Hydrogen storage and complex hydrides

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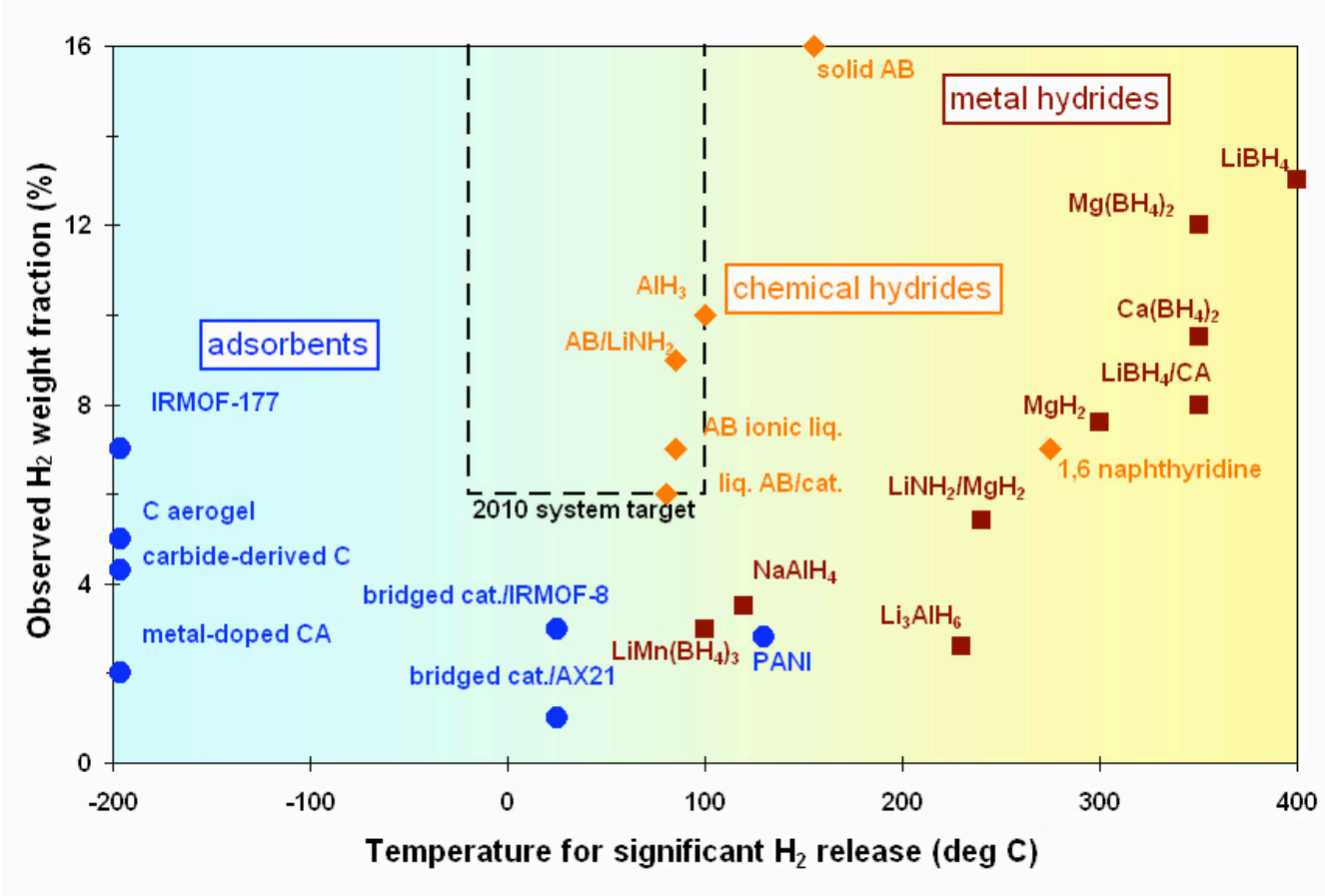
Solid material for hydrogen storage

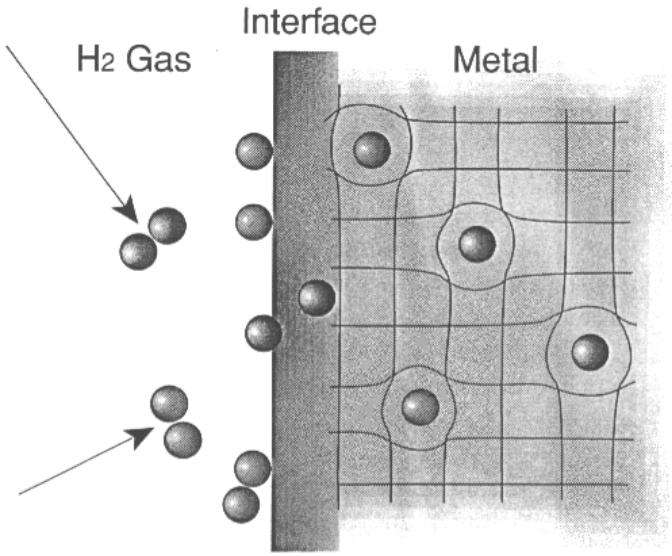


- ***Metal and complex hydrides***
- ***Chemical hydrides***
- ***Nanoporous structures***

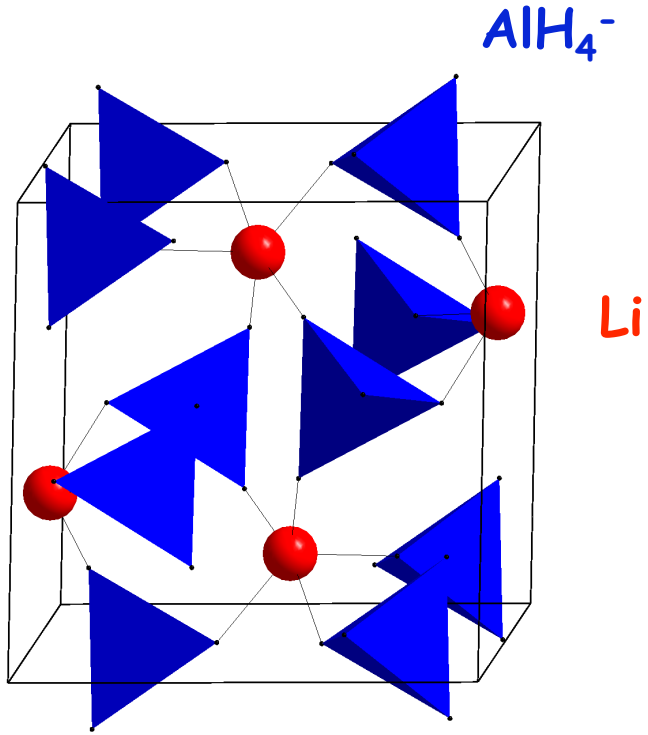
Source: DoE 2007

Storage as hydrides

$$M(s) + x/2\ H_2 \longleftrightarrow MH_x(s) + energy$$

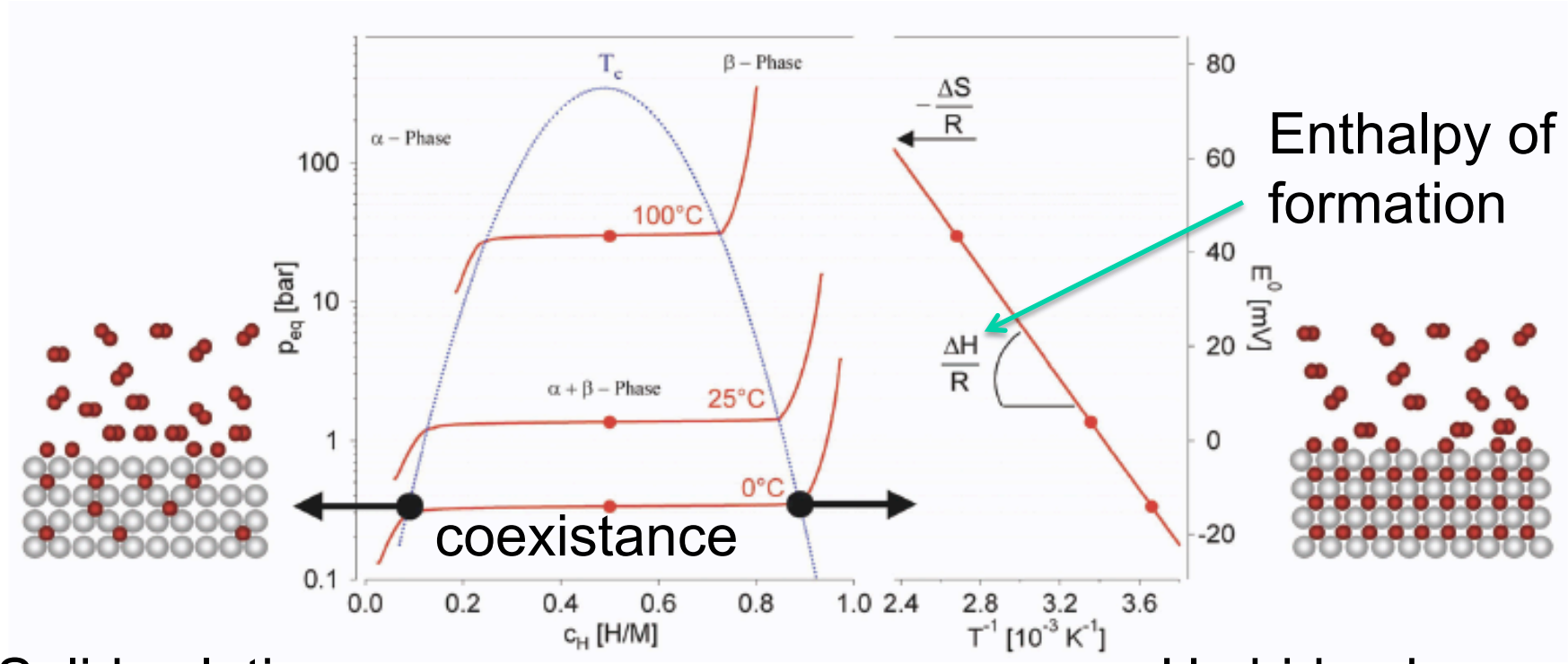


Interstitial metal hydride
(Metal with hydrogen atoms in octahedral-tetrahedral holes)



