NMR studies of metal-hydrides: MgScH$_x$

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Program Scope

Our research program focuses on *in situ* NMR studies of solid-state hydrogen storage systems. In particular, NMR measurements at the high temperatures and/or high pressures of the dehydriding and rehydriding reactions offer the best opportunity of detecting and identifying the mobile species that must be present, as well as the chemical intermediate species that are crucial to the reactions. For example, we expect to identify mobile H atoms in partially dehydrided NaAlH$_4$. From high-field measurements on the nuclear spins of catalytically active species like Ti and Sc, we will determine the local environment of the catalyst atoms in terms of the neighboring nuclear spins, using spin-echo double resonance.

Recent Progress

(a) Kinetics of hydrogen atom hopping in Mg-Sc alloy hydride.
(Poster presentation by Mark Conradi)

Background: The research group of Notten at Philips has recently shown Mg-Sc metastable alloys to be effective systems for hydrogen storage and metal-hydride battery electrodes[1-3]. The motivation behind this alloy system is to capture desirable features of both end-members. At one end, MgH$_2$ has a high hydrogen storage capacity of 8 wt%. However, the binding is of ionic character and this is believed to result in the very slow diffusion kinetics of H in MgH$_2$. The equilibrium H$_2$ pressure is on the low side at 1 atm at T = 278 C, but this is not a severe disability for electrochemical applications. At the other end is ScH$_2$ with approximately 4 wt% storage but the superior diffusion kinetics typical of interstitial metallic hydrides. The H$_2$ equilibrium pressure of the two-phase plateau region is very low at 1 Torr at 740 C.

The Mg-Sc alloy hydrides take on the fluorite structure[3], as does ScH$_2$, for Mg fractions $\leq 80\%$. At higher Mg fractions the structure is rutile-like as for MgH$_2$ and it appears the charging kinetics suffer markedly as a result. The alloys show high storage capacity of 6.7 wt%, in approximate agreement with the simplistic (local) view that each Mg supports 2H and each Sc supports 3H; here the expanded lattice is believed to allow the additional H on Sc beyond the usual ScH$_2$. Mg-Ti alloys have similar behavior to Mg-Sc, but should be much less costly[4]. However, even in thin films for electrochemical applications, the charge/discharge kinetics of MgScH$_x$ are slower than one would like. The kinetic bottleneck may be slow diffusion of H through the alloy or slow kinetics at the electrode surface (despite use of a Pd overlayer).

While gearing-up for *in situ* studies of complex hydrides, we have measured and report here the temperature dependence of the H hopping rate ω_H in MgScH$_x$, as determined by NMR relaxation times.

Methods: Bulk Mg$_{65}$Sc$_{35}$Pd$_{2.4}$ was synthesized by WPK at TUE and loaded with H$_2$ to x = [H]/[M] = 2.2 from the gas phase. Samples were loaded into glass NMR tubes under 0.9 atm of N$_2$ and sealed at a neck with a flame. RF field penetration into the powdered metallic sample was

judged to be good from measurements of rf pulse lengths for $\pi/2$ and π nutations, compared to a water reference sample.

Relaxation times were measured with a homebuilt pulsed, superheterodyne NMR spectrometer with 4 transmitter phases and quadrature-detected receiver. The transmitter power to the probe was about 80 W. Pulse sequences were generated with a combination of TTL hardware and a Pulse Blaster card. The NMR acquisition and analysis software was written locally. T_1 was determined with inversion-recovery and repeated-saturation-recovery schemes. T_2 was measured from the decays of free-induction signals (T_2^*), two-pulse (Hahn) echoes, and CPMG echo trains. Continuous (not chopped) spin-locking with $\gamma B_1/2\pi = 50$ kHz was used to measure $T_{1\rho}$. The relaxation of the dipolar-ordered state (T_{1D}, essentially $T_{1\rho}$ in zero amplitude field) was measured using a phase-alternated version of the Jeener-Broekaert three-pulse method.

