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Comprehensive NMR Study of Magnesium Borohydride

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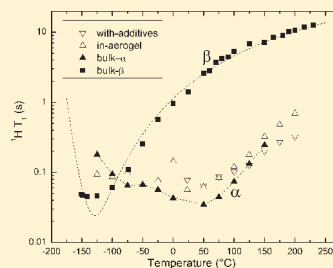
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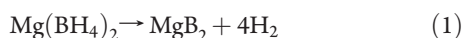
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ABSTRACT: ^1H and ^{11}B NMR measurements were performed to study BH_4 reorientations in four samples of $\text{Mg}(\text{BH}_4)_2$. These include the low (α) and high (β) temperature bulk solid phases, α -phase material with TiF_3 and ScCl_3 additives, and α -phase material incorporated into a carbon aerogel. All four samples show ^1H T_1 minima within our temperature range from reorientational motion of the BH_4 tetrahedra. The β -phase ^1H T_1 minimum occurs at a lower temperature than that for the α -phase, indicating a lower activation energy for reorientations. The α -phase ^1H spectra display the onset of broadening at low temperatures because of the slowing of reorientations but show no indication of line narrowing at high temperatures from translational diffusion. The β -phase ^1H spectra are similar, but here T_{1D} measurements were performed to determine the BH_4 hopping rate. Above 150 $^\circ\text{C}$, a significant narrow component does appear in the ^1H spectra of the aerogel sample, indicating substantially increased diffusive motions in this component.



INTRODUCTION

Complex hydrides, including $\text{Mg}(\text{BH}_4)_2$, are attractive for hydrogen storage applications because they offer high gravimetric and volumetric hydrogen densities.^{1,2} Magnesium borohydride, for example, has a volumetric hydrogen density of 112 g/L, and yields 14.9% hydrogen by weight when fully dehydrided:^{3,4}



A disadvantage of the complex hydrides compared to metallic interstitial hydrides is the high temperatures generally required for dehydriding and the high pressures (and temperatures) required for rehydriding. These factors reflect both high reaction enthalpies and slow kinetics of the reactions. Magnesium borohydride, however, is better than many other complex hydrides in these regards, beginning decomposition at about 270 $^\circ\text{C}$ (compared to temperatures greater than 500 $^\circ\text{C}$ required for many other complex hydrides, such as KBH_4 and NaBH_4).^{4,5} The material has been regenerated with 75% yield using 95 MPa of H_2 and 400 $^\circ\text{C}$.⁶ Diffusion is important to the kinetics of the dehydriding and rehydriding reactions, with faster diffusion yielding faster cycling, but little is known about hydrogen diffusion in bulk $\text{Mg}(\text{BH}_4)_2$.

One method to accelerate the release and uptake of hydrogen or lower the desorption temperature, is the use of catalytic additives.^{7,8} Addition of 5 mol % TiF_3 and ScCl_3 (each) has been reported to increase both the rates and the ultimate amount of hydrogen release from $\text{Mg}(\text{BH}_4)_2$, with 95% of the hydrogen released within two hours at 300 $^\circ\text{C}$ from a sample with additives, versus ten hours required for a sample without these additives.⁴

Another method aims to accelerate the kinetics by reducing the distance that hydrogen must diffuse within the material to reach the surface. By either ball milling the material⁹ or incorporating it into a nanostructure, such as a carbon aerogel,¹⁰ the grain-size can be reduced. Such procedures also tend to introduce defects near the grain boundaries or scaffold walls, which can result in more rapid diffusive motions within the material.¹¹

There are two phases of bulk $\text{Mg}(\text{BH}_4)_2$ that can be obtained depending on the synthesis conditions. The hexagonal (α) phase transforms irreversibly to the orthorhombic (β) phase upon heating to 180 $^\circ\text{C}$. The β -phase is stable at all temperatures up to the final decomposition of the material.¹² In this study, we use ^1H and ^{11}B NMR to examine the atomic motions in both the low (α) and high (β) temperature bulk solid phases of $\text{Mg}(\text{BH}_4)_2$, as well as α -phase material incorporated into a carbon aerogel and an α -phase sample with TiF_3 and ScCl_3 additives.

