FRM II
Forschungs-Neutronenquelle
Heinz Maier-Leibnitz

MLZ
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Complex hydrides for Energy Applications

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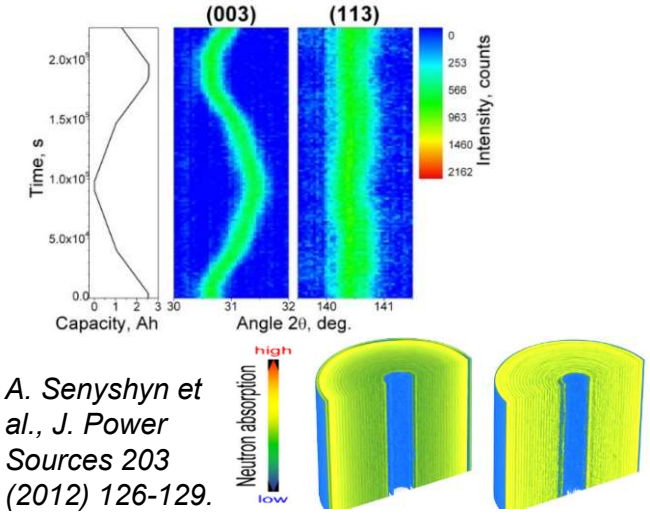
Energy Research with neutrons

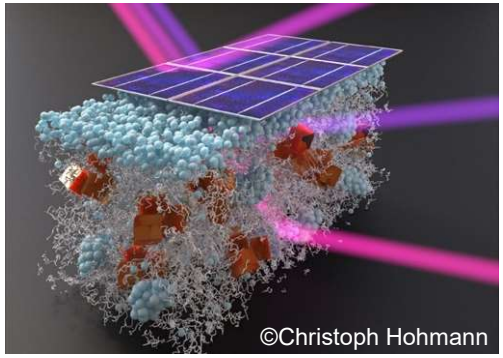
Battery research



A. Senyshyn et al., J. Power Sources 203 (2012) 126-129.

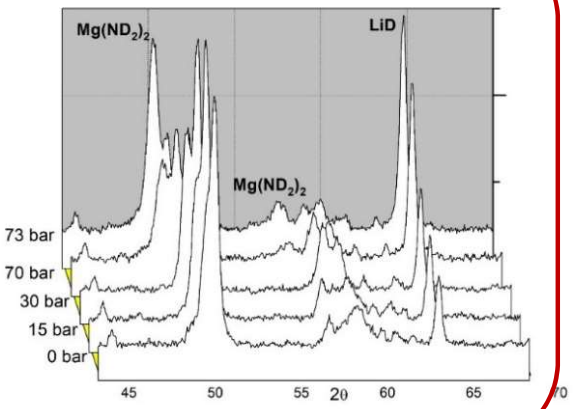
- Diffraction
- Imaging & Analytic techniques
- SANS & Reflectometry
- Spectroscopy
- Positron Source

Next generation solar cells

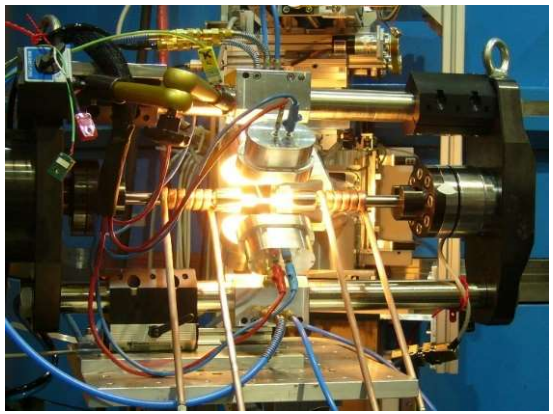


Hydrogen Technology – solid state conductors

F. Dolci et al., Int. J. Hydr. En. 35 (2010) 5448



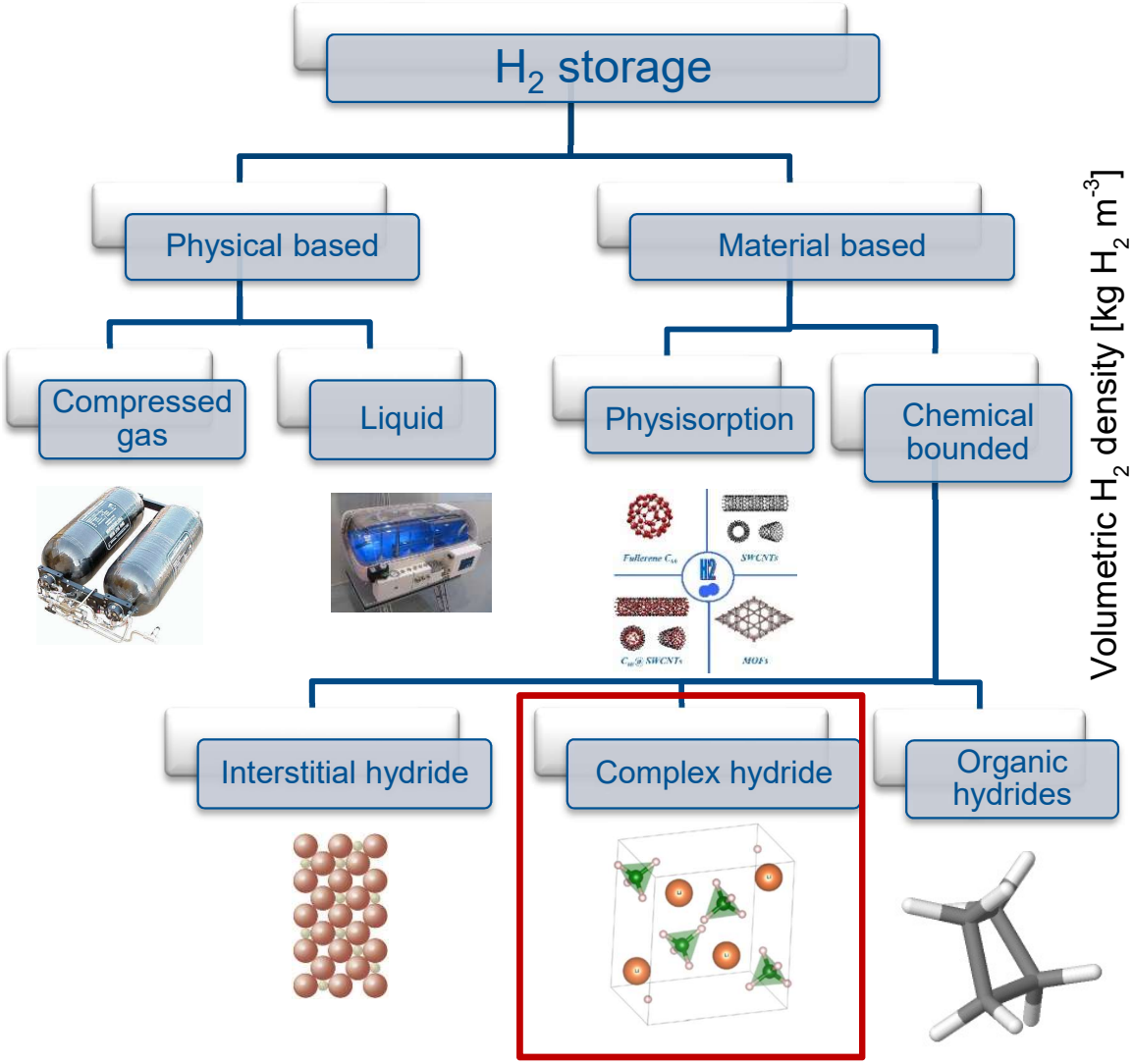
Advanced Materials

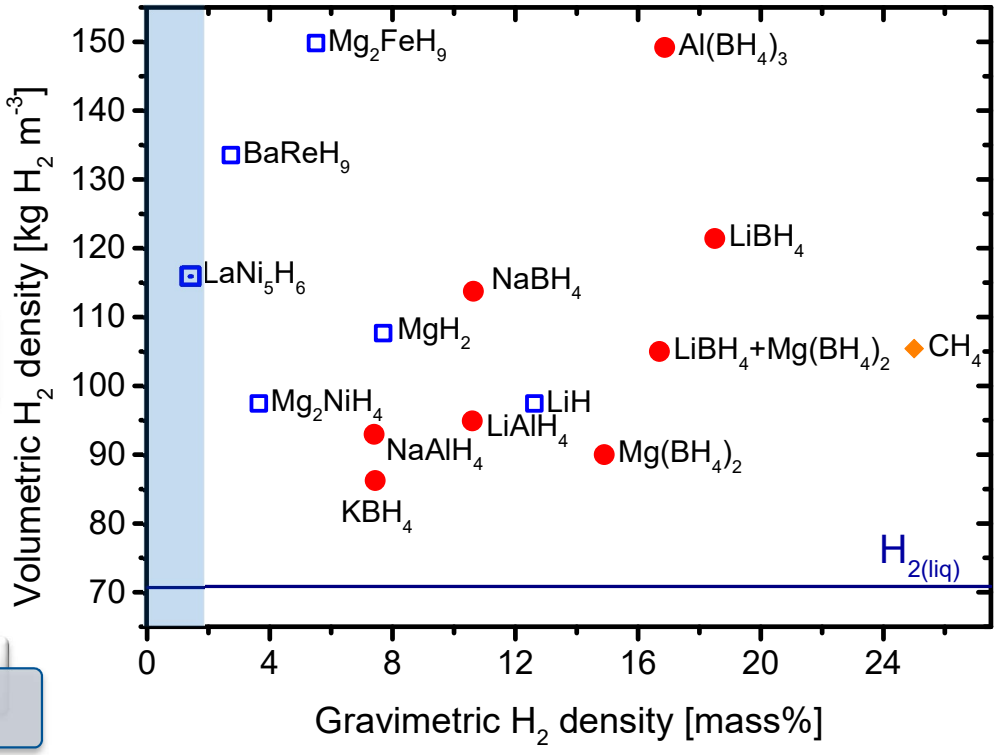


Outline

- Complex hydrides as hydrogen storage materials
- Hydrogen dynamics in $Li_4(BH_4)(NH_2)_3$ studied by QENS
- $Mg(BH_4)_2$ based solid state ion conductors
- Summary

