NMR Studies of the Hydrogen Storage Compound NaMgH₃

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Hydrogen and ²³Na NMR were performed to 400 °C on NaMgH₃ powder produced by reactive ball-milling of NaH and MgH₂. The H resonance shows narrowing already at 100 °C as a narrow line superimposed on the broad, rigid-lattice signal. With increasing temperature, the fraction of spins in the narrow component grows smoothly, approaching 100% near 275 °C. This heterogeneous narrowing suggests a wide distribution of H motion rates. After annealing at 400 °C, the narrow component intensity at temperatures below 200 °C was substantially reduced and both H and ²³Na relaxation rates 1/T₁ were decreased. Thus, it appears that the high rates of H motion, particularly on first heating, are due to regions with poorly organized crystal structure. If this disorder could be maintained, this might be an avenue toward improved reaction kinetics of this or other hydrides. In the annealed sample, the activation energy for H diffusion is approximately 95 kJ/mol.

Introduction

The hydrogen content of NaMgH₃ is 6% (w/w), which makes this material attractive for hydrogen storage. NaMgH₃ is usually synthesized by ball-milling NaH and MgH₂ together in equal mole proportions1–4 or by forming an intimate physical mixture of NaH and MgH₂ and heating under H₂ gas.5 An alternate route is molten-state processing in which the ingredients are melted together under high H₂ pressure.6 NaMgH₃ is expected to be an ionic solid, like its constituents; indeed, an electronic structure study finds a wide band gap.7

Because of the ionic bonding, one might expect H diffusion in NaMgH₃ to be slow. For example, in bulk MgH₂, the rate of H atomic diffusive jumps8 is only 400 s⁻¹ at 400 °C. This motion is too slow to narrow the hydrogen NMR line and was measured with the dipolar slow-motion (T₁D) method. However, NaMgH₃ can be reversibly dehydrided and rehydrided, which is a substantial improvement in kinetics over bulk MgH₂.9 The reaction scheme is two-step.1–4

NaMgH₃ ↔ NaH + Mg + H₂ (1)

NaH ↔ Na + ¹/₂H₂ (2)

with plateau pressures of 1.5 and 0.4 bar for the two steps at 400 °C, respectively. The reversibility of the reactions suggests that H may be more mobile in this system than in MgH₂, for example.

A recent study5 of neutron diffraction and scattering in NaMgD₃ hypothesized that the apparently superior mobility of H or D in this material results from its perovskite structure,10,11,3 which is similar to many oxides ABO₃. Site occupancy factors slightly less than unity on the D-atom sites suggest a non-negligible concentration of D-vacancies, which would increase the rate of D (or H) diffusion. Also, the thermal ellipsoids of the D atoms stretch out toward neighboring D atoms at modestly elevated temperatures indicating that the energy barriers to D-atom jumps may be small. Additionally, the tilt angle of MgD₆ octahedra decreases with rising temperature; by analogy with the oxide perovskites, this is expected to reduce the energy barriers for D-atom diffusive motion.

Here, we present hydrogen and ²³Na NMR data for NaMgH₃; the H line width data, in particular, demonstrate rapid H motion. Changes in the line-narrowing behavior after high-temperature annealing indicate that the narrowing at low temperatures is due in part to regions of initially poorly organized crystal structure.

Experimental Methods

Samples of NaMgH₃ were prepared at Savannah River National Laboratory (SRNL) by addition of equimolar quantities of NaH (Aldrich, as received) and MgH₂ (Alfa Aesar, as received) with four 6.35 mm and two 12.7 mm hardened steel balls in a 65 mL Spex 8000 high-energy ball mill vessel at room temperature for 10 h. The mill was filled with 5.9 L of argon gas to reduce the formation of oxide byproducts. The NaH (Aldrich, as received) was dried under vacuum at 50 °C for 12 h before use. The MgH₂ (Alfa Aesar, as received) was ground to a fine powder in an agate mortar and pestle before use. The reaction scheme is two-step:1

NaH + MgH₂ → NaMgH₃ + H₂

The hydrogen generation reaction was performed at room temperature in a 600 mL vessel with a 10 cm diameter by 30 cm length, while the mixture was agitated by a paddle stirrer at 3000 rpm. The yield of NaMgH₃ was 34% by weight. The product mixture was then ball-milled for 10 h to achieve a uniform product.

The reaction scheme for dehydridation and rehydridation is as follows:

NaMgH₃ → NaH + Mg + H₂

The dehydridation reaction was performed in a 500 mL vessel with a 10 cm diameter by 30 cm length, while the mixture was agitated by a paddle stirrer at 3000 rpm. The yield of NaMgH₃ was 34% by weight. The product mixture was then ball-milled for 10 h to achieve a uniform product.

