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NMR Investigation of Nanoporous γ-$Mg(BH_4)_2$ and Its Thermally Induced Phase Changes

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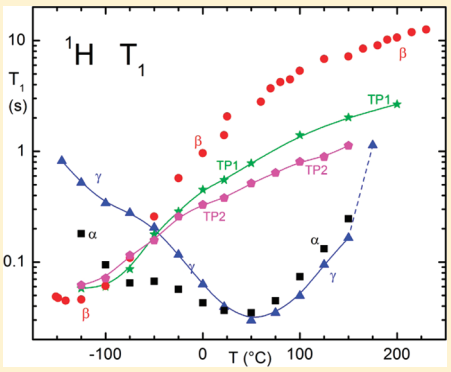
ABSTRACT: The nanoporous polymorph γ-$Mg(BH_4)_2$ with 33% void space has a much lower density than the α and β forms, suggesting that reorientation and diffusion dynamics of BH_4 groups may be enhanced. We report hydrogen NMR line shapes and T_1 and T_{1D} measurements from −125 to 225 °C, along with some ^{11}B results. The main component of the hydrogen NMR line does not show motional narrowing from translational diffusion up to 175 °C, although a small mobile fraction appears at 175 °C. T_{1D} measurements show no evidence for "slow" motions (faster than 10^2 s^{-1}) up to 175 °C, ruling out enhanced overall diffusivity. The hydrogen T_1 is sensitive to reorientations of the BH_4 units. In the γ-phase, a T_1 minimum at 85 MHz is observed at 50 °C, similar to α-phase; the high barrier to reorientation in γ (compared to β-phase where the minimum appears near −135 °C) is confirmed by broadening of the γ-phase hydrogen spectrum at −50 °C and lower temperatures. A sharp increase in T_1 at or above 175 °C signals a transformation of γ-phase to another structure of higher density. T_1 of the transformation product is similar but not equal to that of the β-phase, suggesting the transformation product is primarily β-phase. This is confirmed by powder X-ray diffraction of the transformed material. In situ X-ray powder diffraction studies reveal that γ-$Mg(BH_4)_2$ transforms upon heating in vacuum into the β-phase, and undergoes an amorphization in the presence of gases that can be adsorbed into the pores.



INTRODUCTION

Metal borohydrides are attractive candidates for hydrogen storage[1,2] for transportation and other applications because of their typically large mass fractions[1,3−5] of hydrogen. The utilization of metal borohydrides is often hampered by slow hydrogen release and uptake kinetics,[6−8] which call for fundamental studies of mobility and dynamics of hydrogen and the complex tetrahydridoborate anions, BH_4^-, in this class of materials.

Magnesium borohydride has an extreme structural flexibility (several polymorphs have been observed)[9] and high gravimetric hydrogen storage density of ρ_m = 14.9 wt % H_2, and it stores hydrogen reversibly. It is therefore considered one of the most interesting hydrogen storage materials. However, hydrogen uptake (from the dehydrided state) has up to now only been realized at relatively harsh conditions (400 °C and 950 bar).[10]

A new nanoporous polymorph of magnesium borohydride denoted γ-$Mg(BH_4)_2$ was recently discovered. This polymorph crystallizes with space group symmetry $Id\bar{3}a$ and has a remarkably low material density of ρ = 0.55 g/cm^3 because of a 3D net of interpenetrating channels of ∼8 Å diameter giving ∼33% empty void space.[9] Small molecules such as dichloromethane, nitrogen, or an additional 0.8 H_2 molecules per formula unit can be absorbed in the interior of the γ-polymorph, for example, forming γ-$Mg(BH_4)_2$·0.8H_2 with an extreme hydrogen content of ρ_m = 17.4 wt % H_2. Thus, γ-$Mg(BH_4)_2$ is capable of storing hydrogen both chemically, covalently bonded to boron as BH_4^- anions, and physisorped to the interior of the material in the molecular form as H_2. The highly symmetric cubic γ-$Mg(BH_4)_2$ transforms to a diffraction-amorphous phase at ∼0.5 GPa and to a tetragonal polymorph, denoted δ-$Mg(BH_4)_2$, at ∼2.1 GPa via an extreme volume contraction of 44%. δ-$Mg(BH_4)_2$ has the highest material density for magnesium borohydrides (ρ = 0.99 g/cm^3) and the second highest volumetric hydrogen density for all known hydrides of ρ_V = 147 g H_2/L. The δ-polymorph is stable at ambient pressure and upon heating to ∼150 °C where it transforms back to α-$Mg(BH_4)_2$. It is interesting to note that the structure of α-$Mg(BH_4)_2$ also includes unoccupied voids of 37 Å^3, that is, 6.4% empty space.[11] Above ∼190 °C, α-$Mg(BH_4)_2$ irreversibly transforms to the orthorhombic high-temperature polymorph β-$Mg(BH_4)_2$.[11,12]

