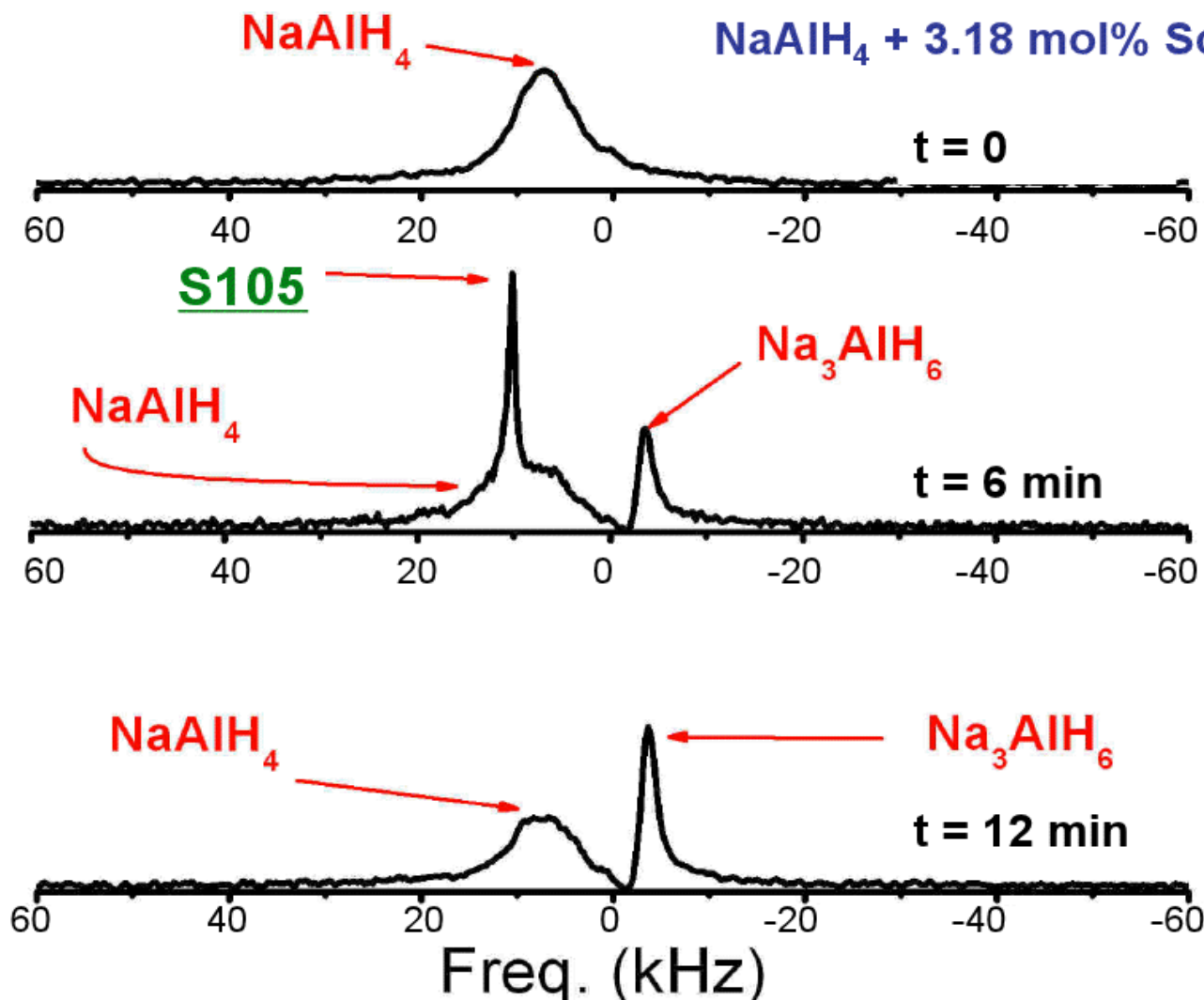


- Internally heated
- Water cooling coils
- Ar over-P surrounds all
- H₂ high-P volume small (less than 12 cc)

