



# FuncHy

## Functional Materials for Mobile Hydrogen Storage

### Synthesis, Stability and Structure of Borohydrides

Philippe Mauron

**FuncHy Workshop 2010**

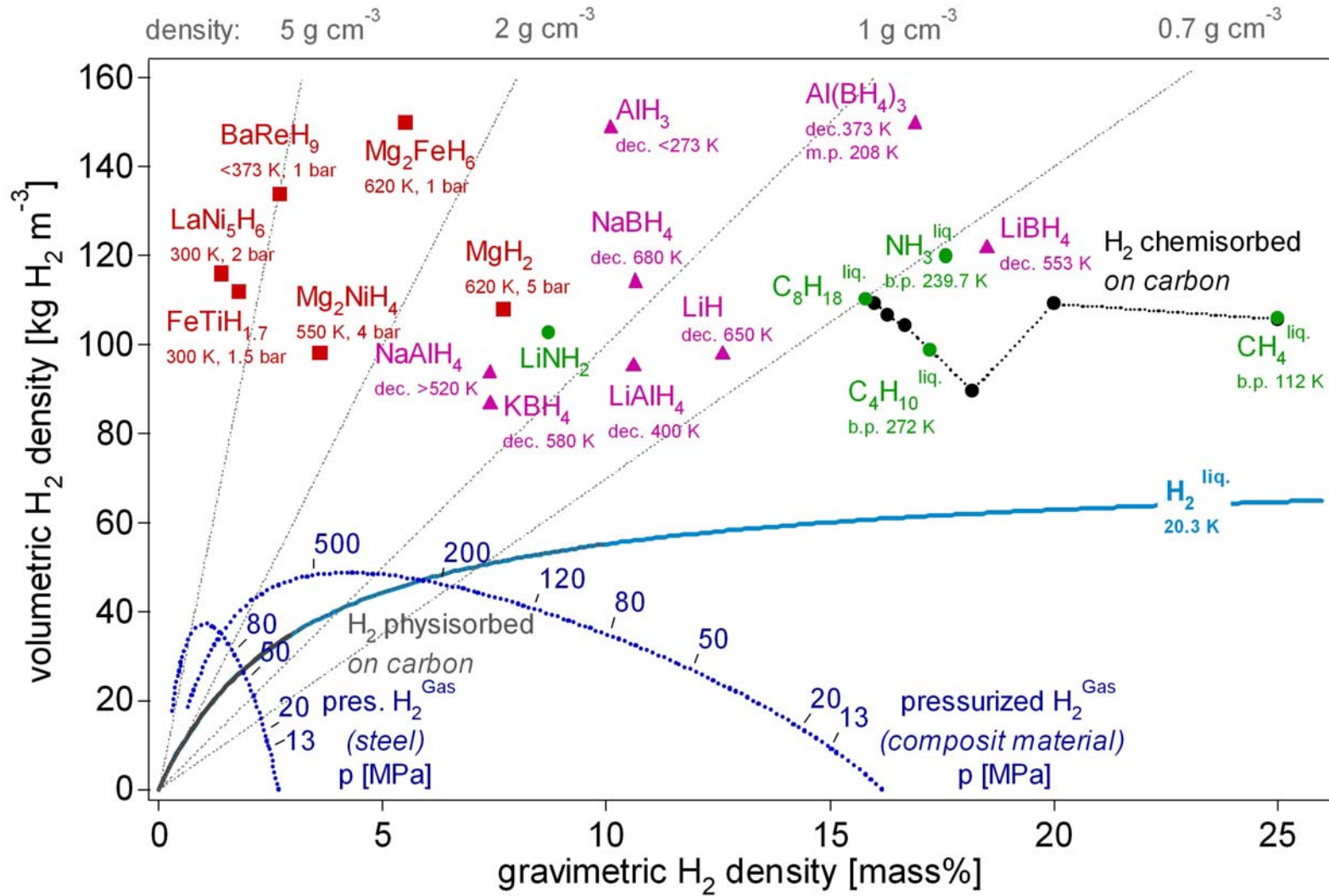
January 25, 2010, Hotel Hirschen, Wildhaus, Switzerland



# Contents

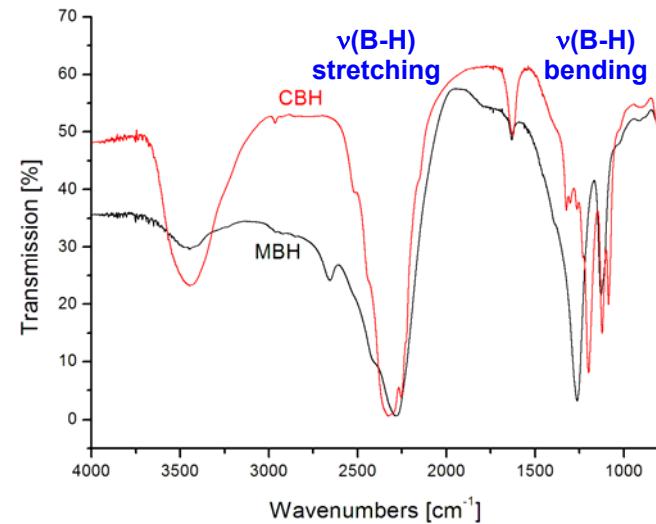
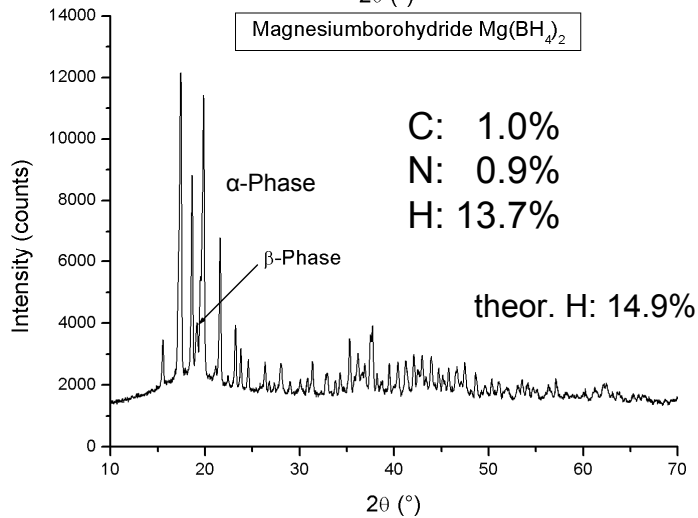
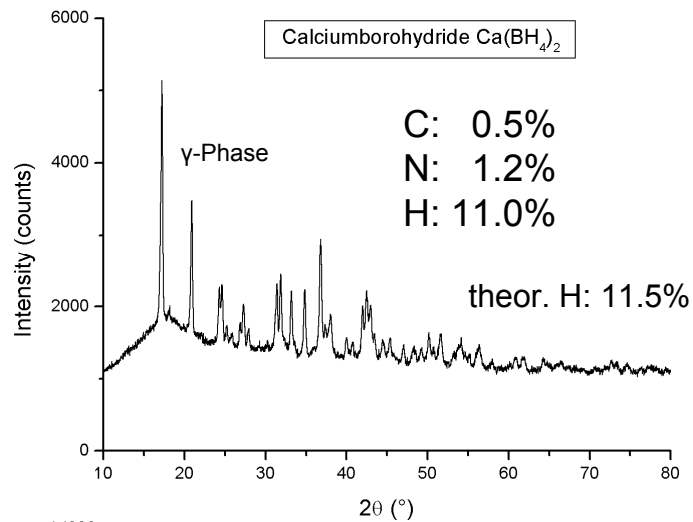
- *Introduction*
- *Synthesis methods of borohydrides and deuterides*
- *Thermal decomposition and reversibility of borohydrides and borohydride compounds*
- *Determination of the stability of borohydrides and borohydride compounds*
- *Crystal structure of borohydrides*
- *Instruments and measuring methods*
- *Conclusion*