The large void space in the γ-phase crystal structure suggests that rapid diffusion of BH_4 units, as observed in $LiBH_4$ but not in α or β-$Mg(BH_4)_2$,[13,14] may occur at an enhanced rate in the γ-phase. One can consider that the existence of large vacant regions in the structure *could* allow diffusion without the need to form vacancy defects, substantially reducing the activation

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energy of the diffusion. Rapid diffusion of BH_4 could have a positive effect on the kinetics of dehydriding and rehydriding of this material. This has prompted our present investigation of hydrogen NMR line shape and T_{1D} (T_{1D}, the decay time of dipolar spin order, is sensitive to motions that are too slow to narrow the line). The hydrogen spin−lattice relaxation time T_1 is also reported because it is determined by and can report upon reorientations of the BH_4 units. We note that related results on γ-$Mg(BH_4)_2$ have appeared recently, with a focus on the BH_4 reorientations.[15]

EXPERIMENTAL METHODS

Dibutyl magnesium, $Mg(n\text{-}Bu)_2$ (1 M solution in heptanes, 25 mL, 25.0 mmol) was added dropwise over a time period of 0.5 h to a solution of $(CH_3)_2S{\cdot}BH_3$ (2 M in toluene, 45 mL, 90 mmol) at room temperature, under stirring and an inert atmosphere. The mixture was left for 3 h with stirring. Then the reaction mixture was filtered using a Schlenk filtration apparatus and the collected solid was washed with toluene (anhydrous, 3 × 10 mL). The solvated product $Mg(BH_4)_2{\cdot}{}^1/_2S(CH_3)_2$ was obtained as a white crystalline solid, collected, and dried for 16 h at room temperature on a vacuum line (4×10^{-2} mbar). The yield of $Mg(BH_4)_2{\cdot}{}^1/_2S(CH_3)_2$ was 1.72 g (81%). The open-pore polymorph γ-$Mg(BH_4)_2$ was obtained by constant heating of $Mg(BH_4)_2{\cdot}{}^1/_2S(CH_3)_2$ at 80 °C on a vacuum line (4×10^{-2} mbar) for 12−16 h. Yield of γ-$Mg(BH_4)_2$ was 1.09 g (81%). This synthesis method is a modified version of previously published protocols.[9,16]

The γ-polymorph of magnesium borohydride was handled in St. Louis in a N_2 atmosphere glove bag and loaded into glass tubes of 5 mm o.d. The tubes were flame-sealed under 0.9 bar N_2 gas. A separate sample was prepared similarly for ^{11}B NMR measurements.

Hydrogen NMR at 85.03 MHz used a home-built spectrometer and a 2.0 T Varian iron-core electromagnet with ^{19}F field stabilization. Boron-11 NMR used a 7.03 T Oxford superconducting magnet, with NMR at 96.1 MHz. For hydrogen and boron, probes with solenoid rf coils were used; temperature control was by thermostatted heated air or cold N_2 gas. Temperature measurement was by type-T thermocouples located within 2 cm of the sample. The temperature ranged from −125 to 225 °C. Two samples transformed at or above 175 °C to a new phase(s) as discussed in the Results section.

Hydrogen NMR line shapes were obtained from free-induction decays following 1 or 2 μs rf pulses; the short pulses avoid spectral distortion. The early time data corrupted by probe ringing and receiver recovery from the rf pulse were obtained by Gaussian extrapolation, as described elsewhere.[17] The hydrogen T_1 was measured using the saturate-wait-inspect approach,[18] with saturation employing forty $\pi/2$ pulses spaced by 1 ms each. The $\pi/2$ pulse time was 8 μs. The Jeener-Broekaert sequence[19] ($\pi/2_{x/-x} - t - \pi/4_y - \tau - \pi/4_y$) was used to measure T_{1D}. The first pulse was phase-cycled between x and $-x$, so the receiver phase was alternated +, −. +, −.... The time t was optimized to yield the largest dipolar-FID (also known as Jeener echo), at t = 6 μs. T_{1D} was obtained as the time constant of the exponential signal decay with increasing τ.