Complex hydride

PCI of intermetallic (AB_xH_n) compound



Solid solution

Hydride phase (lattice expansion)

$$\ln\left(\frac{p_{eq}}{p_{eq}^{0}}\right) = \frac{\Delta H}{R} \bullet \frac{1}{T} - \frac{\Delta S}{R}$$

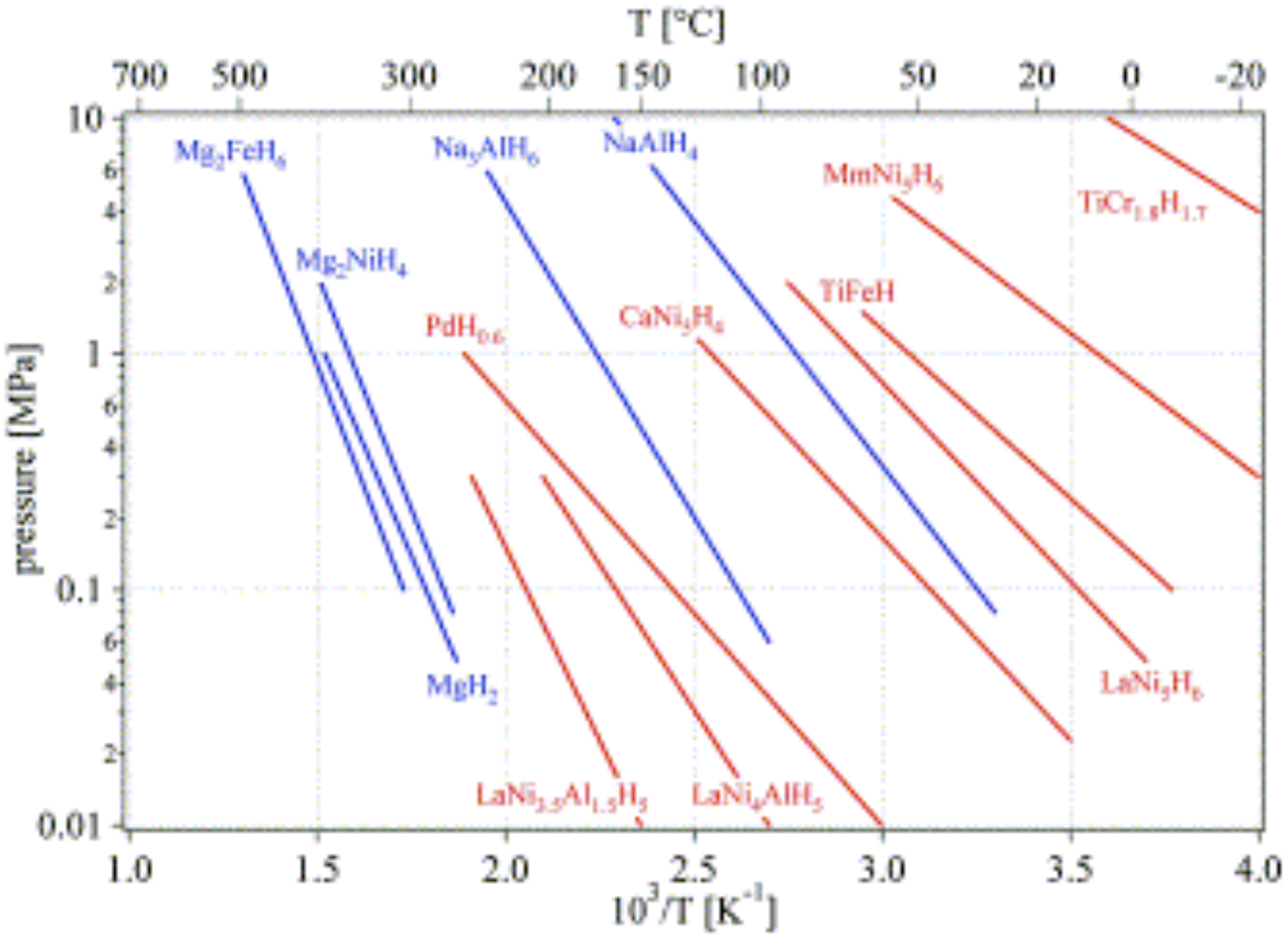
Zuettel (2003)

Exercise

The desired value of enthalpy of formation of our hydride to reach an equilibrium pressure of 1 bar at 27 ^{o}C?

1) Considering ΔS_f = - 130 $JK^{-1}mol^{-1}$ H_2 for all metal-hydrogen systems
2) Answer in kJ mol^{-1} H_2

$$\ln\left(\frac{p_{eq}}{p^{0}_{eq}}\right) = \frac{\Delta H}{R} \bullet \frac{1}{T} - \frac{\Delta S}{R}$$



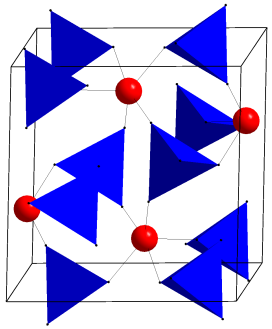
More stable

less stable

Zuettel (2003)

Complex hydrides promising candidates

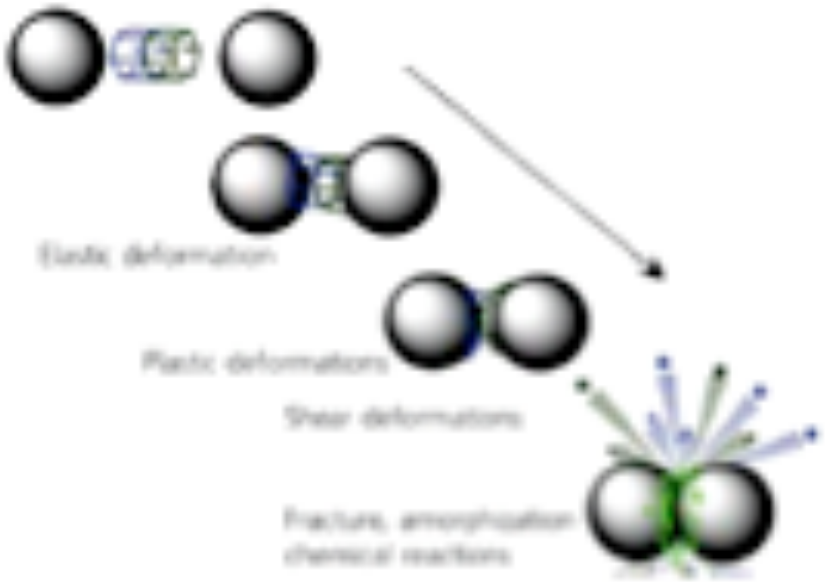
- **> 5 wt% hydrogen:**
  - **$LiAlH_4$: 10.6 wt%**
  - **$NaAlH_4$: 7.5 wt%**
  - **$Mg(AlH_4)_2$: 9.3 wt%**
  - **$LiNH_2/Li_2NH$ reactions (11.5 wt%)**
  - **$LiBH_4$ (18.5 wt%), $NaBH_4$ (10.7 wt%)**
  - **Ammonia-Borane systems: e.g. H_3NBH_3 (19.6 wt%)**



- **Why not used: problems of thermodynamic and kinetics. Not reversible at moderate conditions. Complicated desorption of H_2**

- **Additives (Bogdanović et al., 1997):**
  - **Reversible ($NaAlH_4$ with Ti-additives).**
  - **Reduced desorption temperature.**

High-energy ball-milling…

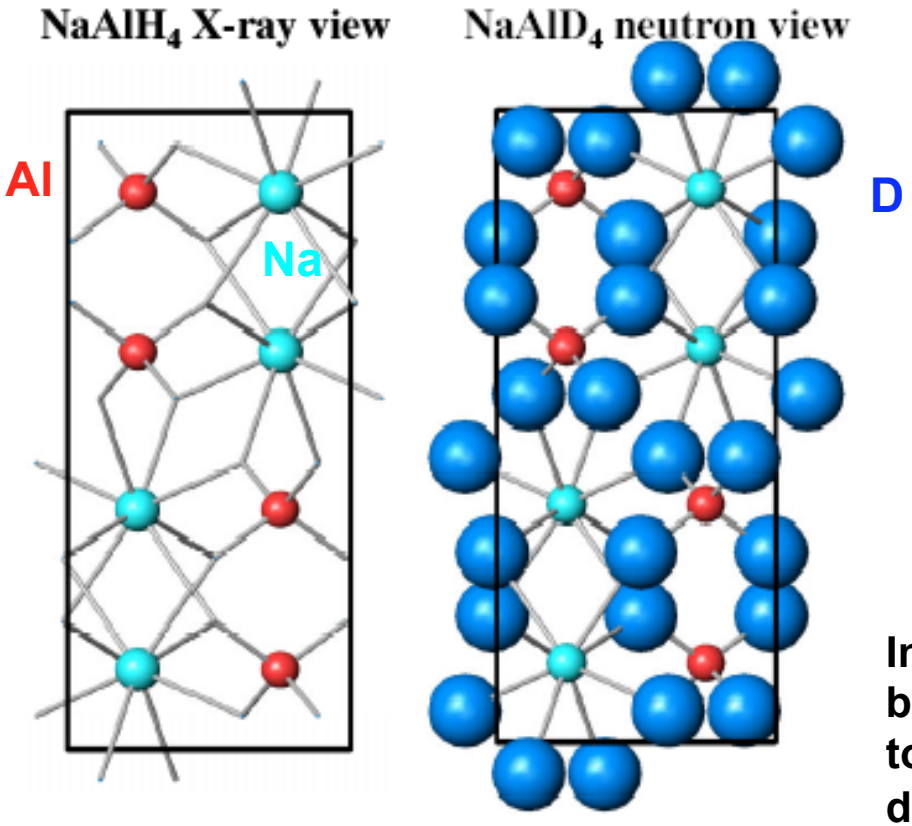


…brings about a broad variety of defects

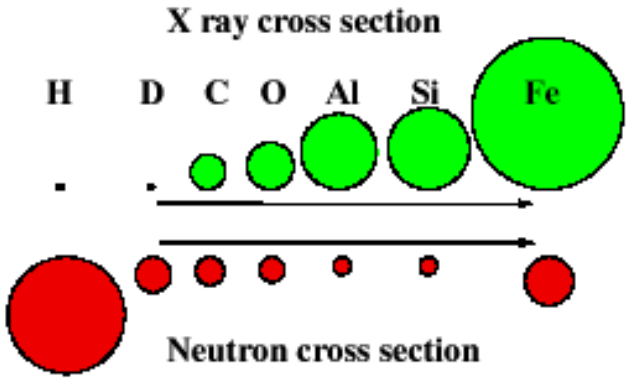
Breaking crystallinity, creating new surfaces, mass transfer = enhanced reactivity of materials towards hydrogen