Hydrogen storage

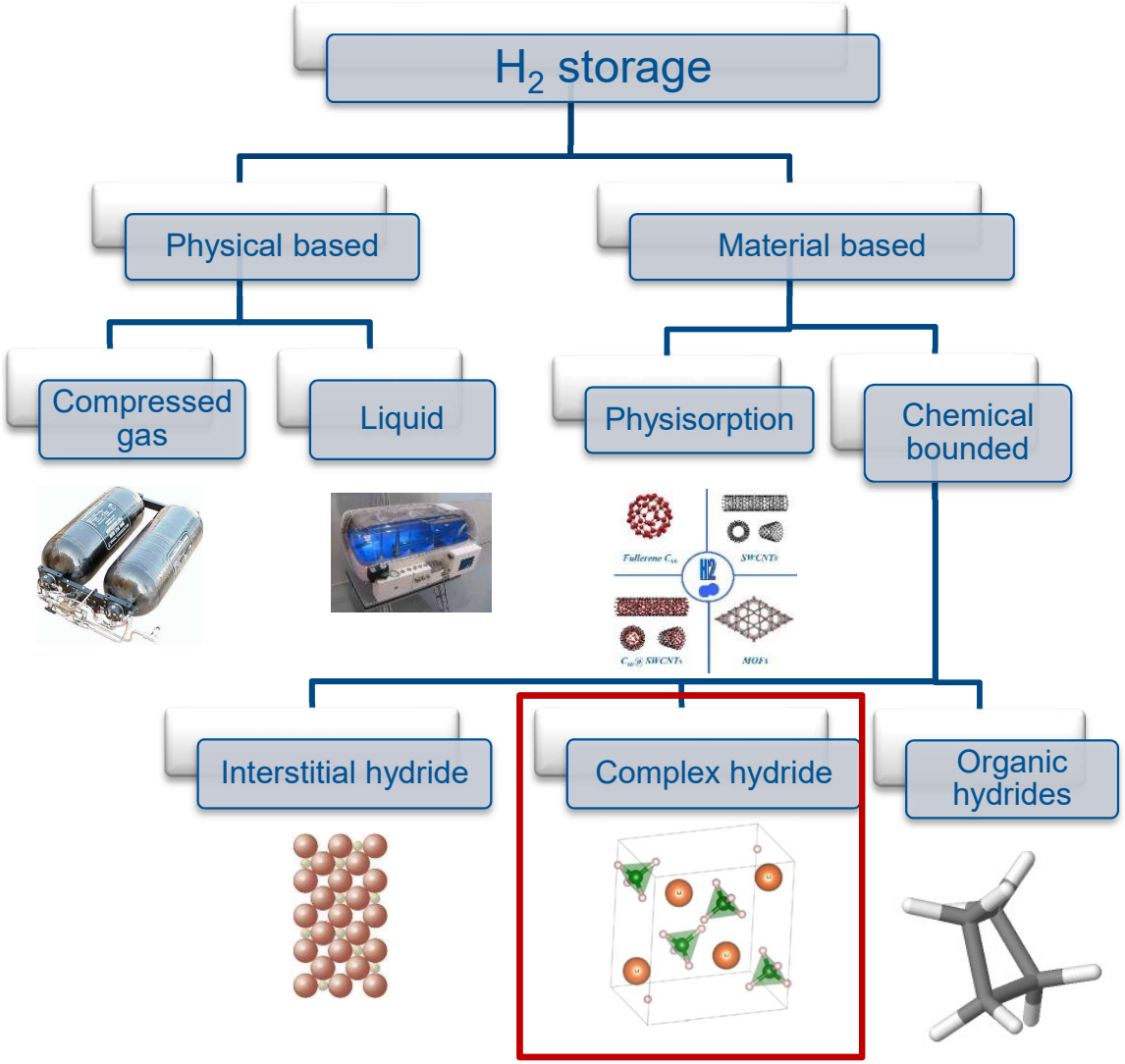




✓ High gravimetric and volumetric content

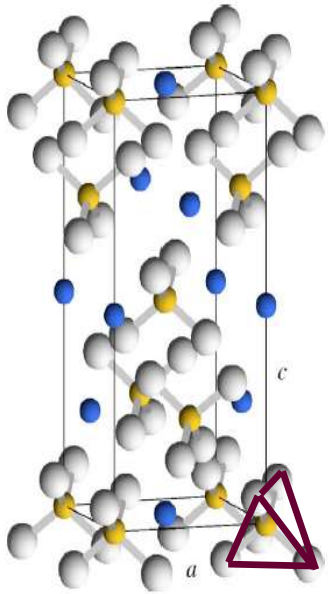
× Poor reversibility

Energy and hydrogen storage



Complex hydrides

- ionic compounds
- solid state reaction to release and reabsorb H_2

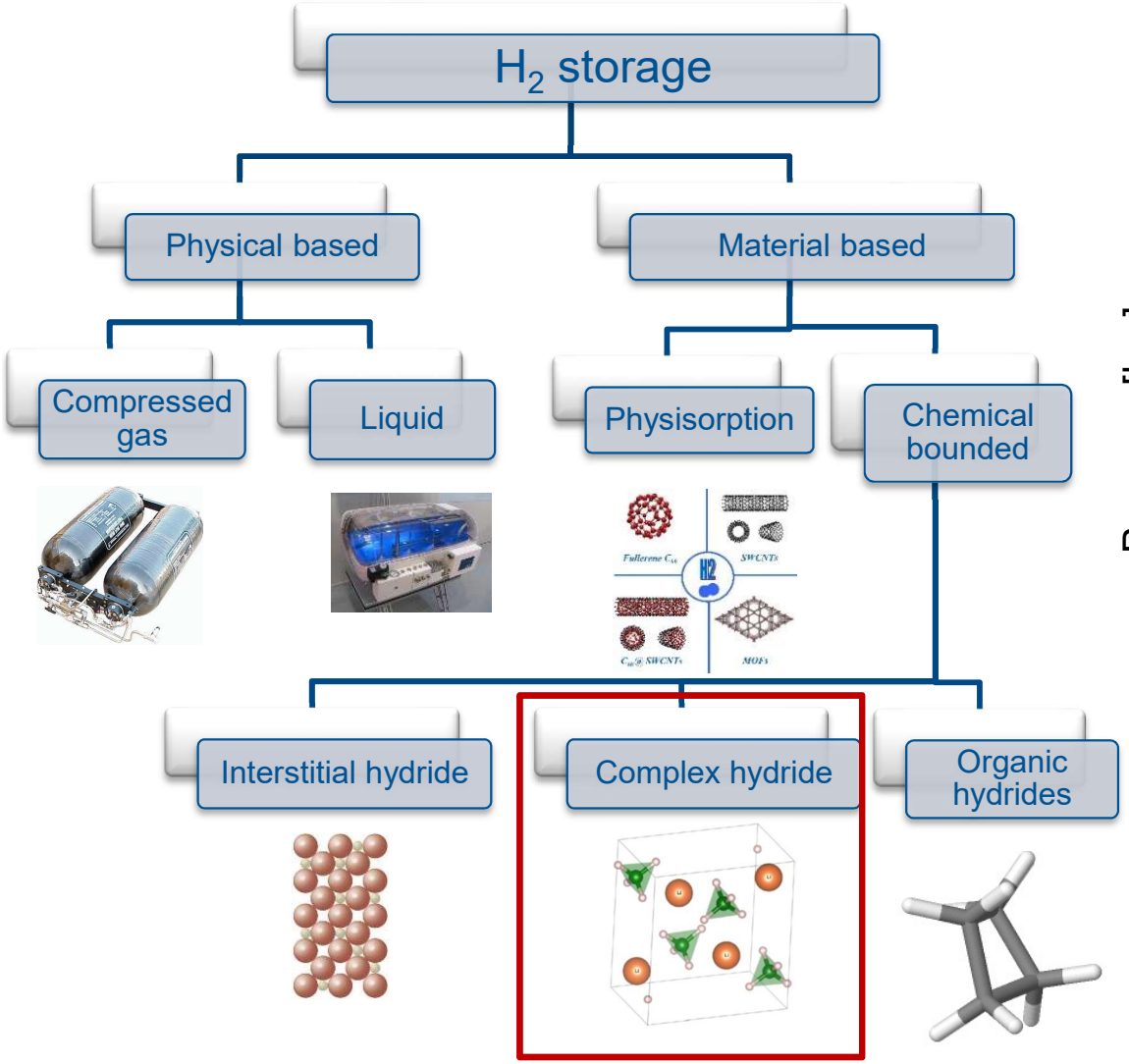


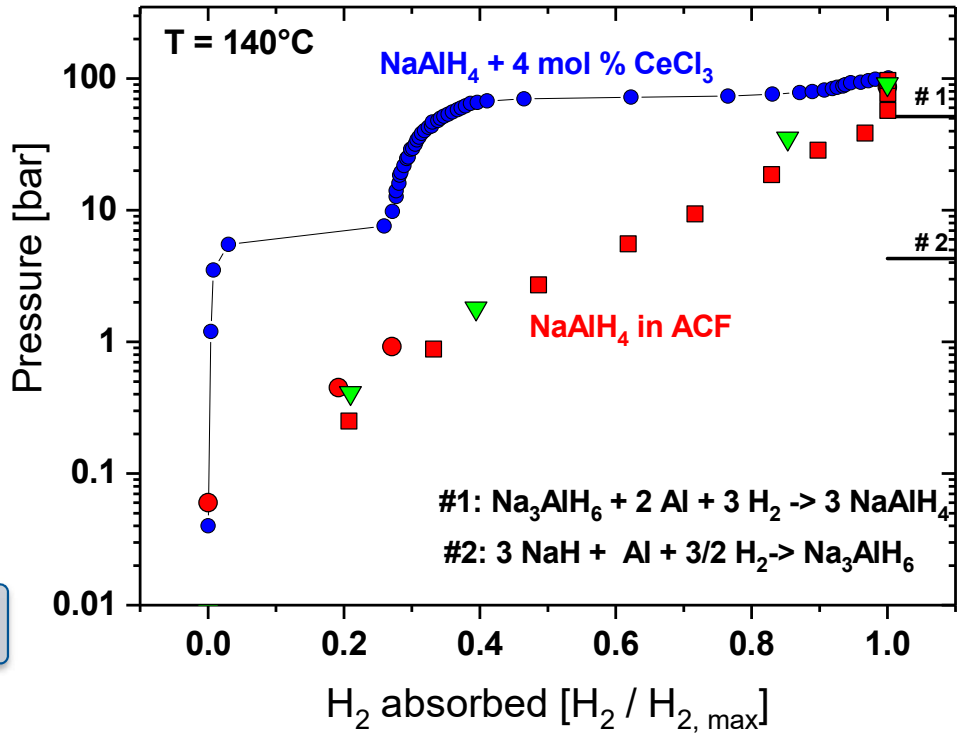
Na^+ $[AlH_4]^-$

$$NaAlH_4 \leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \qquad 3.7\ wt\%\ H_2$$
$$\leftrightarrow NaH + Al + 3/2\ H_2 \qquad 1.8\ wt\%\ H_2$$

Bogdanović, B. et al *Journal of alloys and compounds* 253 (1997): 1-9.

Energy and hydrogen storage





Lohstroh, W. et al. *ChemPhysChem* 11.4 (2010): 789-792.

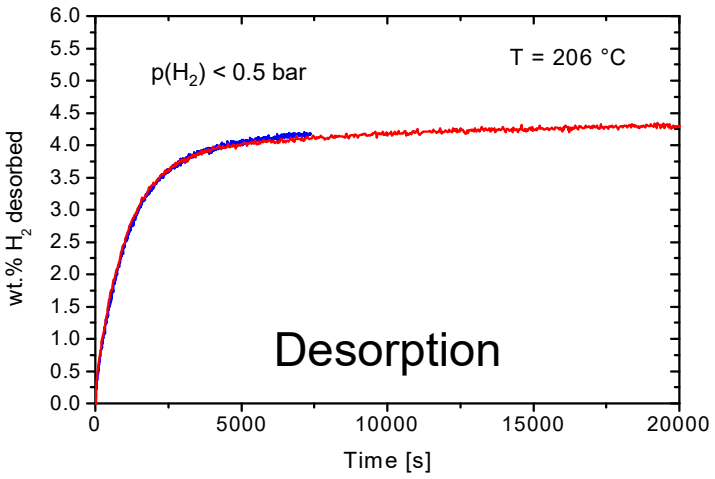
Nitrogen based hydrogen storage materials

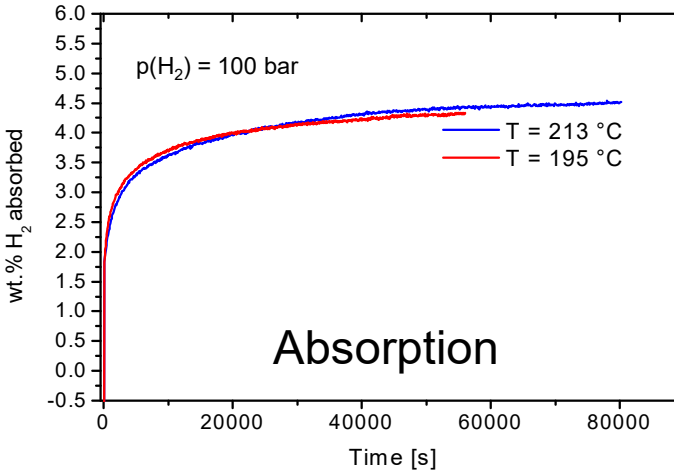
- $6\ Mg(NH_2)_2 + 12\ LiH \longleftrightarrow 3\ Li_2Mg_2(NH)_3 + 3\ LiNH_2 + 3\ LiH + 9\ H_2$

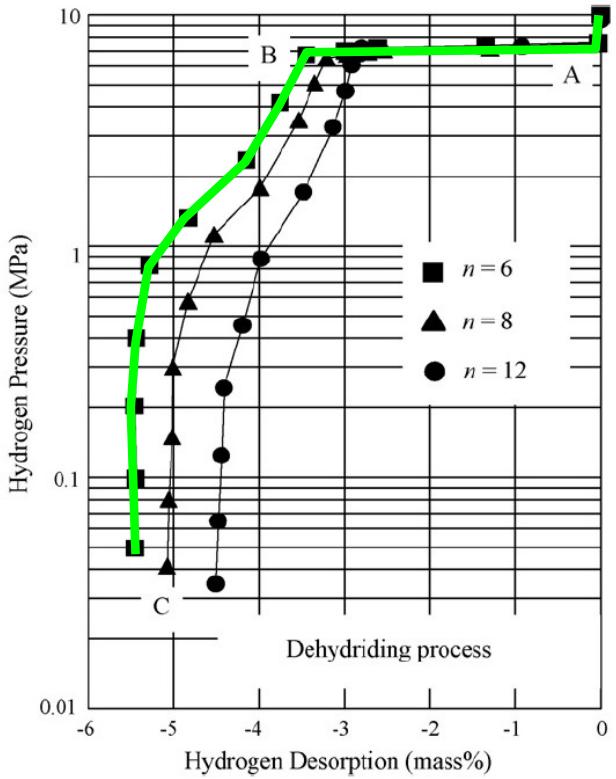
$\longleftrightarrow Li_2Mg(NH)_2 + 9\ H_2 + 3\ H_2$

5.6 wt % H_2, ~39 kJ/mol H_2

[1] W. Luo and E.Rönnebro, *J. Alloys Compd* 404-406 (2005) 392
[2] Leng, Haiyan Y., et al. *The Journal of Physical Chemistry B* 108.26 (2004): 8763-8765
[3] Nakamori, Y. et al. *Journal of Power Sources* 138.1-2 (2004): 309-312.
[4] Weidner, E., et al., *The Journal of Physical Chemistry C* 113.35 (2009): 15772-15777.