References

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temperature under a dry argon atmosphere. The materials were milled for 5 h to promote complete reaction of the binary hydrides. X-ray diffraction (XRD) of the resulting powder indicated conversion to NaMgH₃ from comparison to the XRD data of Ronnebro et al.¹⁰ XRD also found small amounts of NaH and MgO. XRD is only sensitive to crystalline materials, and so amorphous or excessively small grain-size or dissolved impurities would not be detected.

The material was shipped under argon and was stored and handled in a N₂ glovebag. The samples were loaded into borosilicate glass tubes and were flame-sealed under N₂ or Ar gas. For ²³Na NMR, fused silica tubes were used to avoid sodium signals from the glass tubes.

The H NMR was performed in the 2.0 T field of a Varian electromagnet with ¹⁹F field stabilization with H frequency of 85.03 MHz. The 90° radio frequency (rf) pulse duration was about 10 μs. The ²³Na data were obtained at 79.27 MHz in a 7.04 T Oxford cryomagnet. For H measurements, the NMR probe was heated by a temperature-regulated stream of air flowing at 50 L per minute. For ²³Na work, a regulated, noninductive heater surrounded the sample and radio frequency NMR coil. For both H and ²³Na, a type-T thermocouple within 2 cm of the sample indicated the temperature to within ±3 °C. The Q-factors of the probes were kept low for faster recovery from the rf pulses; for both nuclei, the tuned circuit response was about 2 MHz wide, full width at half-maximum (fwhm).

Hydrogen spectra were obtained from free induction decays (FIDs) following short rf pulses of 1–2 μs duration to reduce spectral distortion. The visible portion of the FID (the part not obscured by probe ringing) was extrapolated back to zero time using a Gaussian function joined onto the data as described elsewhere.¹² The ²³Na spectra were also obtained from FIDs.

The relaxation times T₁ were measured using a saturate-wait-inspect strategy.¹³ Saturation was obtained by a train of 10–20 π/2 rf pulses spaced by 1 ms or by a single, long rf pulse that saturated through rf field inhomogeneity. Inspection used a single π/2 pulse and the subsequent FID. Hydrogen T₁ measurements used a continuous (not pulsatile) spin-lock.¹³ The relaxation time T₁ of dipolar spin order¹⁴ was measured with the Jeener–Broekaert sequence¹⁵ with phase alternation (by 180 degrees of the first pulse) to eliminate signals from residual Zeeman order. The typical 90 degree pulse was 10 μs and the 45 degree pulses were 5 μs; the separation of the first two pulses was 2 μs. The amplitude of the Jeener echo following the third pulse decayed nearly exponentially as a function of the time separation between pulses two and three.

Results and Discussion

Hydrogen NMR lineshapes from room temperature to 400 °C are presented in Figure 1a. These data are taken upon rising temperature for an as-prepared sample (that is, upon initial heating). At 23 °C, the resonance displays only a broad component of approximately the same width as MgH₂ indicating that NaMgH₃ is in the rigid lattice limit (no atomic motions or only slow ones) at 23 °C. At only modestly elevated temperatures T such as 100 °C, a distinct narrow component appears. With further increases of temperature, the spectral intensity (area) of the narrow peak increases at the expense of the broad component. The width of the narrow component decreases slowly with rising T. The intensity of the narrow component is much too large to be explained as H₂ gas;¹⁶ the onset temperature is also too low.

We have analyzed the spectra by assuming that they are superpositions of two components, one broad and one narrow.

Furthermore, we assume that the broad fraction is well-described by the 23 °C, rigid-lattice spectrum (that is, it shows no narrowing at all). This procedure is illustrated in Figure 2, where the spectrum observed at 126 °C is fitted in its wings to the 23 °C spectrum, appropriately scaled in intensity. The difference contains only the narrow component. The success of this procedure up to 275 °C demonstrates the essential validity of the above assumptions. Above 275 °C, the broad component is small and difficult to quantify; broad resonances of small intensities (areas) have very small amplitudes (heights).

The spectral decomposition described above and in Figure 2 allows the relative intensities of the narrow and broad components to be determined. We define F, the fraction of the total intensity residing in the narrow component, as

\[ F = \frac{A_N}{A_N + A_B} \]  \hspace{1cm} (3)

where N and B denote narrow and broad areas (A). Provided that the spectra are fully relaxed (longitudinal spin magnetization fully recovered between subsequent rf pulses as we were careful
For the data taken upon initial heating (filled symbols), $F$ increases from essentially zero at 50 °C to essentially one above 275 °C.