180°C

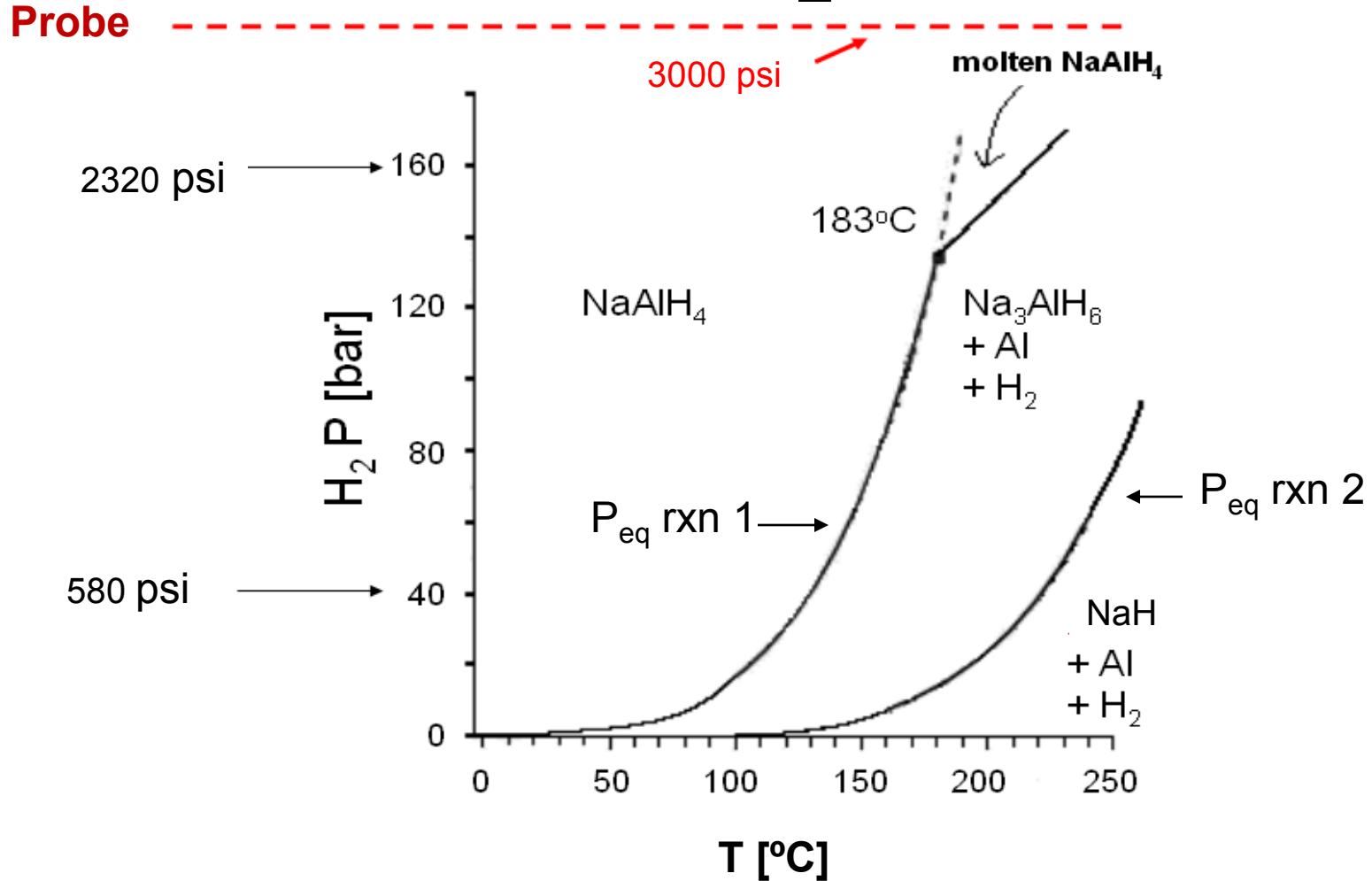
^{27}Al NMR @ 92.3 MHz

$\text{NaAlH}_4 + 3.18 \text{ mol\% ScCl}_3$



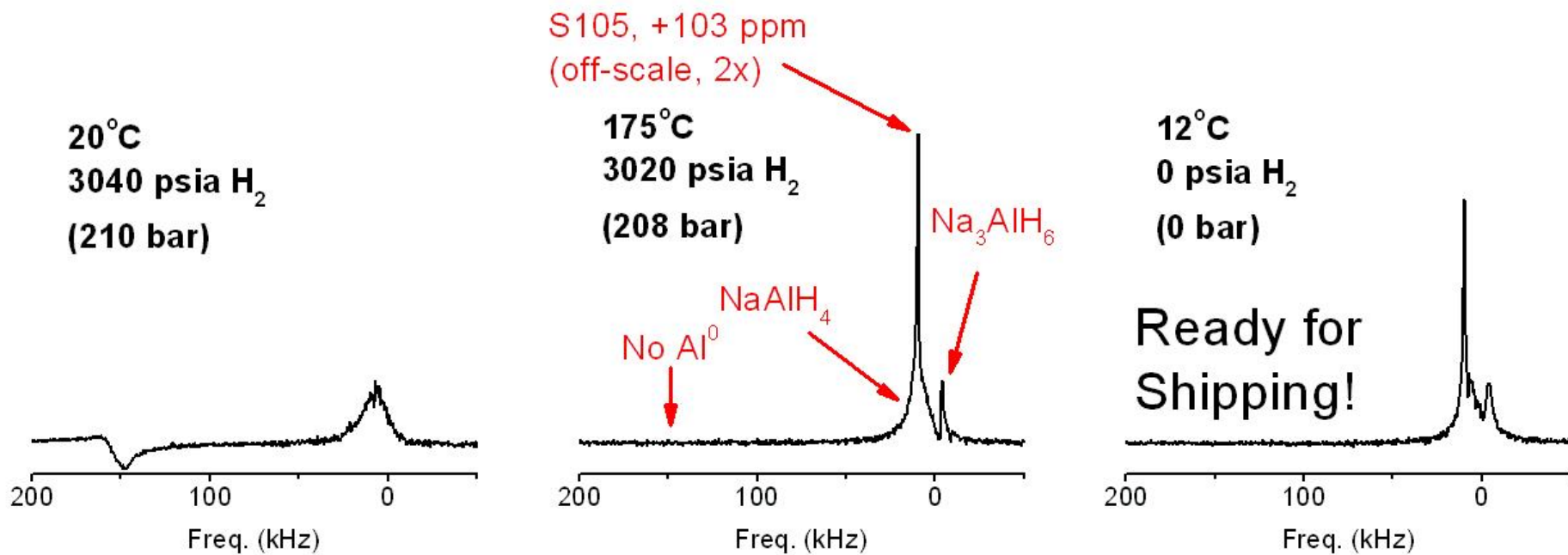
S105 is new and had not been seen before. It is narrow (so is very mobile) and Al-bearing. This could be our missing species responsible for metal-atom transport! But, S105 does not stick around and allow us to identify it.

Equilibrium H₂ 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 “dehydrating away”.
But will we still see S105? Try it and find out!

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

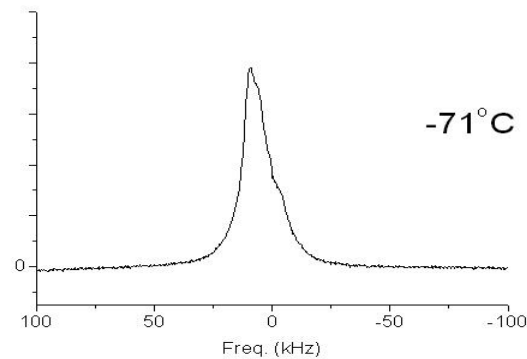
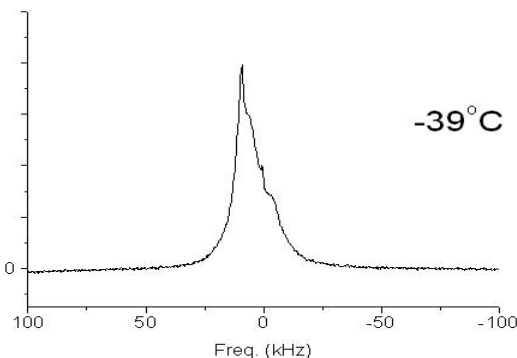
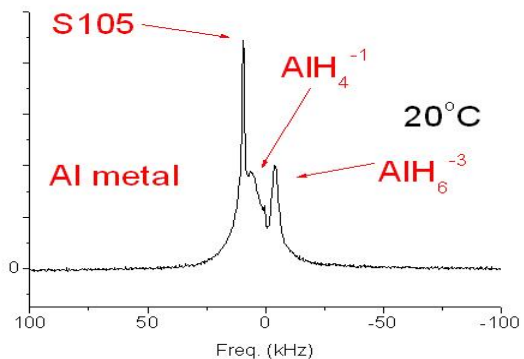


^{27}Al Spectrum, $\text{NaAlH}_4 + 4 \text{ mol\% ScCl}_3$

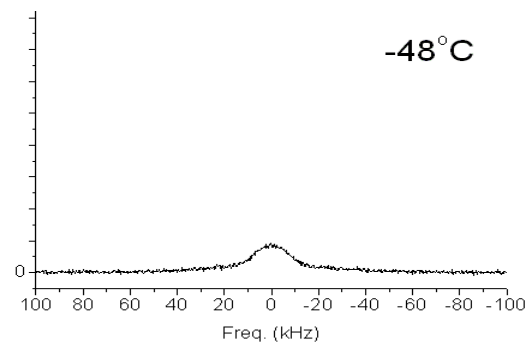
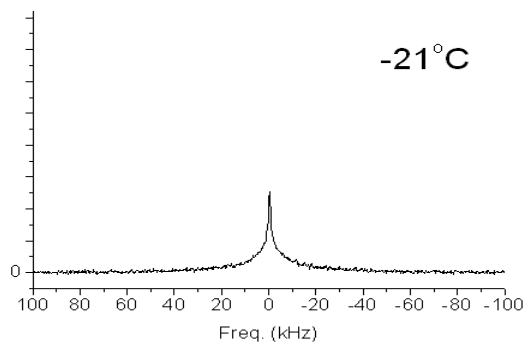
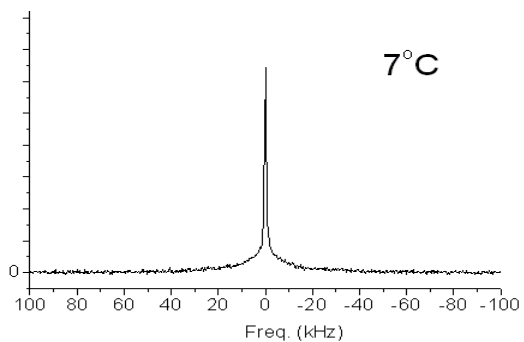
S105 remains at ambient conditions, so it can be studied by magic-angle spinning NMR, x-ray diffraction, etc. S105 can be shipped anywhere, as it is stable.

Note: whenever we see S105, it is accompanied by Na_3AlH_6 (but not Al metal). 6

S105 is Narrowed by Motional Averaging



^{27}Al Cold Spectra, undoped NaAlH_4



^1H , Cold Spectra

so not 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

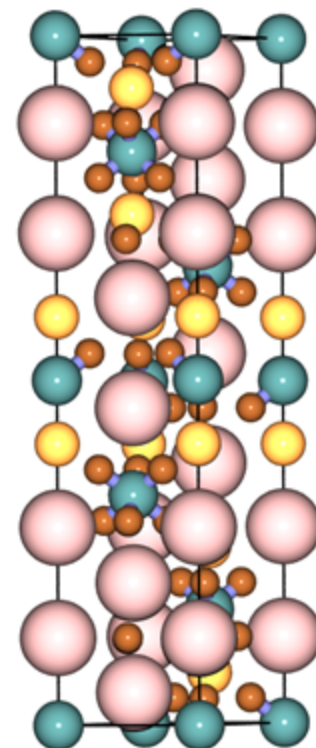
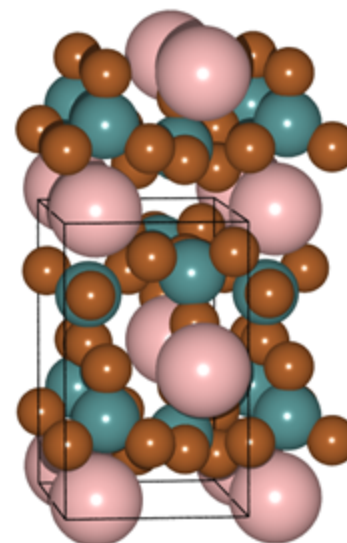
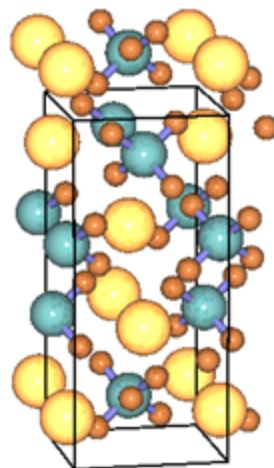
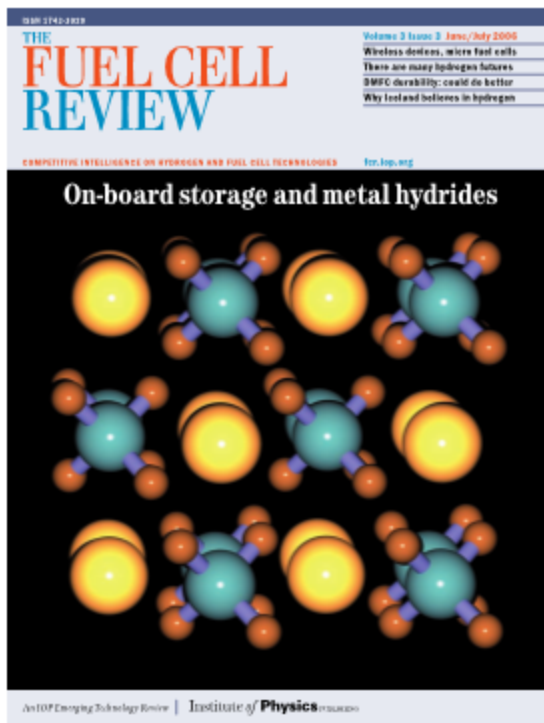
- New species S105 forms under reaction conditions.
 - P,T cycle allows recovery at ambient (doped or bare)
- NMR of S105 says highly mobile, Al_xH_y .
 - Very short ^{27}Al T_1
 - ^{27}Al is motionally narrowed
 - S105 has 15% of ^{27}Al intensity
 - Companion sharp peak in ^1H NMR
 - CPMAS at low-T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

