

IV.I.13 NMR of Hydrogen Storage Systems: Ionic Hydrides and Mobile Species

PI: Mark S. Conradi

Washington University

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In the past, hydrogen storage solids were almost exclusively *interstitial metallic hydrides*. These are noted for their generally good hydrogen diffusion kinetics; here we report ω_H , the rate of atomic-level hydrogen hopping events. This is nicely demonstrated in Figure 1, where ω_H appears on a logarithmic scale for the prototypical ionic system MgH_2 and in the metallic systems ScH_2 , $Mg-ScH_x$, and $LaNi_5H_{6.8}$. Clearly, MgH_2 has much slower dynamics than the metals, and a much higher activation energy. Remarkably, MgH_2 can be converted from the rutile (ionic) structure to the fluorite (metallic) structure with as little as 20% Sc, though Figure 1 is for 35% Sc; the H hopping in the metallic phase is much faster than in MgH_2 and is even a bit faster than in ScH_2 .

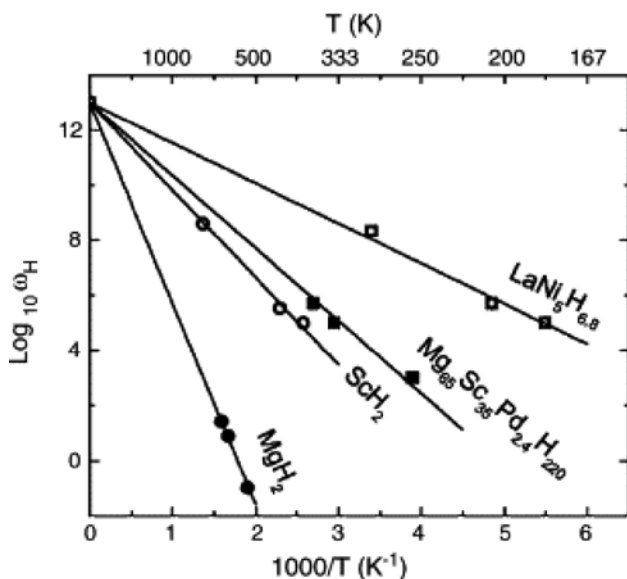


FIGURE 1.

While the metallic hydrides show good H kinetics, an essential feature of any hydrogen storage system, the mass-fraction of H, is too small. Thus, interest has turned to the lightweight hydrides, such as LiH , MgH_2 (7.6 w/w%), $NaMgH_3$, and $LiBH_4$ (18 w/w%). These are all *ionic* or *complex* hydrides. We examined coarse-grained MgH_2 as the prototypical ionic hydride. The rate ω_H of H hopping remains too slow to narrow the hydrogen NMR line up to 400°C, so $\omega_H < 10^5 s^{-1}$. This confirms the reputation of MgH_2 for slow kinetics – rehydriding Mg metal often is halted once a thin skin of MgH_2 forms and blocks further reaction progress.

To detect and measure such slow motions, we turned to the ultraslow motion experiment of Ailion and Slichter. Standard spin Zeeman-order is converted to spin dipolar-order at the start of the experiment. This order is found to decay with time constant T_{1D} . Because dipolar order is a correlation between a spin's orientation and the local dipolar field from its neighbors, and because the local field varies from site-to-site with little correlation, a single atomic jump destroys a given spin's contribution to the dipolar order. Thus, the measured relaxation rate $1/T_{1D}$ is essentially equal to the rate of atomic jumps for a typical H atom.

Results are presented in Figure 2 for coarse-grain MgH_2 . The straight-line region represents thermally activated H motion, from 0.1 s^{-1} at 250°C to 400 s^{-1} at 400°C; these are indeed slow motions. The activation energy is 1.72 eV ($\pm 7\%$), a high value that explains the slow kinetics of MgH_2 . At lower temperatures, the data curve and are no longer controlled by H kinetics; the

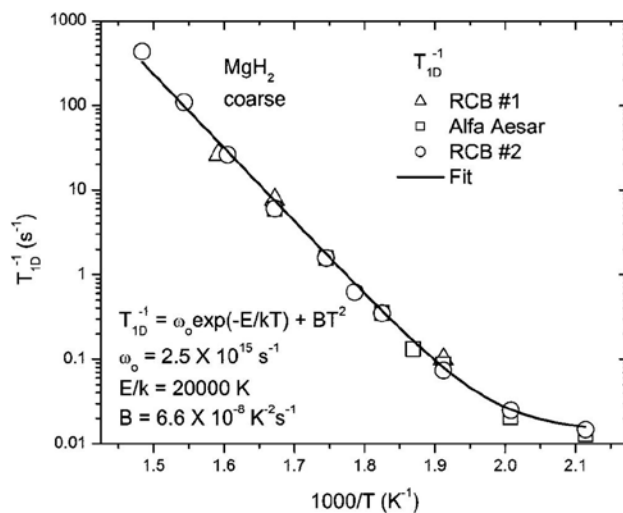


FIGURE 2.

dipolar order decays through coupling to the ^{25}Mg spins and the quadrupolar T_1^{-1} process. The overall fit to the data incorporates both mechanisms and is excellent.