EXPERIMENTAL METHODS

The β -phase material (labeled “bulk β -phase”) was formed by ball milling MgCl_2 and NaBH_4 at The Ohio State University with a 1:3 ratio in dry diethyl ether for three days. The jar was then opened in an argon filled glovebox, and the reaction mixture was transferred to a glass filter. The mixture was filtered at a reduced pressure, and the resulting cakes were washed with diethyl ether. A clear colorless filtrate was evaporated at room temperature, resulting in a viscous liquid. Heating to 100 $^\circ\text{C}$ yielded a white

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solid. The powder was ground with a mortar and pestle, and then heated using an oil bath to 220 °C, and held there for four hours. The powder was ground again, and then heated yet again for another four hours, yielding the final bulk β -phase $\text{Mg}(\text{BH}_4)_2$.

As described elsewhere,⁴ the α -phase material (labeled “bulk α -phase”) was prepared at Sandia National Laboratories by adding 100 mmol of 1 M $\text{Mg}(n\text{-C}_4\text{H}_9)_2$ in heptane dropwise to 400 mmol of $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ in 200 mL of dry toluene. Excess toluene was removed, and the resultant white precipitate $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{S}(\text{CH}_3)_2$ was washed several times with dry toluene and then heated to 160 °C under vacuum overnight to remove complexed $\text{S}(\text{CH}_3)_2$. X-ray diffraction was used to verify that the material was in the α -phase.¹³ The α -phase material with mixed-in additives of 5 mol % TiF_3 and 5 mol % ScCl_3 (labeled “with-additives”) was also created at Sandia by ball-milling these additives together with $\text{Mg}(\text{BH}_4)_2$ in a SPEX 8000 high-energy mill using tungsten carbide balls.

To create the aerogel-incorporated sample (labeled “in-aerogel”), α -phase $\text{Mg}(\text{BH}_4)_2$ from The Ohio State University was used. This α -phase material was created using the same procedure as for the β -phase, except with a final oil bath temperature of only 167 °C. The material was incorporated with a carbon aerogel at United Technologies in a diethyl ether solution. The samples were dried at 100 °C for 48 h, in vacuum followed by desolvation at 140 °C again under vacuum for 24 h, then at 120 °C for 96 more hours. The low temperatures were used to minimize hydrogen loss. The aerogel has an average pore diameter of 16.5 nm.

The NMR experiments were performed at Washington University, using two home-built rf spectrometers controlled by locally written software. The hydrogen work was done at 85.03 MHz in the 2.0 T field of an electromagnet with ^{19}F NMR field stabilization. The ^{11}B NMR was done at 96.15 MHz in a 7.04 T cryomagnet. Both NMR probes used solenoidal rf coils, oriented perpendicular to the static field. For variable temperature hydrogen NMR studies, temperature regulated air or nitrogen gas (for cooling) was blown across the samples. The ^{11}B samples were heated by a noninductive heater in stationary nitrogen gas. Temperatures were measured to ± 2 °C with type-T thermocouples adjacent to the rf coils.

NMR spectra were generated by Fourier transformation of the free induction decay (FID) following a 2 μs pulse. The portion of the FID obscured by probe ringing was replaced by fitting a Gaussian to the unobscured data;¹⁴ this amounts to approximately 2 μs of data for hydrogen NMR and 8 μs for boron NMR. Note that proton decoupling was not used for any of the ^{11}B data.

T_1 was measured using a saturation-recovery sequence.¹⁵ For hydrogen NMR, saturation was achieved via the application of 20 sequential 90° pulses, spaced by 1 ms each. For boron NMR, a long 200 μs pulse saturated through rf field inhomogeneity. For ^1H , the 90° pulse time was measured to be 8 μs . For ^{11}B , a nutation experiment found the maximum signal followed the application of a 10 μs pulse, as compared to 18 μs for a solution-state sample of $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, indicating that our 10 μs pulse on $\text{Mg}(\text{BH}_4)_2$ was exciting only or primarily the central transition. (^{11}B is $I = 3/2$, so one expects an ideal ratio of 2, close to the 1.8 found here.)¹⁶

T_{1D} , the decay time of dipolar spin order, was measured on hydrogen spins with the Jeener–Broekaert sequence.^{17,18} The Jeener echo amplitude was fitted to $A \times \exp(-t/T_{1D})$ to obtain T_{1D} .