What is Species S105?

- We believe S105 is NaAlH_4 with a high vacancy concentration.
- Ozolins *et al.** proposed:
 - $\text{AlH}_3^{\text{v}} \rightarrow \text{H}^- + \text{AlH}_4^- = \text{AlH}_5^{-2}$ complexes (hydrogen rich)
 - $\text{NaH}^{\text{v}} \rightarrow \text{AlH}_3 + \text{AlH}_4^- = \text{Al}_2\text{H}_7^-$ 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 ?

PEGS Method Used to Explore Structural Candidates for S105 Structure

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



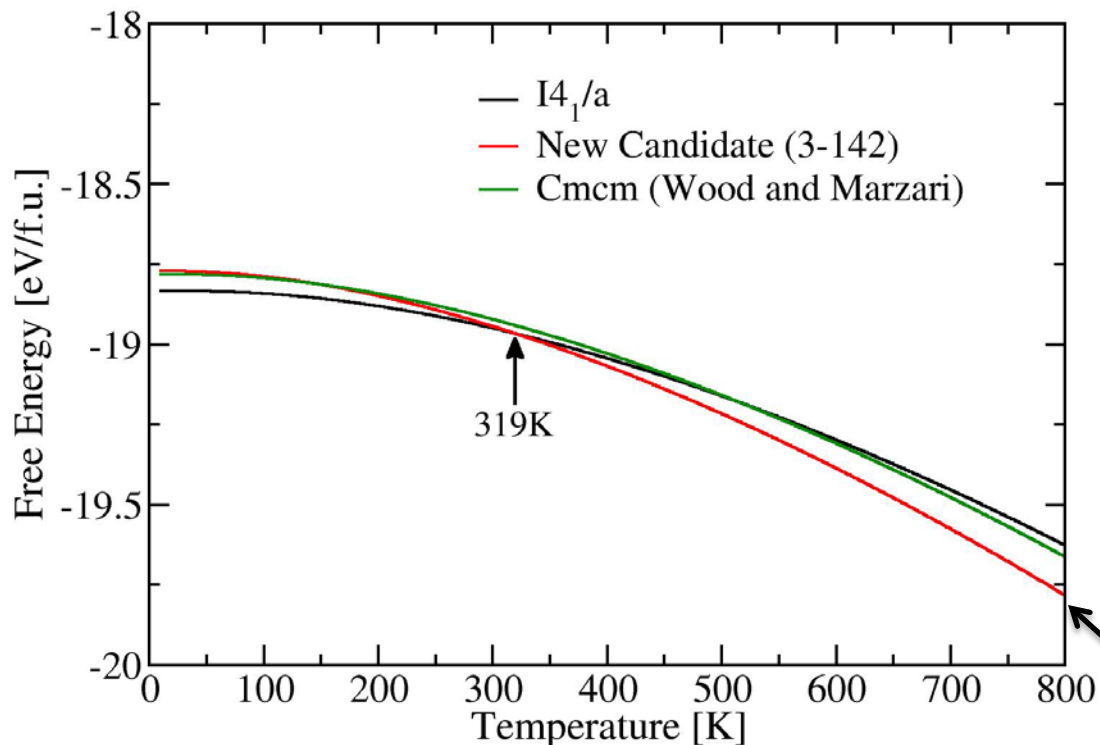
First-principles calculated NMR Shifts using VASP in collaboration with G. de Wijs at Radboud University, Netherlands

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

Bob Corey

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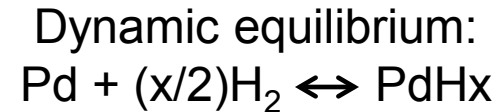
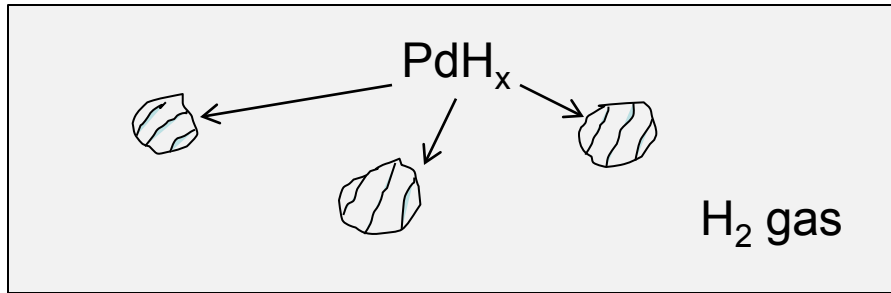
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Hydrogen and Metallurgy Science*

Introduction: PdH_x and Hydride-Gas Exchange



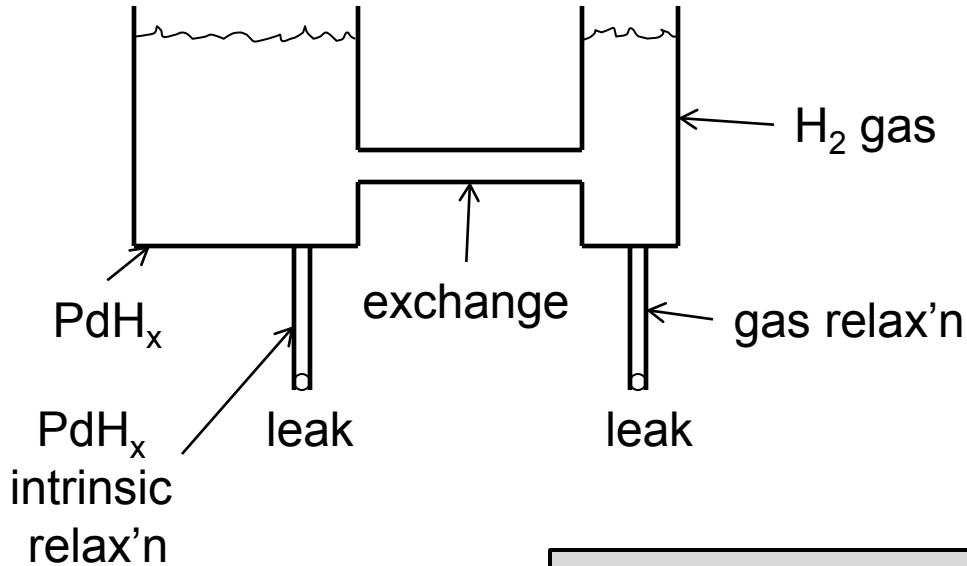
T₁ relaxation:

- T₁ in H₂ gas is short (~ms), because of short H-H bond and favorable τ_C
- Intrinsic T₁ of H in PdH_x ~200 ms. Comes from Korringa and BPP

Idea: If exchange were rapid enough, apparent T₁ of hydride would be reduced. Could measure the exchange rate from apparent hydride T₁.