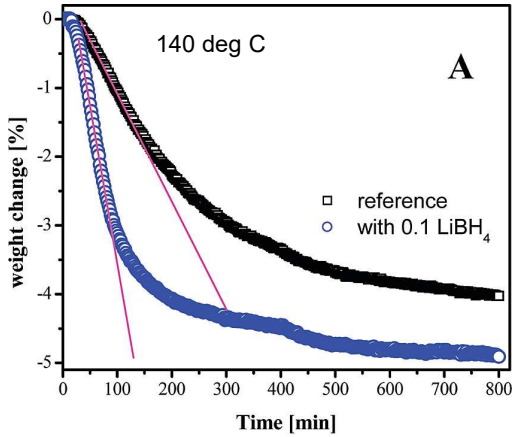


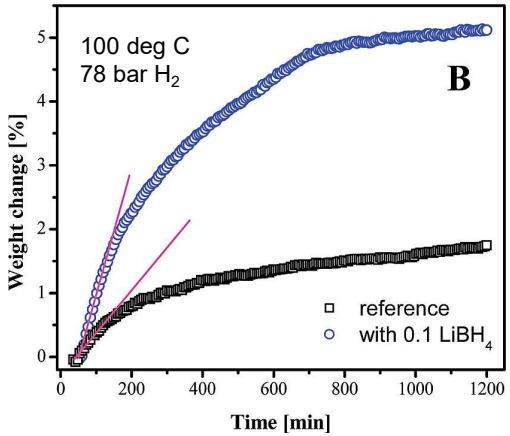
[5] M. Aoki et al., J. Alloys Compd. (2006) doi: 10.1016/j.jallcom.2006.11.141

$Mg(NH_2)_2$ - x LiH - $LiBH_4$ – improved kinetics

- $6\ Mg(NH_2)_2 + 9\ LiH + LiBH_4 \longleftrightarrow 3\ Li_2Mg_2(NH)_3 + Li_4(BH_4)(NH_2)_3 + 9\ H_2$

[1] Hu, J. et al., *Dalton Trans.*, 2010, 39, 9100-9107
[2] Wang, H. et al., Advanced Energy Materials (2017), DOI: (10.1002/aenm.201602456)
[3] Gizer, G. et al. *International Journal of Hydrogen Energy* 44.23 (2019): 11920-11929.

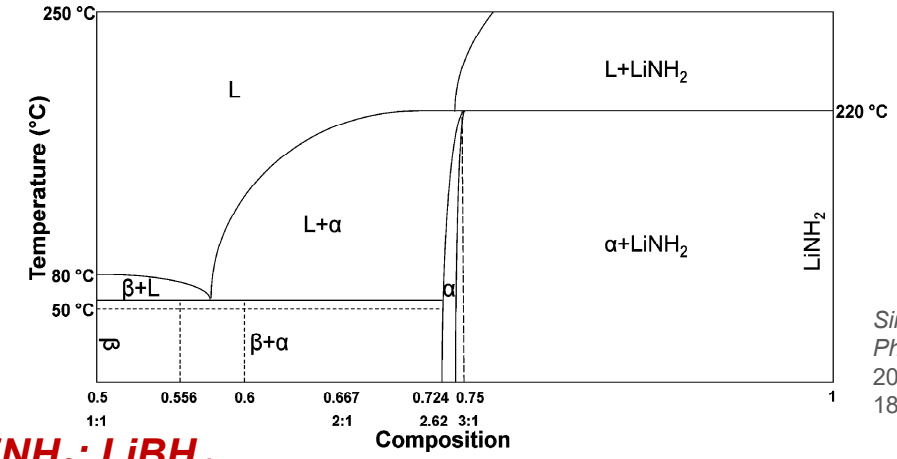




Hu, J. et al., *Chem. Mater.* 2008, 20, 13, 4398-4402

Formation of $Li_4(BH_4)(NH_2)_3$ as driving force for improved kinetics

$LiBH_4$ - $LiNH_2$ inert atmosphere



Singer, J. et al., J. Phys. Chem. C 2009, 113, 43, 18927-18934

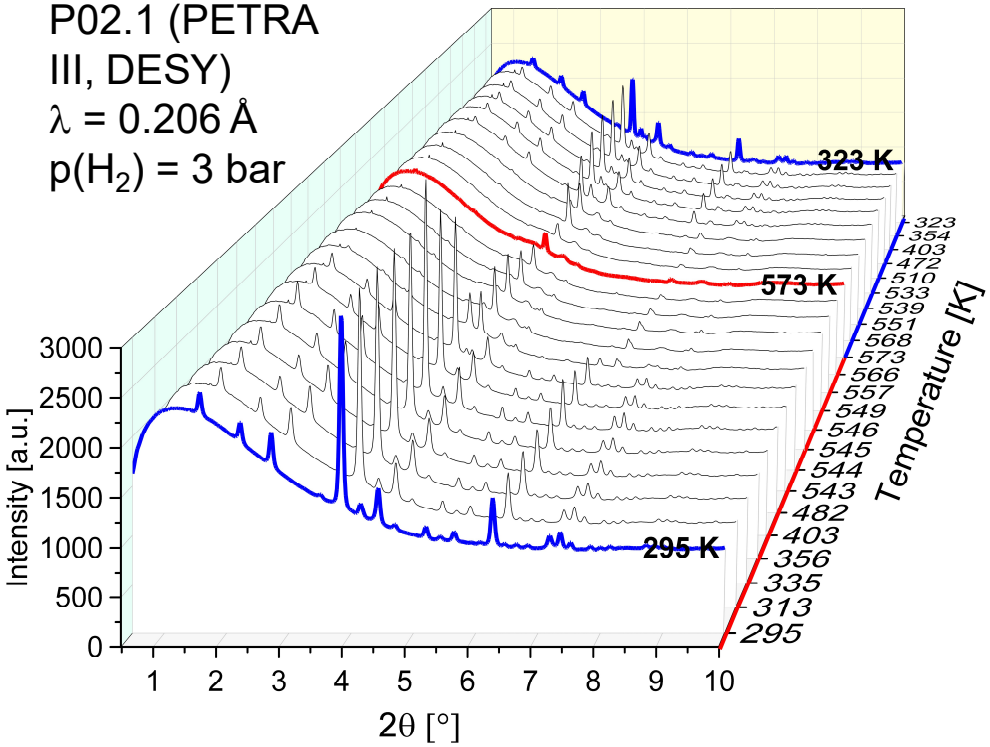
$LiNH_2$: $LiBH_4$

$LiNH_2$

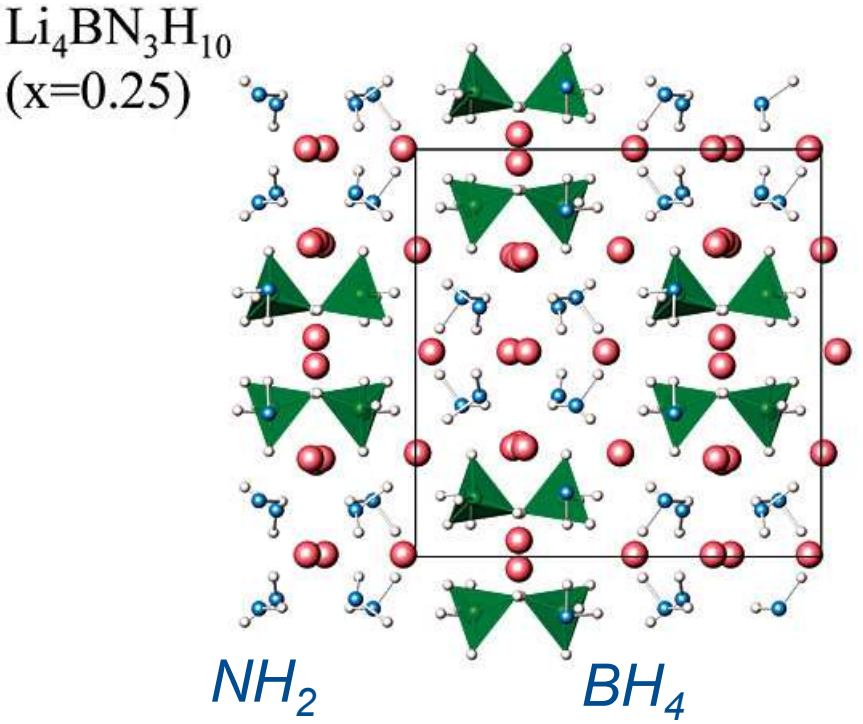
β-$Li_2(BH_4)(NH_2)$ α-$Li_{1+(3-x)}(BH_4)(NH_2)_{3-x}$

$Li_4(BH_4)(NH_2)_3$

- 3 $LiNH_2$ + 1 $LiBH_4$ (ball milled
- P02.1 (PETRA III, DESY)
- λ = 0.206 Å
- p(H_2) = 3 bar



$Li_4BN_3D_{10}$ (*I*213) *a* (Å) = 10.5846(2) Å (@ 5 K)

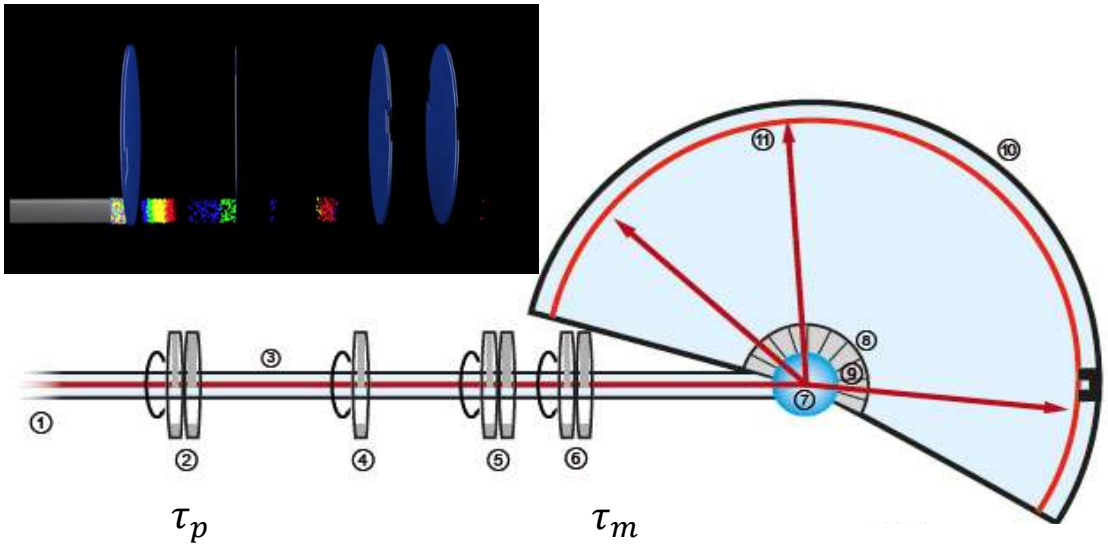


Wu, Hui, et al. *Chemistry of Materials* 20.4 (2008): 1245-1247.