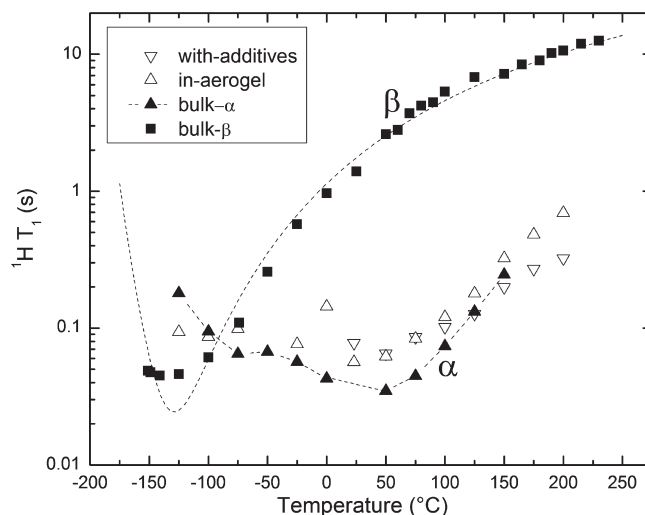


Figure 1. ^1H T_1 for all four samples of $\text{Mg}(\text{BH}_4)_2$. Note the minimum for the bulk β -phase material near -135 °C, and the spread out minima for the three α -phase materials indicative of several activation energies for reorientation. The dashed line tracking the β -phase data points is a theoretical fit with a single activation energy of 123 meV. The dashed line tracking the bulk α -phase data is just to aid the eye.

RESULTS AND DISCUSSION

Hydrogen T_1 . Figure 1 shows the hydrogen T_1 of all four samples we examined as a function of temperature. T_1 of the bulk β -phase is quite distinct from the T_1 of the remaining three materials, all expected to be in α -phase. The β -phase material has a T_1 (filled squares) that increases with temperature over most of the range. A T_1 minimum is evident near our lowest available temperature, around -135 °C. This minimum is due to reorientational motion of the BH_4 anions, in analogy to the behavior seen at similar temperatures in NaBH_4 , KBH_4 , and LiBH_4 .^{19,20}

The β -phase T_1 data were fit using a model with a single activation energy E_a describing the reorientations

$$\frac{1}{\tau_c} = \omega_a \times \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

where τ_c is the temperature-dependent correlation time and ω_a is the attempt frequency. The relaxation time T_1 follows standard relaxation theory

$$\begin{aligned} \frac{1}{T_1} = \hbar^2 \bigg[& \left(\frac{9}{30} \right) \gamma_H^4 \left(\sum \frac{1}{r_{HH}^6} \right) \left(\frac{\tau_c}{1 + \omega_H^2 \tau_c^2} \right. \\ & \left. + \frac{4\tau_c}{1 + 4\omega_H^2 \tau_c^2} \right) + \left(\frac{1}{2} \right) \gamma_H^2 \gamma_B^2 \\ & \left(\left(\sum \frac{1}{r_{BH}^6} \right) \left(\frac{\tau_c}{1 + (\omega_H - \omega_B)^2 \tau_c^2} \right. \right. \\ & \left. \left. + \frac{3\tau_c}{1 + \omega_H^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_B)^2 \tau_c^2} \right) \right) \bigg] \quad (3) \end{aligned}$$

as given by Boden and Abragam.^{21,22} Here, ω_H is the angular resonance frequency of hydrogen, and ω_B is the resonance frequency for boron. We have assumed all the boron are ^{11}B for simplicity, $S = 3/2$. The prefactors provide measures of the strength of the fluctuating dipole interactions, which become

stronger between nuclei with higher gyromagnetic ratios (γ), and as the distance between the nuclei (r) decreases. The parameters r_{HH} and r_{BH} are the H–H and H–B distances, respectively, with our sum performed over a single BH_4 tetrahedron (primarily intramolecular relaxation). Practically, we used the relations $r_{\text{HH}} = 1.63r_{\text{BH}}$, $\gamma_{\text{H}} = 3.11\gamma_{\text{B}}$ to reduce the fitting formula to

$$\frac{1}{T_1} = A \times \left[(0.04797) \left(\frac{\tau_c}{1 + \omega_{\text{H}}^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_{\text{H}}^2 \tau_c^2} \right) + (0.0515) \left(\frac{\tau_c}{1 + (\omega_{\text{H}} - \omega_{\text{B}})^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_{\text{H}}^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_{\text{H}} + \omega_{\text{B}})^2 \tau_c^2} \right) \right] \quad (4)$$