One of the samples transformed above 175 °C has been studied by X-ray powder diffraction without breaking the sealed NMR tube. Mo Kα radiation from the Rigaku UltraX-18 rotating anode generator was diffracted on the sample in Debye−Scherrer geometry. The diffraction data were collected with the MAR345 image plate diffractometer and transformed into 1D profile using Fit2D software and calibration measurements of LaB_6.

A separate set of in situ diffraction measurements was done on fresh samples of γ-$Mg(BH_4)_2$ heated under various atmospheres. The experiments were performed at the Swiss-Norwegian Beamlines at the ESRF, using calibrated monochromatic radiation of ∼0.7 Å wavelength, MAR345 detector, and the gas system[20] (courtesy of P. Llewellyn). The conditions applied to fresh samples of γ-$Mg(BH_4)_2$ were two experiments in vacuum (∼10^{-1} and 10^{-3} mbar, respectively), heating from RT to 250 at 3 °C/min rate; two experiments at 1 bar of argon, heating from RT to 216 and 300 °C respectively, at 2 °C/min rate; and one experiment at 44 bar of hydrogen, heating from RT to 250 at 3 °C/min rate. In all cases, there was an excess amount of gas, compared to the milligram quantities of γ-$Mg(BH_4)_2$. The 2D data series were integrated into 1D patterns as described above, and analyzed using FullProf software.

RESULTS

Line Narrowing. Hydrogen NMR spectra of γ-$Mg(BH_4)_2$ are presented in Figure 1. At 22 °C up through 150 °C, the resonance is partially narrowed and the line width is constant, demonstrating that BH_4 reorientations are rapid on the 10^{-5} s time scale throughout this temperature range. This picture is confirmed by T_1 measurements (see below). At −75 and −145 °C, the line becomes broader because at least some of the BH_4 reorientations are slowing through the relevant time scale at these lower temperatures, in agreement with an earlier report.[15] The absence of further line narrowing above 22 °C indicates that translational diffusive hops remain slower than 10^{-5} s.

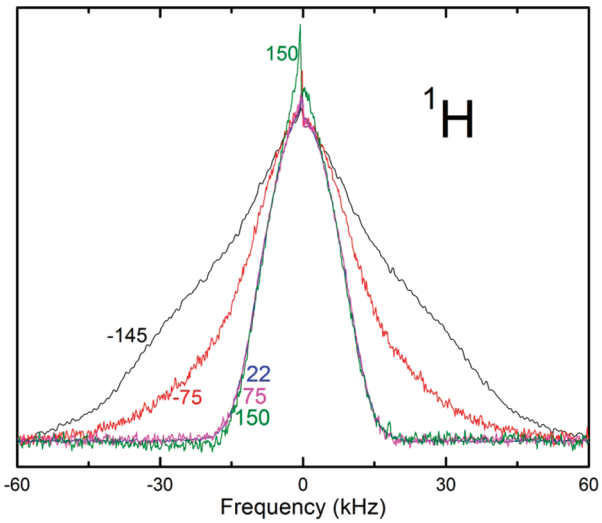

Figure 1. Hydrogen NMR spectra of γ-$Mg(BH_4)_2$ at several temperatures. At −75 and −145 °C, pronounced broadening is due to slowing of the BH_4 reorientations. At and above 22 °C, no further narrowing of the main resonance occurs, ruling out rapid BH_4 translational diffusion. At the highest temperature, a narrow component appears, reflecting a small fraction of mobile spins, probably from residual solvent.

A small narrow component of the hydrogen spectrum becomes evident at 150 °C and grows larger at 175 °C (spectrum not shown). The component disappears upon return to lower temperatures, proving that it is not H_2 gas from partial decomposition of the borohydride.[21] We believe this narrow component to be from residual solvent in the sample.

T_{1D}. The measurement of T_{1D}, the spin−lattice relaxation time in the dipolar-ordered state, allows the measurement of motions which are too slow to narrow the resonance.[22,23] Motions at rate ω which substantially (∼100%) modulate the dipolar interaction result in a T_{1D} relaxation time of order $1/\omega$. In addition, other "leaks" such as lab-frame T_1 processes often reduce T_{1D}.

Data for T_{1D} in γ-$Mg(BH_4)_2$ appear in Figure 2, together with β-phase data[14] for comparison. In β, the T_{1D} exhibits the strong decrease with increasing temperature that is the signature of thermally activated diffusive hopping motion. As discussed elsewhere,[14] at the highest temperature of 225 °C the hopping rate in β is about 400 s^{-1}, still much too slow to narrow the resonance. In the γ-phase up to 175 °C, no such thermally activated region is evident. Thus, any translational diffusive motions of the BH_4 groups remain slower than 10^2 s^{-1}, a limit based on the ∼10 ms maximum value of T_{1D}.