# Intro

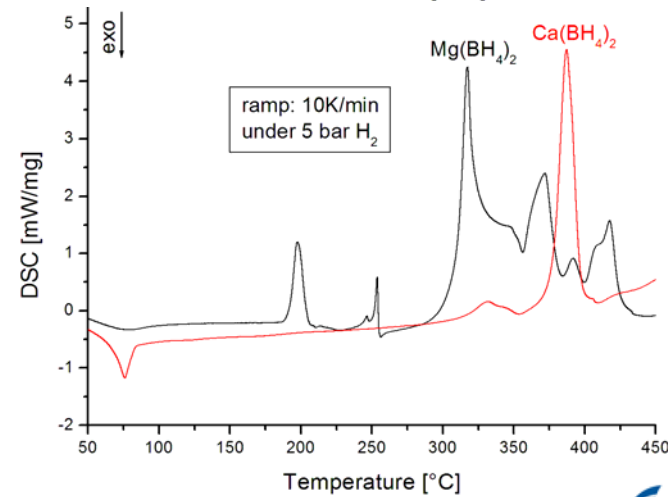




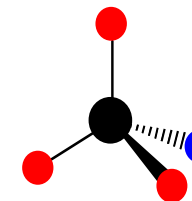
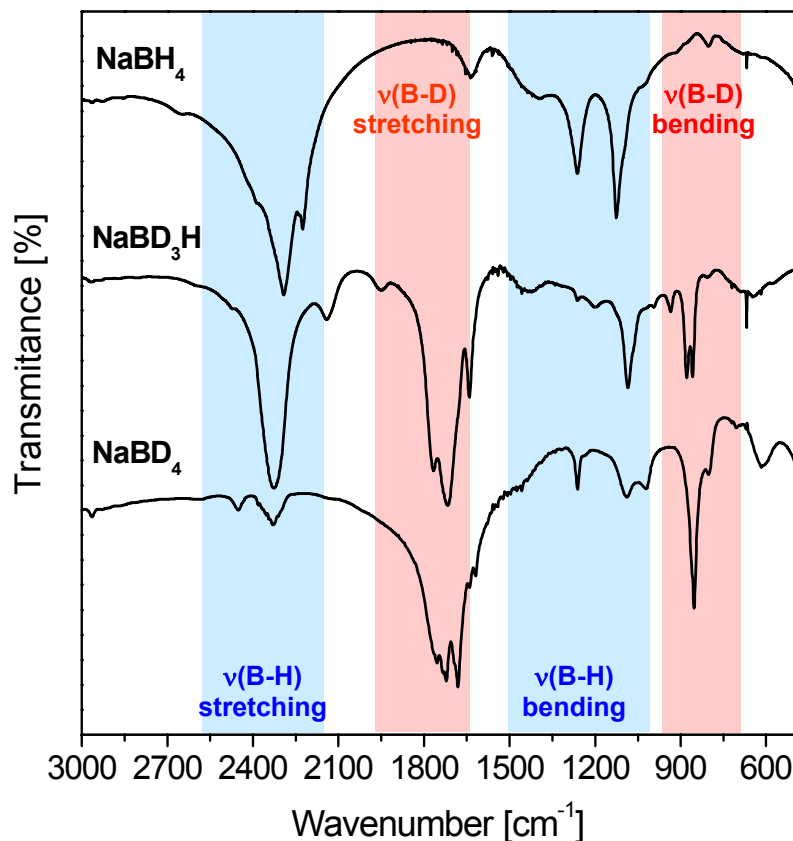
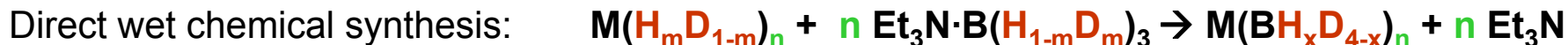
**XRD**



**IR**



**DSC**



	$\text{BH}_4^-$	$\text{BHD}_3^-$	$\text{BD}_4^-$
<b>B-H stretch. modes</b>	2290 ( $A_1$ ) 2283 ( $T_2$ )	2283 ( $A$ )	
<b>B-D stretch. modes</b>		1695 ( $T_2$ ) 1639 ( $A_1$ )	1695 ( $T_2$ ) 1639 ( $A_1$ )
<b>Deformation modes</b>	1239 ( $E$ ) 1123 ( $T_2$ )	1065 ( $E$ ) 864 ( $E$ ) 859 ( $A$ )	877 ( $E$ ) 852 ( $T_2$ )

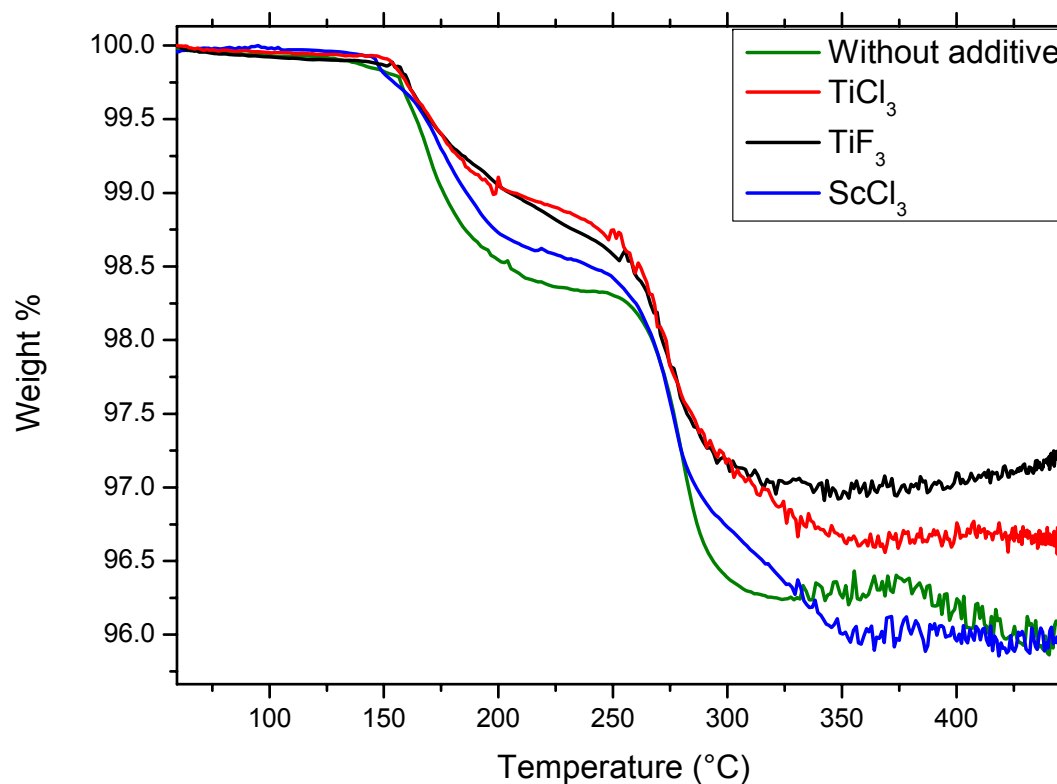
FT-IR

H. Hagemann, V. D'Anna, P. Carbonnière, E. G. Bardají and M. Fichtner,  
*J. Phys. Chem. A*, 113, 2009, 13932.



$2\text{LiBH}_4 + \text{MgCl}_2$  were milled in 10bar  $\text{H}_2$  for 12h with and without the presence of 1% molar ratio of three different additives.

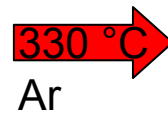
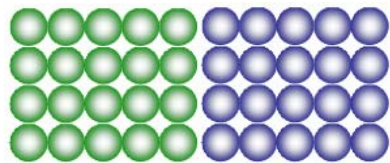
Formation of  $\text{Mg}(\text{BH}_4)_2$  was confirmed by Raman and XRD



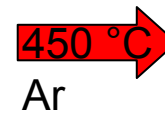
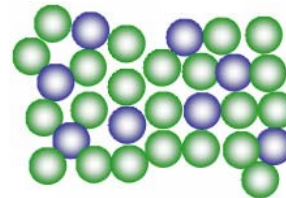
Results indicated that reaction's yield decreased in all cases except for  $\text{ScCl}_3$ .

## ■ Synthesis of $\text{LiBH}_4$ and $\text{LiBD}_4$ from the elements

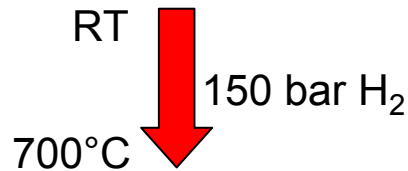
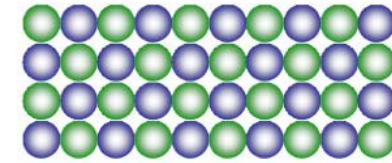
Li (0.2 g) + B (0.2 g)  
stoichiometric ratio Li/B  $\approx$  1.6



$\text{LiB}_3 + x \text{Li}$



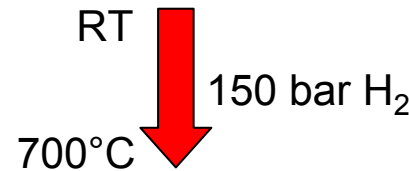
$\text{Li}_7\text{B}_6 + x \text{Li}$



$\text{LiBH}_4 + x \text{LiH}$

B:

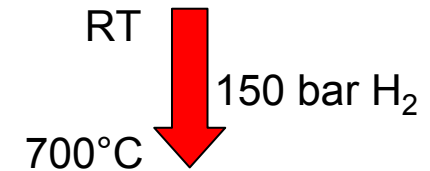
- Strong crystalline lattice
- Cage like structure of boron
- strong  $\text{H}_2$  absorption step at melting point of LiH ( $689\text{ }^\circ\text{C}$ )



$\text{LiBH}_4 + x \text{LiH}$

\* $\text{LiB}_3$ :