Using neutrons to ”see” hydrogen

Powder neutron diffraction (PND)

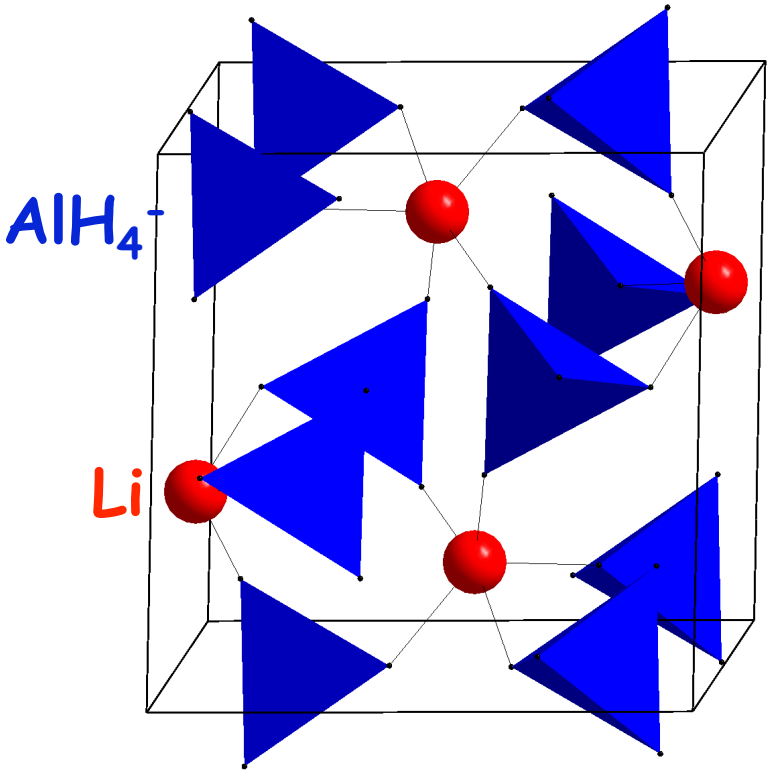


JEEP-II



In contrast to X-ray, neutrons are scattered by the nuclei of the atoms. X-ray data tends to give erroneously short metal-hydrogen distances and incertainties in determination of hydrogen coordinates

Structural characteristics

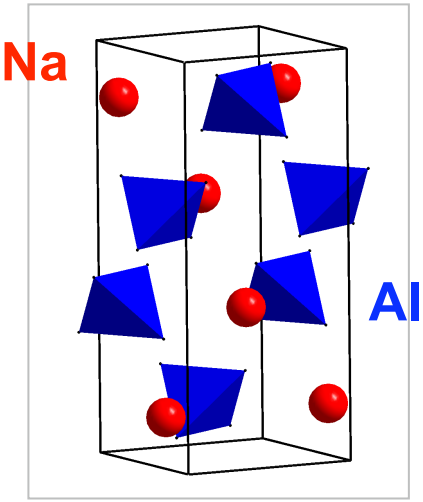


$M^{n+}(AlH_4)^-_n$

- Anions: AlH_4^-, AlH_6^{3-}, BH_4^-, MgH_3^- etc. Covalent bonded.
- Metal ions: Alkaline, alkaline earth or 3*d* elements. Ionic bonded.

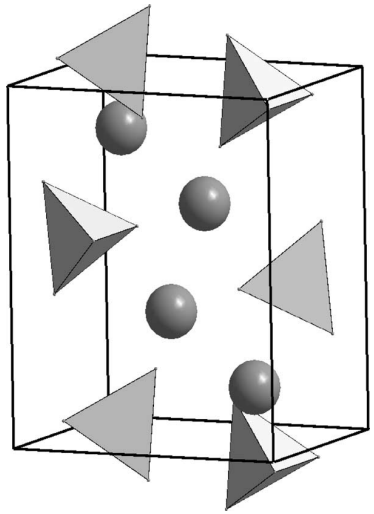
Combined neutron and X-ray diffraction

$NaAlD_4$



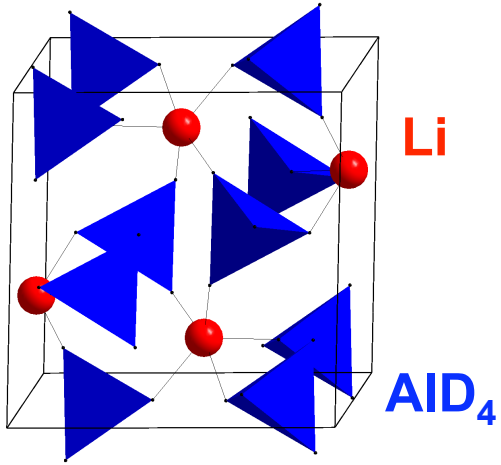
- AlD_4^- tetrahedra
  - Al-D: 1.626 Å (at 295 K).
- Na^+: surrounded by 8 D atoms from 8 different AlD_4^-

$KAlD_4$



- AlD_4^- isolated tetrahedra
  - Al-D: 1.618 Å (at 295 K).
- K^+: surrounded by ten D atoms

$LiAlD_4$



- AlD_4^- tetrahedra connected via Li.
- Li^+ : surrounded by a trigonal bipyramid of 5 D from 5 different AlD_4^-

The variation in the crystal structures of $MAlH_4$ arise from the difference in the size of the alkali cations of Li, Na and K, which result in coordination numbers of 5, 8 and 10, respectively.

Hauback, Brinks, Jensen, Murphy, Maeland (2003) Hauback, Brinks, *et al.* (2005) Hauback, Brinks, Fjellvåg (2002)

Dehydrogenation and rehydrogenation- Undoped alanates

Desorption ALANATES, e.g. $NaAlH_4$ (7.5 wt%):

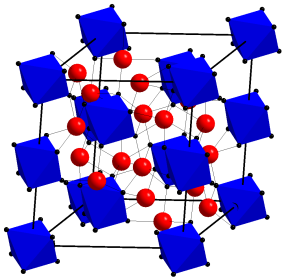
$3\ NaAlH_4 \rightarrow Na_3AlH_6 + 2\ Al + 3\ H_2$	3.7w%	180-230°C
$Na_3AlH_6 \rightarrow 3\ NaH + Al + 3/2\ H_2$	1.9wt%	230-250°C
$NaH \rightarrow Na + ½\ H_2$	1.9wt%	425°C

The reaction temperatures depend strongly on the heating rate

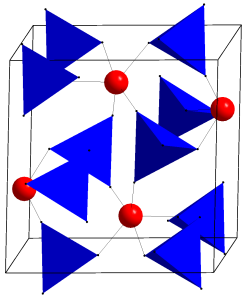
Study of dehydrogenation $LiAlD_4$ - *In-situ* PXD