We investigated a number of ball-milled MgH_2 materials supplied by collaborators at Savannah River, Université de Québec Trois Rivieres, and GKSS (Germany). Lineshape data are presented in Figure 3a for the most “accelerated” system – MgH_2 with 0.5 mol% Nb_2O_5 from GKSS. Already at 100°C , a line-narrowed component appears, indicating a small fraction of mobile H atoms (here “mobile” means $\omega_{\text{H}} > 10^5 \text{ s}^{-1}$). With increasing temperatures, the fraction of intensity in the narrowed line (see graph in Figure 3b) increases up to ~31% at 400°C . Two aspects are worthy of note: mobile H atoms appear already at low temperature (100°C) and the sample is *inhomogeneous*, with some slow-moving H and some fast moving. Presumably, the sample inhomogeneity reflects a very broad distribution of local environments, due to the aggressive mechanical activation process.

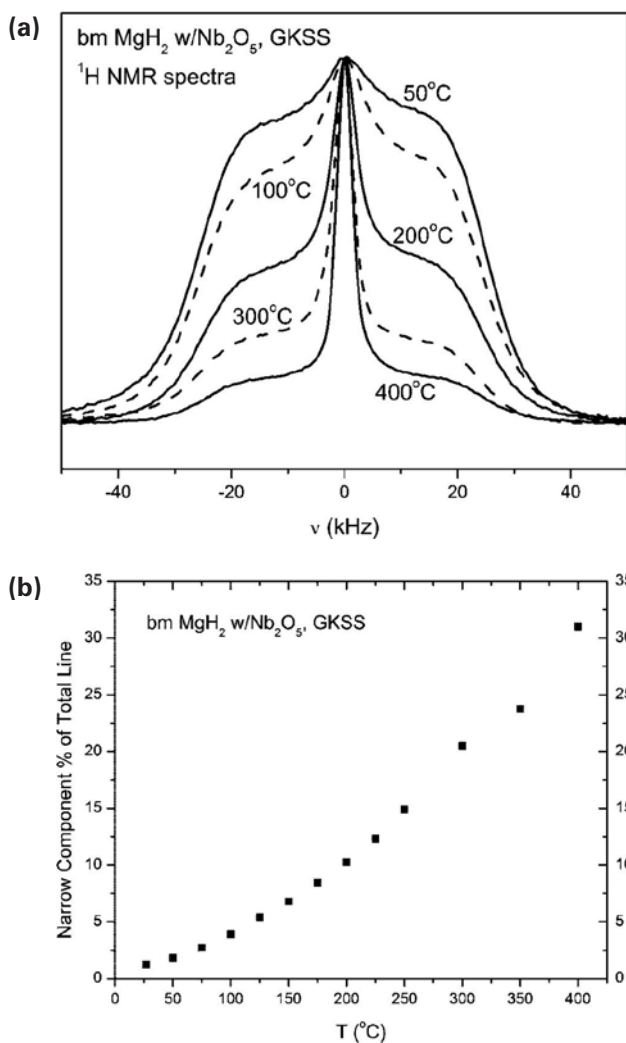


FIGURE 3.

In addition, the relaxation time T_1 decreases from 3,000 s to 0.1 s in the ball-milled GKSS material. This rapid relaxation, only weakly temperature dependent, demonstrates a large concentration of unpaired electron spins from mechanical rupture of the bonds.

The behavior of ball-milled MgH_2 is similar to NaMgH_3 , ball-milled from 1:1 NaH and MgH_2 . The hydrogen NMR line narrows starting below 100°C . The narrowing is inhomogeneous up to 275°C , beyond which the rest of the line narrows rapidly. The T_1 of NaMgH_3 is a few seconds, remarkably short for such a ‘rigid’ spin system; presumably, a large concentration of unpaired electrons are present here as well.

