In Situ NMR Studies of Hydrogen Storage Systems

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Mg-Sc Alloy Hydride – Rationale

- MgH_2 has high H content (8 wt%), ionic bonding, very slow kinetics.

- ScH_2 has lower H content (4 wt%), metallic character, better kinetics, very low equilibrium pressure (1 Torr at 740 C).

- Mg-Sc alloy embodies some of each:
  - good reversible H content, over 2 H per metal, 6.7 wt%,
  - fluorite structure of ScH_2,
  - adequate kinetics,
  - low P_{eq} (~10^{-7} atm at R.T.) may not be issue for electrochemical applications.

- Problem: MH batteries with thin film Mg-Sc electrodes show slow kinetics,
  - even with Pd overlayer.

Is it a surface effect?

Is it slow bulk diffusion?

NMR Relaxation Time Measurements

Spectrometer: Home-built, 4-phase transmitter with 80 W output, quadrature-detected receiver.

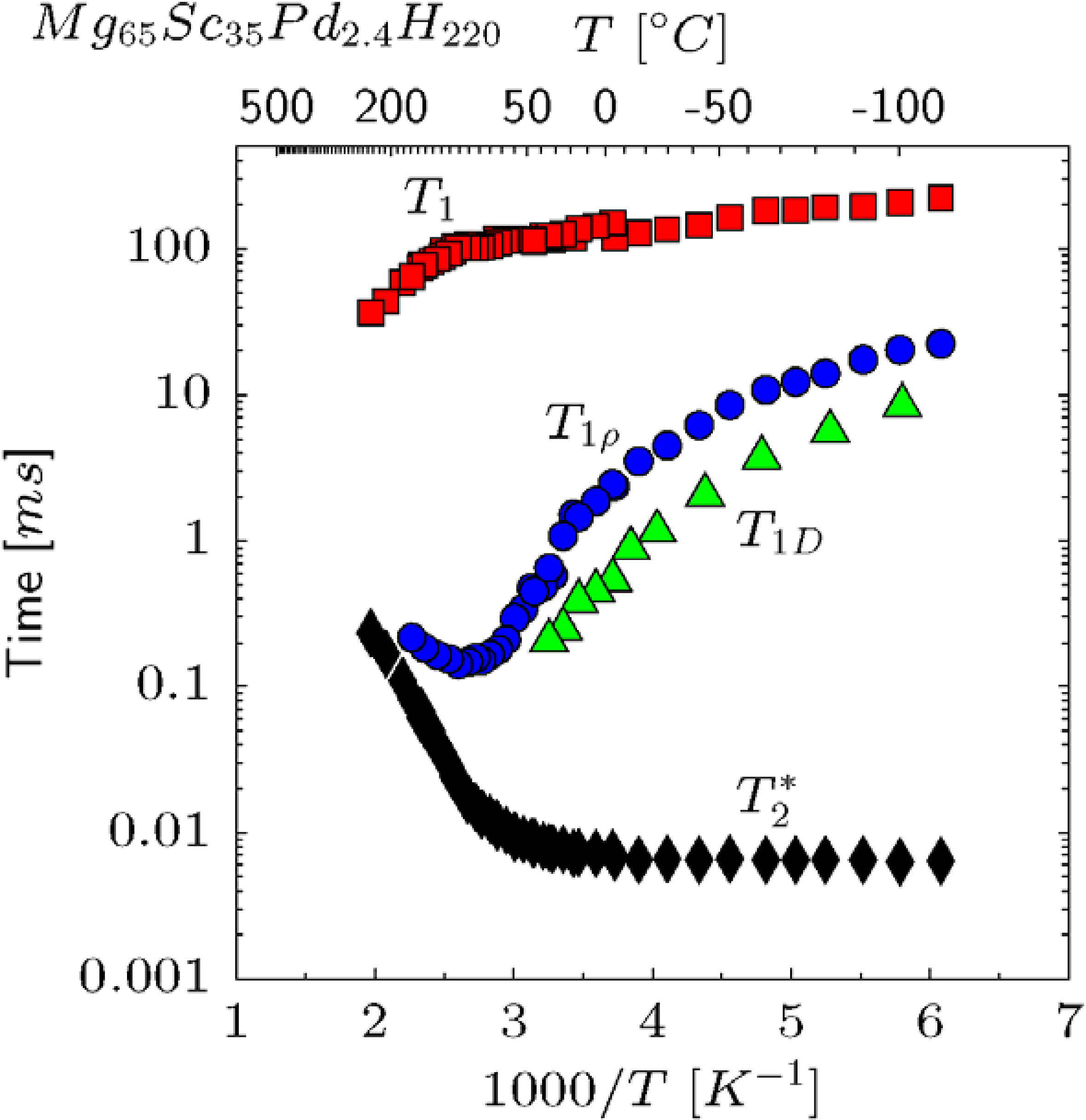
Samples: Synthesized and loaded with H_2 gas at TUE by WPK in Netherlands.
Sealed into glass NMR tubes.