The fitting routine treated ω_{a} , A , and E_{a} as adjustable parameters. The dashed line tracking the β -phase data in Figure 1 represents the model fit. Our fit corresponds to an activation energy of 123 ± 4 meV and an attempt frequency of $(1.1 \pm 0.3) \times 10^{13} \text{ s}^{-1}$. The high quality fit evident in Figure 1 indicates that the simple model has the correct essential features. We note that the fit and resulting parameters E_{a} and ω_{a} are only weakly sensitive to the relative weighting coefficients of the HH and HB terms in eq 4. In the vicinity of the T_1 minimum, the data are flatter (weaker temperature dependence) and shallower (larger minimum T_1) than the fit; this suggests the physical system may have motions described by multiple activation energies.

The remaining three samples all show a hydrogen T_1 minimum around 50 °C, with a second shallower minimum at somewhat lower temperatures visible in the bulk α -phase sample and possibly also visible in the in-aerogel sample. Skripov et al. reported similar behavior in their study of the bulk α -phase; they were able to model the T_1 data by considering reorientations of the BH_4 groups.²³ In particular, they accounted for their T_1 data by assuming three different types of jump processes, with rotation around the 2-fold axis connecting the B and Mg atoms representing the fastest process, and rotations around two other 2-fold axes perpendicular to the B–Mg line being the slower processes. The activation energies for the motions were 116–362 meV. Note that the minimum for the bulk β -phase material occurs at a lower temperature and thus the BH_4 reorientations have a smaller activation energy (than the average of the motions in the bulk α -phase): this simply reflects that the β -phase material has substantially different packing.³ However, the depth of the minimum is approximately the same as that for the α -phase material, which is expected since the minima result from reorientational modulation of the same primarily intramolecular dipole interactions.²¹ Our measurements do not extend low enough in temperature to allow a full analysis of the β -phase T_1 data in terms of multiple motion processes.

The in-aerogel material was never heated above 140 °C during the incorporation process, so it is expected to be in the α -phase initially, as confirmed by the similarity of its hydrogen T_1 to that of bulk α -phase. It is important to note that the aerogel T_1 data (and spectra) were taken beginning at room temperature and continuing up to 225 °C, where some conversion to β -phase may have occurred. Then the sample was cooled to 0 °C and data were taken going down to –150 °C. The 0 °C T_1 point seems abnormally high compared to the nearby data points, possibly indicating partial conversion to the β -phase during heating.

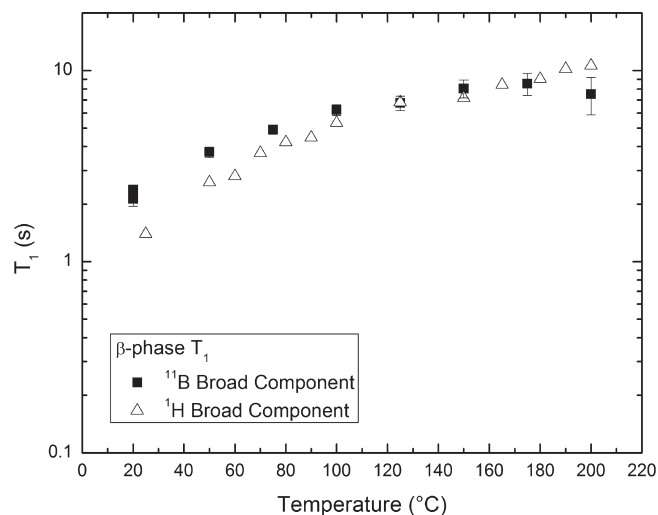


Figure 2. ^{11}B and ^1H T_1 as a function of temperature for the bulk β -phase $\text{Mg}(\text{BH}_4)_2$ material. The similar trend with temperature for both nuclei confirms that a similar process is controlling both T_1 values.

In Figure 2, ^{11}B and ^1H T_1 values are compared for the bulk β -phase material, with very similar temperature dependences evident. This is as expected, since the boron T_1 is driven primarily by ^{11}B – ^1H intramolecular dipole interactions, and the hydrogen T_1 is controlled by ^{11}B – ^1H and ^1H – ^1H intramolecular dipole couplings, and all of these are modulated by the same reorientational correlation time. The approximate agreement of the ^{11}B and ^1H T_1 temperature dependences can be taken as a confirmation that BH_4 reorientations control both relaxation times.