- Interstitial solution of Li in B
- Expanded and stressed B lattice
- Decripitation of B particles
- $\text{H}_2$  absorption already at  $550\text{ }^\circ\text{C}$



$\text{LiBH}_4 + x \text{LiH}$

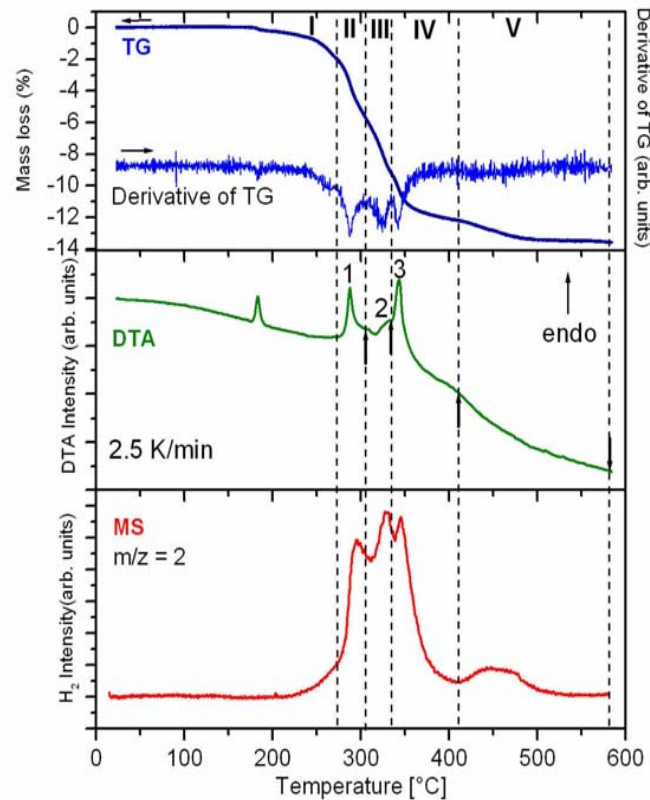
\*\* $\text{Li}_7\text{B}_6$ :

- New phase formation
- $\text{H}_2$  absorption already at  $550\text{ }^\circ\text{C}$

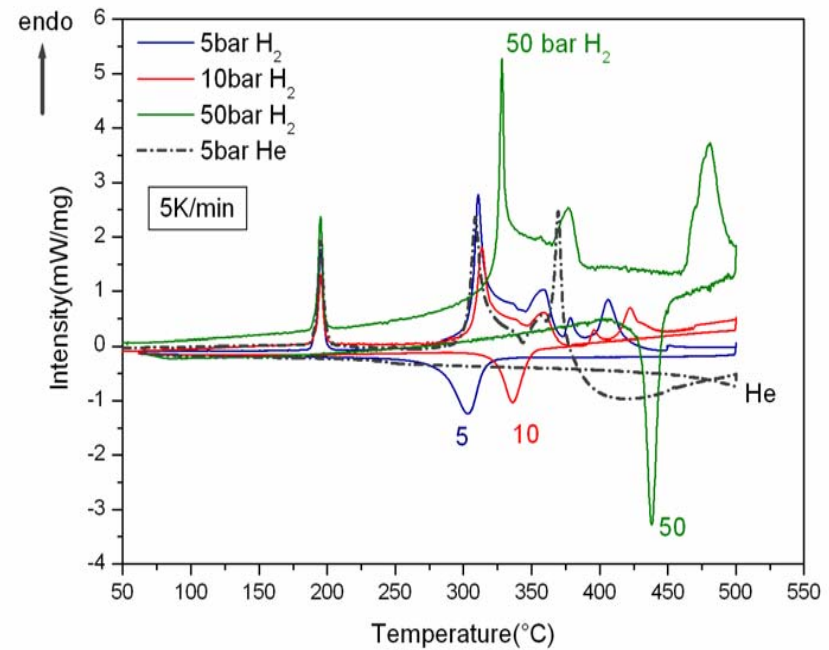
\*Meden et al, *J. Phys. Chem.* (1995) 99, 4252, \*\*Ernst et al, *J. Electrochem. Soc.* (1982) 129, 1513

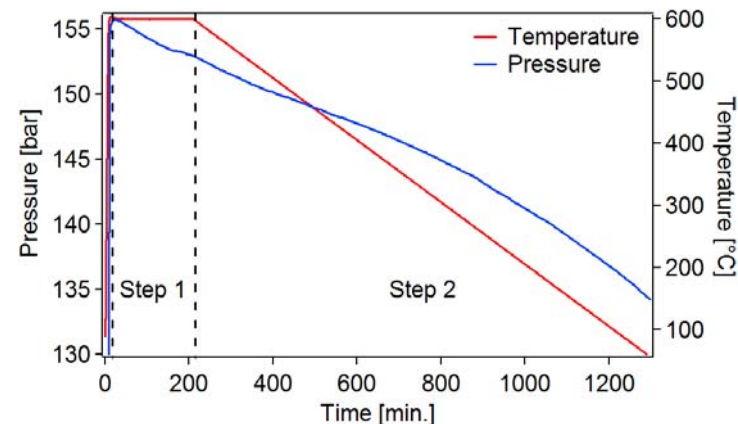
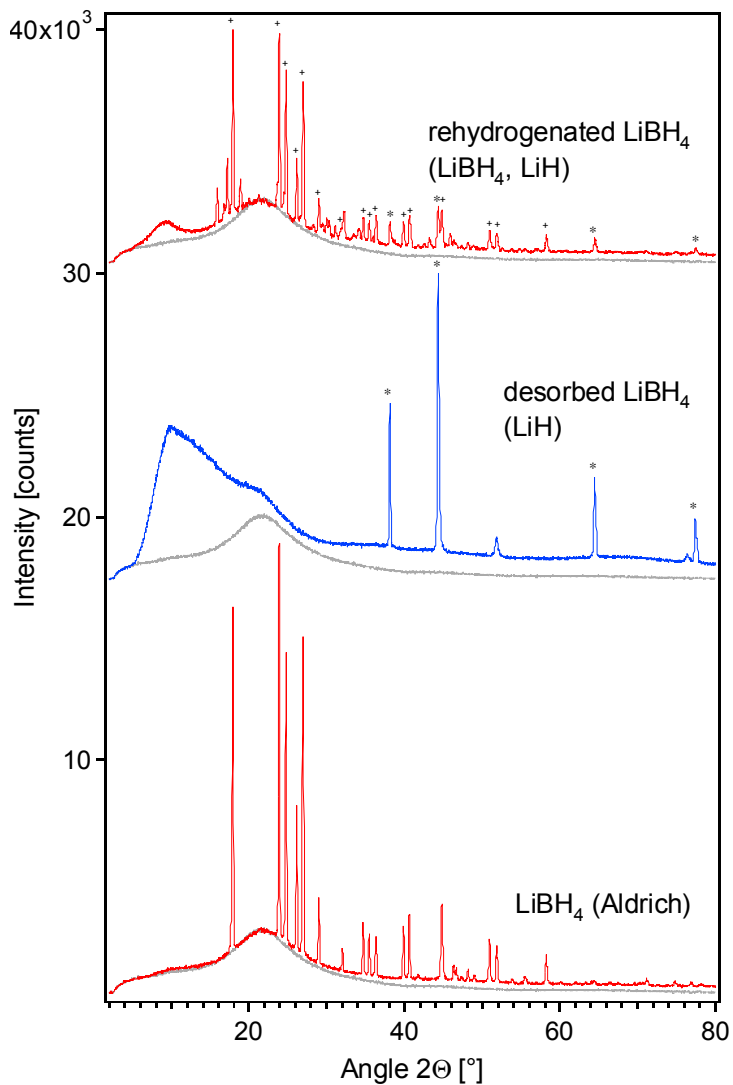
O. Friedrichs et al. *Acta Materialia* 56, 949 (2008)