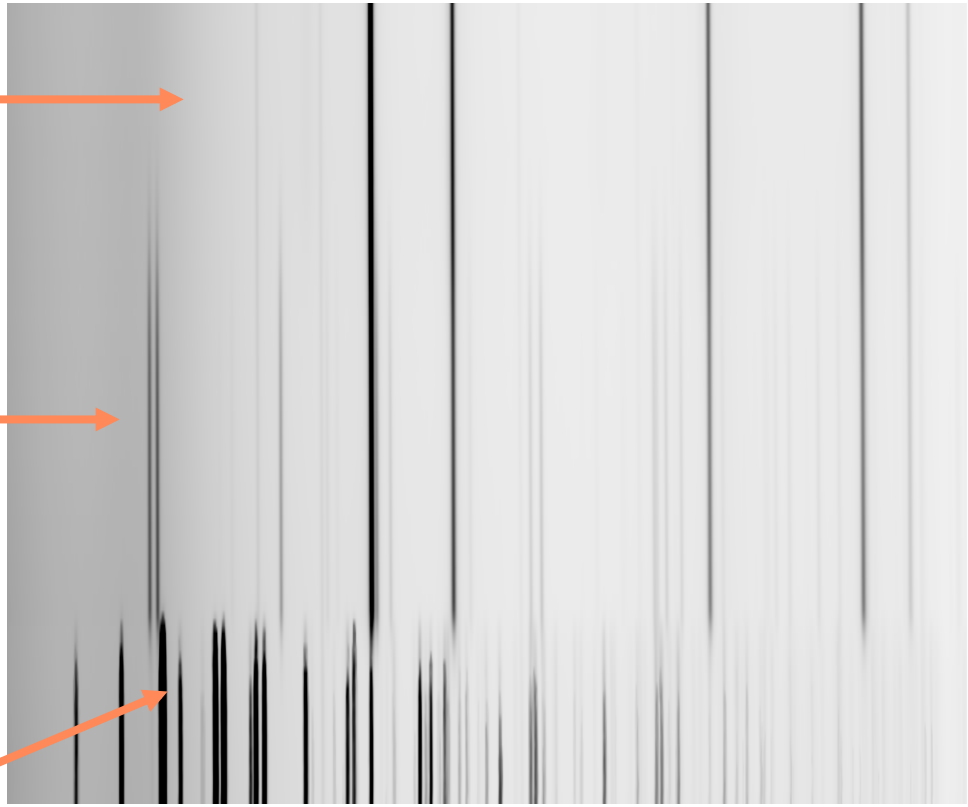
220°C
LiD +Al

160°C
Li_3AlD_6+Al



130°C
$LiAlD_4$



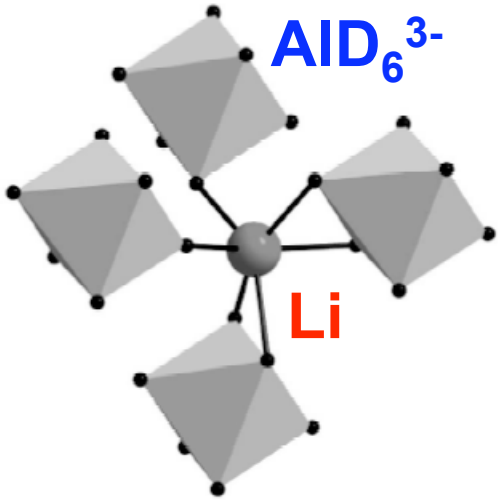


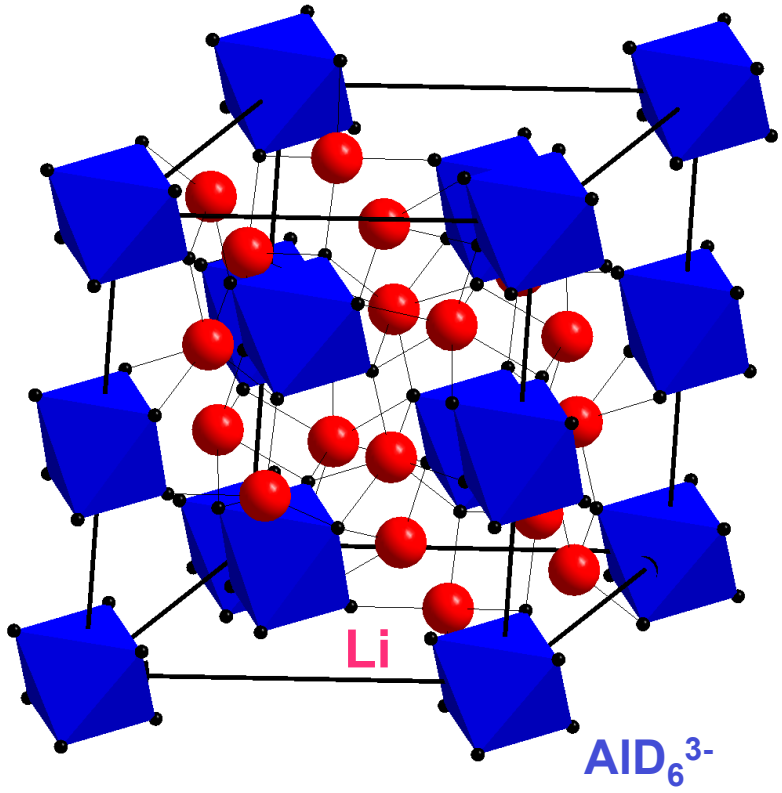
- **$3LiAlH_4 = Li_3AlH_6 + 2Al + 3H_2$ 150ºC (R1) 5.3 wt%**
- **$Li_3AlH_6 = 3LiH + Al + 3/2H_2$ 210ºC (R2) 2.6 wt%**
- **$3LiH + 3Al = 3LiAl + 3/2H_2$ 350ºC (R3) 2.6 wt%**

Brinks, Hauback, Fjellvåg, Norby (2003)

Li_3AlD_6

- Isolated octahedra **AlD_6^{3-}**:
  - Al-D: 1.754 and 1.734 Å.
- **Li**: 6-coordinated:
  - Li-D: 1.892-2.120 Å.





Each Li atom is connected to two corners and two edges of AlD_6^{3-} octahedra with in total six D atoms in the coordination sphere

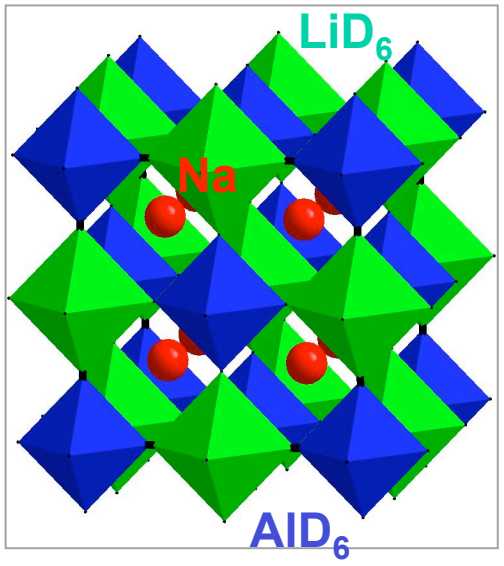
The structure can be described as a distorted bcc structure of AlD_6^{3-} units with all tetrahedral sites filled with Li Brinks, Hauback (2003)

Mixed alanates Na_2LiAlD_6 and K_2NaAlH_6

- Synthesized **from $NaAlD_4$ + $LiAlD_4$**
- Synthesized by ball milling $KH+NaAlH_4$
- Both *Fm-3m*.
- Different size of octahedron AlD_6^{3-} and LiD_6^-
  - **K in tetrahedral sites**
  - **Na in octahedral sites**

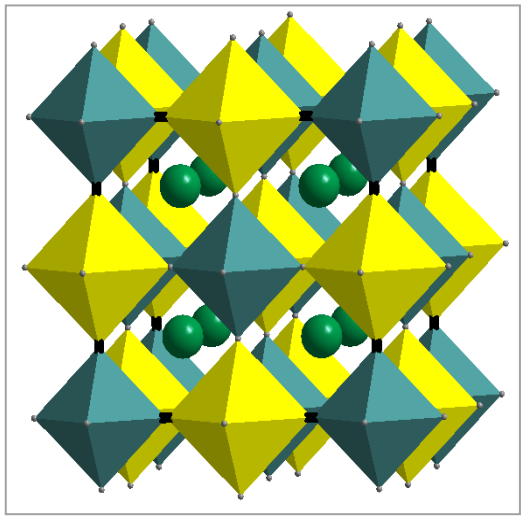
Isostructural to Na_2LiAlD_6

Na_2LiAlD_6



Theoretical 3.5 wt%

K_2NaAlH_6

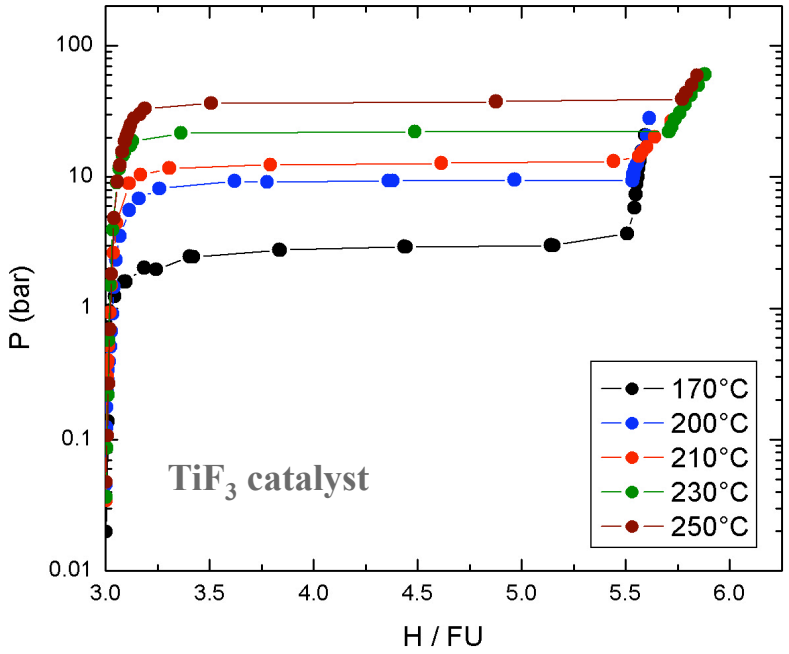


Theoretical 2.2 wt%

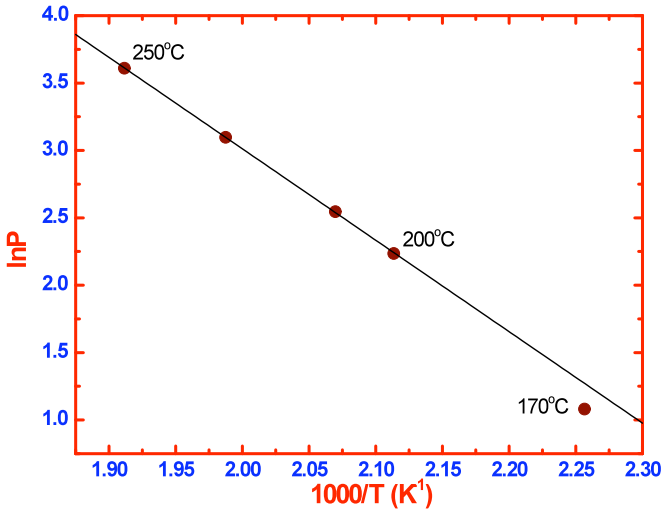
Brinks, Hauback, Jensen, Zidan (2005)
Sørby, Brinks, Fossdal, Thorshaug, Hauback (2006)

TiF_3 in Na_2LiAlH_6: thermal data

PCT data



van't Hoff plot



<u>Adjustment of the stability</u> of complex hydrides by anion substitution (H/F). $Na_3AlH_{6-x}F_x$ less stable than Na_3AlH_6

- Na_2LiAlH_6: (Diss enthalpy) ΔH^0 = 56.4 kJ/mol H_2 (more stable)
- Na_3AlH_6: ΔH^0 = 47 kJ/mol H_2 (Bogdanovic 2000)

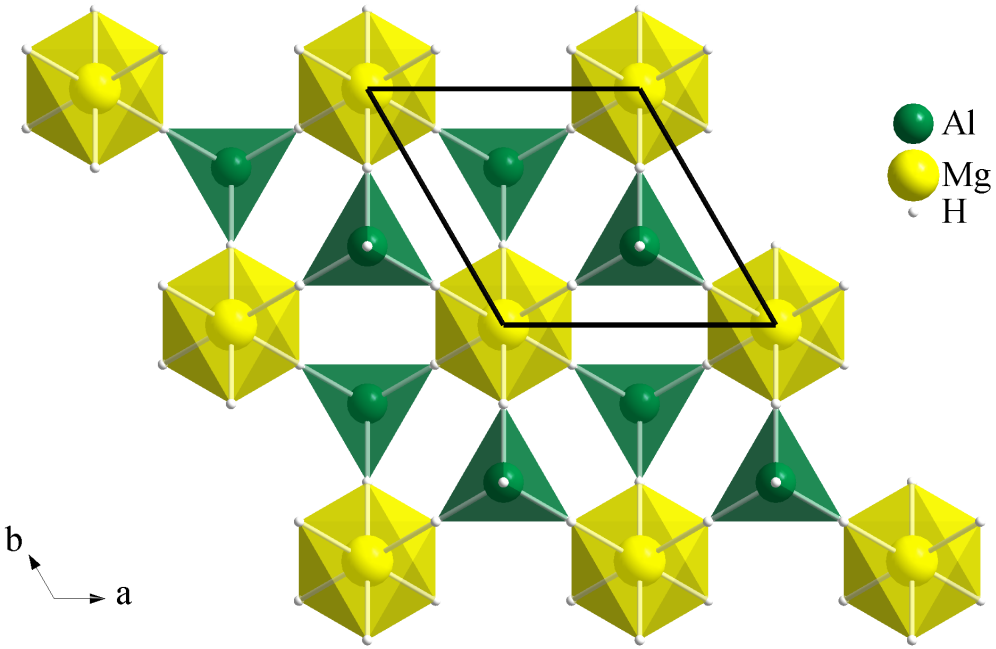
Reversible (2.8 wt%) decomposition, sample rehydrogenated in 1-2 h at 200 °C

$Na_2LiAlH_6 = 2NaH + LiH + Al + 3/2H_2$

Fossdal, Brinks, Hauback (2005)

$Mg(AlH_4)_2$

- Isolated AlH_4^- tetrahedra.
- Mg surrounded by 6 H.
- MgH_6 octahedra share one corner with each of six AlH_4^- tetrahedra.
- Sheet like structure along *c*-axis.
- Al – H: 1.561, 1.671 Å.