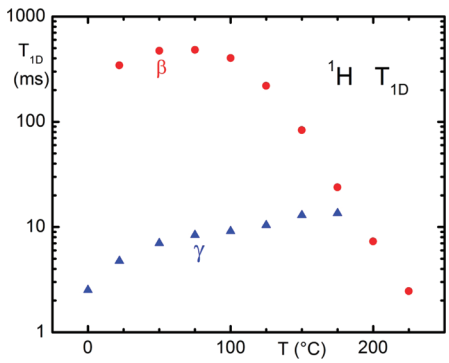

Figure 2. Hydrogen NMR measurements of T_{1D} in γ-$Mg(BH_4)_2$, together with β-polymorph data from reference 14 for comparison. In γ-phase, there is no sharp decrease in T_{1D} at elevated temperatures that would signal thermally activated diffusive hopping with rates 10^2 s^{-1} or faster.

T_1. Data for hydrogen T_1 in γ-$Mg(BH_4)_2$ are displayed in Figure 3. A deep minimum in T_1 near 50 °C appears, indicating that the rate of reorientations is about 1.6 ω_o here, where $\omega_o = 2\pi f_o$, with f_o being the 85.03 MHz resonance frequency (so a reorientation rate of approximately 0.85 × 10^9 s^{-1} at 50 °C).[24,25]

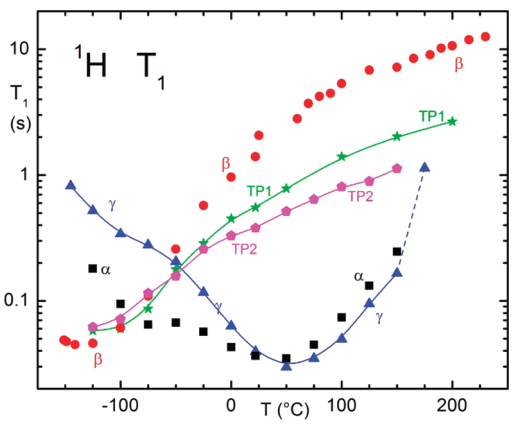

Figure 3. Hydrogen NMR T_1 of $Mg(BH_4)_2$. Results are shown (triangles) for γ-phase material from −150 to 175 °C; the sharp increase above 150 °C (dashed line) shows the transformation to a new structure, TP1. The transformation was completed at 225 °C; T_1 of the transformation product TP1 down to −125 °C appears (stars). A second sample was transformed to yield TP2 (pentagons). See text for description of temperature cycling histories. For comparison, T_1 of α-phase (squares) and β-phase (circles) is shown, from refs 26 and 14.

At lower temperatures, T_1 of the γ-phase increases in a manner that suggests a secondary minimum (not well resolved) near −100 °C. This behavior is similar to that of α-$Mg(BH_4)_2$, also presented in Figure 3 (but at the nearby frequency of 90 MHz), though in α-phase this is more pronounced.[26,27] We note that the α-phase also displays a T_1 minimum near 50 °C. The α-phase T_1 data were interpreted[26,27] in terms of three BH_4 reorientational motions, with activation energies of 0.12, 0.20, and 0.36 eV. The *average* activation energy for the α-phase is thus much larger than that for the β-phase (0.12 eV), in accordance with the much higher temperature of the T_1 minimum in α-phase than in β-phase[14] (−135 °C, see β data in Figure 3).

We have not attempted to fit our γ-phase hydrogen T_1 data to a model with multiple motions.[26] But the comparison with the α- and β-phase data makes it clear that the reorientations in the γ-phase are described by at least two activation energy barriers. And the temperatures of the T_1 minima show the average reorientations in γ are described by a large activation energy, similar to that of α-phase and much larger than that of β-phase.

The appearance of large energy barriers to BH_4 reorientation in α-phase results in line broadening below −50 °C.[14,26] Similarly, the γ-phase spectra in Figure 1 exhibit noticeable additional broadening at −75 °C and below.