## TGA-MS-DTA 2.5 K/min, He

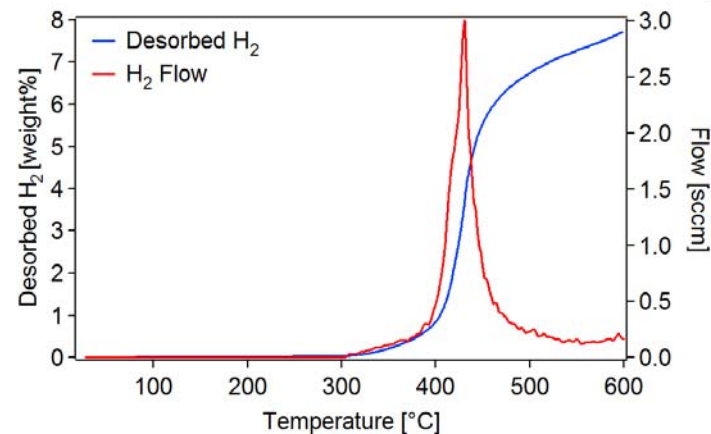


## HP-DSC

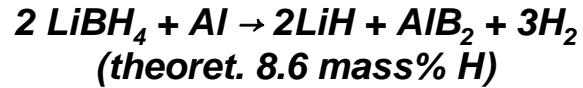




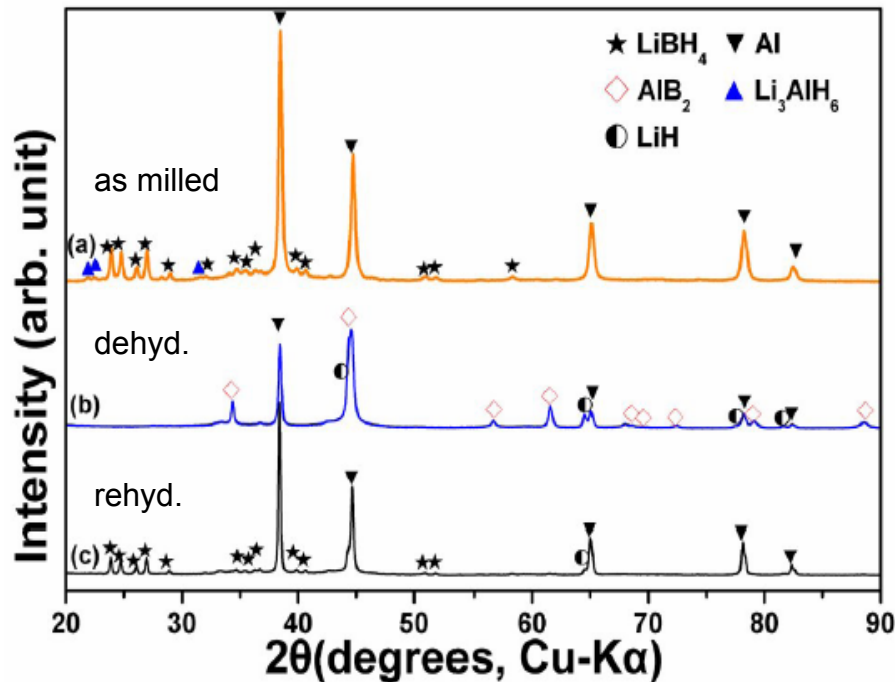
- absorption at 600 °C and 155 bar of  $\text{H}_2$  for 200 min.
- Cooling down to room temperature (0.5 °C/min.)



- One desorption peak with a maximum at 430 °C



thermod.  $T_{\text{Dec}} (1 \text{ bar H}_2) = 130^\circ\text{C}$  (CALPHAD)

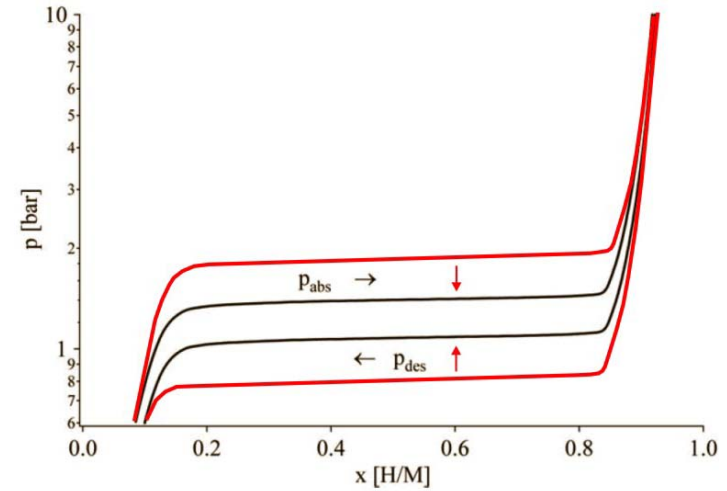
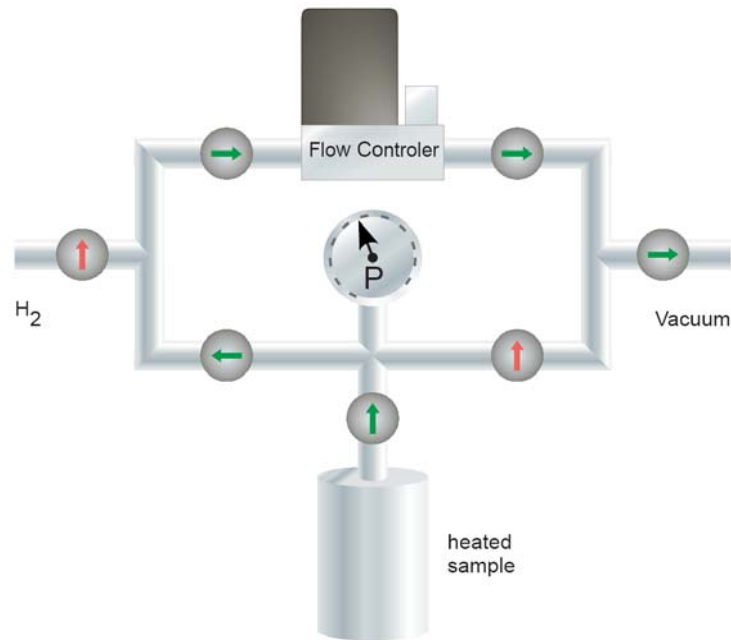


Cycling:  $2.2 \text{LiBH}_4 + \text{LiAlH}_4 + 0.1 \text{TiF}_3$

	Hydrogen <sup>a</sup>	T	P
1 <sup>st</sup> Des.	7.5 wt%	623 K	0.9 bar
1 <sup>st</sup> Abs.	-	573 K	100 bar
2 <sup>nd</sup> Des.	3 wt%	623 K	0.9 bar
2 <sup>nd</sup> Abs.	1.3 wt%	518 K	100 bar
3 <sup>rd</sup> Des.	1.2 wt%	623 K	0.9 bar
3 <sup>rd</sup> Abs.	3.5 wt%	563 K	100 bar
4 <sup>th</sup> Des.	2.8 wt%	623 K (350°C)	0.9 bar
4 <sup>th</sup> Abs.	4.5 wt%	563 K (290°C)	100 bar

(ca. 60%)

- Principle of the dynamic pcT system

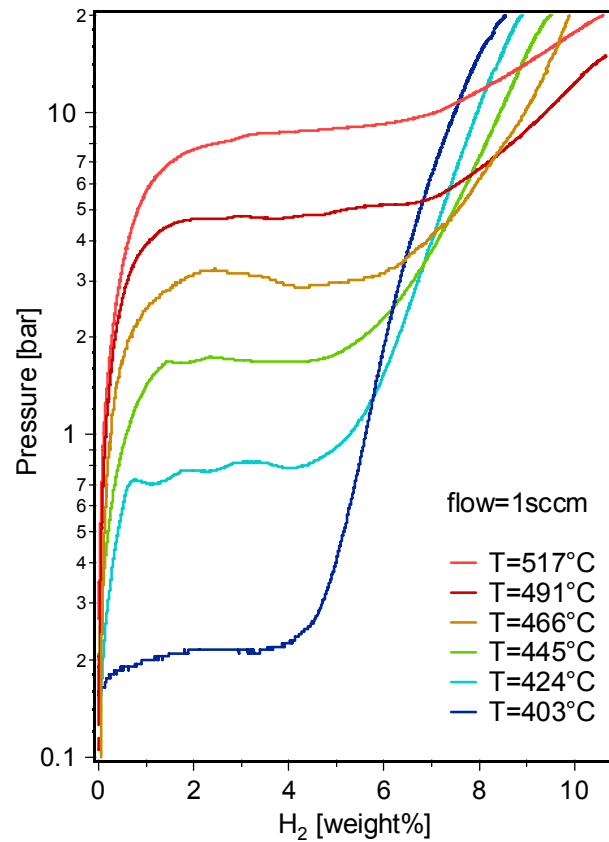
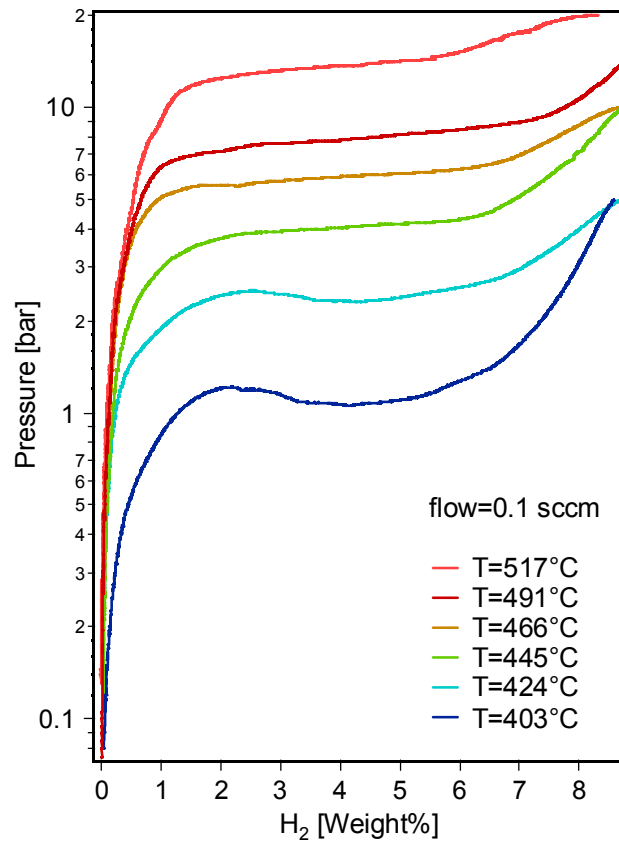


- $\Delta p$  is a function of flow / kinetics
- Reaction always goes in one direction !