Sequences:

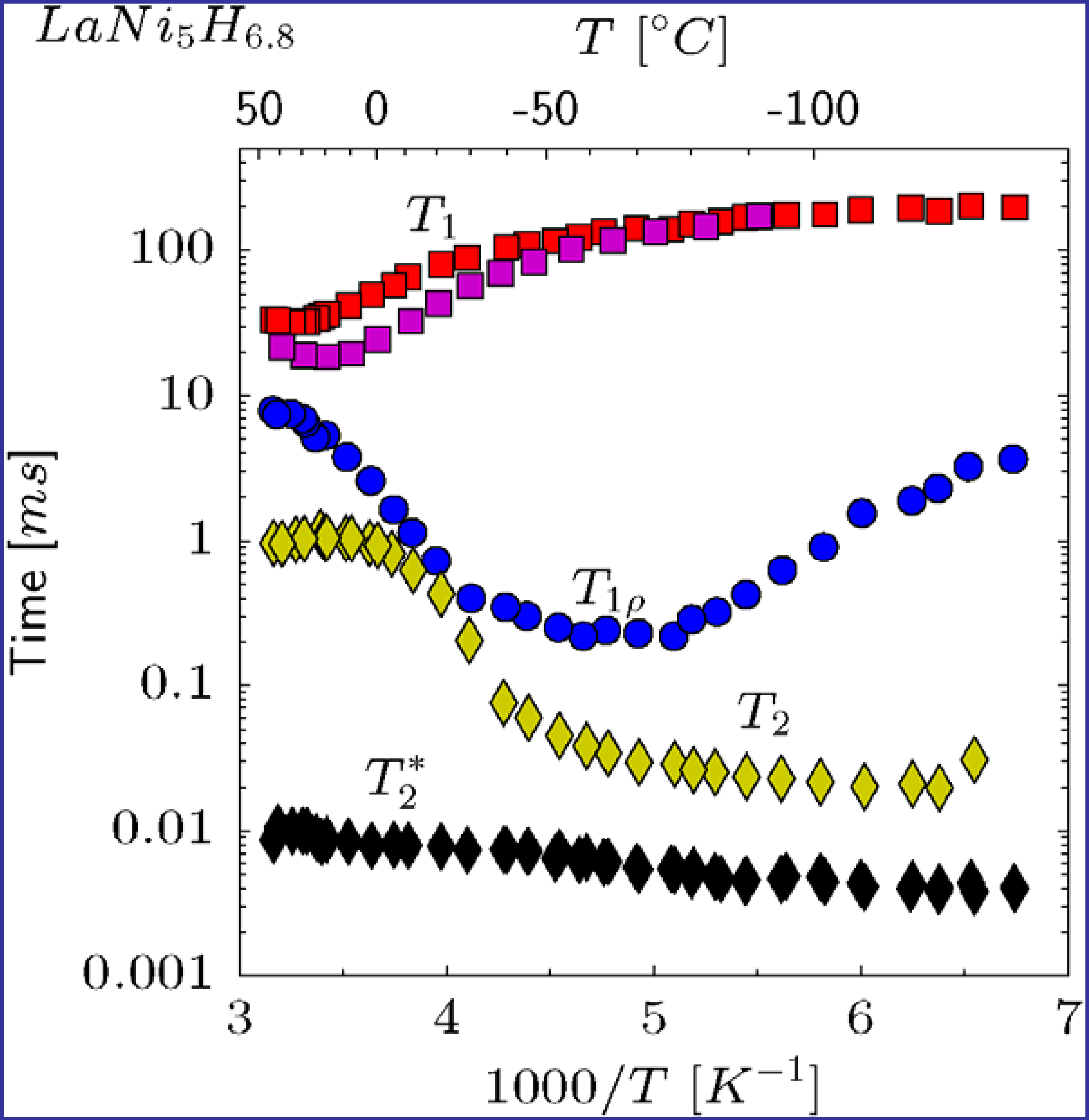
T_1 from 180-τ-90 and $(90\text{-}t)_n$-τ-90
T_2 from free induction decays, 2-pulse echoes, and CPMG echo trains.
$T_{1\rho}$ from CW (not chopped) spin-locking.
T_{1D} (T_1 of dipolar-ordered state, essentially T_1 in zero field) from phase-alternated Jeener-Broekaert: $90_{x,-x}$-t-45_y-τ-45_y.