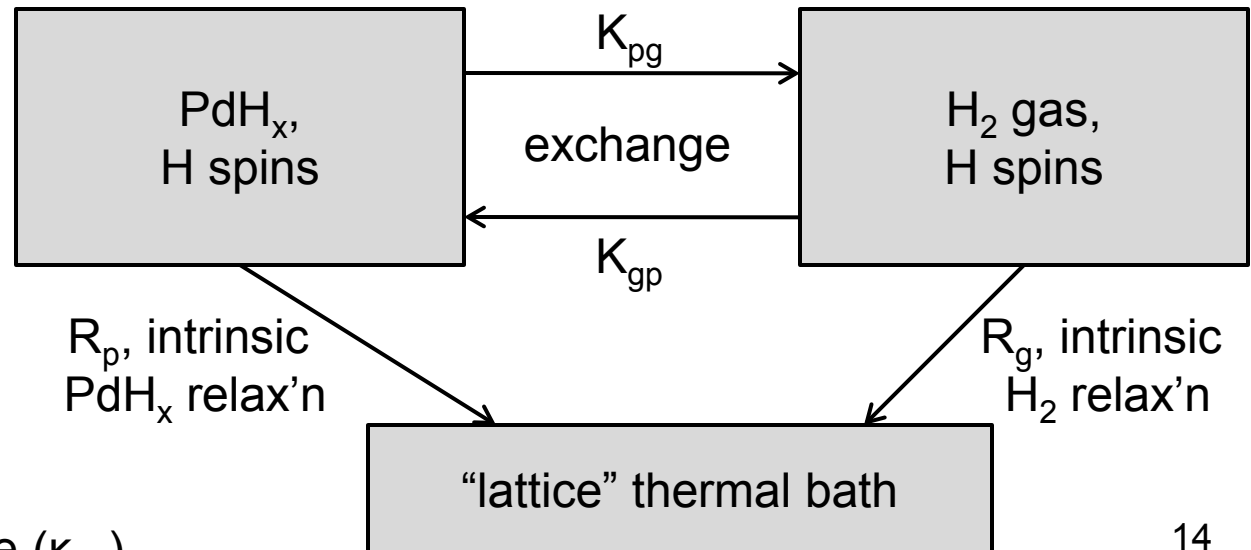
Simple case, limit: If T₁^{gas}=0, gas spins always at equilibrium. An H going from PdH_x to gas phase will be replaced by a fully relaxed H from the gas.

2 bucket analogy



H nuclear spins in PdH_x can relax via:

- intrinsic relaxation mechanism, or
- by exchanging with (very rapidly relaxing) gas phase.



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

Summary of all the equations

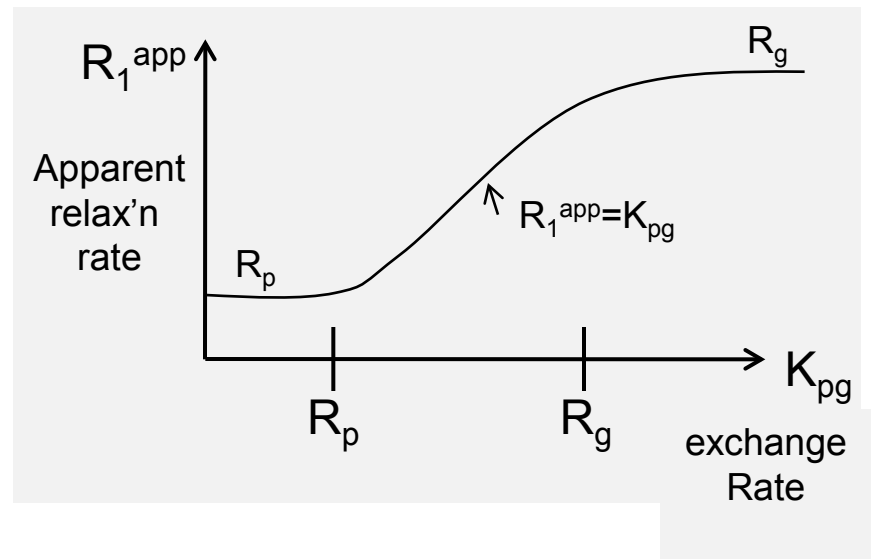
1. For maximum impact of exchange on hydride phase apparent T_1 , want $N_g \gtrsim N_p$. (Need lots of gas around PdH_x powder particles)

2. $\left(\frac{1}{T_1}\right)^{app} = \boxed{R_1^{app} \text{ is } \cong K_{pg}}$, exchange rate, provided

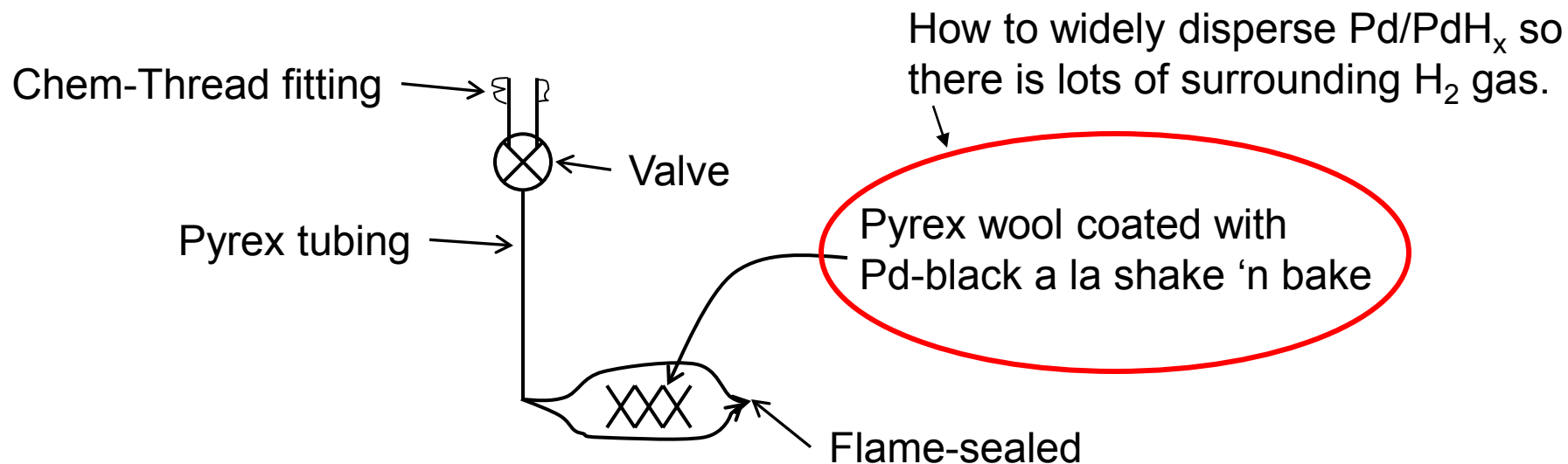
$$R_p \lesssim K_{pg} \lesssim R_g \left(\frac{N_g}{N_g + N_p}\right)$$

or, for $N_g \gg N_p$,

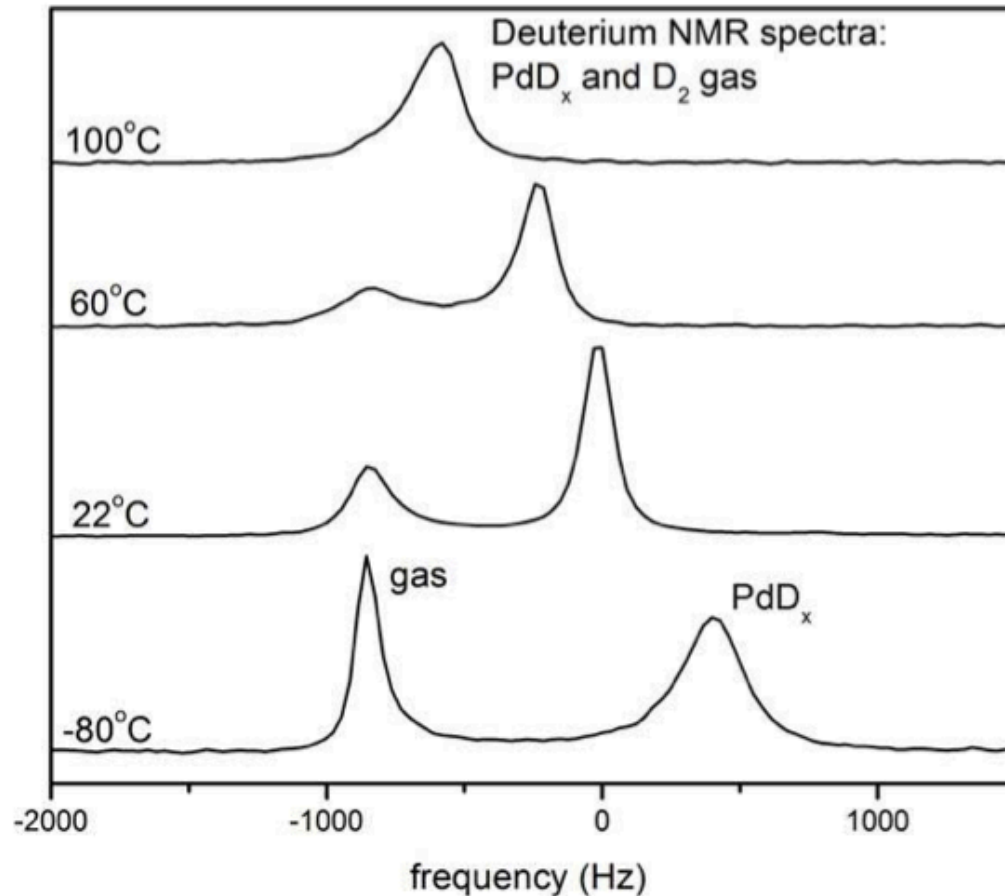
$$\boxed{R_p \lesssim K_{pg} \lesssim R_g}$$