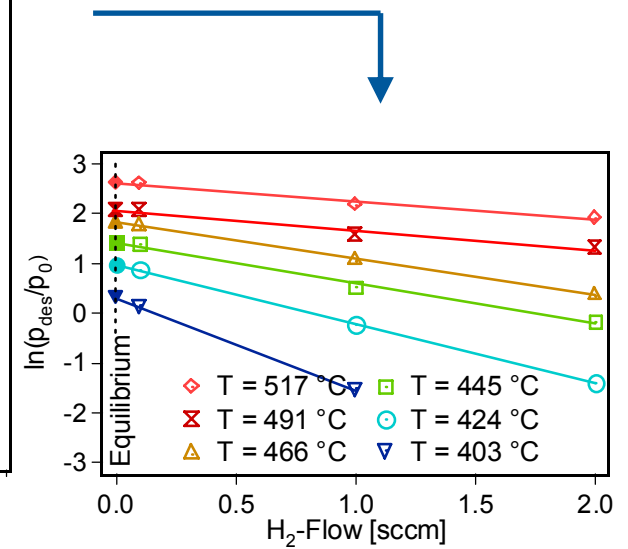
pcT-Instrument with small internal volume ( $\sim 3 \text{ cm}^3$ )  
for precise measurements of small sample amounts



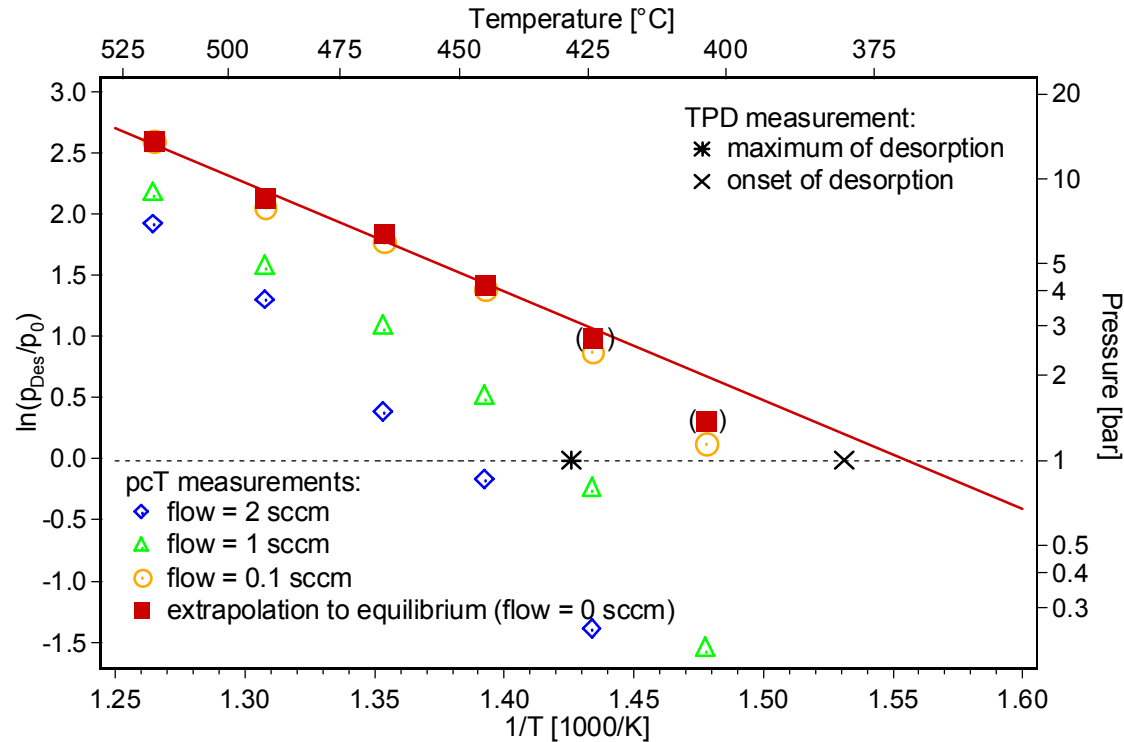
- pcT-measurements of the desorption of LiBH<sub>4</sub> → LiH + B + 3/2 H<sub>2</sub> (13.9 wt%)



Extrapolation to equilibrium at a flow of 0 sccm.



- Van 't Hoff plot for the desorption of LiBH<sub>4</sub> → LiH + B + 3/2 H<sub>2</sub> (13.9 wt%)



$$\ln\left(\frac{p_{eq}}{p_0}\right) = \frac{\Delta_r H}{R} \cdot \frac{1}{T} - \frac{\Delta_r S}{R}$$

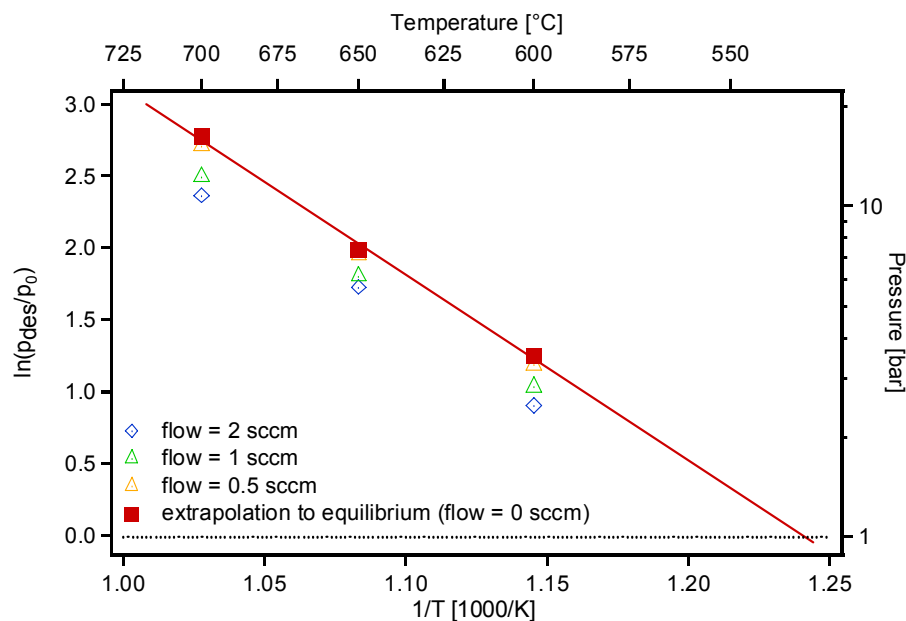


$$\Delta_r H = -74 \text{ kJ mol}^{-1} \text{ H}_2$$

$$\Delta_r S = -115 \text{ J mol}^{-1} \text{ H}_2 \text{ K}^{-1}$$

$$T_{dec} = 370 \text{ °C}$$

▪ pcT of desorption of

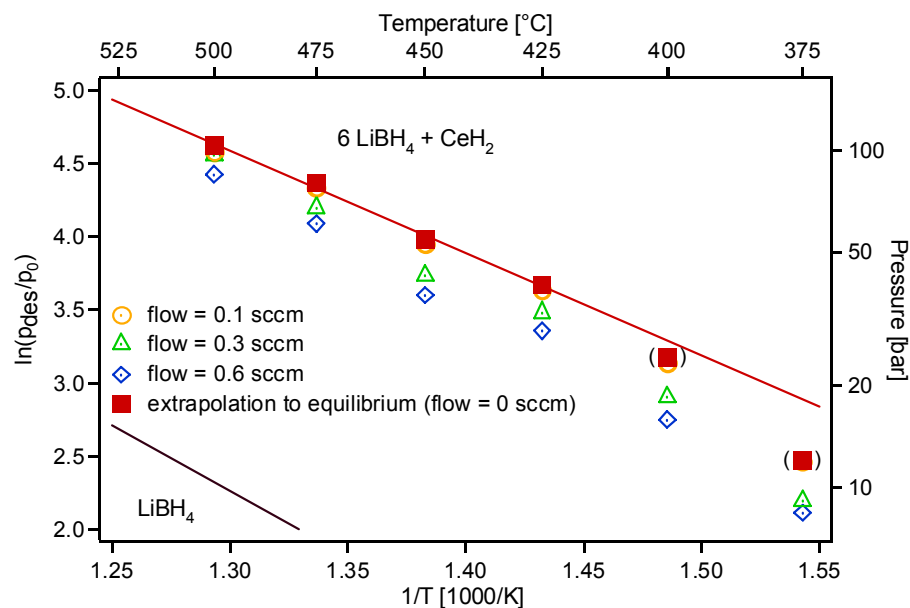
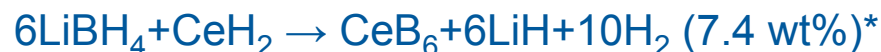