We also note that beginning at 150 °C, a narrow component in the ^1H and ^{11}B spectra (not shown) of the bulk β -phase material becomes resolvable. By fitting two Gaussian functions to the saturation recovery spectra and determining the area of each Gaussian component during recovery, we calculated separate T_1 values for the narrow and broad spectral components. The more mobile boron atoms corresponding to the narrow line had a much shorter T_1 (by approximately 2 orders of magnitude), and T_1 decreased with increasing temperature. The ^1H T_1 of the narrow component was also shorter, approximately 1 s. We believe this narrow component is the result of an impurity, as further discussed below.

^1H Spectra and T_{1D} . We now turn to ^1H spectra and slow motion measurements for the four samples.

β -phase. For the bulk β -phase sample, at 50 °C the ^1H spectrum consists of a single line, approximately Gaussian in shape, with a full width at half of maximum height (fwhm) of approximately 21.3 kHz. The line changes little with increasing temperature until a narrow component, fwhm ~ 800 Hz, begins to appear on top of the broader resonance around 150 °C. (In the ^{11}B spectra, the broad component has a fwhm of ~ 3.4 kHz, the narrow component a FWHM of ~ 400 Hz.) By 200 °C, this ^1H narrow component represents approximately 9% of the spectral area. Its narrow width suggests it may correspond to released gas,^{24,25} but this temperature is too low for significant hydrogen release. The ^1H T_1 of the narrow component is also too long for hydrogen gas.²⁴ Thus, we believe the narrow resonance to be an impurity signal. We suspect it to be the same impurity recorded in the boron spectra and T_1 (see above) because both narrow components appear at the same temperature and have similar fractions of the total resonance intensity.

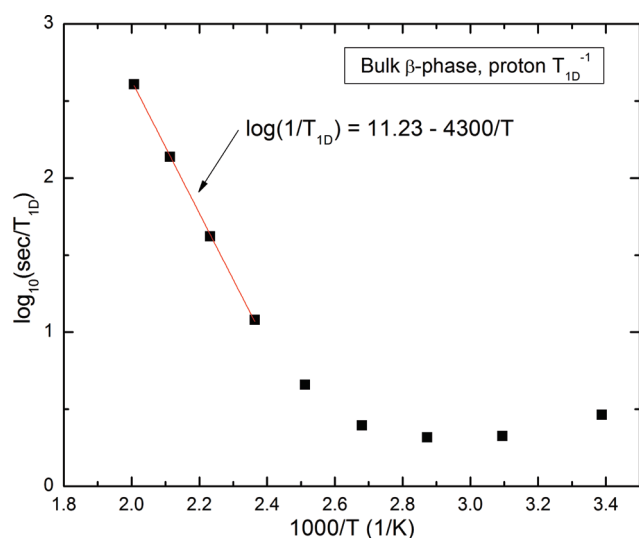


Figure 3. Proton T_{1D}^{-1} on log scale as a function of reciprocal temperature for the bulk β -phase. The fit to the high temperature data indicates BH_4 hopping with an activation energy of 0.85 eV.

Because the BH_4 translational diffusion in the bulk β -material was too slow to narrow the line, we made a measurement of T_{1D} for the bulk β -phase, presented in Figure 3. As discussed by Slichter,^{18,26} for slow motion, the relaxation is in the strong collision regime in which $1/T_{1D}$ is approximately equal to the atomic hopping frequency. Similar to the example of LiBH_4 , this is jump diffusion of BH_4 units.²⁷ At lower temperatures (to the right in Figure 3), T_{1D} is being limited by laboratory frame T_1 relaxation and is thus no longer a good measure of the hydrogen hopping rate. (A spin flip caused by T_1 relaxation will destroy dipolar order, just as a hydrogen site-to-site hop will.) In particular, at room temperature $1/T_{1D}$ is equal to 2.91 s^{-1} . At this temperature, for protons, $2/T_1$ is 1.43 s^{-1} , and for boron $2/T_1$ is 0.94 s^{-1} . (The factor of 2 is present because spin flips of either spin in an interacting pair can invert the dipole interaction.) So in this region the laboratory-frame relaxation is not negligible and the measured $1/T_{1D}$ can no longer be treated as purely because of slow jumps of BH_4 units.

