

LiBH₄

NMR of Hydrogen Storage Materials

David Shane,
Washington University in St. Louis

Bob Corey, South Dakota School of Mines and Technology
Bob Bowman, Jet Propulsion Laboratory
Mark Conradi, Washington University in St. Louis

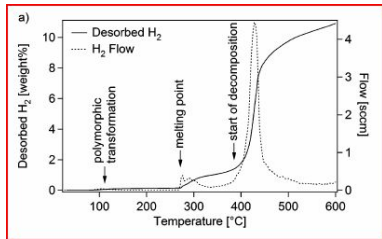
November 8, 2008

The Good



- Composed of light metals, 18.4% hydrogen by mass
- $\text{LiBH}_4 \leftrightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2$, releases 13.8% hydrogen
- Has an overall ionic structure, with BH_4 built of covalent bonds

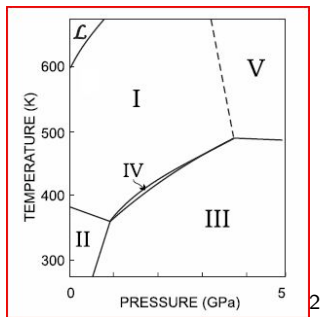
The Bad



- Doesn't really begin releasing hydrogen until melt at 270°C.
- Produces undesirable decomposition products: B₂H₆
- Rehydriding requires extreme conditions: 600°C, 150-350 bar

¹Mauron et. al., J. Phys. Chem. B 2008, 112, 906-910

Description of LT Phase

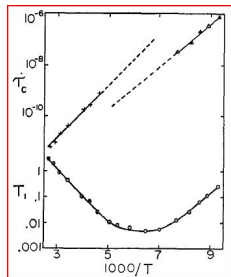


- The LT phase (II) is orthorhombic, and exists up to around 110°C.
- The HT phase (I) is hexagonal and orientationally disordered.

²Dmitriev et. al., Physical Review B 77, 174112 (2008)

Classic Work by Tsang and Farrar

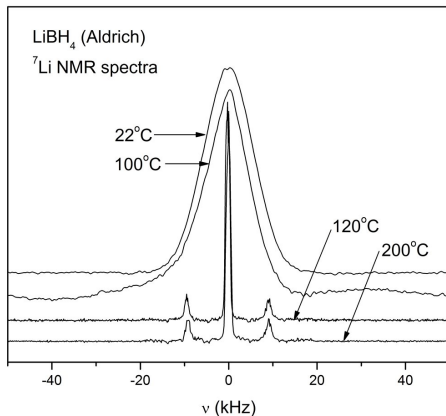
- Tsang and Farrar observed a broad proton T_1 minimum (160K, 19MHz).
- They hypothesized two types of BH_4 tetrahedra.
 - $2T_1^{-1} = T_{1a}^{-1} + T_{1b}^{-1}$
 - From this they fit the T_1 data.
- Therefore, rapid BH_4 reorientations control the hydrogen T_1 here.
- BH_4 rotation is fast enough to average the intramolecular dipole-dipole interactions.



3

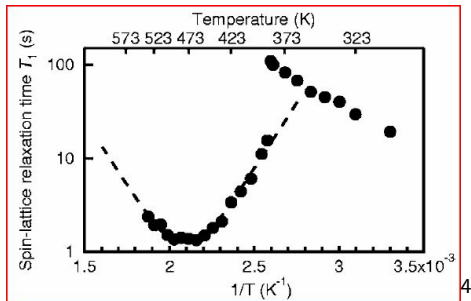
³Tsang and Farrar, Journal of Chem. Phys. 50, 8 (1969)

Lithium Spectra



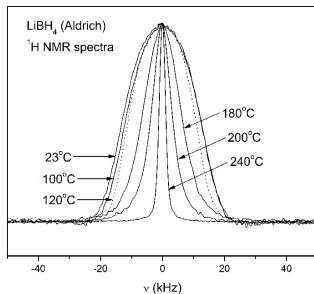
- The lithium line sharpens greatly after the phase transition, indicating rapid Li diffusion.