The T_1 of ^{11}B in γ- and β-$Mg(BH_4)_2$ is shown in Figure 4. In γ-phase, a T_1 minimum occurs at 50 °C, similar to that of the hydrogen T_1, in Figure 3. This is expected since BH_4 reorientations modulate the primarily intramolecular H−B dipole interactions which drive ^{11}B relaxation, just as the reorientations modulate the H−H and H−B dipole interactions driving hydrogen spin relaxation. The present hydrogen and boron T_1 data are in substantial agreement with that of Skripov et al[15] where the temperature ranges overlap (the present data extend to higher temperatures).

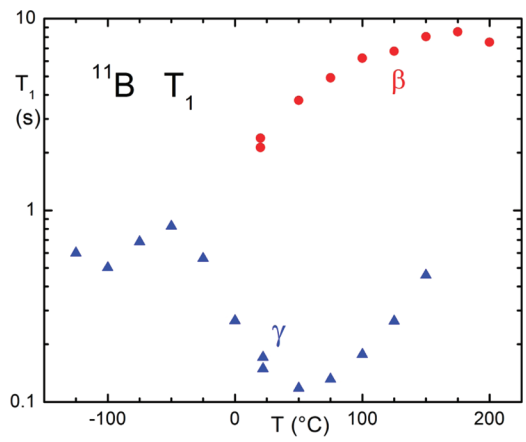

Figure 4. Boron-11 T_1 for γ-$Mg(BH_4)_2$, with β-polymorph data from ref 14 for comparison. The minimum near 50 °C for γ-phase is due to BH_4 reorientations, just as in the γ-phase hydrogen T_1 of Figure 3.

Phase Transformation. The hydrogen T_1 increases by a large step in heating from 150 to 175 °C (see dashed line in Figure 3), suggesting that γ-phase has transformed at least

partially.[9] The material was then cooled to 22 °C and heated again several times (once to 225 °C). After the second heating (to 175 °C), the transformation product (TP1) showed stable behavior (reproducible T_1 values on subsequent heatings). Data for T_1 of TP1 appear in Figure 3.

The T_1 minimum of TP1 near −125 °C is similar to that[14] of β-$Mg(BH_4)_2$, though the TP1 values remain smaller at higher temperatures than the β values. This suggests that TP1 is a structure similar to β, but is not pure β-phase itself. A second possibility is that the material is only partially transformed—a small fraction of remaining γ (with its very rapid relaxation near room temperature) could decrease the TP1 T_1 below the β-phase T_1, as in Figure 3. A third possibility is that the heating generated unpaired electron spins that result in additional nuclear relaxation. However, we were unable to explain the data of Figure 3 by assuming a constant relaxation rate resulting from the electron spins, which would yield

$$(1/T_1)_{TP} = A + (1/T_1)_\beta \quad (1)$$

From the high-temperature data, A must be about 0.3 s^{-1}. But this value is much too small to fit the discrepancy between T_1 of β and TP1 at −25 °C, for example. Of course, the electron spin-generated relaxation may not be constant, but it is unlikely[25] to be strongly temperature dependent. Overall, this third possibility seems unlikely.

A second sample of γ-$Mg(BH_4)_2$ from the same batch was transformed by heating. At 225 °C, little change in T_1 was evident after 2 h. But at 250 °C for 1 h, T_1 increased a large amount; subsequent T_1 measurements on this second transformed material appear as TP2 in Figure 3. The results are similar to (but not the same as) those of TP1. This and the higher temperature required for phase transformation suggest some variability in the process, the source of which is not known.

Material TP2 was examined by powder X-ray diffraction using a rotating anode X-ray source. Diffraction data (not shown) unambiguously reveal that the only crystalline component of the transformed material is β-phase. A more detailed study of the temperature-induced transformation of the γ-phase was done by synchrotron X-ray diffraction of separate (fresh) samples of the γ-phase under various gas atmospheres. It reveals a number of additional observations: (1) γ-$Mg(BH_4)_2$ transforms upon heating in vacuum into the β-phase, and (2) γ-$Mg(BH_4)_2$ amorphizes upon heating under argon or hydrogen atmospheres.

This different behavior can be explained by the effect of gas molecules entering the pores on the stability of the porous phase. The amorphization occurs at temperatures below 100 °C, while the transformation into the β-phase takes place (under vacuum) only at higher temperatures. Considering the reported small isosteric heat of adsorption for hydrogen in γ-$Mg(BH_4)_2$ (~6 kJ/mol), the physisorption of H_2 above room temperature should be practically excluded. However, the presence of hydrogen gas evidently has a profound effect on the thermal stability of the porous phase. On the other hand, 0.9 bar of nitrogen in the NMR tube has no destabilizing effect, likely due to the presence of a very small amount of gas compared to the amount of γ-$Mg(BH_4)_2$ in the sealed NMR tube.