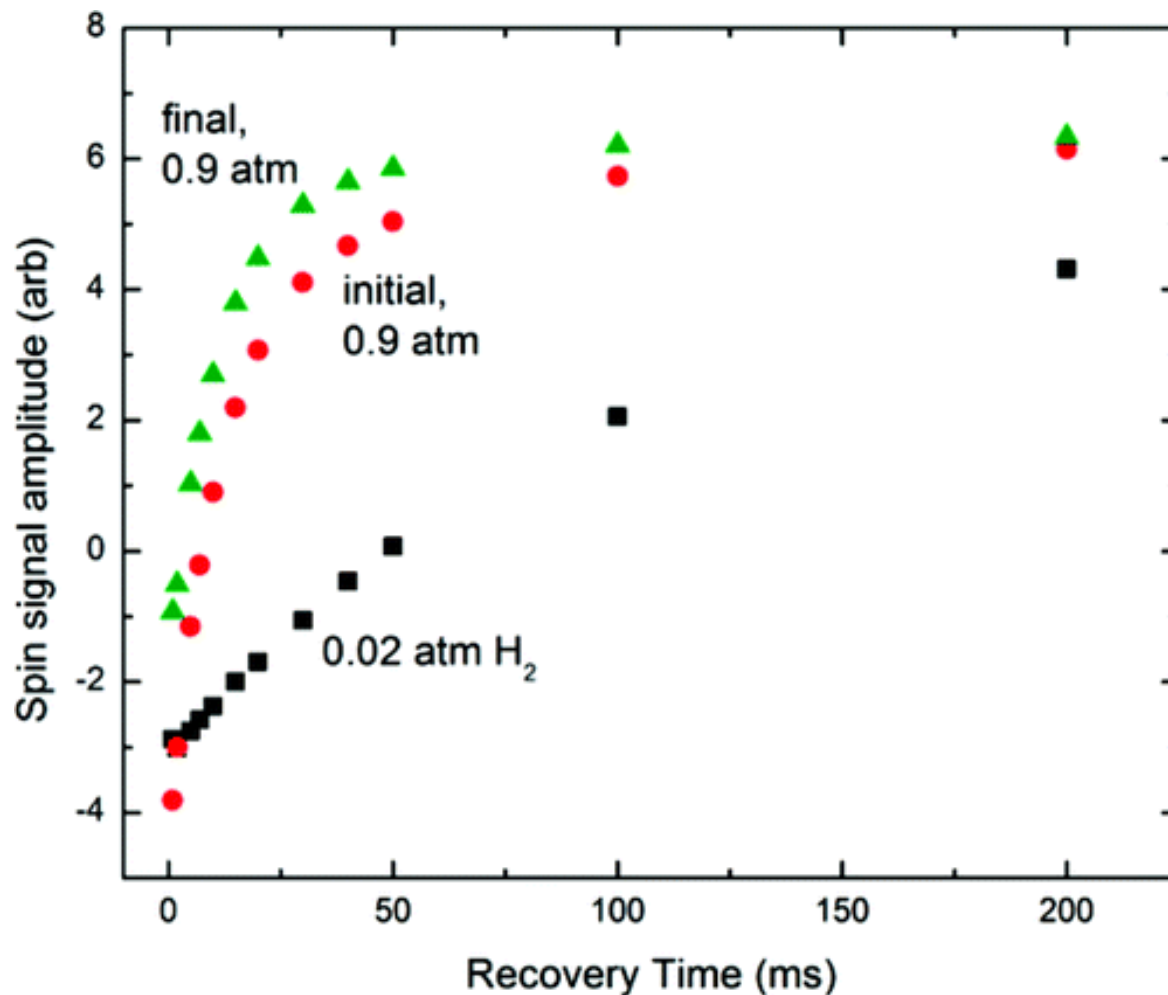
Sample Preparation



- Evacuate at 150°C overnight
- At 100°C, add 5 Torr H₂ and evacuate; 8 times
- At room-T, hydride to 0.9 bar and evacuate
- At room-T, hydride to 0.9 bar (and seal).

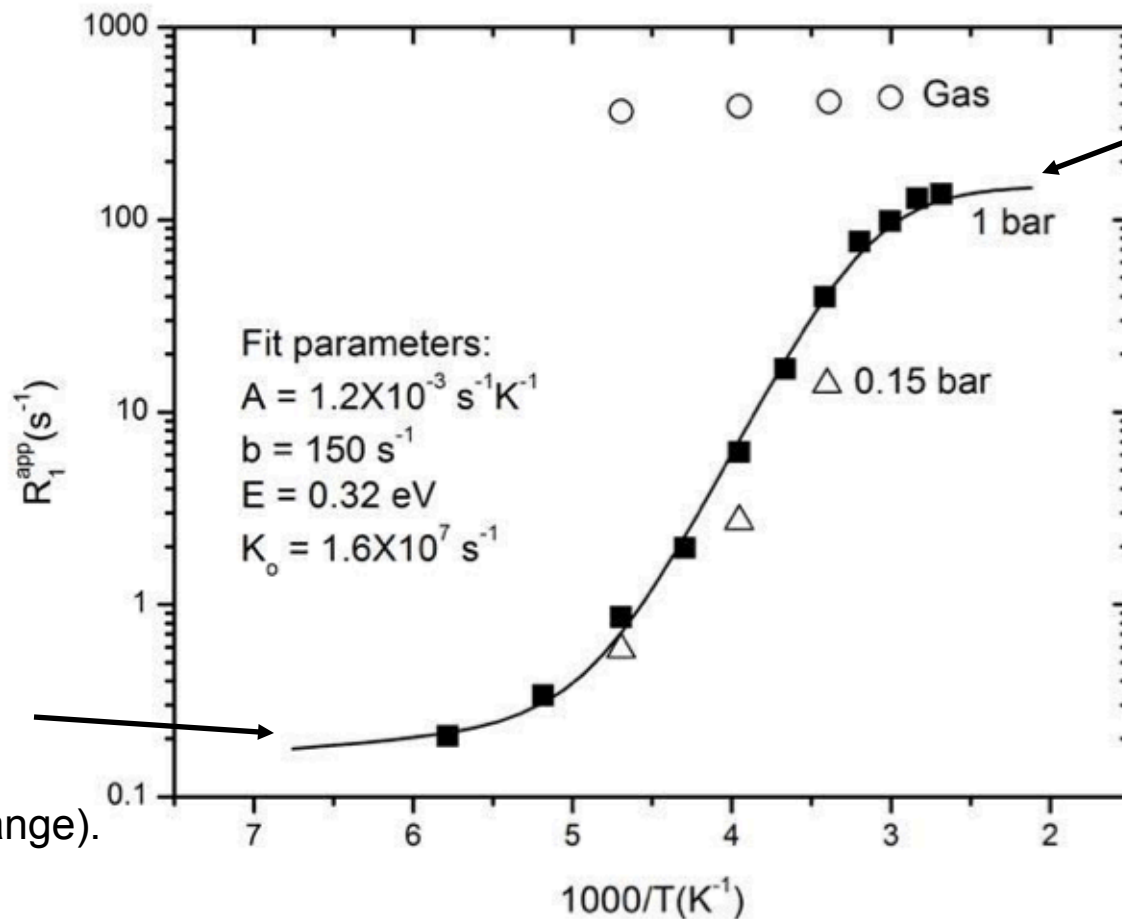


Deuterium NMR spectra of PdD_x and the surrounding D₂ gas at several temperatures. The 22°C spectrum shows that there are about half as many D nuclear spins in the gas as in the deuteride. At -80°C, PdD_x broadens due to the slowing of the internal motions. At 60°C, the gas resonance is broadened by gas-deuteride exchange; by 100°C, the resonances are partially merged.