Lithium T_1



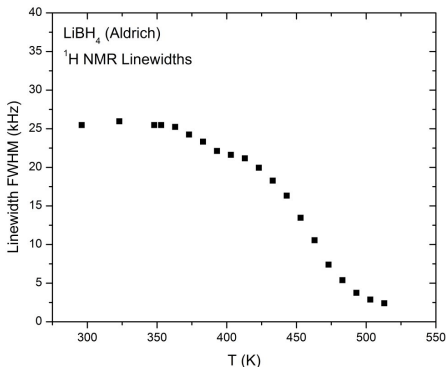
- Others observed a T_1 minimum near 200°C at 116 MHz, also showing rapid lithium hopping ($\sim 10^9$ hops/sec).

Proton Spectra



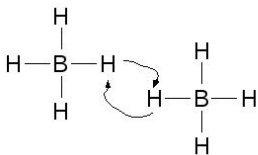
- Even at room T, the proton NMR spectrum is narrower than similar materials, showing the BH₄ reorientations are already partially averaging the dipolar interactions.

Proton Spectra

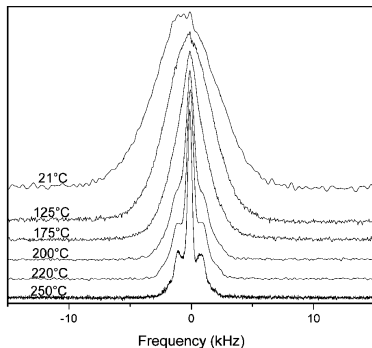


- The linewidth undergoes two part narrowing.
- Stage 1: Li hopping averages away the Li-H dipole interaction.
- Stage 2: H translational diffusion must be present to drive the linewidth to zero.

Boron-11 lineshapes

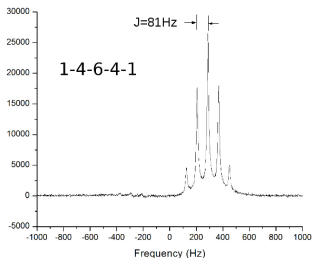


- Do the hydrogens move by BH₄ diffusion, or by exchanging between BH₄ units?
 - If B remain stationary, the static B-B dipole interaction would broaden the line.
 - A Van Vleck calculation of M_2 yields a FWHM of 1525 Hz - versus the measured 400 Hz before melt.
 - So, B atoms move too, so BH₄ units are diffusing.



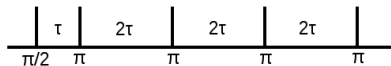
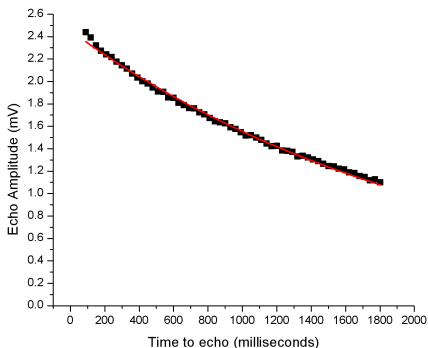
Boron-11 data

- Swiss group proposed (based on Raman spectroscopy) that H translation, not BH_4 translation occurs in the HT phase.



- LiBH_4 solid exchanging with D_2 gas.
- Raman sees BH_4 , BH_3D , &c.
- Observation of J-coupling in melt shows hydrogens are not exchanging over NMR time scales of $\frac{1}{\text{linewidth}} \sim 50\text{ms}$ (lower limit of exchange lifetime).

B-11 CPMG



- $\tau = 15\text{ms}$, time for complete dephasing
- The echoes decayed with time constant 2.2s .
- Proton $T_1^H = 10\text{s}$, so we expect the boron T_2 limited by $T_1^H/4$.

Conclusions

LT Phase:

- In the LT phase, BH_4 reorientation is rapid and controls T_1 .
- Li motion gradually increases, narrowing the proton line and decreasing proton T_{1D} .

HT Phase:

- In the HT phase, the Li motion increases greatly, sharpening the Li spectrum and causing a T_1 minimum.
- Above 170°C the hydrogen motion becomes fast enough to further narrow the proton line.
- The boron spectrum indicates that both B and H diffuse.
- Observation of J-coupling in the melt shows that the BH_4 units remain intact.