It is interesting to note that the β-phase formed upon heating the porous polymorph shows on further heating an evolution of the powder pattern toward the disappearance of diffraction peaks with odd h, k, and l indices. This structural evolution, which is not fully interpreted yet on the microscopic level, may explain the observed T_1 variation between TP1, TP2, and β-phase samples. A more thorough investigation of the phase transformations using in situ X-ray diffraction is under way.

The transformation caused an increase in the line width measured at 22 °C. The spectra of the original γ-phase and the transformation product (TP1) are displayed in Figure 5, with

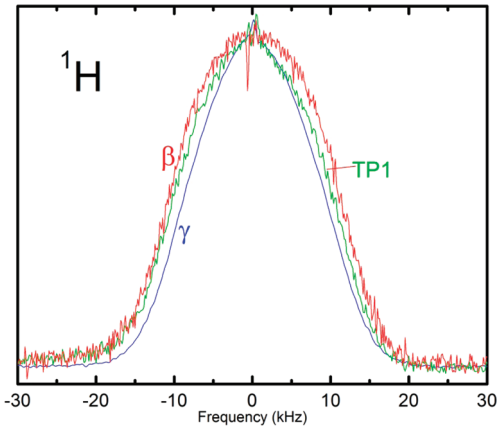

Figure 5. Hydrogen NMR spectra, all at 22 °C. Data are presented for γ-phase and β-phase (from ref 14) materials, as well as the transformation product TP1, formed from γ by heating to 225 °C.

the β-phase spectrum for comparison. In terms of full-width at half maximum (fwhm), the original γ-phase line width is only 89% as large as the TP1 line width. This is in accordance with TP1 being a denser phase than γ, so with stronger dipolar spin interactions (which vary as $1/r^3$). We note that the spectrum of the transformation product TP1 at 22 °C is not as wide as in β-phase (Figure 5). This supports the view that the TP1 structure is somewhat different than β-phase *or* that TP1 is a phase mixture. It was previously found[15] that the γ line width is smaller than that of β at room temperature, in accordance with the present data (Figure 5).

Magic-angle spinning (MAS) ^{11}B NMR was used to examine the transformed material, TP1. Essentially all the signal resides in a single peak at −40 ppm, corresponding to BH_4 groups. Only a very small amount of impurity or decomposition product is present. Thus, TP1 is the product of a phase change and not a chemical reaction.

■ CONCLUSIONS

Hydrogen NMR line shapes reveal no motional narrowing due to translational self-diffusion in the main part of the resonance, up to 175 °C. "Slow" motion measurements by means of the hydrogen T_{1D} indicate the absence of translational motions faster than 10^2 s^{-1} up to this temperature. Thus, despite the large amount (33%) of open volume in γ-$Mg(BH_4)_2$, we find no evidence for rapid diffusion.

The hydrogen T_1 is controlled by the rate of BH_4 reorientation. Observation of a deep minimum in T_1 at 50 °C demonstrates that the mean rate of reorientation is about 10^9 s^{-1} at 50 °C. The T_1 behavior of γ-phase is similar to that reported in α-phase, where activation energies for BH_4 reorientation were found to be 0.12, 0.20, and 0.36 eV. By comparison, in β-phase $Mg(BH_4)_2$, a T_1 minimum occurs at −135 °C and is described by an 0.12 eV activation energy. Thus, the *mean* activation energy for BH_4 reorientation in γ-phase is high, as in α-phase. The ^{11}B T_1 shows a minimum at 50

°C, as well. This is as expected because the intramolecular B−H dipole interaction, modulated by BH_4 reorientations, drives (in part) both the hydrogen and ^{11}B spin−lattice relaxations.

Our γ-phase material transformed to another phase upon standing at 175 °C for 2 h in one case. Subsequent heating to 225 °C completed the transformation. A second sample of γ-phase $Mg(BH_4)_2$ transformed during 1 h at 250 °C. T_1 of the transformation products down to −125 °C were found to be similar but not equal to T_1 of β-$Mg(BH_4)_2$. The data suggest that the transformation products are largely β-phase. Boron-11 magic-angle spinning NMR of the recovered transformation product demonstrates the transformed material is not significantly dehydrided; essentially all the boron atoms remain as BH_4. Powder X-ray diffraction shows that material TP2 has a crystallographic structure equal to that of the β-polymorph; an amorphous component can not be ruled out.

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Notes

The authors declare no competing financial interest.

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