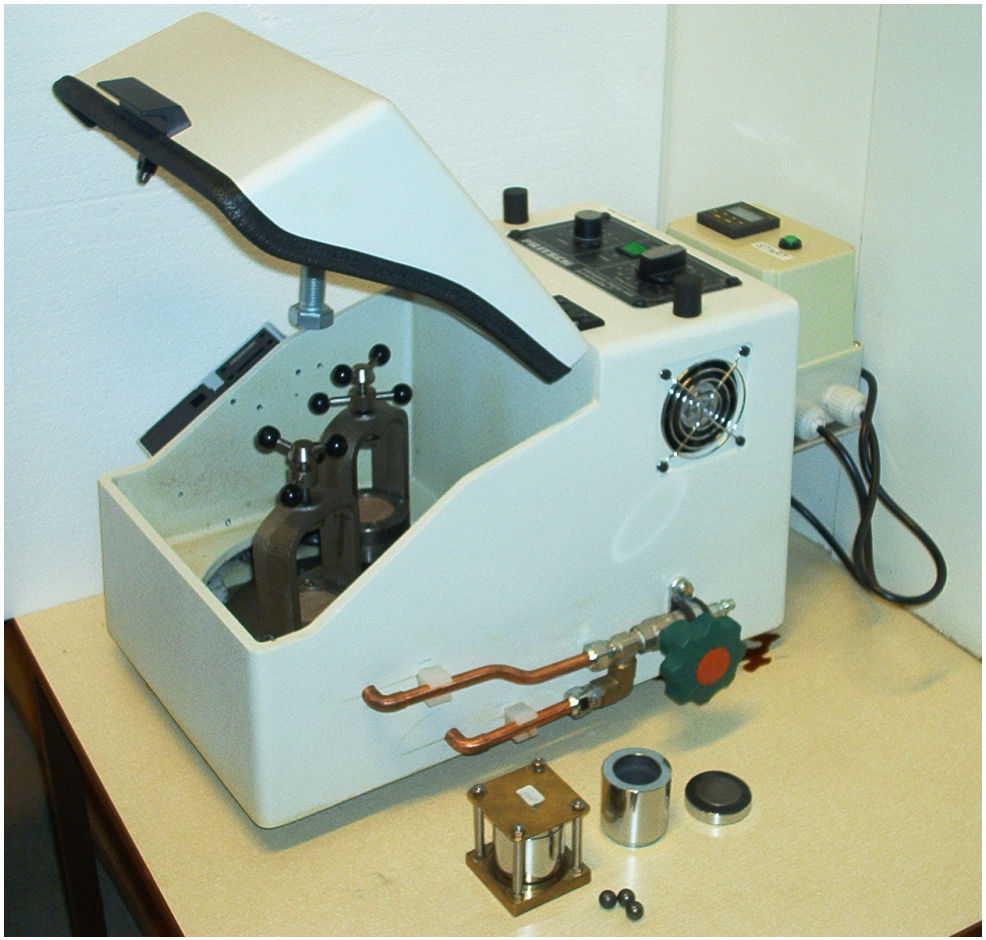


- $Mg(AlH_4)_2$: Solvent-free and fast synthesis
- reversibility not sufficient (kbar pressures for rehydrogenation at RT)

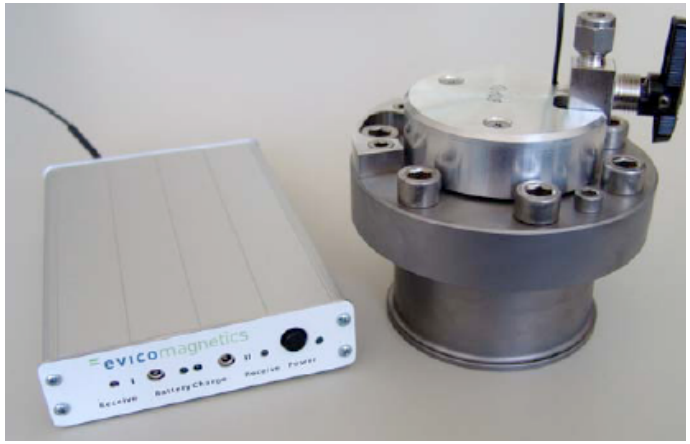
Sheets interconnected by van der Waals forces

Fichtner et al. (2003)
Fossdal, Brinks, Fichtner, Hauback (2005)

Additives in alanates



P7 ball milling apparatus



ball milling (Fritsch P6) in Ar, high-pressure vial with pressure/temperature monitoring system (evico magnetics)

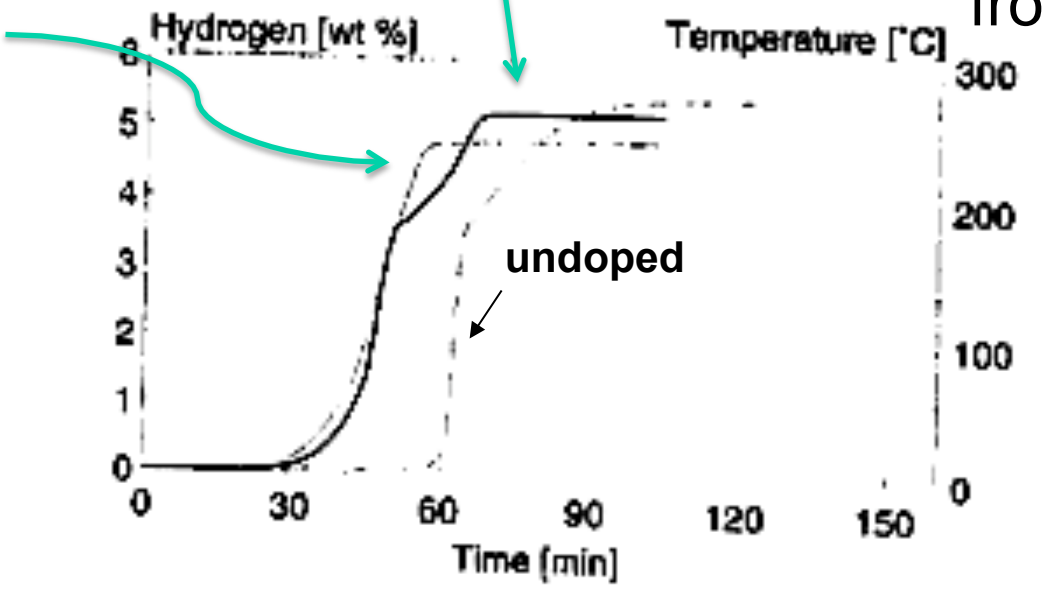
Effect of additives – $NaAlH_4$ +Ti-compounds

The undoped $NaAlH_4$ sample at 160 °C delivers H_2 at an almost negligible rate and, even at 200 °C, the H_2 evolution takes 22-24 h until completion. In contrast samples doped with $Ti(OBu)_4$ is completed at 160 °C within 6-8 h and at 180 and 200 °C within 2-3 and 1 h respectively