LiBH_4 has much faster atomic motions. At all temperatures above -100°C , the tetrahedral BH_4 units reorient rapidly, as shown in earlier work. At a solid-solid transition at 109°C , the Li^+ motion increases dramatically. As in Figure 4, the ^7Li resonance narrows so that quadrupolar satellites at ± 10 kHz are clearly resolved. Thus, the high-temperature (HT) phase may be superionic, though the Li^+ motion is $\approx 10^9 \text{ s}^{-1}$, far below the liquid-like rates of some superionics.

The H and ^{11}B resonances also narrow from 170 – 240°C , well into the HT phase (see Figures 5, 6, and 7). The activation energy extracted from H linewidth and T_{1D} data is 0.72 eV, $\pm 5\%$. The narrowing of the ^{11}B resonance is crucial: if the BH_4 units were not diffusing and the H were moving by exchanging between neighboring BH_4 units, the ^{11}B linewidth could not decrease below that predicted from B-B dipolar interactions. This limiting width is calculated to be 1,600 Hz, while the narrowest line in Figure 7 is 300 Hz (all values FWHM). So, the BH_4 are diffusing as intact units.

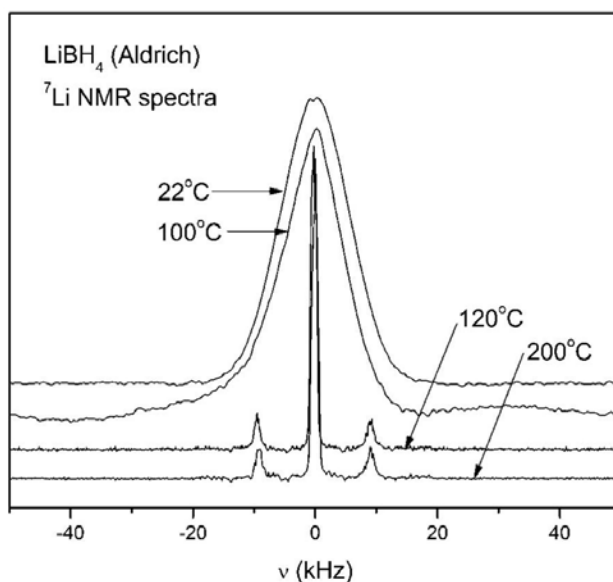


FIGURE 4.

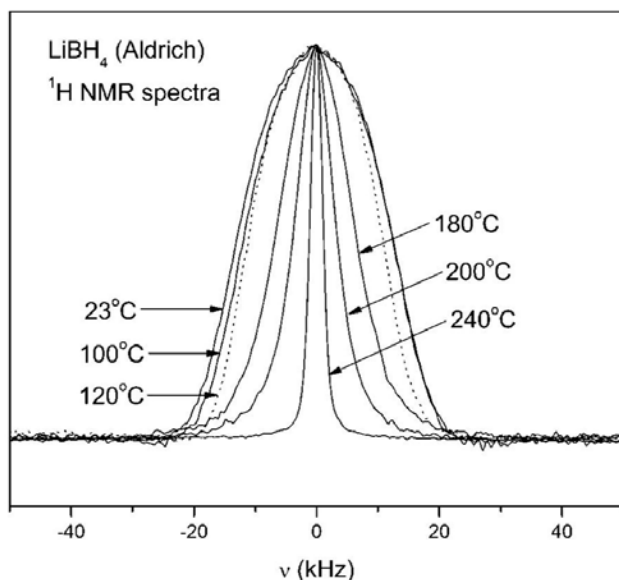


FIGURE 5.

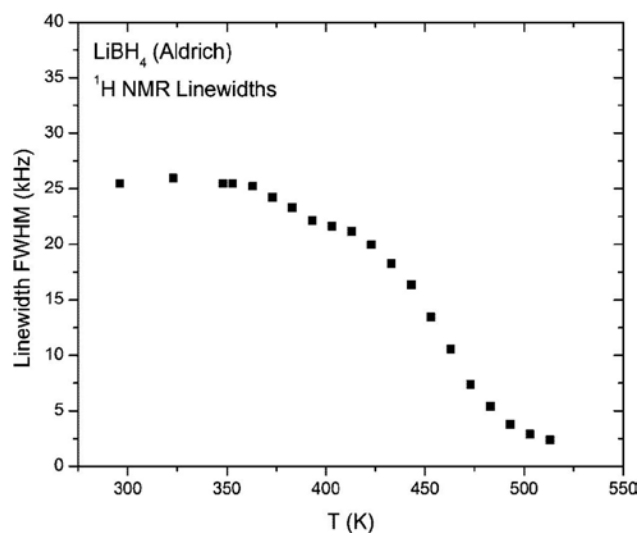


FIGURE 6.