At higher temperatures, $1/T_{1D}$ is a good measure of the hopping rate. The motion rate increases from approximately 12 hops per second at 150°C , to 400 hops per second at 225°C . By fitting the data to

$$\frac{1}{T_{1D}} = \omega_a \times \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

we determined the hopping attempt frequency, ω_a , and the hopping activation energy, E_a . We find that ω_a is equal to $1.7 \times 10^{11} \text{ s}^{-1}$, with E_a equal to 0.85 eV. Attempt frequencies are notoriously difficult to measure, because they are the result, in effect, of extrapolating the measured data to infinite temperature. Our value seems low compared to typical vibration frequencies, like 10^{13} s^{-1} . When we force the fit to $\omega_a = 10^{13} \text{ s}^{-1}$, the activation energy increases to 1.01 eV; the quality of the resulting fit is not badly reduced compared to the fit in Figure 3. The short-range of the data in Figure 3, from which the activation energy is determined, translates into a large uncertainty in the activation energy of $\pm 20\%$. We remark that the maximum hopping rate ($1/T_{1D}$ in Figure 3), about 400 s^{-1} , is much too slow to narrow the resonance (narrowing would require $\sim 10^5 \text{ s}^{-1}$).

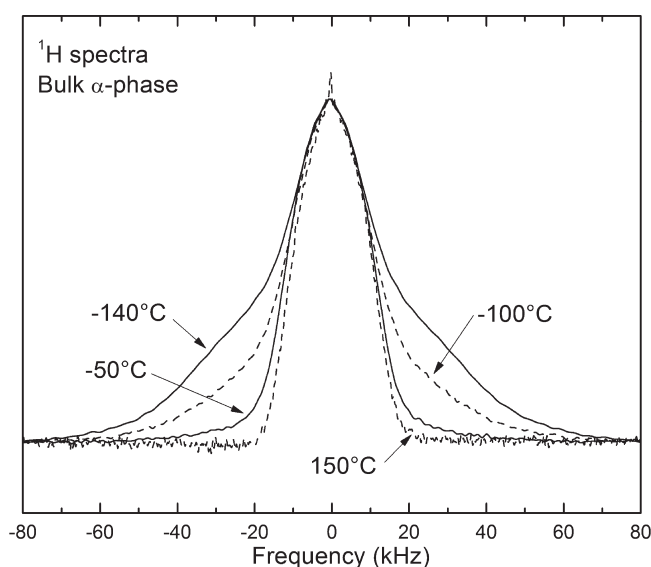


Figure 4. Bulk α -phase $\text{Mg}(\text{BH}_4)_2$ proton spectra. Note the broad wings present at low temperatures, where some of the BH_4 reorientations have slowed to less than of order 10^5 s^{-1} . Very little additional narrowing occurs at elevated temperatures, until a very small narrow component appears on top of the broader resonance near 150°C .

α -phase. Figure 4 shows hydrogen spectra of the α -phase material from -140 to 150°C . At low temperatures, we observe an additional broadening that sets in below about -50°C . The broadening is the result of slowing of the BH_4 reorientations with the largest activation energy (recall the T_1 minimum stretching from -75 to 50°C in Figure 1). No significant further narrowing occurs up to 150°C , indicating no translational diffusion of BH_4 groups on the 10^{-5} s time scale.²² The data we present here is again in accordance with that presented by Skripov et al. in Figure 2 of ref 23. T_{1D} data were taken for the α -phase but simply tracked the temperature dependence of the α -phase laboratory-frame T_1 (much shorter than the β -phase T_1), and thus cannot provide a measure of the hopping rate.

The hydrogen spectra for the α -phase material with TiF_3 and ScCl_3 additives are nearly identical to the bulk α -phase spectra of Figure 4. The T_1 data (Figure 1) are also very similar to that of the bulk α -phase; the T_1 minimum is slightly shallower (larger minimum T_1), suggesting the existence of a broader distribution of reorientation rates in the additive-doped material. There is no NMR signature of an enhanced mobile fraction of H spins (such as a narrowed resonance component) that could explain or be correlated with the observed improved hydrogen release as compared to bulk $\text{Mg}(\text{BH}_4)_2$.⁴ Work at Sandia has indicated that the sample with additives begins releasing trace amounts of hydrogen at around 200°C – 250°C .