- **α- $Li_4(BH_4)(NH_2)_3$**
- **T_{melt} > 500 K (DSC 493 K)**
- **Recrystallisation to α-phase + $LiNH_2$**

Aslan, Neslihan, et al. *Advanced Engineering Materials* 23.11 (2021): 2100620.

Hydrogen dynamics – Quasielastic scattering



Nuclide	σ_{coh}	σ_{inc}
^{1}H	1.75	**80.26**
Mg	3.63	0.08
^{7}Li	0.45	0.78
^{11}B	5.56	0.21

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega \mathrm{d}E'}\right) = \frac{1}{\hbar}\frac{k_i}{k_f} N \left[\frac{\sigma_{\mathrm{inc}}}{4\pi} S_{\mathrm{inc}}(\mathbf{Q},\omega) + \frac{\sigma_{\mathrm{coh}}}{4\pi} S_{\mathrm{coh}}(\mathbf{Q},\omega)\right]$$

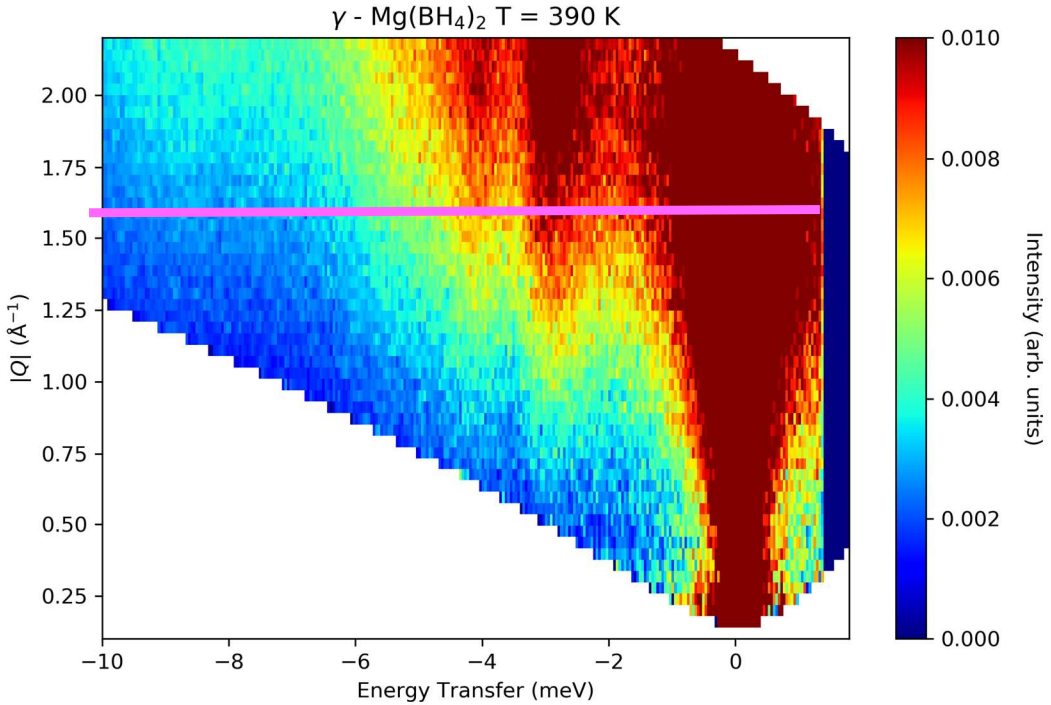
$\propto$ self correlation function

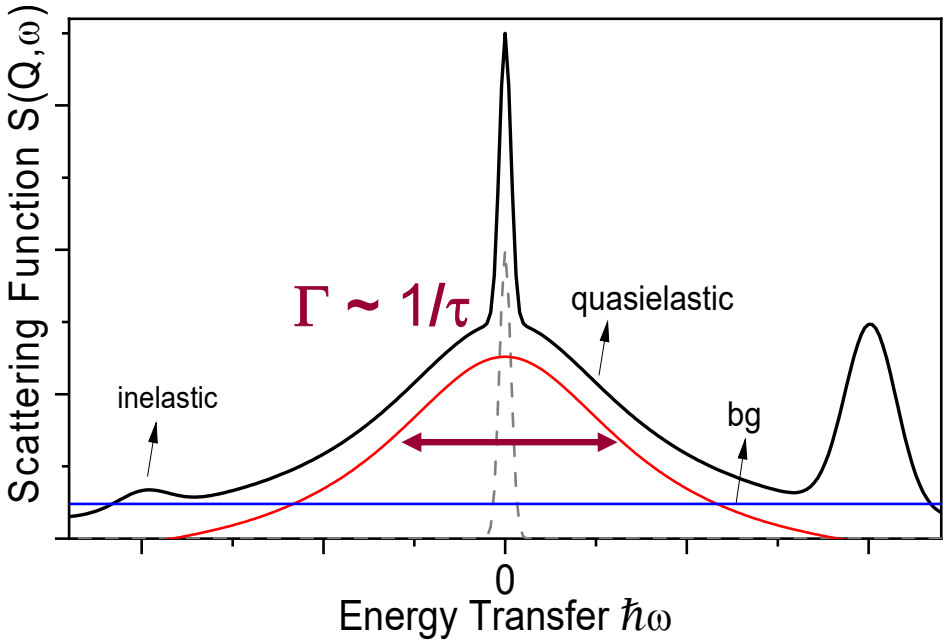
Hydrogen dynamics – Quasielastic scattering

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega \mathrm{d}E'}\right) = \frac{1}{\hbar}\frac{k_i}{k_f} N \left[\frac{\sigma_{\mathrm{inc}}}{4\pi} S_{\mathrm{inc}}(\mathbf{Q},\omega) + \frac{\sigma_{\mathrm{coh}}}{4\pi} S_{\mathrm{coh}}(\mathbf{Q},\omega)\right]$$