2 mol% $Ti(OBu)_4$

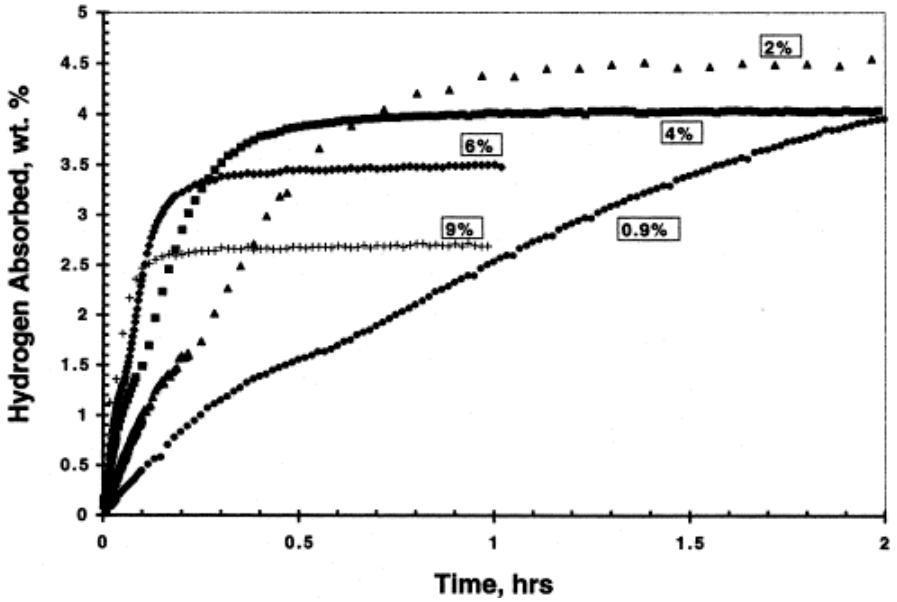
2 mol% $TiCl_3$

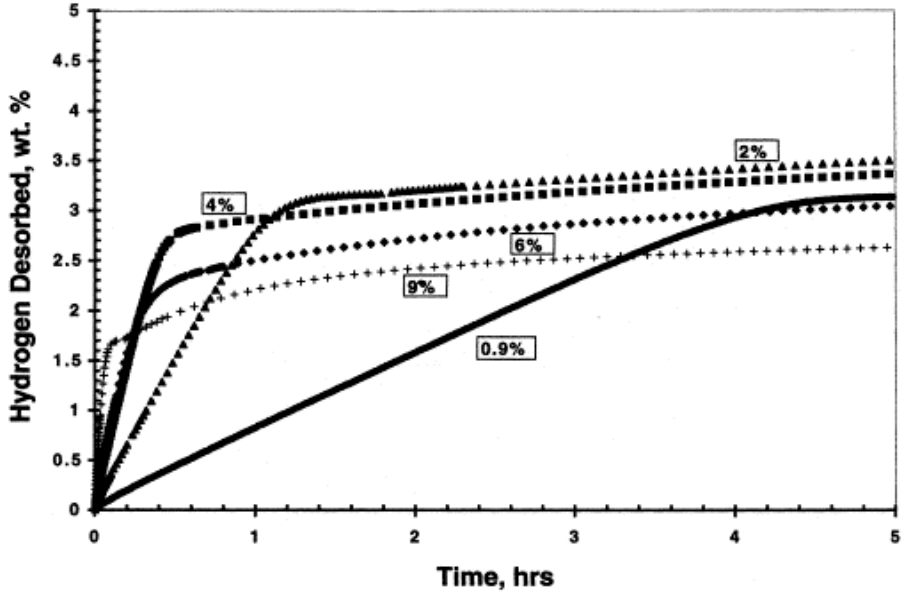
Dehydrogenation from RT to 270 °C



Bogdanovic et al. (1997)

Effect of mol % $TiCl_3$ in $NaAlH_4$ (ball milled)





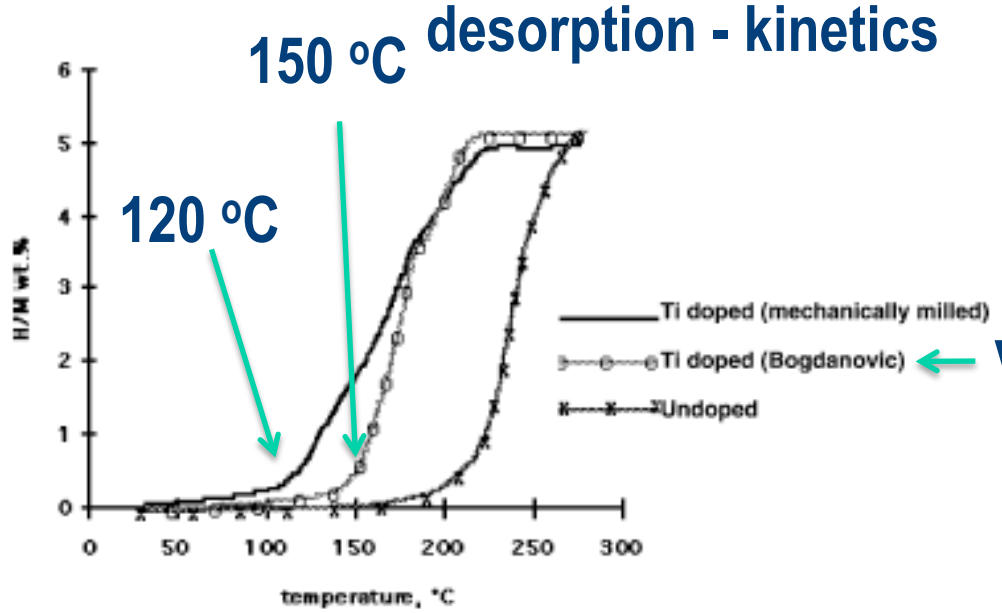
H_2 absorption (from NaH + Al)
T=125°C, P=8 MPa = 80 bar

H_2 desorption (from $NaAlH_4$)
T=125°C

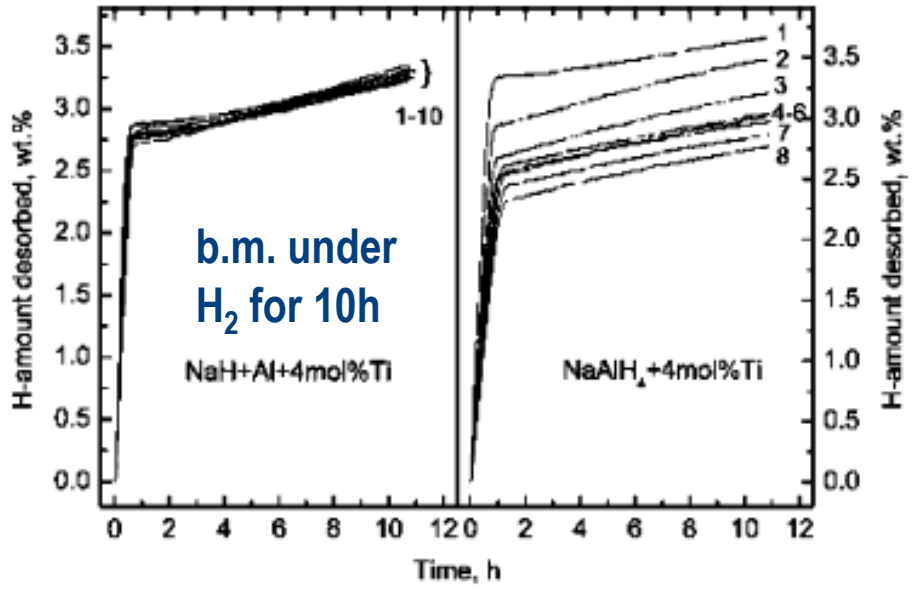
Multiple order-of-magnitude increases in kinetics. Decrease desorption temperatures

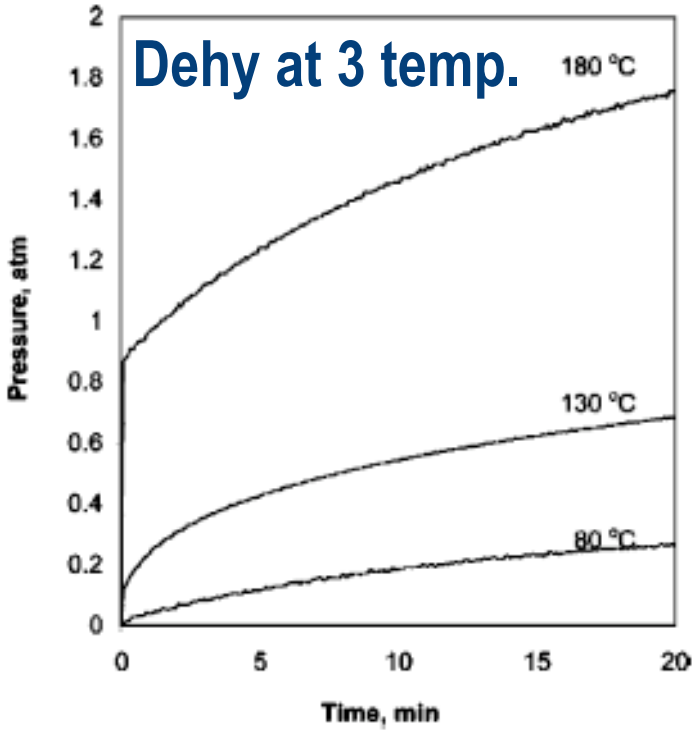
Bogdanovic et al. (1997); Sandrock et al. (2002); Srinivasan, Brinks, Hauback, Jensen (2004)

Doped $NaAlH_4$



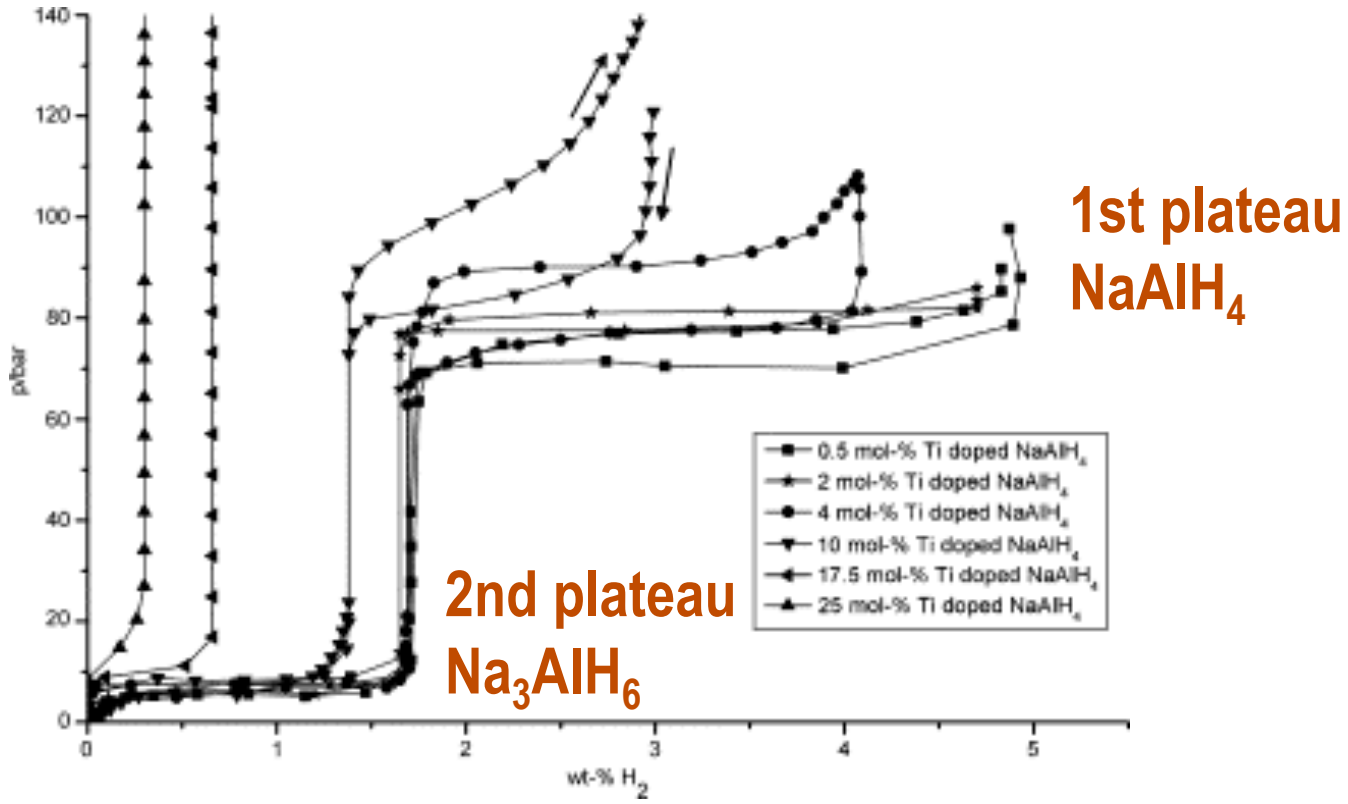
Via wet chem.