Faster relaxation of green and red shows effect of PdH_x exchanging with H₂ gas.

Magnetization recovers as functions of time following spin inversion. Palladium black well-dispersed on glass wool; with 0.9 atm H₂ (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.



Relaxation rate limited by T_1 of D_2 gas.

Relaxation rate equals that of PdDx (no exchange).

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(BH₄)₂

Mitch Eagles

Bo Sun

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Bo Richter

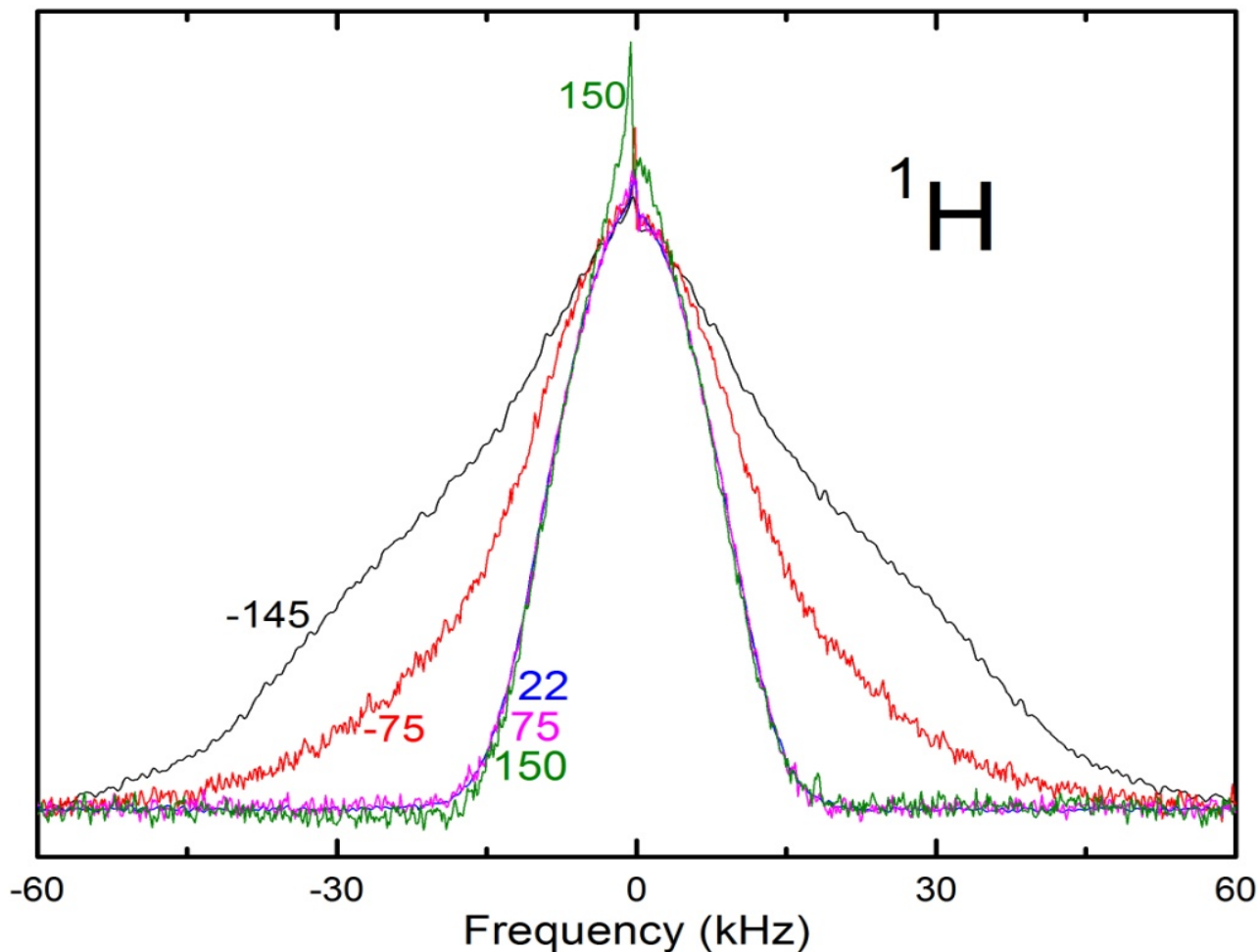
Torben R. Jensen

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Yaroslav Filinchuk

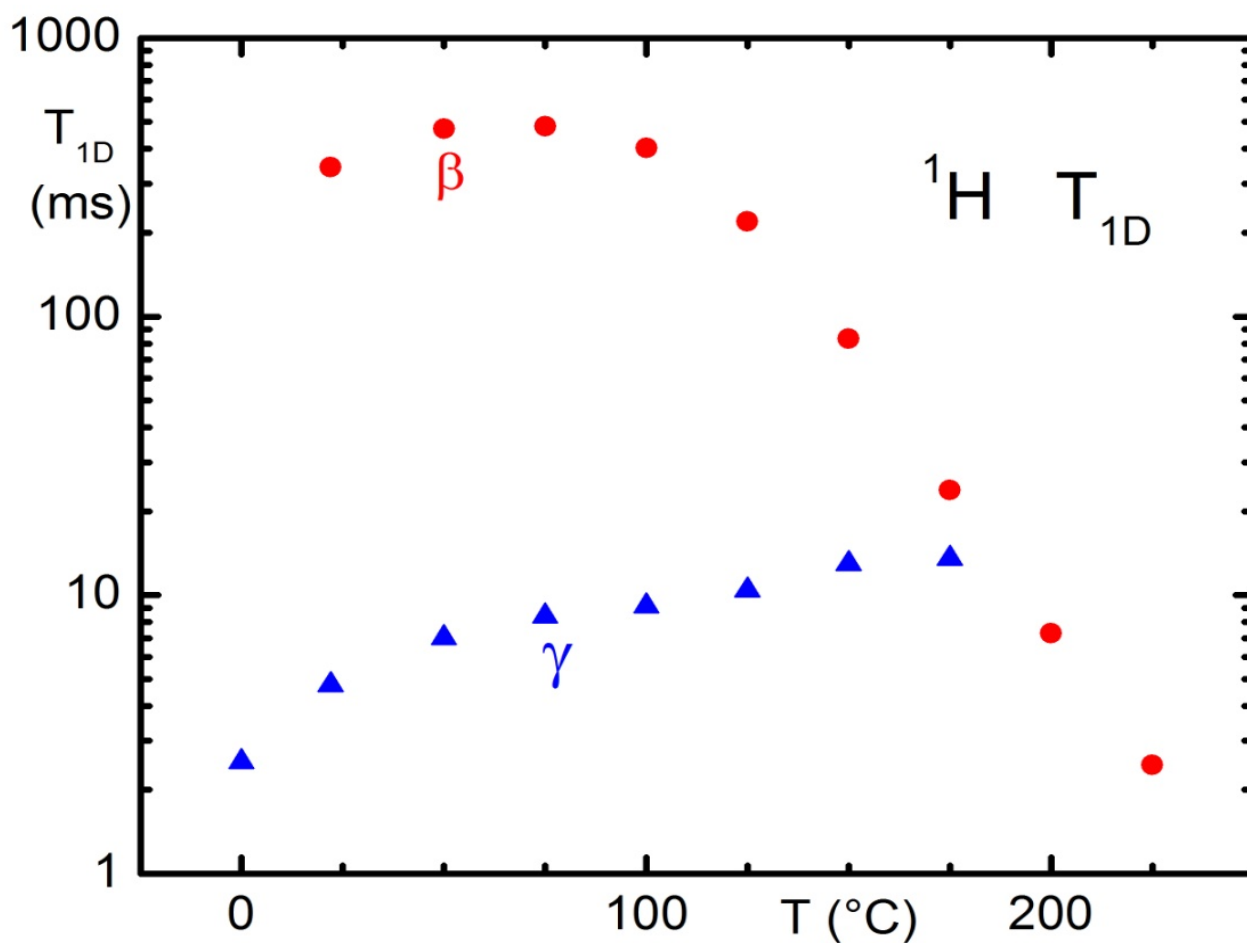
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γ -Mg(BH₄)₂ has 33% open volume (!), so we may expect enhanced rate of diffusion (of BH₄⁻, for example). Diffusion of these species is crucial to dehydriding and rehydriding reactions.



No line narrowing
up to 150°C [no sign of enhanced
BH₄⁻ diffusion.