$\propto$ self correlation function

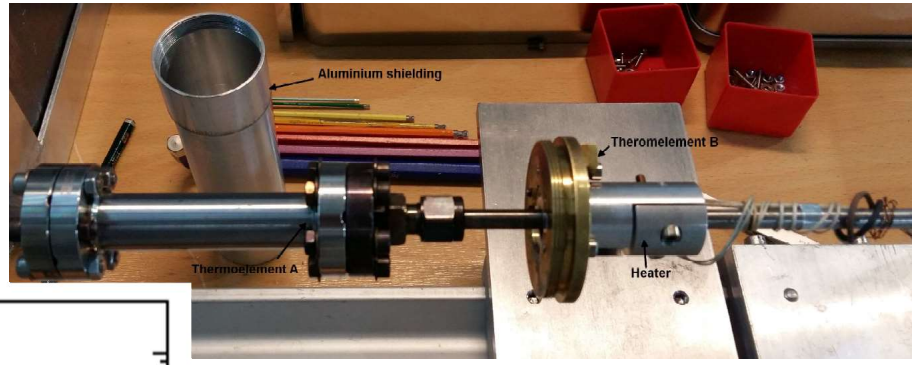
$\propto$ pair correlation function

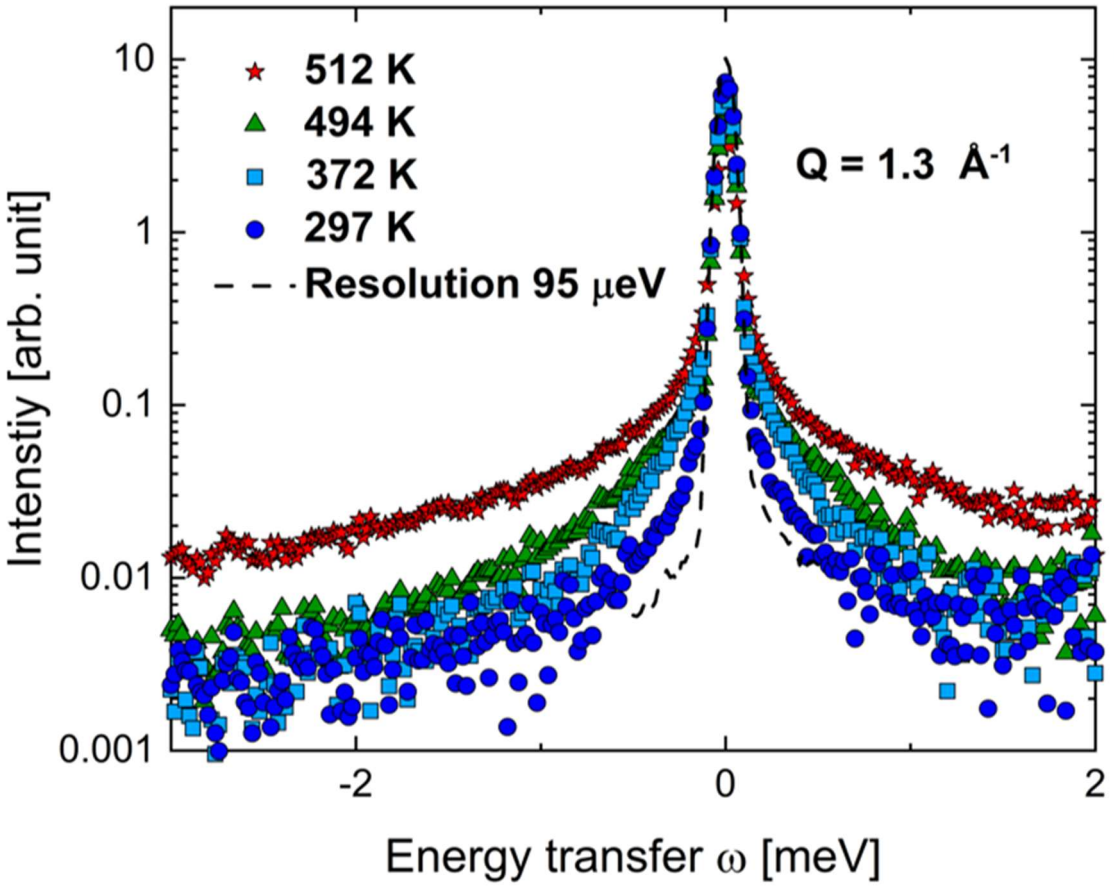




$Li_4(BH_4)(NH_2)$ – QENS

- Fully protonated – BH_4 and NH_2 entities
- $p(H_2)$ = 3 bar



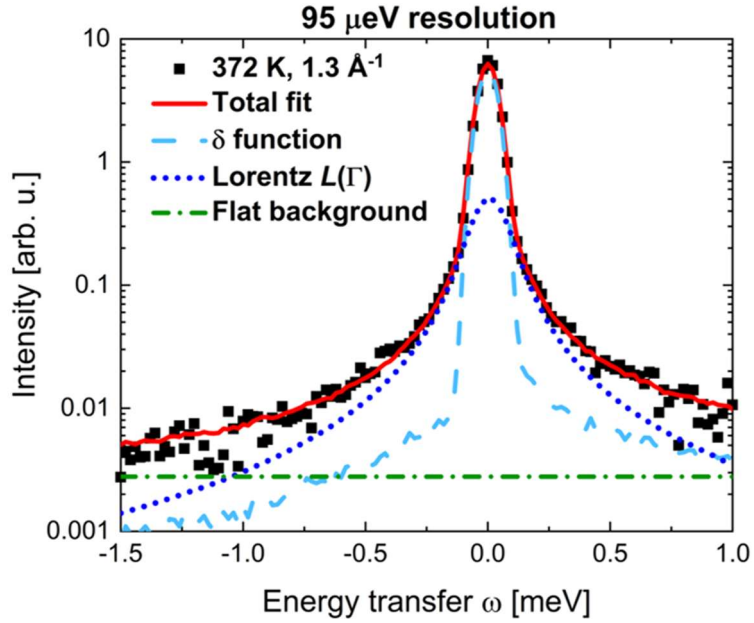


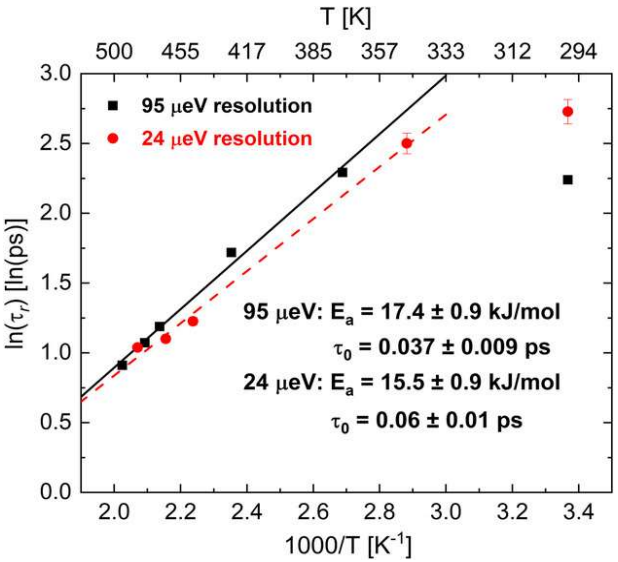
$Li_4(BH_4)(NH_2)$ – QENS

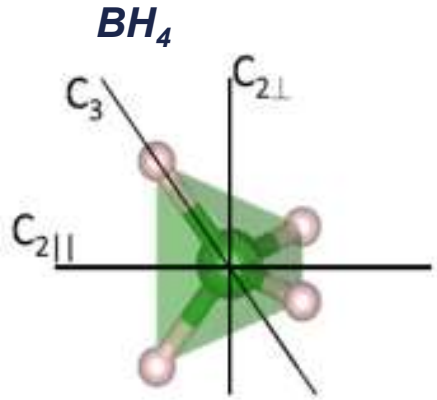
$$S(Q,\omega) = R \otimes \left[A_0(Q)\delta(\omega) + \sum A_n(Q)\mathcal{L}_n(Q,\omega) \right] + bg$$

Below 500 K

- Γ Independent of Q
- Elastic contribution



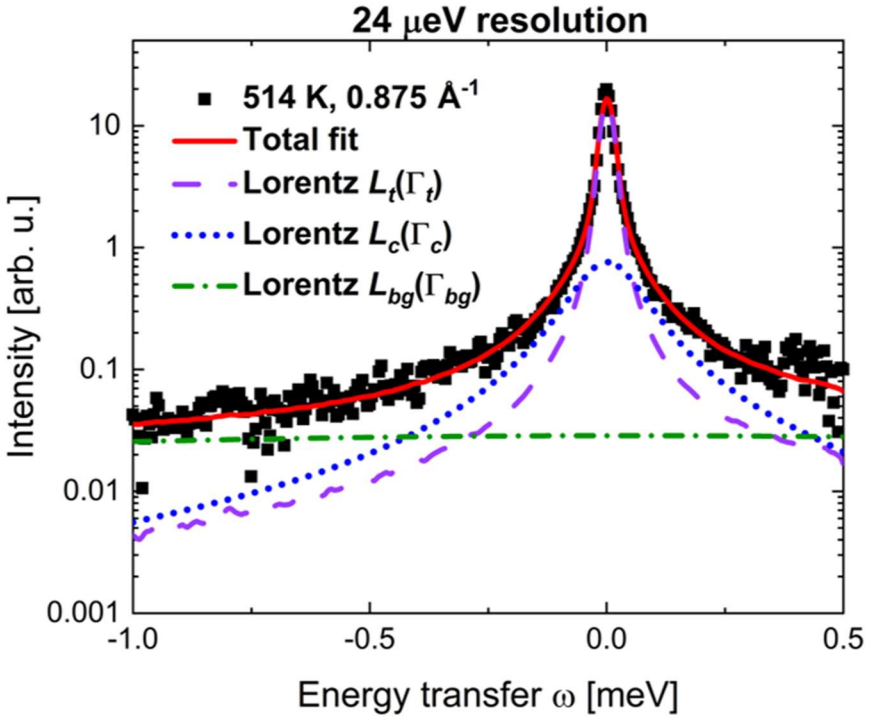




- ***Thermally activated localized motion (rotations of BH_4)***

Aslan, Neslihan, et al. *Advanced Engineering Materials* 23.11 (2021): 2100620.

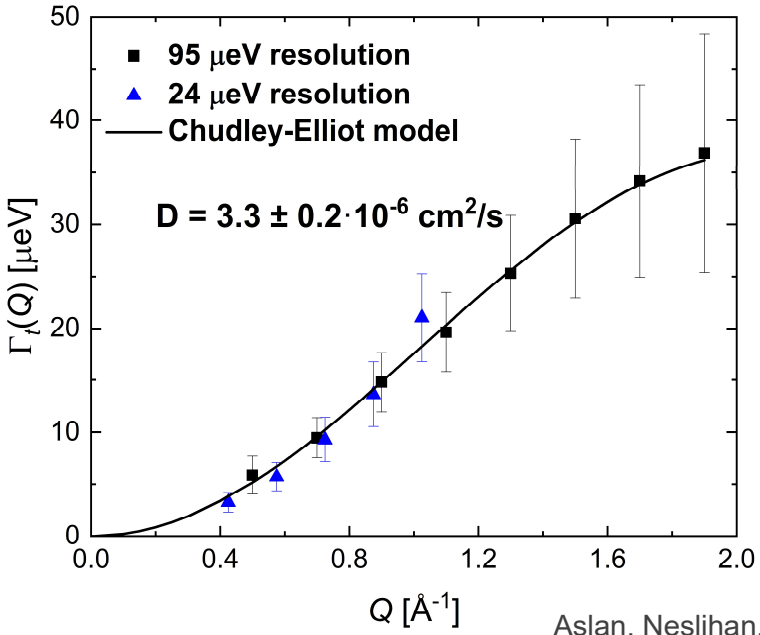
$Li_4(BH_4)(NH_2)$ above 500 K



- ***Long range diffusive motion of hydrogen entities***
- ***Jump diffusion model***

Chudley-Elliot Model:

$$\Gamma_t = \frac{6\hbar D}{l^2}\left(1 - \frac{\sin(Ql)}{Ql}\right)$$



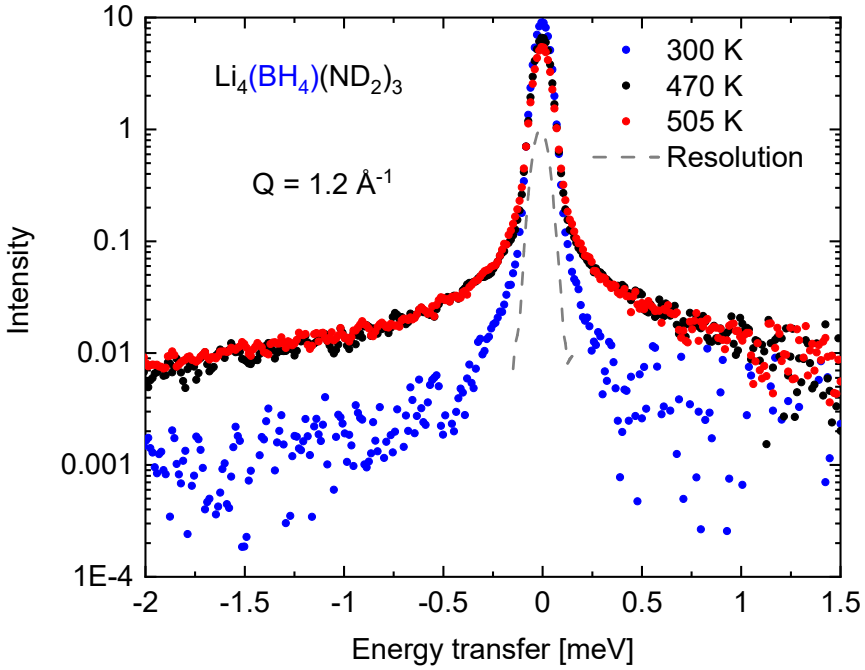
- 2 Lorentzians: $S_{rot} \otimes S_{trans}$
- Γ_t increasing with Q
- No elastic contribution

$$S(Q,\omega) = R \otimes [A_0(Q)\mathcal{L}_t(Q,\omega) + A_1(Q)\mathcal{L}_1(Q,\omega)] + bg$$

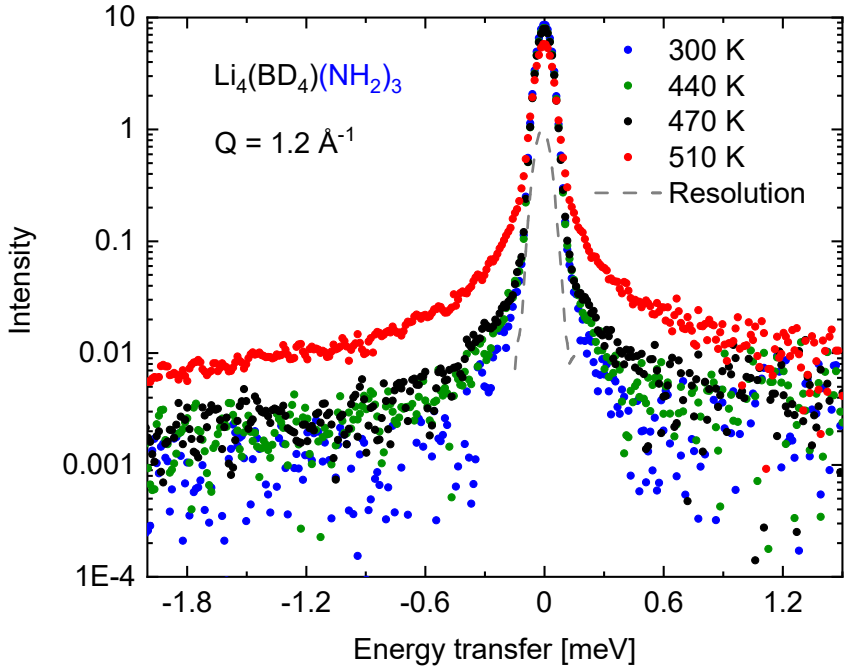
Aslan, Neslihan, et al. *Advanced Engineering Materials* 23.11 (2021): 2100620.