$$\Delta_r H = -108 \text{ kJ mol}^{-1} \text{ H}_2$$

$$\Delta_r S = -133 \text{ J mol}^{-1} \text{ H}_2 \text{ K}^{-1}$$

$$T_{\text{dec}} = 534 \text{ }^\circ\text{C}$$

▪ pcT of desorption of



$$\Delta_r H = -58 \text{ kJ mol}^{-1} \text{ H}_2$$

$$\Delta_r S = -114 \text{ J mol}^{-1} \text{ H}_2 \text{ K}^{-1}$$

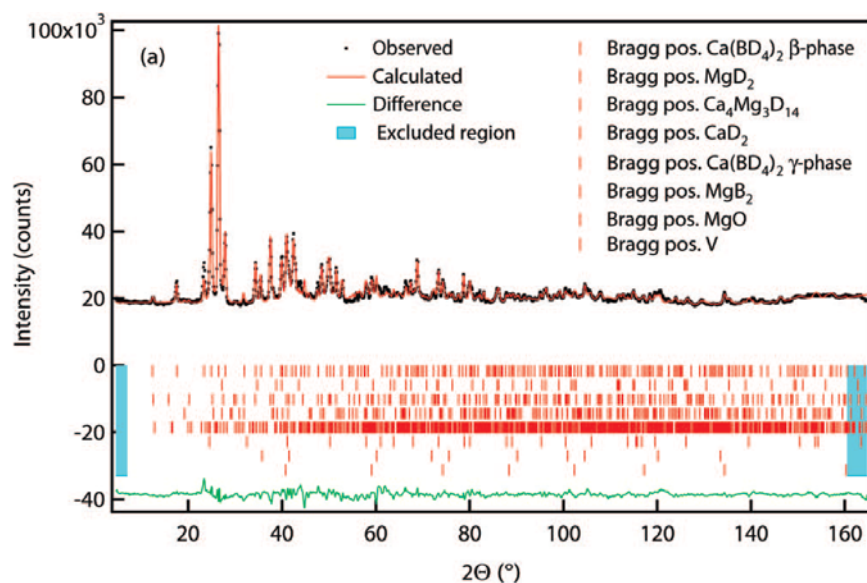
$$T_{\text{dec}} = 236 \text{ }^\circ\text{C}$$

\*S.-A. Jin et al. Phys Chem C 112 (2008)

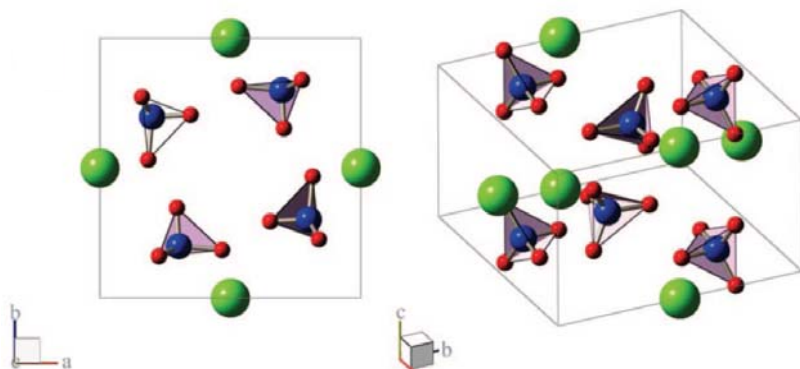
P. Martelli, submitted to Phys Chem B (2010)

Ph. Mauron et al., to be submitted

## Neutrons (beta phase, 480K)

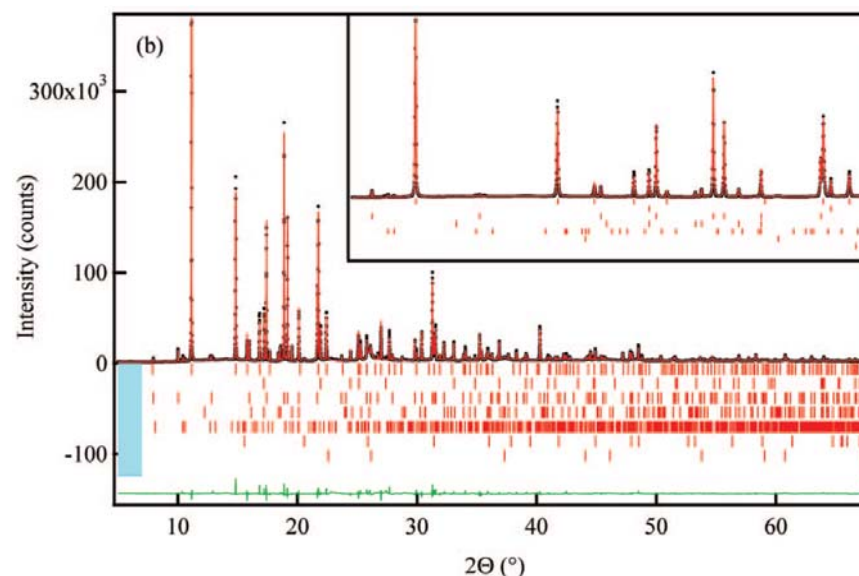


## Ab initio calculation (lowest energy for #84)



F. Buchter et al., *Phys Chem B* 112, 8042 (2008)

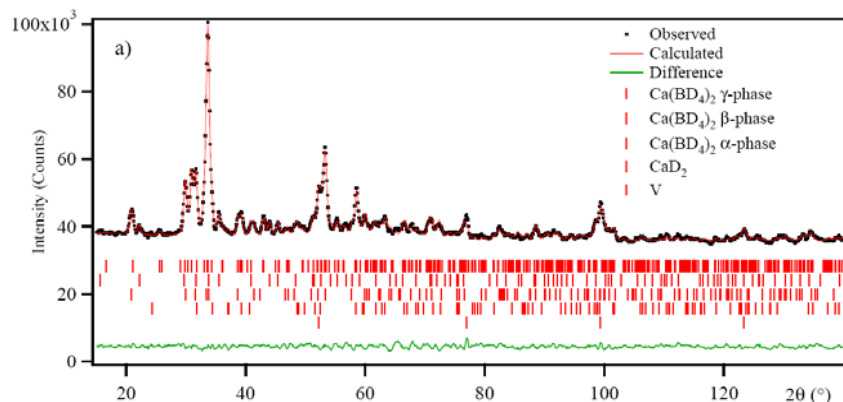
## Synchrotron (beta phase, 480K)



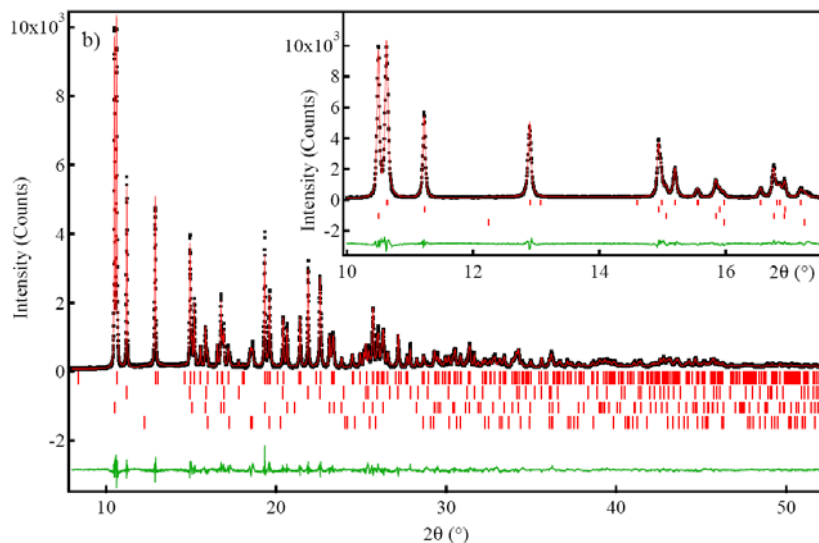
## Exp. results from combined refinement (#84)

Space Group $P4_2/m$ (no. 84); $Z = 2$				
site	$x/a$	$y/b$	$z/c$	$B_{iso}$ (Å <sup>2</sup> )
Experimental; $T = 480$ K; $a = 6.9468(1)$ Å, $c = 4.3661(1)$ Å				
Ca/2c	0.5	0	0.5	3.9(2)
B/4j	0.302(4)	0.200(5)	0	3.3(4)
D1/4j	0.295(8)	0.347(9)	0	11.0(11)
D2/4j	0.468(7)	0.185(5)	0	11.0(11)
D3/8k	0.226(5)	0.161(5)	0.800(6)	11.0(11)