All measurements at 53 and 21 MHz in Varian iron-core electromagnet.

Results for $Mg_{65}Sc_{35}Pd_{2.4}H_{220}$



For Comparison: Results in $LaNi_5H_{6.8}$



Guide to Interpreting NMR Results

ω_H ≡ rate of H hopping motion

- Motional averaging of local dipolar fields is evident as increase of T_2 with temperature.
  At onset, $\omega_H \sim 10^5\ s^{-1}$ (approx. the low-T linewidth).

- At $T_{1\rho}$ minimum, $\omega_H \sim 5 \times 10^5\ s^{-1}$ (about 1.6 γB_1).

- At T_1 minimum at 21 MHz,
  $\omega_H \sim 2 \times 10^8\ s^{-1}$ (about 1.6 γB_0).

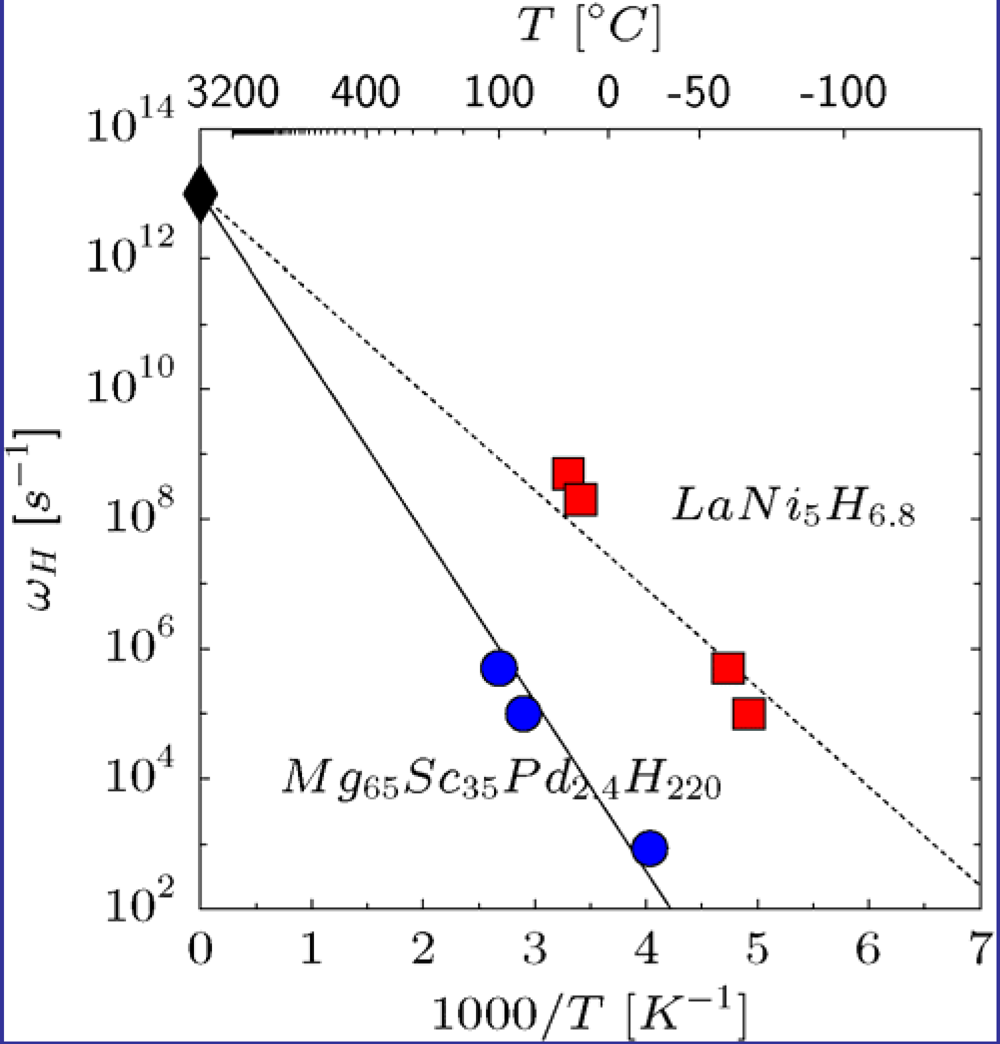
- T_{1D} is approx the mean time between hops,
  $T_{1D} \sim 1/\omega_H$, a strong-collision result.