Two aspects of the line narrowing in NaMgH$_3$ are remarkable. First, it starts at a very low temperature, 100 °C; one may compare with MgH$_2$, where extrapolation of the hopping rate determined by $T_{1D}$ relaxation measurements yields $\omega_H \sim 10^5$ s$^{-1}$ (onset of line narrowing) only at 550 °C. In connection with this comparison, both systems have similar equilibrium H$_2$ pressures$^{1-4,10}$ at 400 °C (1.5 and 22 bar for NaMgH$_3$ and MgH$_2$, respectively). The second aspect is that the line narrowing is heterogeneous and is spread across a wide temperature range. That is, the material must not be uniform, with some regions or H atoms having greater H mobility than others. The simplest model of this is to assume that, for some reason, the motion rates $\omega_H$ of H atoms are (1) widely distributed and (2) thermally activated functions of temperature as is usual. Thus, with increasing temperature, the entire broad distribution slides toward faster rates $\omega_H$ so that an increasing fraction $F$ of hydrogen atoms will display line narrowing ($\omega_H > 10^5$ s$^{-1}$). A similar description has been proposed$^6$ for ball-milled MgH$_2$ with Nb$_2$O$_5$ additive.

The data discussed so far in Figures 1a and 3 were obtained upon initial heating and increasing temperature. The data set shown as open symbols in Figure 3 were obtained upon heating from room temperature after the sample had sat at 400 °C for 30 min. All subsequent measurements, upon cooling or repeated warming, agree with these data showing that the sample was thoroughly annealed at 400 °C. Here, the narrow fraction $F$ in Figure 3 is much smaller in the 100–200 °C interval, with $F$ rising more steeply in the vicinity of 275 °C, heading toward one. Corresponding spectra from annealed material are shown in Figure 1b. The annealed spectrum at 400 °C is narrower than the first-heating data at 400 °C; this simply reflects changing field homogeneity (an instrumental effect) as confirmed by first-heating data upon a fresh sample (not shown).

We present further evidence of annealing in Figure 4 where two spectra, both measured at 125 °C, are compared. One is upon initial heating and the other is after annealing by exposure to 400 °C. The relative intensity of the narrow component is much smaller in the annealed material. This suggests that the as-milled NaMgH$_3$ has imperfections in the atomic-level structure and that these imperfections are partially removed at 400 °C. Presumably, the reaction between NaH and MgH$_2$ is not yet complete after ball milling. The imperfections are at least partially responsible for the remarkable line narrowing at modest temperature, below 200 °C, in the as-milled material.

Relaxation data appear in Figure 5. Here, the data were taken on annealed NaMgH$_3$ and refer to the narrow spectral component (whenever two components are evident). $T_2^*$ is the 1/e decay time of the long component of the FID. Above 350 °C, the spin–echo envelope decay time $T_2$ becomes somewhat longer than $T_2^*$ indicating, that some static (refocusable) source of broadening, such as field inhomogeneity, depresses $T_2^*$ in this region. The rotating-frame relaxation time $T_{1p}$ was measured by recording the decay of signal amplitude as a function of spin-
Figure 5. Hydrogen relaxation times $T_1$, $T_2$, and $T_{1p}$ for an annealed sample of NaMgH$_3$. The data refer to the narrow spectral component when two components are distinguishable. The solid curve was calculated using eqs 4 and 5.

lock duration.$^{13}$ The spin signal decayed nearly exponentially as a function of spin-lock duration. $T_{1p}$ presents a broad minimum near 300 °C increasing by only a factor of 3.5 over the wide range of 225–400 °C. If the spin system is described by a single hydrogen motion rate $\omega_H$, standard relaxation theory leads to a relaxation rate of approximately$^{19}$

$$T_{1p}^{-1} = M_2 \frac{1}{\omega_H} \frac{1}{1 + 4\omega_H^2 / \omega_B^2}$$

(4)

where a Lorentzian spectral density is assumed and $\omega_1$ is the angular frequency of nutation, $\gamma B_1$ (with $B_1$ the rf field strength). $M_2$ is the second moment that characterizes the squared strength of the fluctuating dipole interactions. This predicts a maximum relaxation rate and minimum $T_{1p}$ when the hopping rate $\omega_H$ is 2$\omega_1$ or 3 × 10$^5$ s$^{-1}$ here. The H hopping rate $\omega_H$ was taken according to the thermal activation expression

$$\omega_H = \omega_0 \exp(-E/kT)$$

(5)