Measurements in molten LiBH_4 at 285°C rule out rapid H-exchange between BH_4 units. As displayed in Figure 8, the ^{11}B spectrum has 5 lines of intensity ratio 1:4:6:4:1. This is unambiguous evidence that each BH_4 has long-lived spin states of the 4 H atoms (i.e., 4 up, 3 up + 1 down, 2 up + 2 down, etc.). Rapid exchange would lead to collapse (averaging, narrowing) of the 5-line pattern. From the linewidth in Figure 8, the BH_4 lifetime against H-exchange is at least 16 ms. From spin-echo experiments, the lifetime is at least several seconds. Thus, exchange in the melt is slow; in the solid the exchange will be even slower. Thus the previously observed isotopic scrambling of BH_4 , BH_3D , BH_2D_2 , etc does not occur through rapid H-exchange.

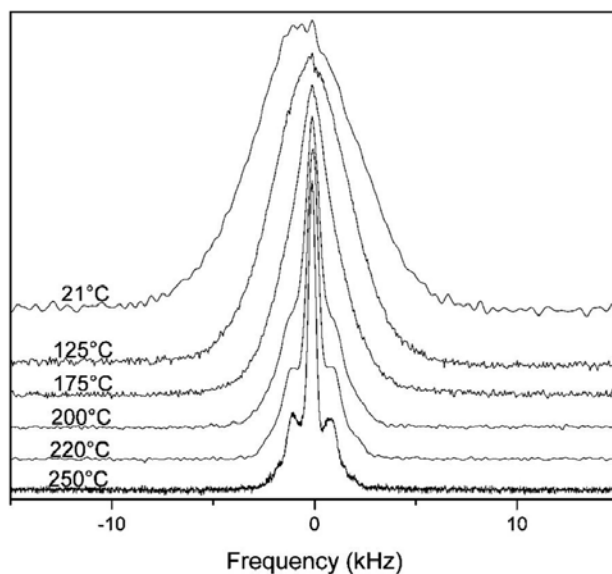


FIGURE 7.

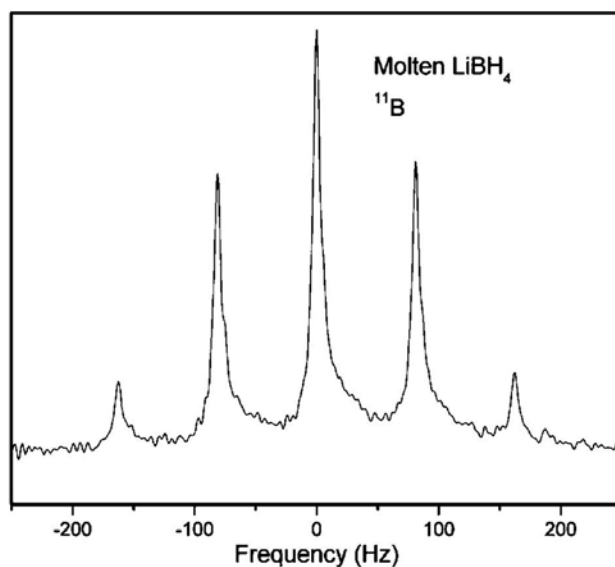


FIGURE 8.

Separate NMR isotope scrambling experiments starting with mixed LiBH_4 and LiBD_4 powders find nearly complete isotopic mixing in 30 minutes or less. Thus, in the melt, H-exchange falls in between the several second and 30 minute time scales.

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People Working on DOE Project

Robert L. Corey

visiting professor from South Dakota School of Mines and Technology, 2 months per year, 22%

Robert C. Bowman, Jr.

RCB Hydrides LLC.

Bowman is a consultant and is co-investigator.

Graduate Students:

- Timothy Ivancic, full support.
- David T. Shane, full support.

Undergraduate student:

Charles McIntosh, summer student, 3 months.

Collaborators at other institutions:

- Ragaiy Zidan, Ashley Stowe (now at Y12, Oak Ridge), Savannah River National Laboratory.
- Son-Jong Hwang, California Inst. Of Technology, Chemistry NMR Facility, sub-contract leader.
- Jacques Huot, U. Quebec Three Rivers.
- Martin Dornheim, Rudiger Bormann, Jose Bellosta von Colbe, GKSS in Germany.