The spectra for the in-aerogel material are somewhat different and are presented in Figure 5. The -125°C , 175°C , and 225°C data were all normalized to have the same maximum height, before a vertical shift was added for clarity. The height of the 25°C line was adjusted to make it clear that its line width was approximately equal to the width of the broad component at 175°C . The line at 25°C is nearly identical in shape to the bulk α -phase line at 25°C . At higher temperatures, a substantial narrow component develops, increasing to 26% of total spectral area at 225°C . Although we may have had partial conversion to the β -phase, this is still a much higher fraction of mobile spins

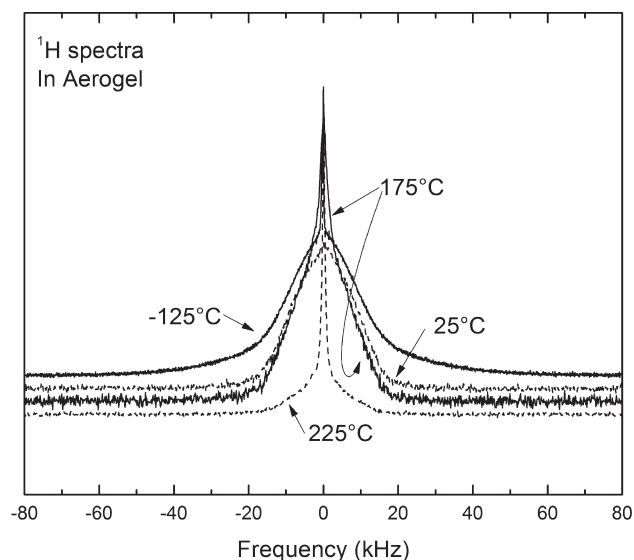


Figure 5. Proton spectra for the in-aerogel sample, offset vertically for clarity. At lower temperatures, broad wings form as reorientations slow, similar to the lineshapes of bulk α -phase material in Figure 4. At higher temperatures a substantial narrow component appears, not seen in other samples. The -125°C spectrum, taken after the 225°C spectrum, also contains a small narrow component likely indicative of some gas release.

than was observed in β -phase $\text{Mg}(\text{BH}_4)_2$. This result is similar to data observed on LiBH_4 incorporated into an aerogel polymer scaffold, where a narrow component was prominent already in the ^1H spectra at room temperature, while no narrow component appeared in the bulk.¹¹ There, the fraction of spins in the narrow component also increased with temperature. The narrow fraction was found to depend on the pore size of the aerogel, with smaller pores and correspondingly larger surface to volume ratios yielding a larger narrow fraction, indicating that the spins near the walls undergo increased motion. We believe we are observing a very similar effect in $\text{Mg}(\text{BH}_4)_2$ incorporated into the aerogel.

As shown in Figure 5, a small narrow component remains in the ^1H in-aerogel spectra upon cooling from 225°C . This remaining narrow component has a very short ^1H T_1 , on the order of 1 ms, suggesting that it may be indicative of some H_2 gas release at the high temperature.²⁴

CONCLUSIONS

In the β -phase $\text{Mg}(\text{BH}_4)_2$ material, reorientational motion of the BH_4 groups produces an ^1H T_1 minimum near -135°C . This is substantially colder than the T_1 minimum in the bulk α -phase, indicating a lower average activation energy for BH_4 reorientation; a fit to the β -phase T_1 data yields an activation energy of 0.12 eV. Although this motion averages away intramolecular interactions, intermolecular interactions remain, resulting in a nearly temperature-independent ^1H line width of approximately 20 kHz from -125°C up to temperatures of 225°C . T_{1D} measurements do show that the BH_4 hopping rate increases with temperature, with an activation energy of about 0.85 eV.

All three α -phase samples show similar ^1H T_1 behavior, again controlled by BH_4 reorientations, but with a higher average activation energy. Low-temperature broadening in the ^1H spectra is evident as the reorientations slow down. At higher temperatures, ^1H spectra for the bulk α -phase and with-additives material

change little, but a significant narrow component develops for the in-aerogel sample, likely representing increased motion of spins near the carbon scaffold walls.

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