The attempt frequency $\omega_0$ was set to 2 × 10$^{14}$ s$^{-1}$, and the activation energy was 95 kJ/mol as determined below. The second-moment $M_2$ was adjusted to make the calculated minimum value of $T_{1p}$ agree with the measurements. The theoretical curve in Figure 5 has stronger temperature dependences than the data suggesting that there is a distribution of hydrogen hopping rates $\omega_H$ even in annealed material. The data also show that $\omega_H$ remains on the order of 10$^5$–10$^7$ s$^{-1}$ at these temperatures. This specifically rules out liquidlike (10$^{11}$–10$^{12}$ s$^{-1}$) hopping rates and the fast motion rates typical of superionic conducting solids.$^{20,21}$ In Figure 5, the weak temperature dependence of $T_2$ toward lower temperatures reflects our selection of the narrow component of the resonance.

Line-narrowing data and $T_{1D}$ (relaxation time of dipolar spin order) were determined for an annealed NaMgH$_3$ sample as in Figure 6. The Jeener–Broekaert three-pulse method$^{15}$ was used to create and measure dipolar spin order and to measure its decay time, $T_{1D}$. To within a factor of 2, the rate $\omega_H$ of H hopping motion between sites is predicted to equal 1/$T_{1D}$, the strong collision result of Slichter and Allion that applies for motions too slow to narrow the line.$^{14,22}$ At higher temperatures, line narrowing is expected to follow (Δf is in Hz units, fwhm)

$$\Delta f = (\pi/1.39)(\Delta f_{RL})^2 / \omega_H$$

(6)

once narrowing is well-developed as shown elsewhere.$^{23}$ The static, rigid-lattice line width (fwhm) is $\Delta f_{RL}$ again in Hz units. The data in Figure 6 that are circled were selected to be in the middle of thermally activated regions, where the above assumptions hold most closely. This screening is done to avoid, for example, the intrinsic inaccuracy of using Jeener–Broekaert to measure short $T_{1D}$ values near the onset of narrowing (here, one can no longer neglect the time for the spin system to reach internal equilibrium). This also avoids line width measurements near the onset of narrowing as well as lines that are so narrow that field inhomogeneity is no longer unimportant.

The H hopping rate $\omega_H$ was determined from $\omega_H = 1/T_{1D}$ or from eq 6 for the circled data points in Figure 6. The values were fit to the thermal activation expression, eq 5, as shown in Figure S1 of the Supporting Information. The values so determined are $\omega_0 = 2 \times 10^3$ s$^{-1}$ (factor of 10 uncertainty in each direction) and activation energy $E = 95$ kJ/mol (0.98 eV, $E/k = 11,400$ K, all ±7%). The activation energy is much smaller than that determined$^8$ for bulk MgH$_2$, 166 kJ/mol; the lower energy may partly explain why NaMgH$_3$ can be reversibly hydrided,$^{1,4}$ but bulk MgH$_2$ generally cannot.

The reasonable value of attempt frequency demonstrates the success of our procedure. We have used $T_{1D}$ and narrowed line width data points which describe the largest fraction of the resonance. That is, the $T_{1D}$ data describe the broad component (the selected points in Figure 6 are at or below 200 °C, where the area of the narrow component of the annealed line shape is small as in Figures 1b and 3) and the selected line width data are from temperatures (325, 350, and 375 °C) where essentially only the narrow component is present. While the discrepancy between the data and the calculated curve in Figure 5 indicates the presence of a distribution of H motion rates even in annealed material, we believe the thermal activation parameters taken from the data of Figure 6 describe the average H motion rate.
Calculations of H diffusion in NaMgH$_3$ have been performed by Hao and Sholl.\textsuperscript{24} The calculations are based on the methodology of Van de Walle applicable to ionic and complex hydrides.\textsuperscript{25,26} The identity of the dominant point defects depends on the Fermi energy (through the requirement of electrical neutrality) and the chemical potential of H atoms.\textsuperscript{24} The calculations identify the mobile defects in NaMgH$_3$ as H interstitials.\textsuperscript{24} Concerted motion of a H interstitial onto a H lattice site (pushing that H into a new interstitial site) is predicted to have a very low migration energy of about 0.12 eV (\textsuperscript{3}Na, first heating) is predicted to have a very low energy (through the requirement of electrical neutrality) and the chemical potential of H atoms.\textsuperscript{24}\textsuperscript{27} The calculations identify the mobile defects in NaMgH$_3$ as H interstitials.\textsuperscript{24} Concerted motion of a H interstitial onto a H lattice site (pushing that H into a new interstitial site) is predicted to have a very low migration energy of about 0.12 eV (\textsuperscript{3}Na, first heating).