## Neutrons (gamma phase, 300K)



## Synchrotron (gamma phase, 300K)



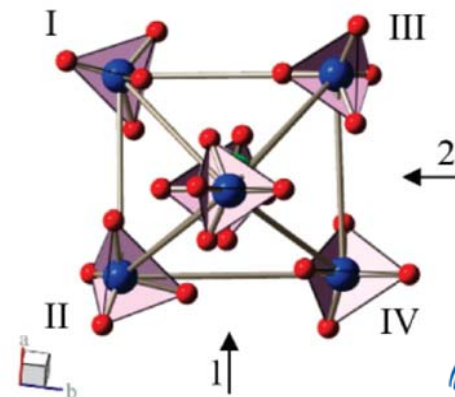
F. Buchter et al., *Phys Chem C* 113, 17223 (2009)

## Exp. results from combined refinement (#61)

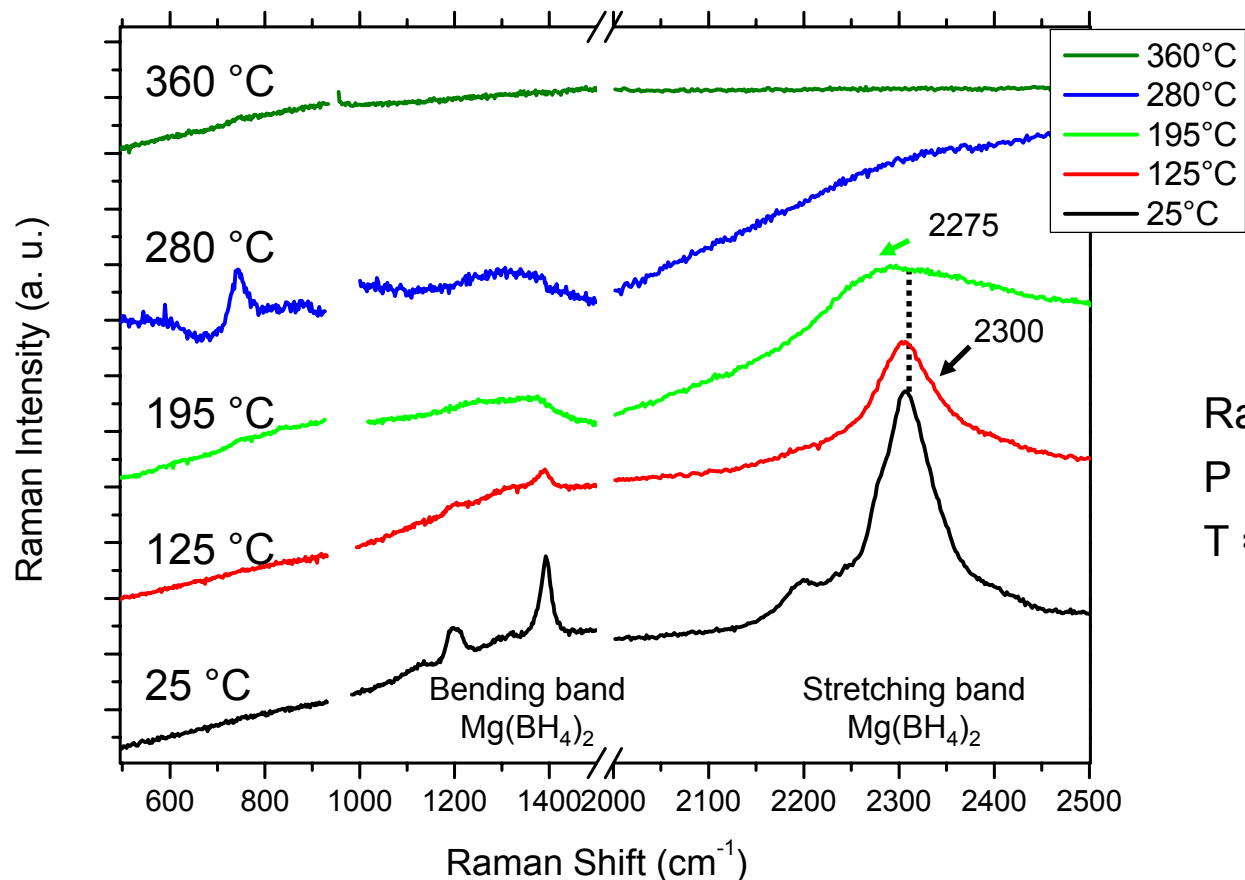
Experimental;  $T = 300$  K;  $a = 13.0584(8)$  Å,  $b = 8.3881(4)$  Å,  
 $c = 7.5107(4)$  Å,  $Pbca$  (#61)

site	$x/a$	$y/b$	$z/c$	$B_{\text{iso}}$ (Å <sup>2</sup> )
Ca/8c	0.6276(7)	0.379(1)	0.366(1)	2.7(2)
B1/8c	0.225(4)	0.410(6)	0.480(5)	1.6(7)
D11/8c	0.264(7)	0.344(10)	0.348(12)	4.9(7)
D12/8c	0.265(6)	0.347(12)	0.596(12)	4.9(7)
D13/8c	0.237(6)	0.535(9)	0.473(13)	4.9(7)
D14/8c	0.136(7)	0.368(10)	0.480(10)	4.9(7)
B2/8c	0.503(3)	0.842(5)	0.817(6)	1.6(7)
D21/8c	0.524(6)	0.688(9)	0.798(11)	4.9(7)
D22/8c	0.409(6)	0.867(13)	0.814(12)	4.9(7)
D23/8c	0.542(6)	0.862(10)	0.956(12)	4.9(7)
D24/8c	0.542(7)	0.921(10)	0.708(12)	4.9(7)

## Ab initio calc. (lowest E, highest Sym. for #61)

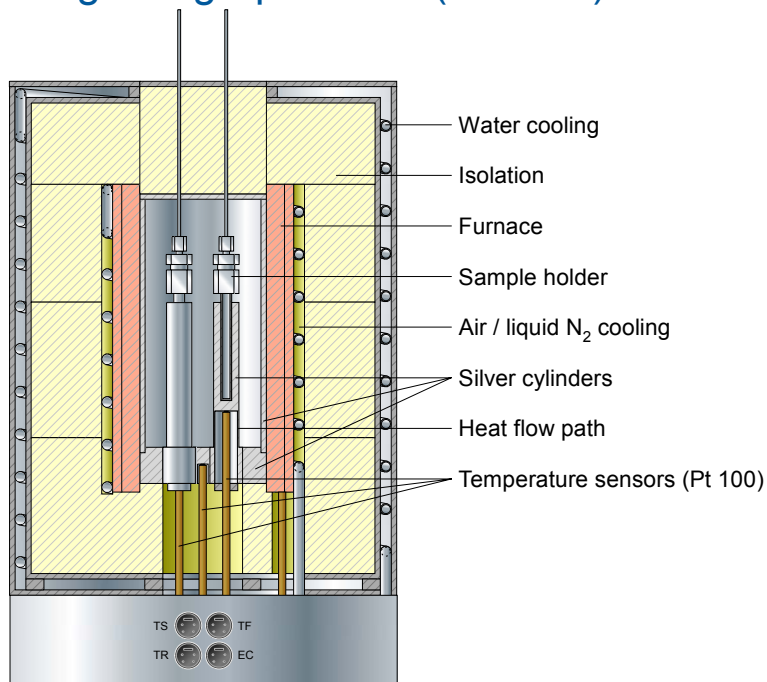


In-situ Raman measurements of  $\text{Mg}(\text{BH}_4)_2 + 2\text{LiCl}$  heating up to  $360^\circ\text{C}$  in Ar atmosphere



Stretching mode shift to the left hand due to the anharmonic effect and finally it disappears due to the decomposition of  $\text{Mg}(\text{BH}_4)_2$