Notes:

In $MgScH_x$, could not reach T_1 minimum.
After 1 hour at 300 C, irreversible changes in alloy occurred.

In $LaNi_5H_x$, magnetic precipitates (presumably Ni)
distort field uniformity and keep T_2 of FID very short (~10 μs).

Relaxation Map – Compares ω_H in $MgScH_x$ and $LaNi_5H_{6.8}$



Fit is to

$\omega_H = 10^{13}\ s^{-1} \exp((-E_a/k)/T)$

Activation energies:

$MgScH_x$ $E_a/k = 6000$ K

$LaNi_5H_x$ $E_a/k = 3500$ K

Here we have taken ω_H to be $10^{13}\ s^{-1}$ at T = ∞, providing us an extra datum point.

$MgScH_x$ Conclusions

- Rate of H hopping, ω_H, is same in two systems only for much higher temperature in $MgScH_x$.

- At same temperature, motions in $MgScH_x$ are $\cong$ 3000× slower than in $LaNi_5H_x$.

- This explains slow kinetics seen in battery charge/discharge with $MgScH_x$ thin film electrodes

- Future:
- Examine Mg-Ti alloy hydride. Made as thick thin-film, so limited quantity available, so use microcoil and high B_0 field.

- Vary Mg:Sc ratio to see effect on H kinetics. Is fluorite-rutile transition near 80% Mg the primary controlling factor?

- Try deuterium magic-angle spinning (MAS-NMR) to resolve distinct resonances for distinct hydrogenic sites.

The New Breed of H_2 Storage Compound

- Interstitial metallic hydrides show rapid diffusion, but wt% storage is inadequate.

- $NaAlH_4$, $LiBH_4$ imides and amides have covalent and ionic bonding.

- Where are the mobile species? How does H get out?

- Especially during rehydride:
  $NaH + Al + 3/2\ H_2 \rightarrow NaAlH_4$.
  But how? Where are mobile Al, Na species?

- *In situ* NMR is measured *at* rxn conditions.
  Not ambient-NMR on samples recovered from rxn.