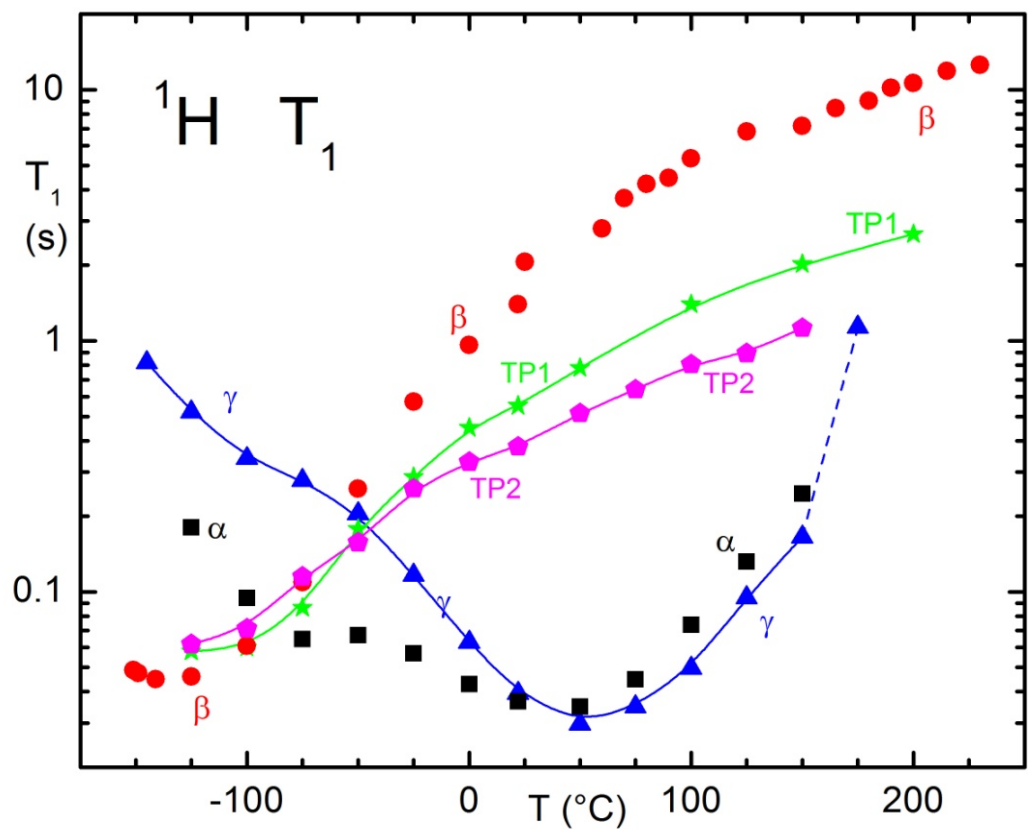
Hydrogen NMR spectra of γ -Mg(BH₄)₂ at several temperatures. At -75 and -145°C, pronounced broadening is due to slowing of the BH₄ reorientations. At and above 22°C, no further narrowing of the main resonance occurs, ruling out rapid BH₄ translational diffusion. At the highest temperature, a narrow component 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 $\gamma\text{-Mg}(\text{BH}_4)_2$, 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.



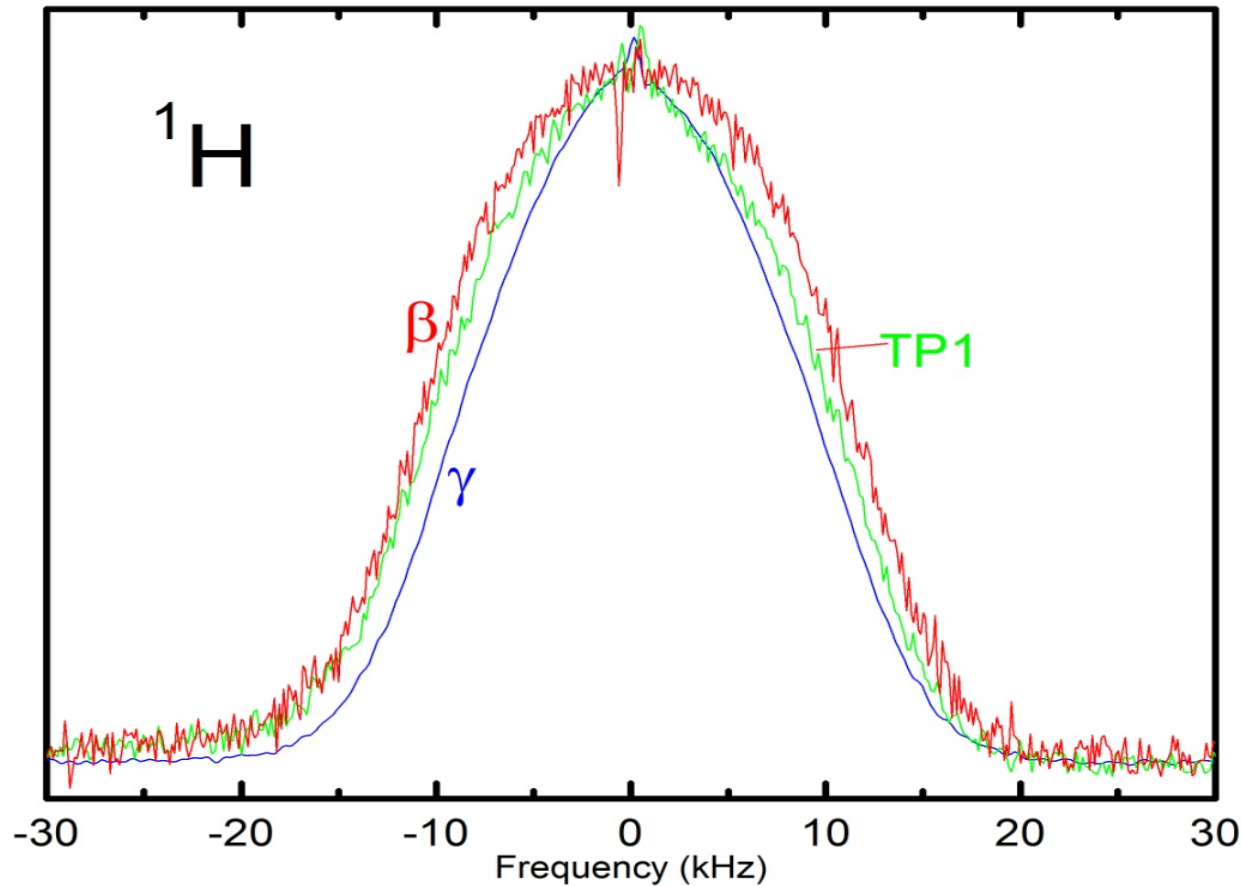
T_1 is controlled fully by BH_4^- reorientations.

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: $\gamma < \text{TP1} < \beta$
Linewidth reflects density because dipole interactions vary as $1/r^3$.

Conclusions

- Despite the large 33% of vacant space in γ -Mg(BH₄)₂, there is no sign of BH₄⁻ diffusion up to 150°C.
- Neither line narrowing nor short T_{1D} is found.
- BH₄⁻ 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 T₁ behavior and from x-ray diffraction).