Partial Deuteration

- $Li_4(BH_4)(ND_2)_3$



- $Li_4(BD_4)(NH_2)_3$



NEUTRONS FOR SOCIETY

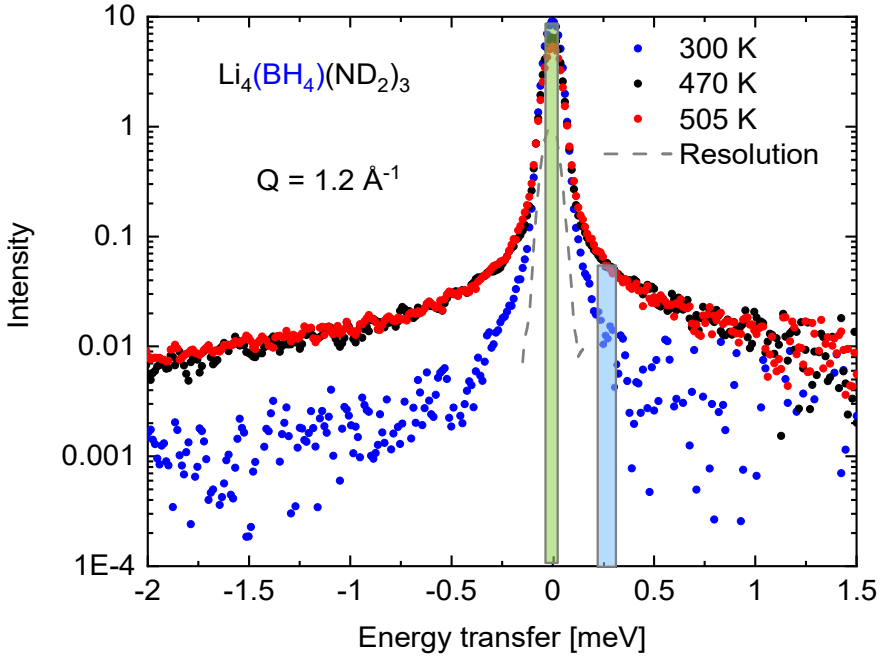
IN6 Sharp

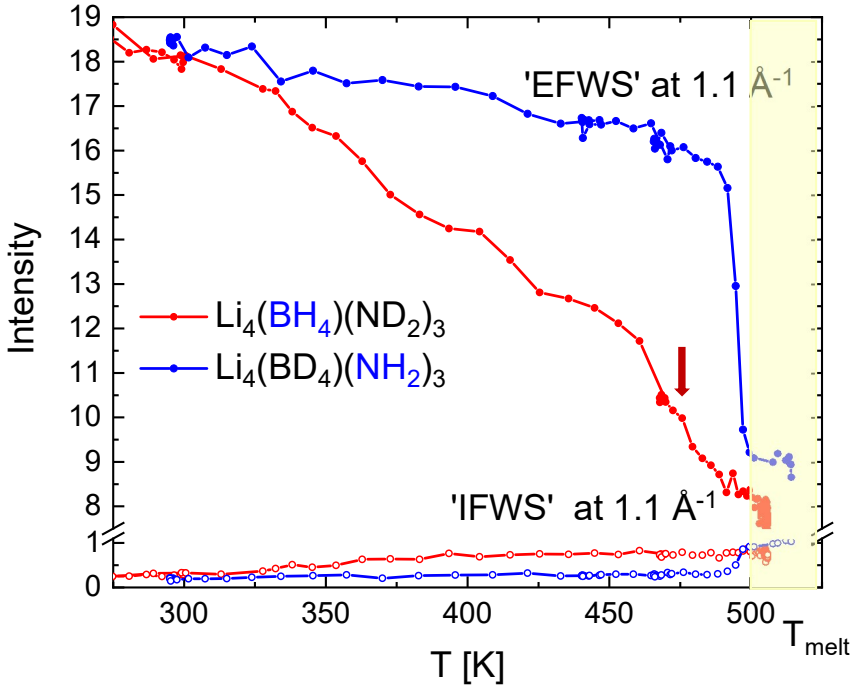
- ***QENS below T_{melt} originates mainly from BH_4 entities***
- ***Temperature dependence varies for the two partially deuterated samples***

N. Aslan et al. (2021)

Partial Deuteration

- ***Temperature dependence***



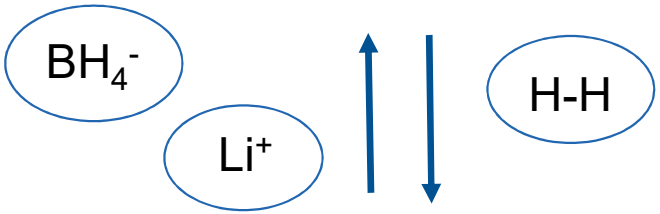


- ***$Li_4(BD_4)(NH_2)_3$***
  long range diffusion above T_{melt}
- ***$Li_4(BH_4)(ND_2)_3$***
  gradual transition
  long range diffusion starting around 470 K

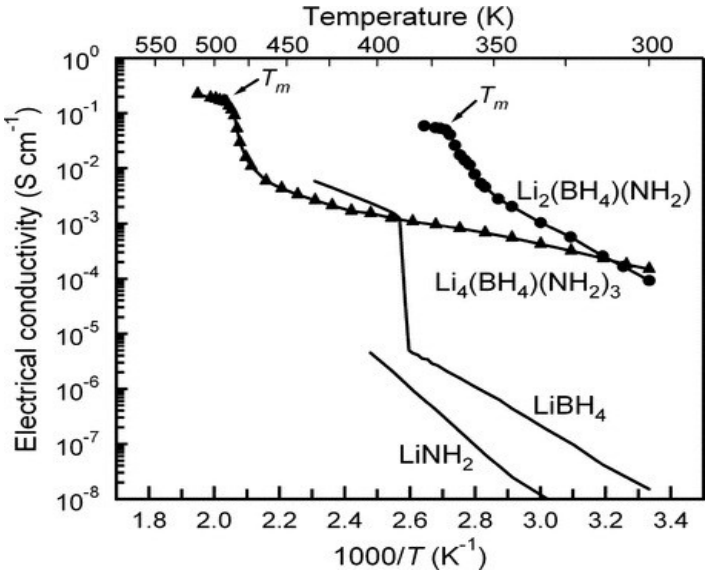
N. Aslan et al. (2021)

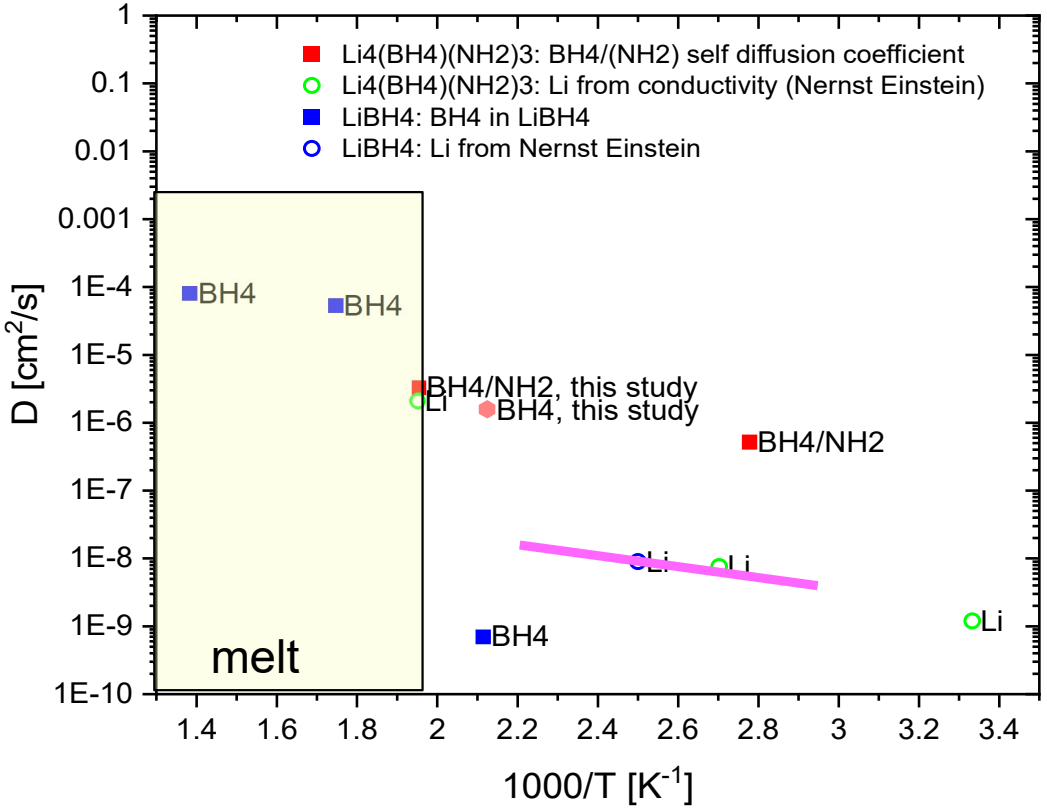
Diffusivity

$$6\ Mg(NH_2)_2 + 9\ LiH + LiBH_4$$



$$3\ Li_2Mg_2(NH)_3 + Li_4(BH_4)(NH_2)_3 + 9\ H_2$$





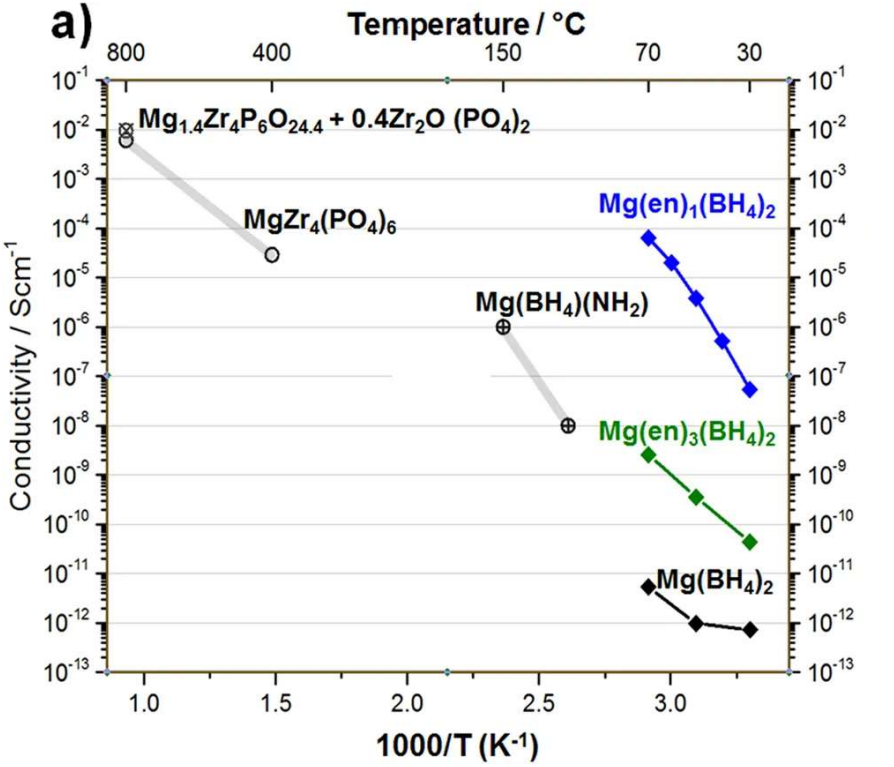
[1] Matsuo, M. et al, *Advanced Energy Materials* 1.2 (2011): 161-172.
[2] Martelli, P. et al., T*he Journal of Physical Chemistry A* 114.37 (2010): 10117-10121.
[3] Burankova, T. et al., *The Journal of Physical Chemistry C* 121.33 (2017): 17693-17702.
[4] Borgschulte, A., et al. , *Physical Chemistry Chemical Physics* 12.19 (2010): 5061-5066.
[5] M. Matsuo et al., *Appl. Phys. Lett.* 91 (2007): 224103.

Hydrogen Mobility and Ionic Conductivity – $Mg(BH_4)_2$ as solid state ion conductor

- High gravimetric $Mg(BH_4)_2$

  14.9 wt% H_2
- rich structural phase diagramm (e.g. $Mg(BH_4)_2$: α, β, β‘, γ, ε, ε‘, δ)
- potential solid state ion conductors – high cation mobility concurrent with BH_4 dynamics

Mg^{2+} conductivity in $Mg(BH_4)_2$

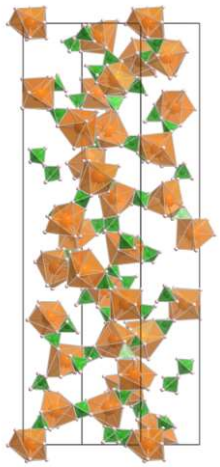


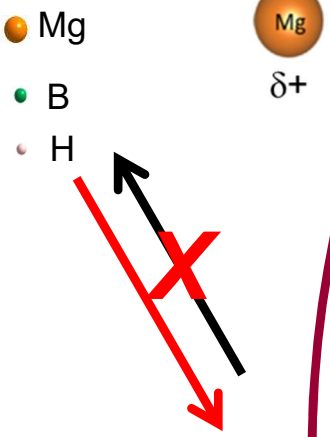
Elsa Roedern et al., Scientific Reports 7, 46189 (2017)

$Mg(BH_4)_2$: α-, β- and γ- polymorph

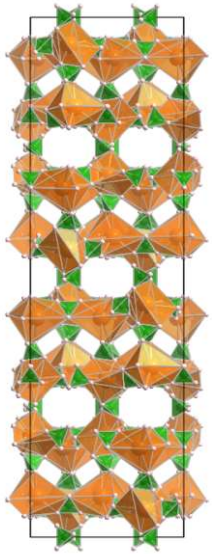
Low temperature α - $Mg(BH_4)_2$

- hexagonal $P6_122$
- Cell volume: 3434 Å^3
- 6 non-eq. BH_4 positions
- Contains voids (37 Å^3)