Results: The relaxation times for $Mg_{65}Sc_{35}Pd_{2.4}H_{220}$ are presented as a function of reciprocal temperature in the figure below. The data can be understood by realizing that T_2 begins to increase (motional averaging) when the H atomic hopping rate ω_H is about 10^5 s^{-1}. The $T_{1\rho}$ minimum corresponds to $\omega_H = 5 \times 10^5$ s^{-1}, and a T_1 minimum at 21 MHz would reflect $\omega_H = 2 \times 10^8$ s^{-1}, but evidently the available temperature range is too low to reach such a fast rate of H motion. One sample was heated to 300 C for about one hour and suffered irreversible changes (e.g., T_1 was different upon returning to 25 C). The time T_{1D} is, to within a factor of two, equal to the mean hopping time, $1/\omega_H$, a strong-collision result.
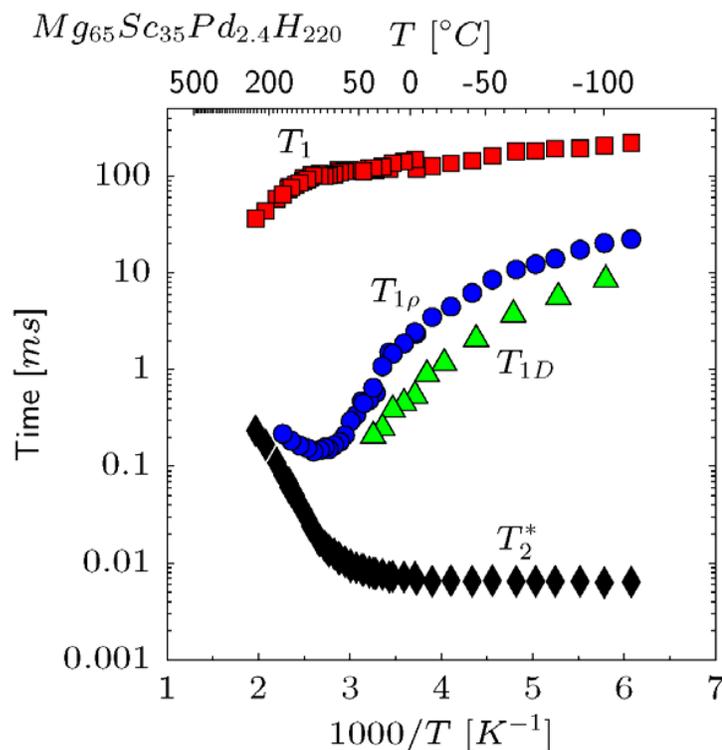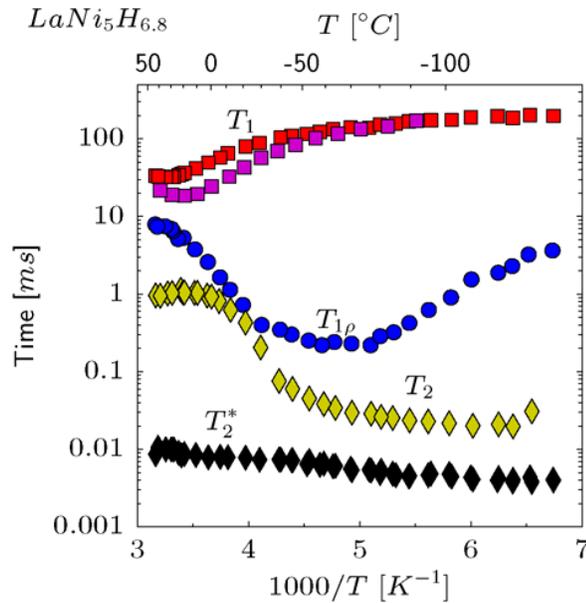
For comparison, similar data for $LaNi_5H_{6.8}$ are presented in the above figure. This material was synthesized at JPL and hydrided at WU by MPM. Comparing the figures, it is obvious that specific features such as the $T_{1\rho}$ minimum occur at much higher temperatures in $MgScH_x$ than in $LaNi_5H_{6.8}$. Thus, at a given temperature the H motion in $MgScH_x$ is much slower (by factor of ~3000) than in $LaNi_5H_x$. This demonstrates that slow internal kinetics are a substantial reason for the slow kinetics of MgSc film electrodes.

The relaxation map of the lower figure shows the log of ω_H as a function of reciprocal temperature for both materials. The data points are from a T_1 minimum, $T_{1\rho}$ minima, and the onset of line narrowing (lengthening of T_2). In each case, the attempt frequency ω_a is approximated as 10^{13} s^{-1}, corresponding to $1/T= 0$, providing an additional point on each line. The straight line fits correspond to $\omega_H = \omega_a \exp(-\Delta E /kT)$; the activation energies $\Delta E/k$ are 6000 K and 3500 K for $MgScH_x$ and $LaNi_5H_x$, respectively. This approach is more reliable than obtaining activation energies from the temperature dependence of one relaxation time (e.g., T_1 or $T_{1\rho}$) in cases with broad distributions of hopping rates at a fixed temperature (particularly true of $LaNi_5H_x$).
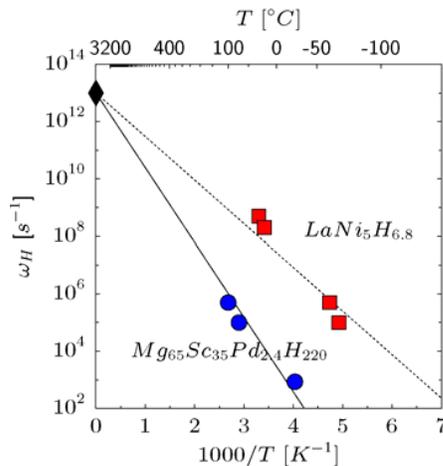
Future Plans

The study of new interstitial metallic alloys will be extended to Mg-Ti[4], because Ti is so much less costly than Sc. Only a small quantity of Mg-Ti is expected to be available, requiring measurement in a microcoil at high field strength. The H kinetics in Mg-Sc hydride will also be studied as a function of the Mg:Sc ratio, to test the view that the rutile-fluorite structural transition controls the H hopping rate. When $MgScD_x$ is available, deuterium magic-angle spinning NMR will be used to try to resolve distinct resonance lines for distinct hydrogenic sites.

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