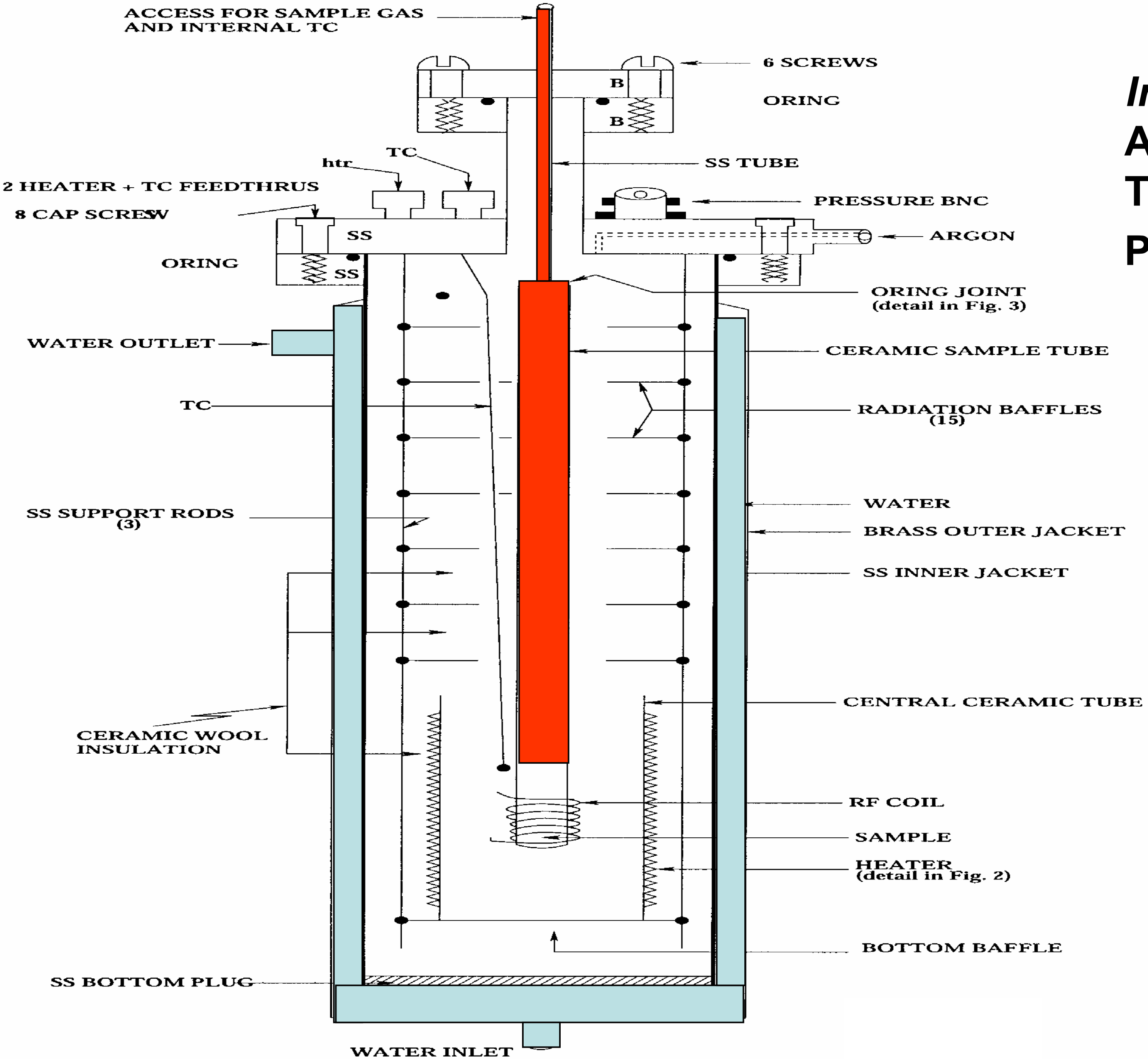
- Need $T \leq 300$ C and $P \leq 100$ atm.

- Unlikely to do magic-angle spinning (MAS-NMR) at these rxn conditions. But we can *complement* static-sample *in situ* NMR with MAS-NMR on recovered material.

In Situ NMR Apparatus

$T \leq 300$ C

$P \leq 100$ atm



Future Plans for *In Situ* NMR

- $NaAlH_4$
  look for mobile H species,
  distinguish by long T_2, so “last remaining signal”.

- Sc-catalyzed $NaAlH_4$
  Sc-45 is much better for NMR than Ti-47 and Ti-49.

- Look with MAS-NMR at Caltech (14 Tesla) at Sc-catalyzed $NaAlH_4$.

- Build version of *in situ* NMR for high-field (8.4 T) and “metal” atoms:
  ^{23}Na, ^{27}Al, ^{7}Li, ^{15}N.