- Drawing of high-pressure (200 bar) DSC



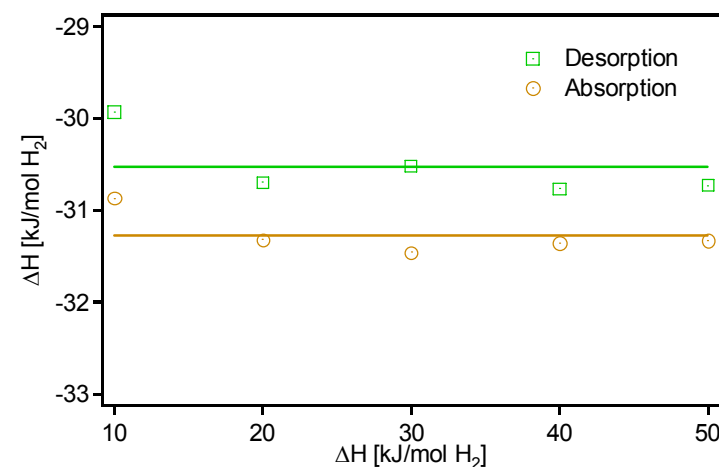
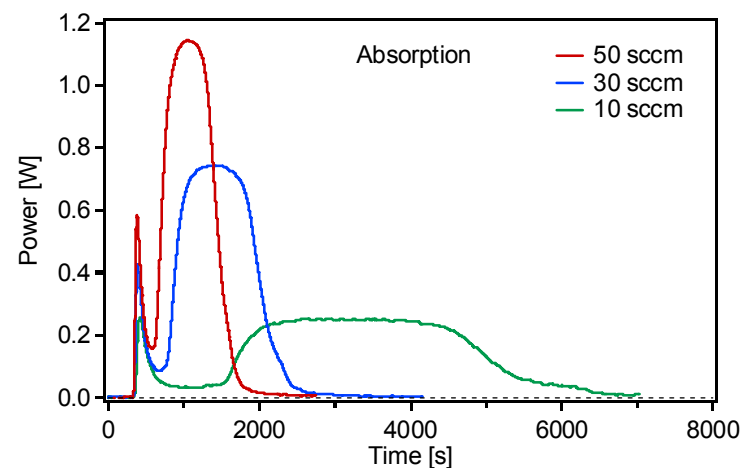
$$\Delta H_{\text{abs}} = -32.3 \text{ kJ/mol H}_2$$

$$\Delta H_{\text{des}} = -31.3 \text{ kJ/mol H}_2$$

Literature\*:

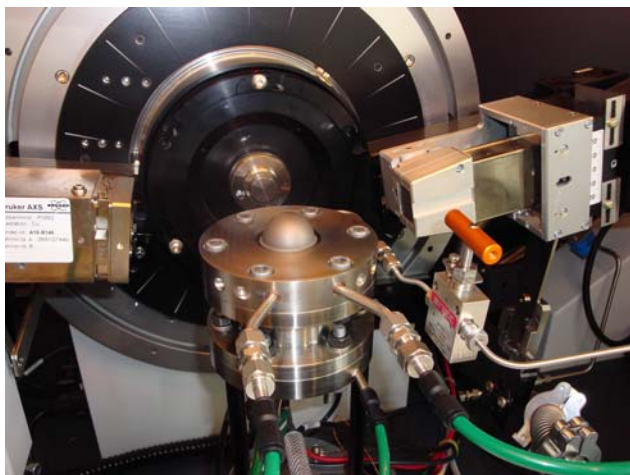
$$\Delta H_{\text{abs}} = -(32.1 \pm 0.1) \text{ kJ/mol H}_2$$

- LaNi<sub>5</sub>H<sub>6</sub> as reference material (T=60 °C)

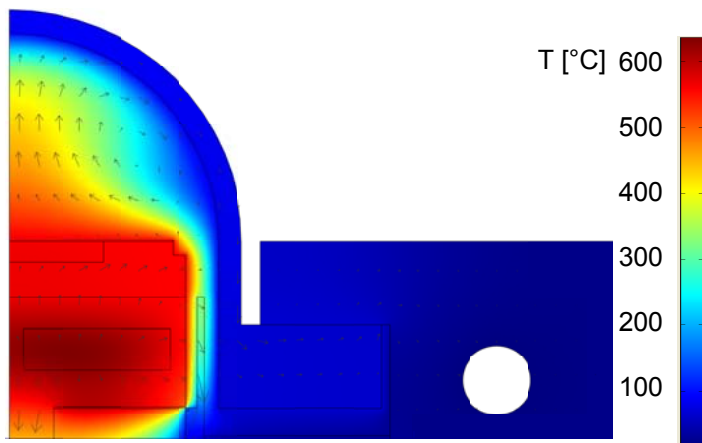


\*W.N. Hubbard, *Chem Thermodynamics* 15, 785 (1983)  
 Ph. Mauron et al. *Rev Sci Inst* 80, 083901 (2009),

- Foto of HP-XRD Cell in XRD hutch (200 bar)

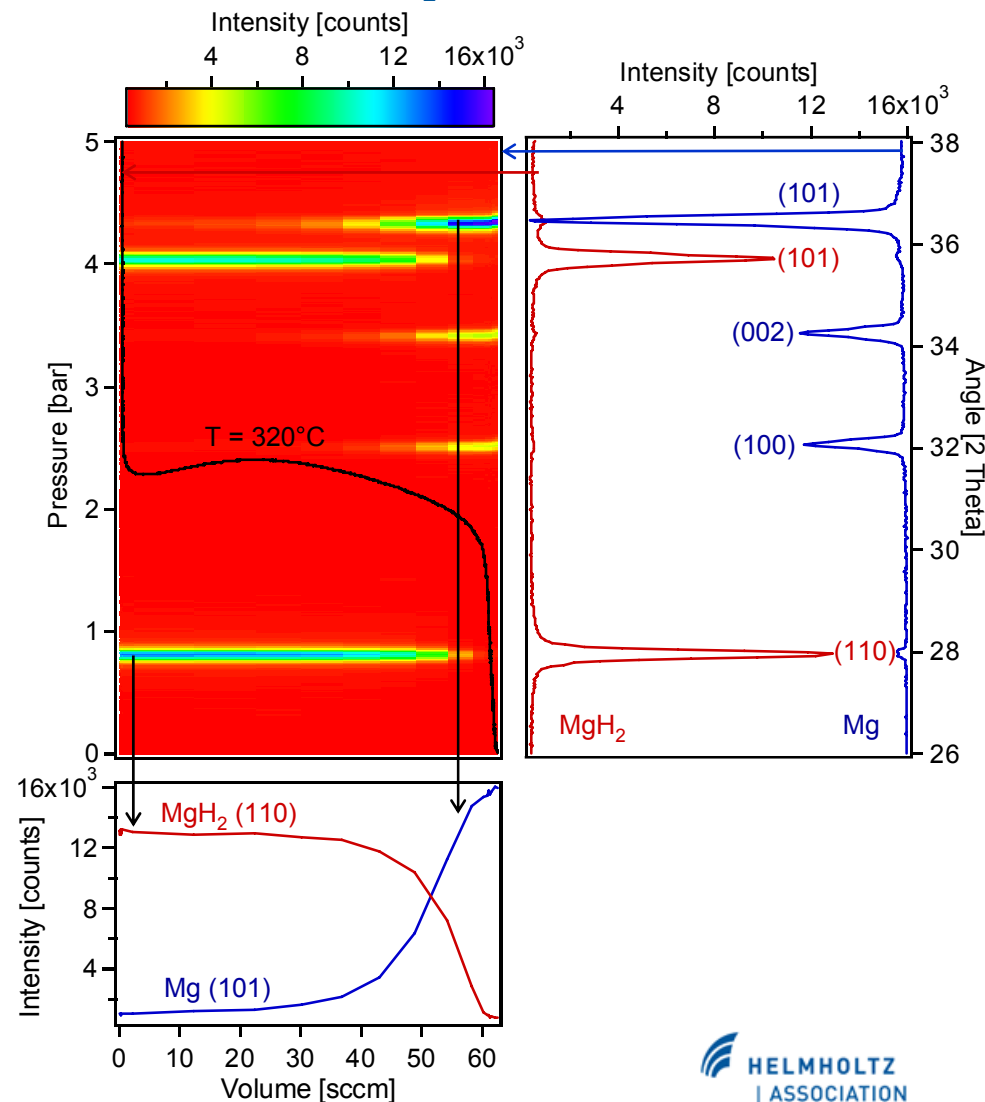


- Simulation of Temp. and Heat flow (COMSOL)



Ph. Mauron et al. to be submitted to Rev Sci Inst

- Desorption of  $MgH_2$  at 320 °C



# Summary

- *Borohydrides and deuterides were successfully synthesized with different methods:*
  - *wet chemical method ( $Mg(BH_4)_2$ ,  $Ca(BH_4)_2$  and deuterides)*
  - *metathesis reaction ( $Mg(BH_4)_2$ ,  $Ca(BH_4)_2$  and deuterides)*
  - *directly from the elements and indirectly via  $LiB_3$  and  $Li_7B_6$  ( $LiBH_4$ ,  $LiBD_4$ )*
- *The desorption of  $LiBH_4$ ,  $MgBH_4$  and  $CaBH_4$  was investigated*
- *The reversibility of  $LiBH_4$ ,  $LiBH_4 + Al$  has been shown*
- *The Stability of different borohydrides and a borohydride metal hydride system was determined by dynamical pcT ( $LiBH_4$ ,  $NaBH_4$ ,  $LiBH_4 + CeH_2$ )*
- *The crystal structure of  $\beta$ - and  $\gamma$ - $Ca(BH_4)_2$  was determined*
- *A high pressure in-situ Raman- and XRD cell and a high pressure DSC were constructed*

# Contributors



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Materials Science & Technology

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**Thanks for your attention !**