T > 490 K

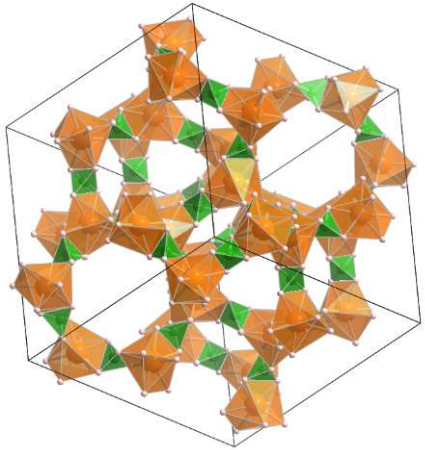


High temperature β - $Mg(BH_4)_2$

- Orthorhombic *Fddd*
- Cell volume: 7543 Å^3
- 5 non-eq BH_4 positions
- Anomalous thermal expansions

Precusor for Mg^{2+} conductors

Porous (low temperature) γ - $Mg(BH_4)_2$



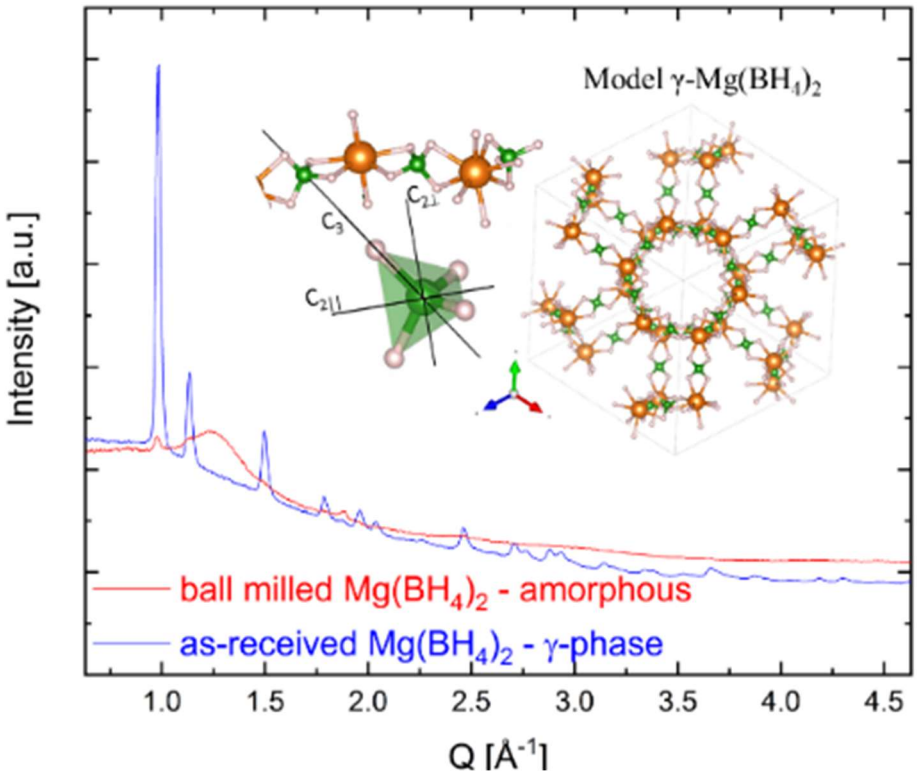
- Cubic Ia-3d
- Cell volume: 3912.57 Å^3
- 1 non-eq BH_4 positions

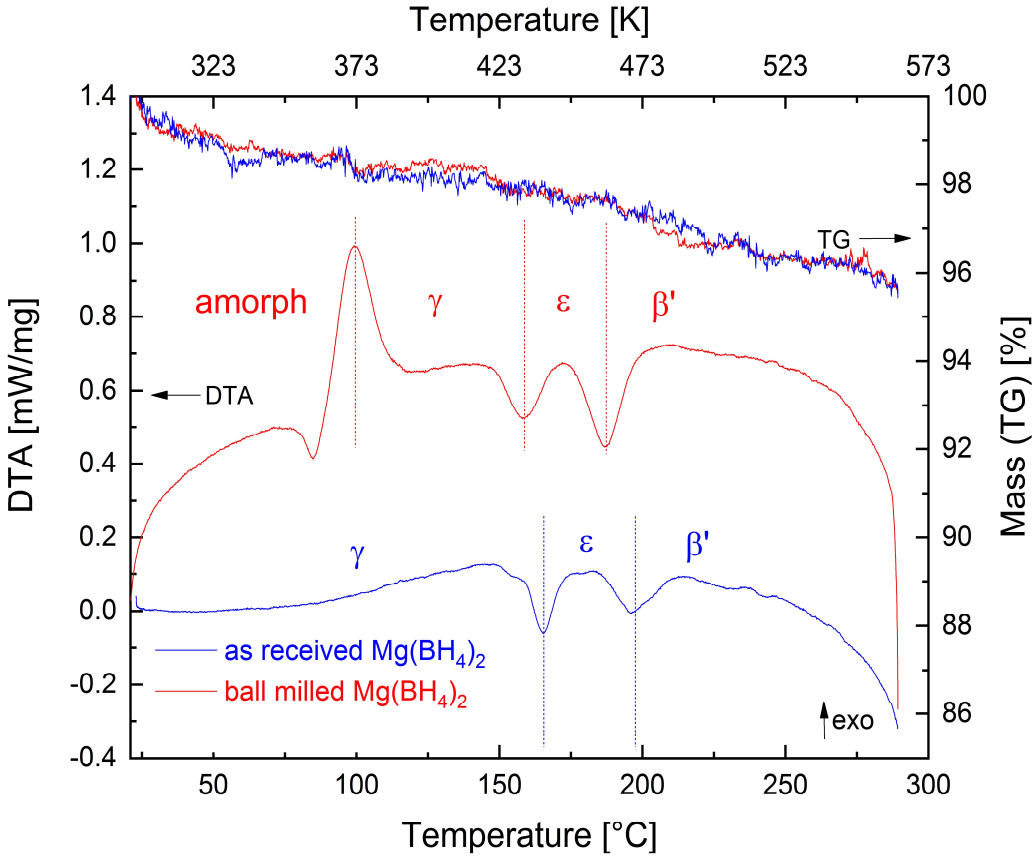
Filinchuk Y. et al, *Chem. Mater.* **2009**, 21, 925–933
Filinchuk Y. et al, Angew. Chem. Int. Ed. **2011**, 50, 11162-11166

γ- $Mg(BH_4)_2$: as received and ball milled

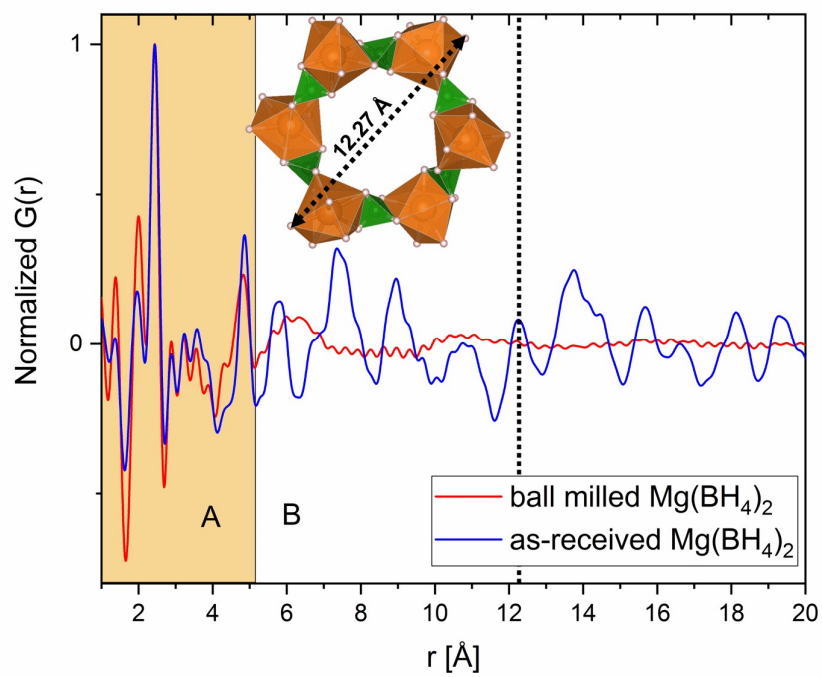
after ball milling:

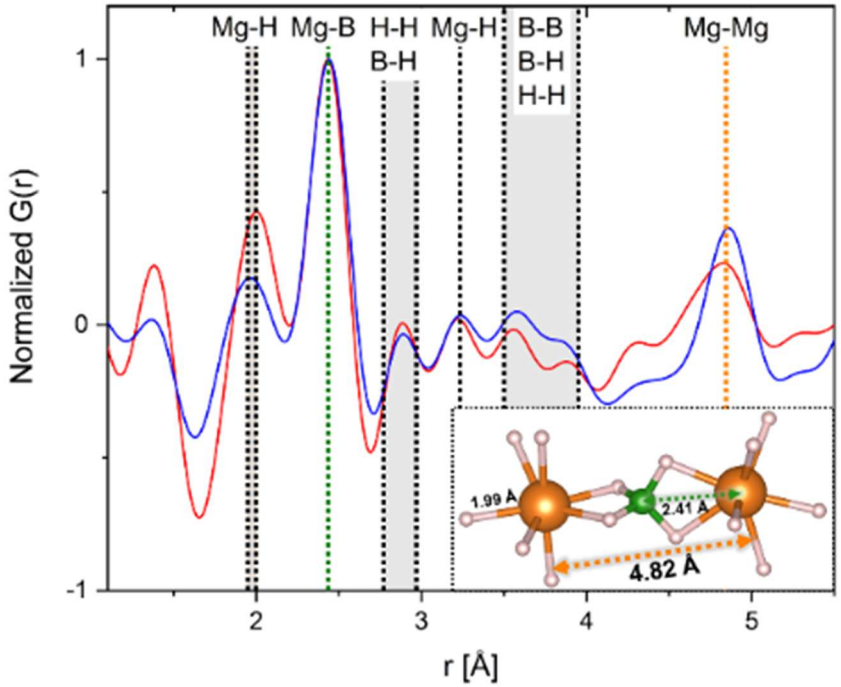
- XRD – no long range order
- recrystallization around 373 K