The 23Na lineshapes were unremarkable. The shapes were approximately Gaussian with line widths decreasing continuously from 6 kHz (fwhm) at room temperature to about 1.5 kHz at and above 350 °C. The Na–Na Van Vleck dipole–dipole second moment,\textsuperscript{30} relevant to the case where the H diffuses rapidly, was calculated treating the 23Na as like spins; assuming a Gaussian shape, the corresponding line width is 1520 Hz, which is in good agreement with the measurement. Above 300 °C, a second, overlapping peak was evident. This peak was identified as NaH from its chemical shift relative to NaMgH$_3$; growth smoothly with increasing temperature reaching ~100% near 275 °C. Because of the continuous growth of the narrowed line, it cannot be identified with hydrogen atoms residing at surfaces or grain boundaries or in one of the two crystallographically inequivalent sites. The explanation of continuous growth of the narrowed feature must involve a broad distribution of H motion rates at any temperature.

Figure 7. Relaxation time $T_1$ for hydrogen and for $^{23}$Na in NaMgH$_3$ upon first heating (filled symbols) and after annealing at 400 °C (open symbols).

An observed decrease in $T_1$ upon cryo-grinding of pharmaceutical solids may also be due to unpaired electrons.\textsuperscript{31} The bulk magnetic susceptibility of one as-milled NaMgH$_3$ sample in a glass tube was determined with a superconducting quantum interference device (SQUID) magnetometer. The susceptibility (negative and temperature independent) of an empty glass tube was used to correct the NaMgH$_3$ result. The corrected result was paramagnetic (positive and varying as 1/T) and corresponds to one free $g = 2$ electron spin per approximately 550 formula units. This concentration is reasonable to result in the observed relaxation rates.\textsuperscript{30} The methodology of the calculation was checked with a small sample of TEMPO free radical, giving one free electron per molecular unit, to within the uncertainty.

We thank a reviewer for pointing out related behavior in nanocrystalline LiTaO$_3$, LiNbO$_3$, and Li$_2$O.\textsuperscript{34–36} In the case of lithium niobate, two-component $^7$Li lineshapes appear\textsuperscript{15} with the relative intensity of the narrow component increasing with temperature similar to Figure 3. The enhanced rate of lithium motion is also evident in the $^7$Li $T_1$ and electrical conductivity.

**Conclusions**

In as-prepared NaMgH$_3$, the H NMR line develops already at 100 °C a narrow resonance superimposed on a broad, rigid-lattice background. The fraction of intensity in the narrow feature grows smoothly with increasing temperature reaching ~100% near 275 °C. Because of the continuous growth of the narrowed line, it cannot be identified with hydrogen atoms residing at surfaces or grain boundaries or in one of the two crystallographically inequivalent sites. The explanation of continuous growth of the narrowed feature must involve a broad distribution of H motion rates at any temperature.

Annealing at 400 °C changes the narrowing behavior. The narrowed component below 200 °C is much reduced in intensity, and so the increase toward ~100% at higher temperatures is now steeper. This is confirmed by examining H spectra at 125 °C before and after annealing at 400 °C. In addition, the
relaxation rate $1/T_1$ also decreases substantially after annealing. The changes upon annealing indicate that much disorder exists in the material as prepared. If the disorder could somehow be maintained, this might be a useful method of improving the dehydriding and rehydriding reaction kinetics of NaMgH$_3$, or related hydrides.

In the annealed material, the broad minimum in the rotating-frame relaxation time $T_1$ demonstrates the existence of a distribution of $H$ motion rates $\omega_H$ at any given temperature. In annealed NaMgH$_3$, the line width and $T_1D$ data can be described by an average $H$ motion rate $\omega_H$ with Arrhenius parameters, activation energy $E = 95$ kJ/mol ($E = 0.98$ eV; $E/k = 11,400$ K), and attempt frequency $\omega_0 = 2 \times 10^{14}$ s$^{-1}$.

The longitudinal relaxation rates $T_1^{-1}$ of H and $^{23}Na$ are too fast to be explained by the observed H motions, most of which are $10^3$–$10^7$ s$^{-1}$ or slower at our temperatures. Besides, the slow and weak variations of $T_1$ with temperature rule out such an explanation. We believe unpaired electron spins determine the relaxation rates $T_1^{-1}$ as in other ball-milled systems, including MgH$_2$. A measurement of bulk magnetic susceptibility corresponding to one free electron per 550 formula units confirms the presence of a sufficient concentration of these relaxation centers.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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