NaH – a simple ionic hydride

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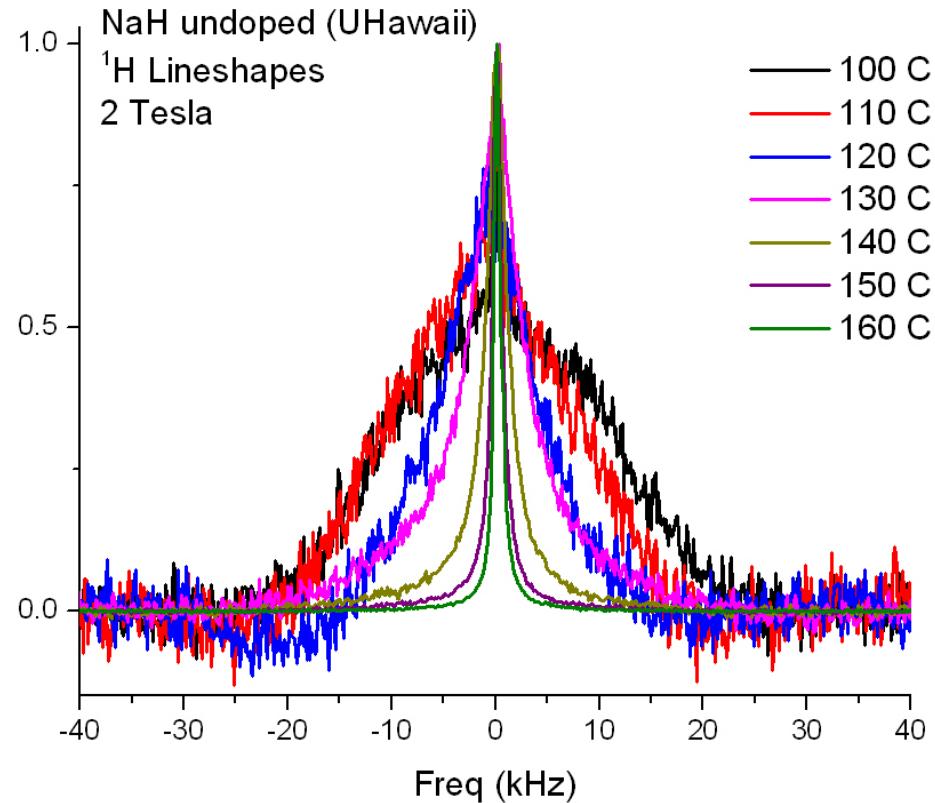
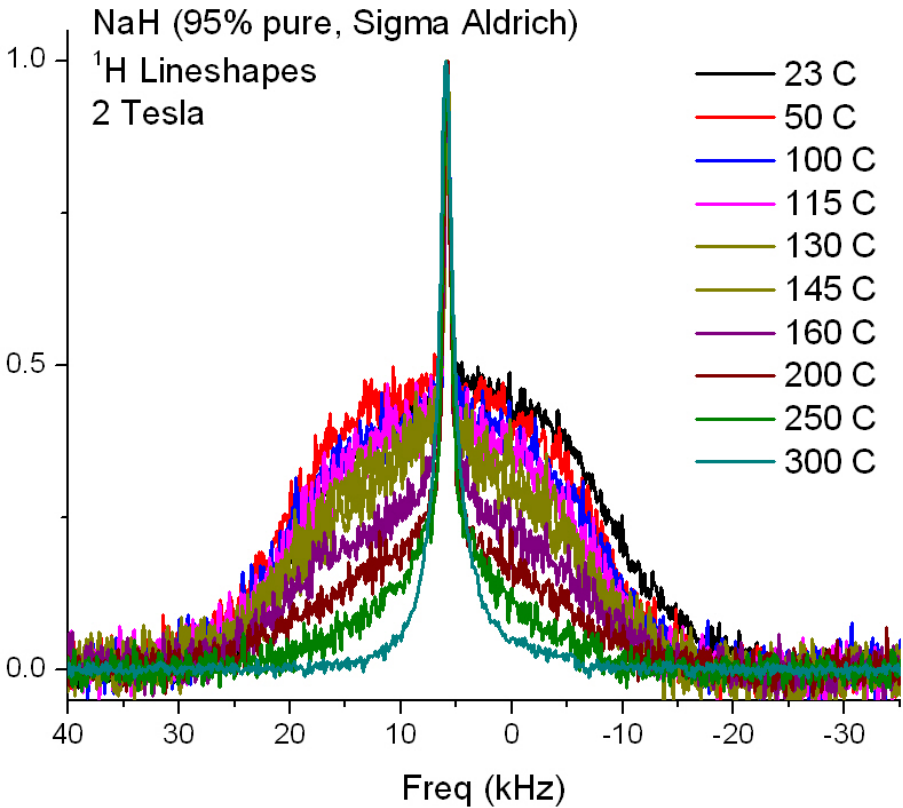
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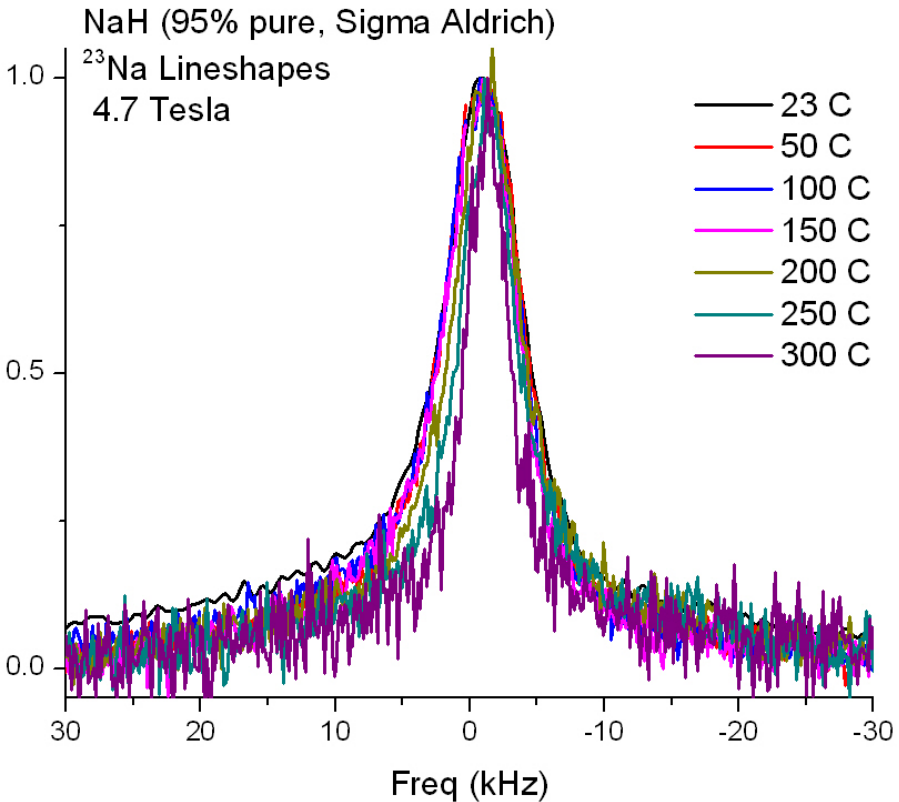
Washington U. Physics Dept.

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

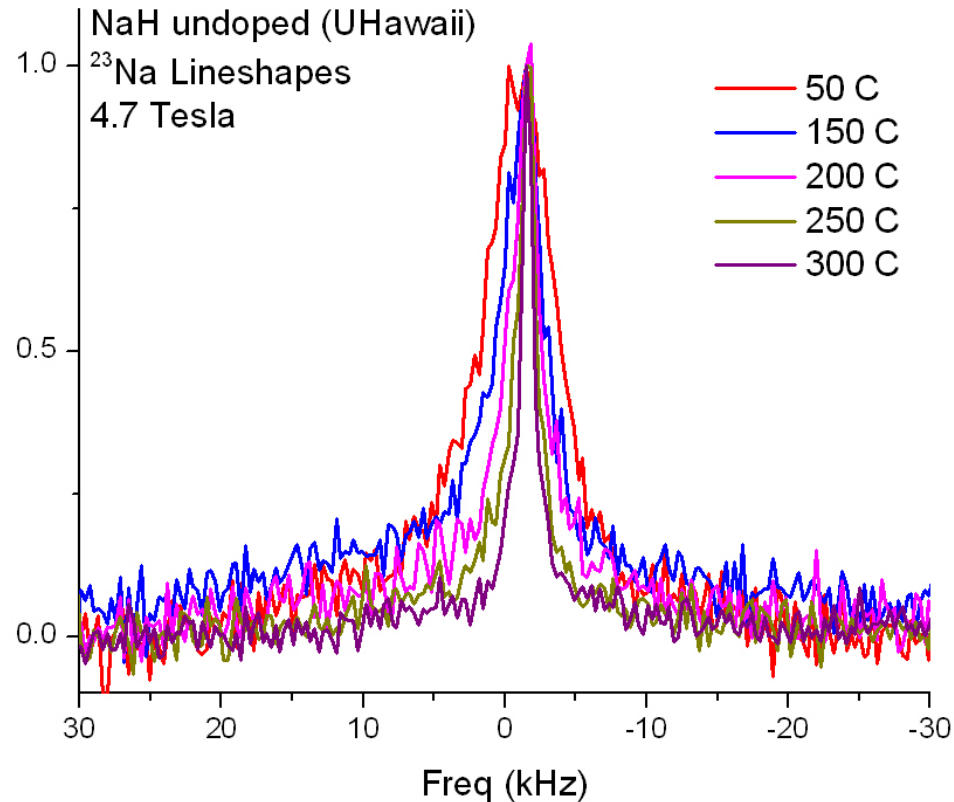


As T increases, the fraction of H that is mobile (line narrowed) grows. Fraction of immobile H decreases. In other ionic hydrides, we identified mobile H as those near defects (grain boundaries, for example). Immobile H are in crystallite interiors. Above 250°C, the remaining broad component motionally 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 ^{23}Na 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.