γ- $Mg(BH_4)_2$: as received and ball milled





PDF: Mg-B-H building blocks remain intact

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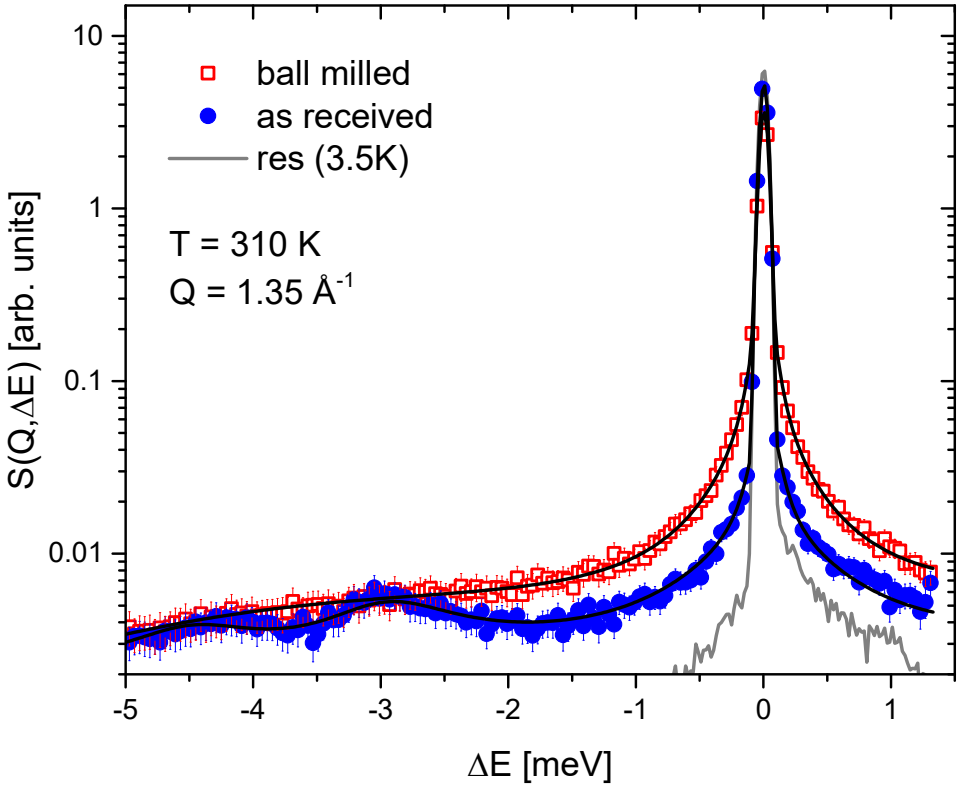
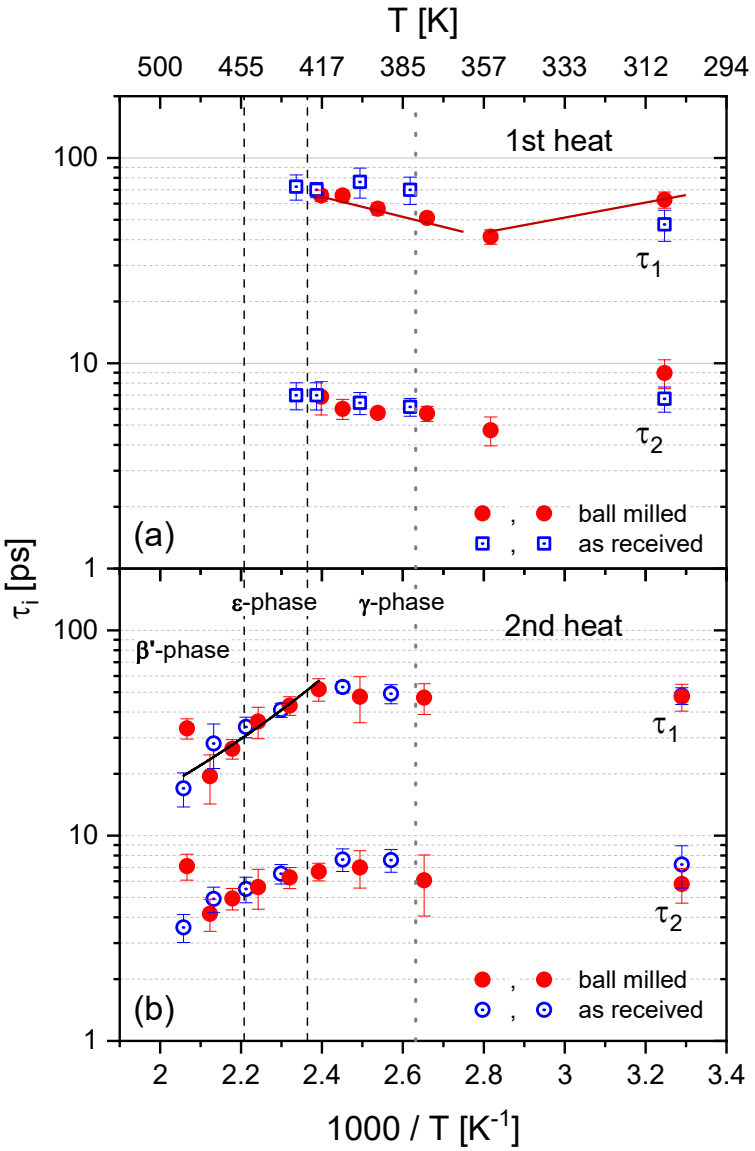
10.1038/s41598-020-65857-6

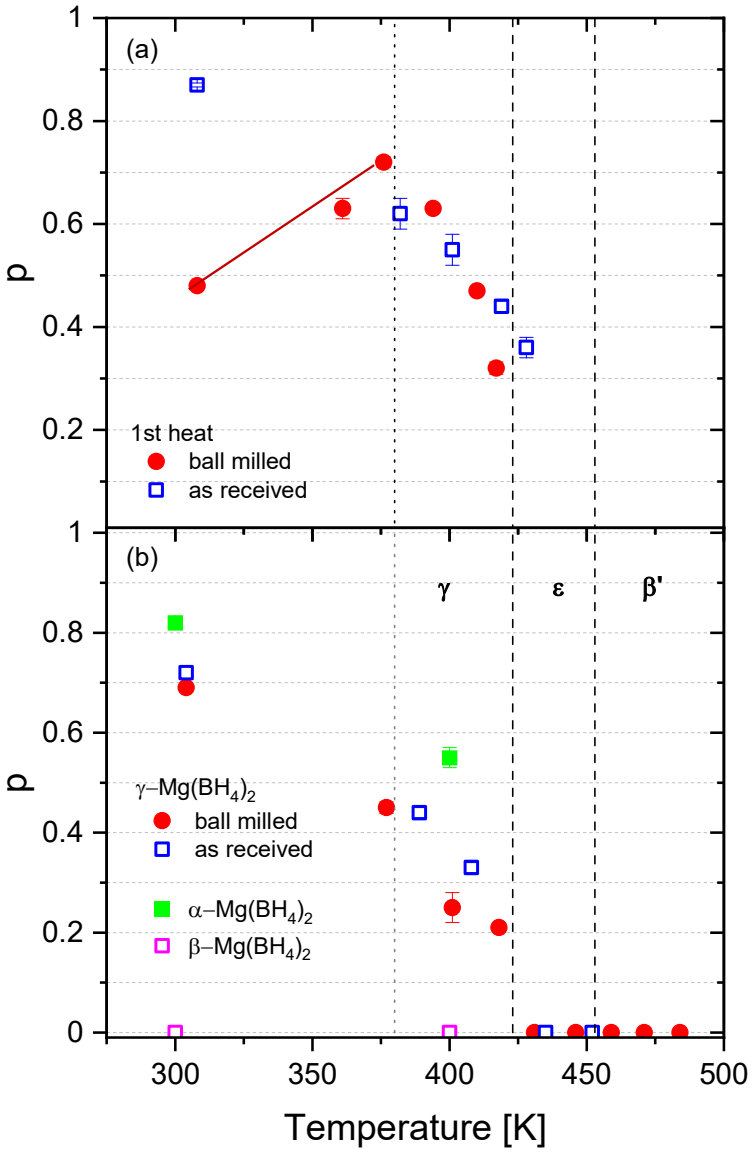
γ- $Mg(BH_4)_2$: as received and ball milled

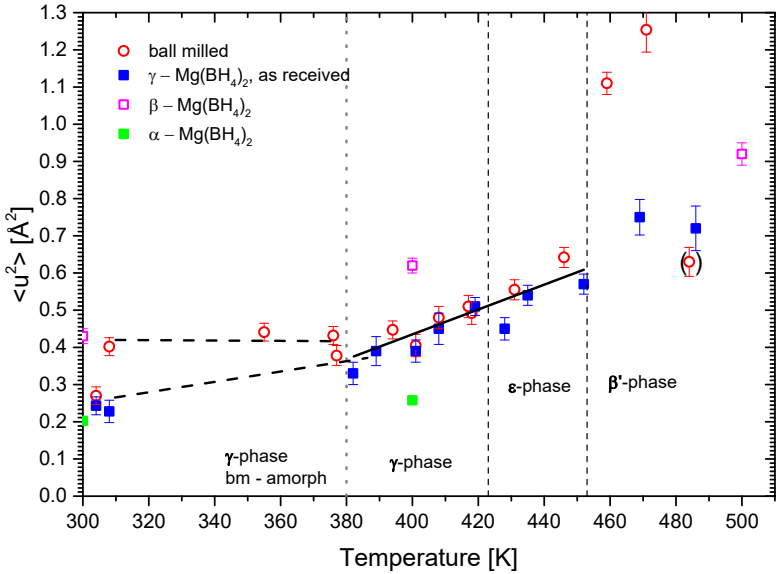




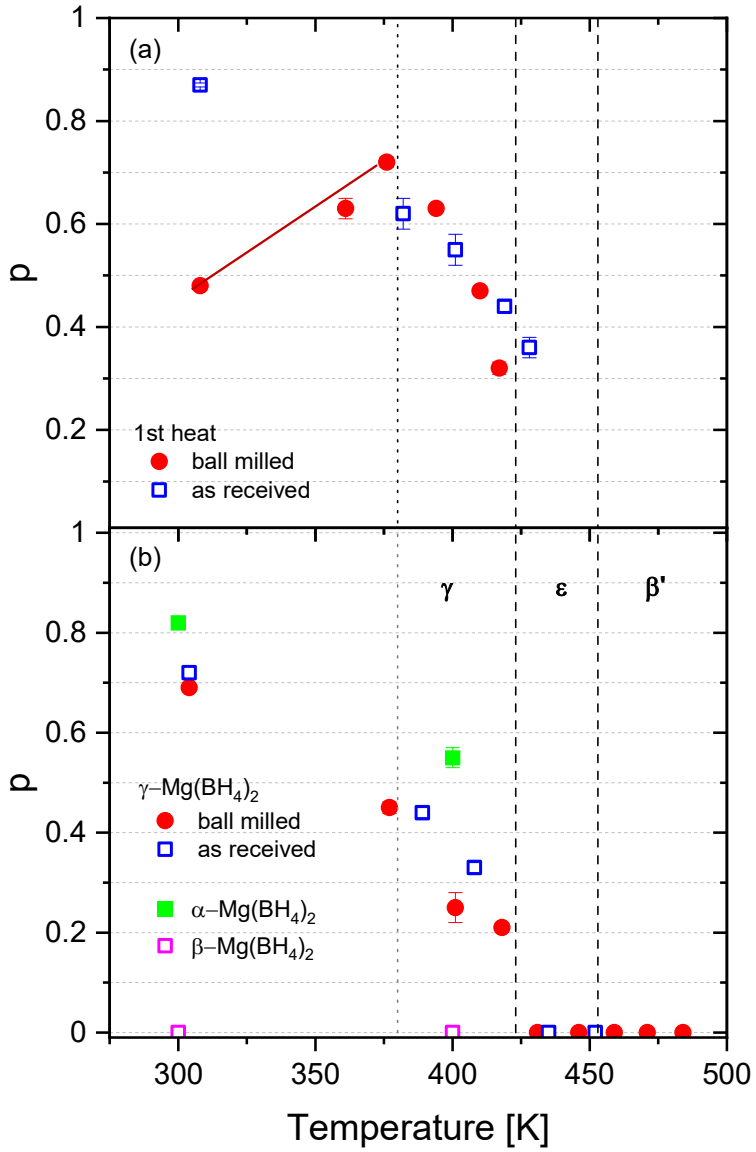
- ***Rotational jump diffusion of BH4 entities***
- $\tau_{1/2}$
- ***Fraction of hindered rotations, p***

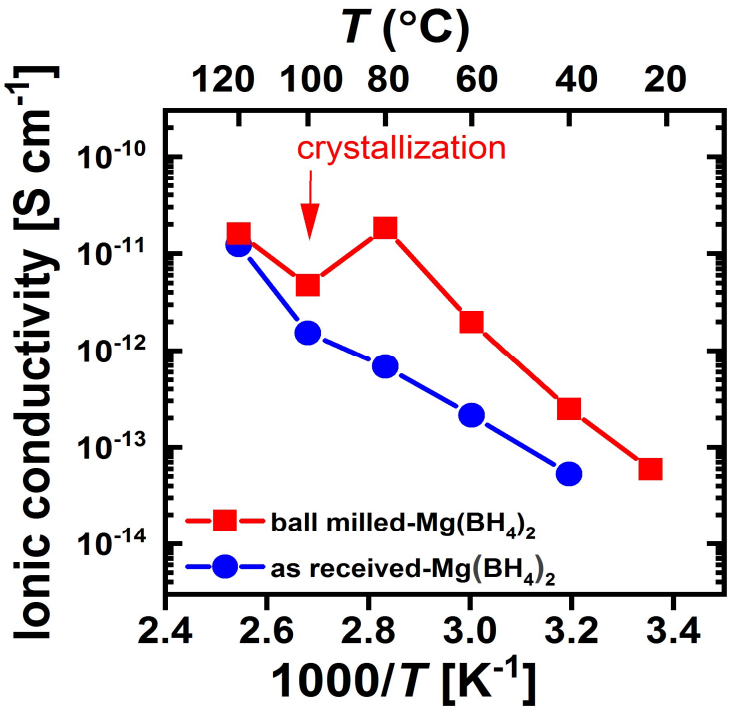
γ- $Mg(BH_4)_2$: as received and ball milled





γ- $Mg(BH_4)_2$: as received and ball milled





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