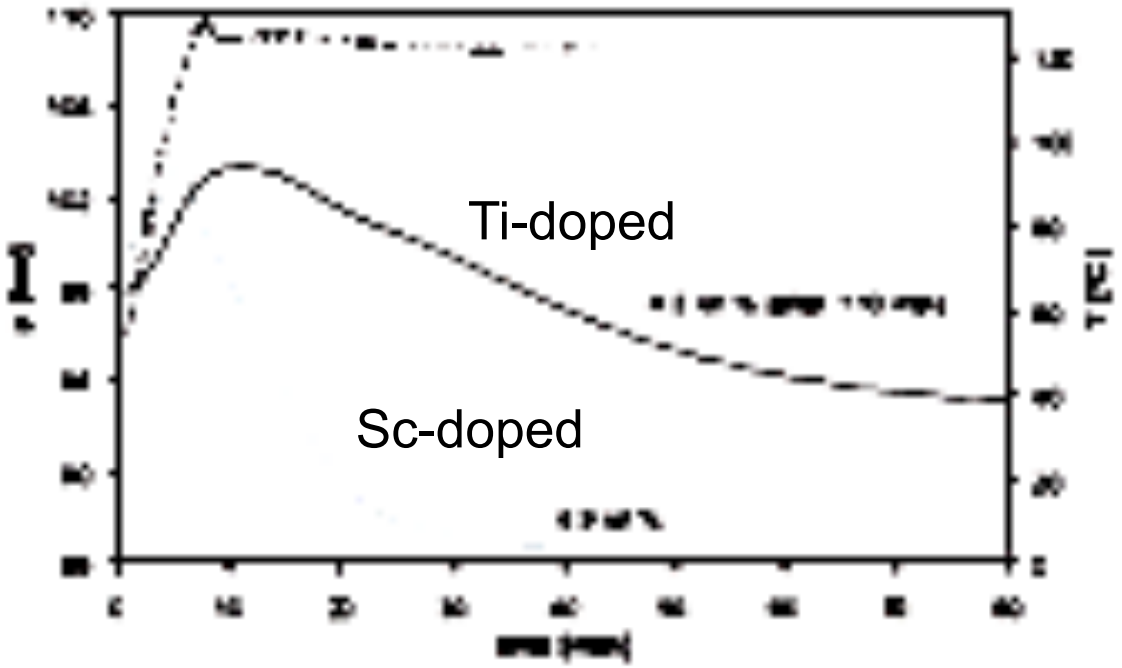
$NaAlH_4$+2mol%$Ti(OBu)_4$

PCI at 160 ºC for 6 different mol% doping level of Ti



Bogdanovic *et al.*, (2007)

Others additives $NaAlH_4$



Bogdanovic at al. (2006)

In comparison to $TiCl_3$-doped $NaAlH_4$, $ScCl_3$ and $CeCl_3$ dopants reduce hydrogenation times by a factor of 2 at high pressure and by a factor of 10 at low pressure.

As $TiCl_3$ is the best Ti-precursor compound (together with Ti-nanoparticles), trichlorides of the first-row transition metals are investigated as alternative dopants. $ScCl_3$ results highly efficient, both with respect to storage capacity and kinetics.

Borohydrides

Hydrogenated form	Dehydrogenated form	Hydrogen capacity wt. %	g H_2/L	$-\Delta H$, kJ/mol H_2	Decomp. temp., °C calc.	obs.
$LiBH_4$	LiH + B	13.9	93	75	402	470
2 $LiBH_4$ + MgH_2	3 LiH + MgB_2	11.4		46	225	315
2 $LiBH_4$ + Al	2 LiH + AlB_2	8.6			188	
7 $LiBH_4$ + 1.75 Mg_2Sn + 0.25 Sn	Li_7Sn_2 + 3.5 MgB_2	6.3		46	184	
$NaBH_4$	NaH + B	7.9	85.5	90	609	595
2 $NaBH_4$ + MgH_2	3 NaH + MgB_2	7.8		62	351	
$Be(BH_4)_2$	Be + 2B	20.8	126	27		123
$Mg(BH_4)_2$	Mg + 2B	14.9	113	40		323
$Ca(BH_4)_2$	2/3 CaH_2+1/3CaB_6	9.7	108	75.5		360
$Ca(BH_4)_2$ + MgH_2	CaH_2+ MgB_2	8.3			159	
$Zn(BH_4)_2$	Zn + 2B*	8.5				85
$Al(BH_4)_3$	Al + 3B*	16.9	121	6		150
$Sc(BH_4)_3$	ScB_2 +B (?)	13.5				260
$Ti(BH_4)_3$	TiB_2 +B*	13.1				25
$Mn(BH_4)_2$	Mn + 2B	9.5				
$Zr(BH_4)_4$	ZrB_2 + 2B (?)	10.7	108			250

*Formation of diborane observed.

Synthesis tetrahydroborate

Direct reaction in etheral solvents:

$$2MH + B_2H_6 \longrightarrow MBH_4$$

Direct synthesis from the metal, boron and hydrogen:

(550-700 ^{0}C, 30-150 bar)

$$M + B + 2H_2 \longrightarrow MBH_4$$

Metathesis reaction:

$$MgCl_2 + 2MBH_4 \longrightarrow Mg(BH_4)_2 + 2MCl$$

$LiBH_4$

- Dehyd. $LiBH_4 = LiH + B + 3/2\ H_2$ (13.9 wt%)
  - P_{eq} = 1 bar @ 410°C
  - Reversibility at 600 °C and 350 bar
  - Slow kinetics < 600°C (can be improved by additives or by #)
- $NaBH_4$ and KBH_4 more stable (670/830°C)

$LiBH_4$ "destabilized" by stabilizing the products

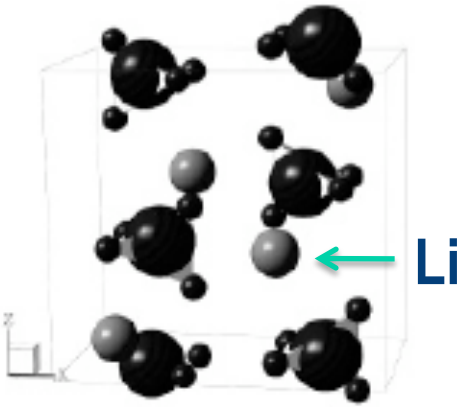
- $LiBH_4 + ½\ Mg = LiH + ½\ MgB_2 + 3/2\ H_2$ (des. Temp. reduced by 30 K)
- $LiBH_4 + ½\ MgH_2 = LiH + ½\ MgB_2 + 5/2\ H_2$ (rehyd. at T< 300 °C, 50 bar)
- Cycled at 330°C
- $TiCl_3$,VCl_3 used as catalyst

J.J. Vajo, S.L. Skeith J. Phys. Chem. B 2005

Low- and high-temperature structures of $LiBH_4$

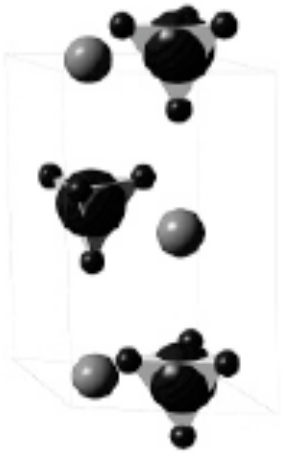
$LiBH_4$ AT 293K (20°C)

Orthorhombic symmetry
space group: **Pnma (#62)**
a = 7.17858(4) Å
b = 4.43686(2) Å
c = 6.80321(4) Å
Vol: 216.685 Å^3, Z = 4



$LiBH_4$ AT 408K (135°C)

Hexagonal symmetry
space group: **$P6_3mc$ (#186)**
a = 4.27631(5) Å
b = a
c = 6.94844(8) Å
Vol: 110.041 Å^3, Z = 2



Dehydrogenation reactions

Alkali metal borohydrides:

$M(BH_4) \longrightarrow MH + B + 3/2H_2$

$A(BH_4) \longrightarrow AB + 2H_2$

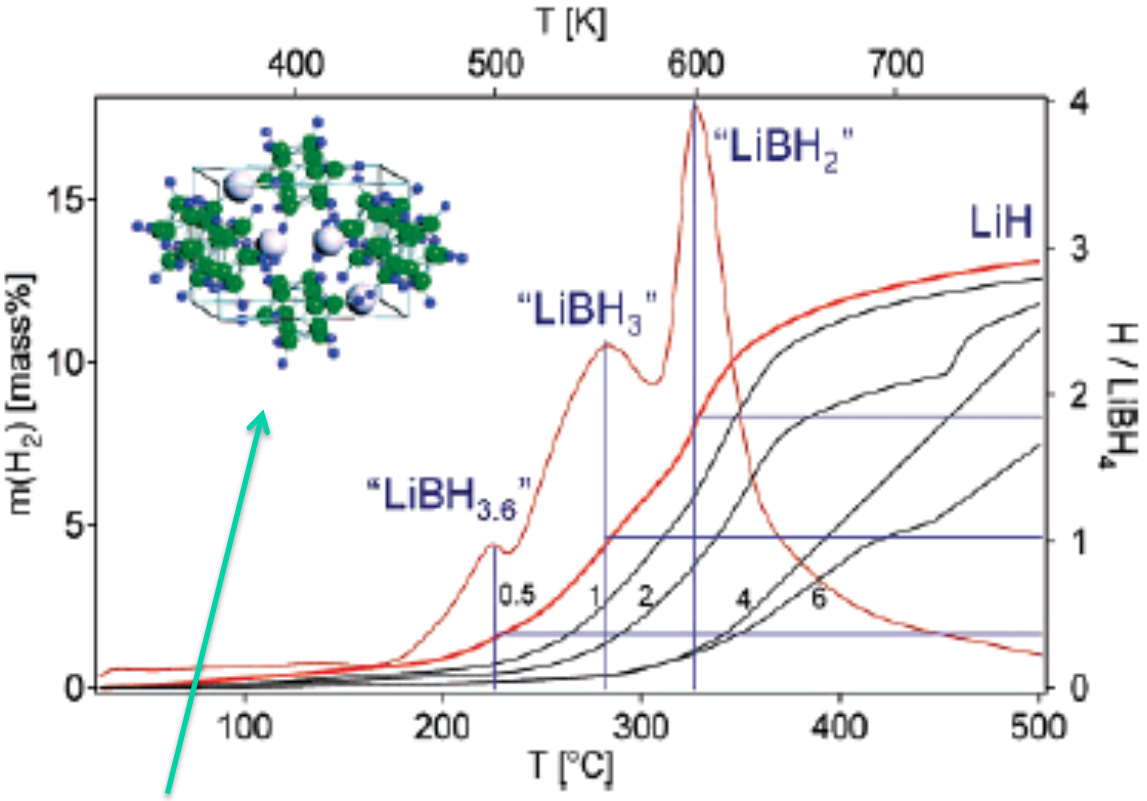
Alkaline earth borohydrides:

$M(BH_4)_2 \longrightarrow MH_2 + 2B + 3H_2$

$M(BH_4)_2 \longrightarrow MB_2 + 4H_2$

$M(BH_4)_2 \longrightarrow 2/3MH_2 + 1/3MB_6 + 10/3H_2$

Thermal desorption from $LiBH_4$



Various heating rates (0.5-6 °C min^{-1})

several intermediate steps
-110 °C polymorphic transformation
- 280 °C melting
- 490 °C hydrogen $LiBH_2$ (50%)
- at 680 °C des of 3 of the 4 H

$Li_2B_{12}H_{12}$ cluster confirmed by Raman and XRD

Borohydrides

Pro: High gravimetric storage density (wt.% H_2)

Cons:

- Alkali (e.g. $LiBH_4$): ⟶ thermodynamically too stable
- alkaline earth: ⟶ kinetically too slow
- transition metal: ⟶ unstable and/or irreversible

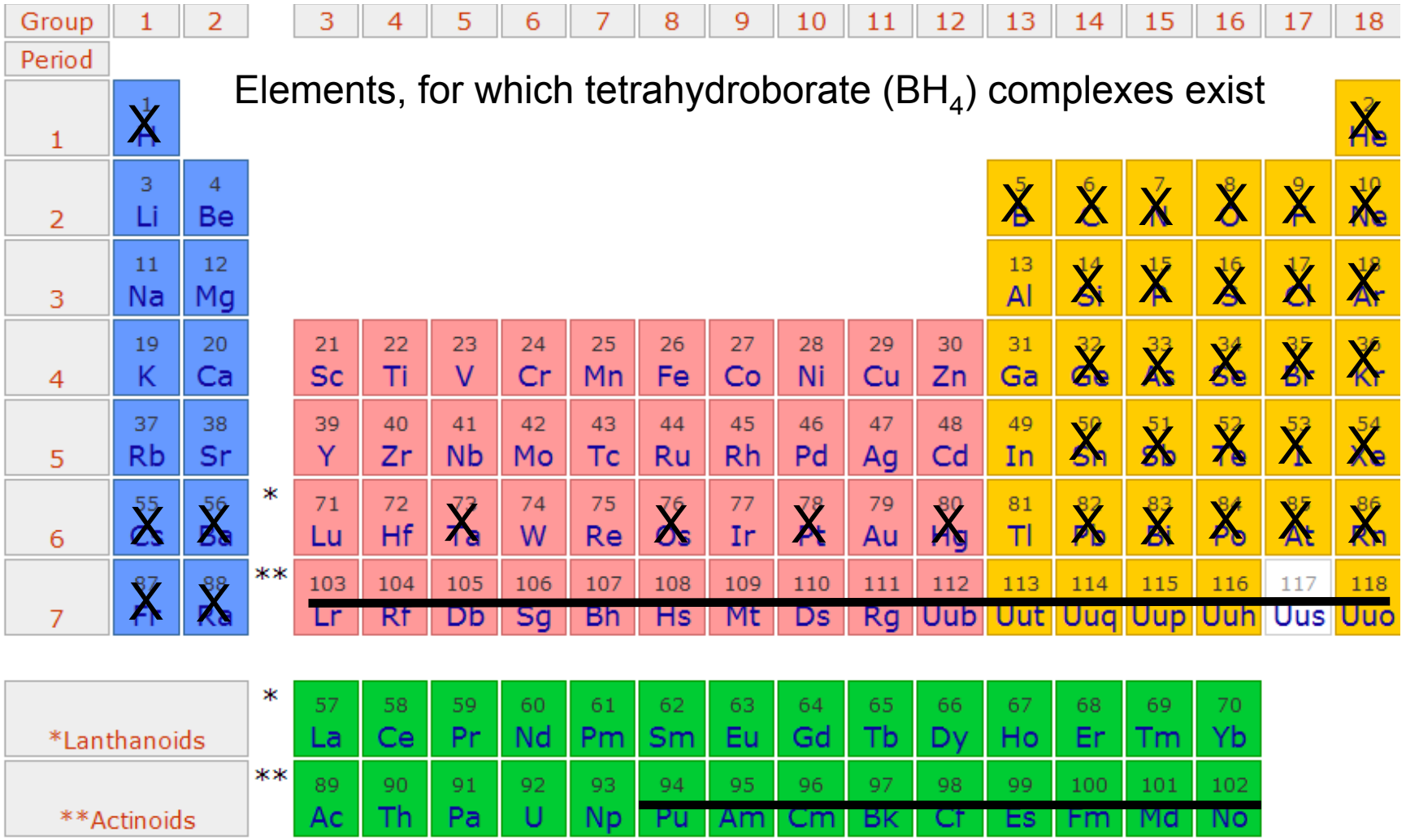
} CHALLENGE

Diborane B_2H_6 release

??? SOLUTION ???

Make new borohydrides or modify existing ones

Elements, for which tetrahydroborate (BH_4) complexes exist



Exercise @ find relation heat of formation borohydrides versus Pauling electronegativities of cations

Predicted heat of formation borohydrides ΔH_{boro}

$LiBH_4$ = - 161 kJ mol^{-1} BH_4

$CuBH_4$ = 76

$NaBH_4$ = - 155

KBH_4 = - 198

$Zr(BH_4)_4$ = - 54

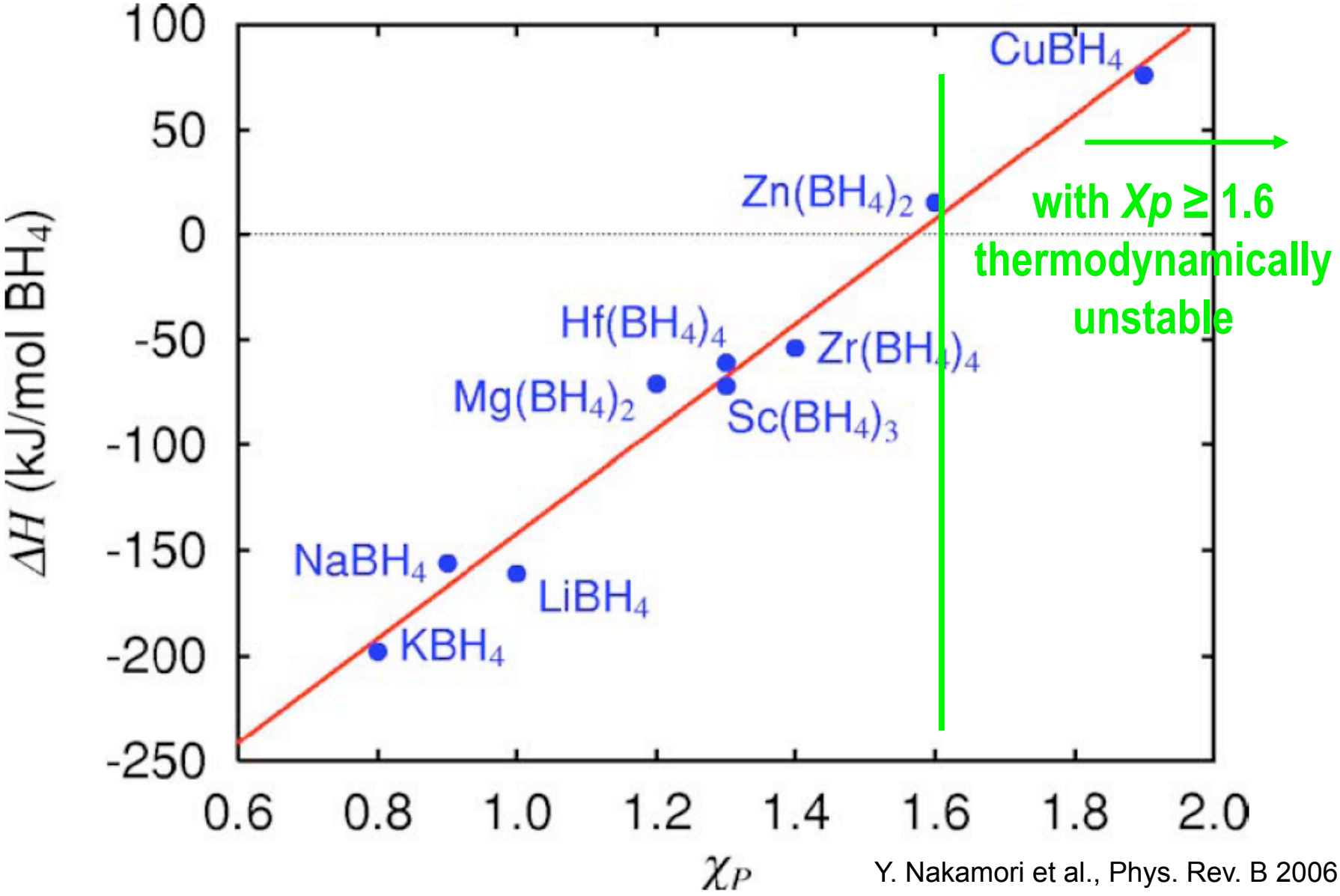
$Hf(BH_4)_4$ = - 61

$$\frac{1}{n}M + \mathrm{B} + 2\mathrm{H}_2 \rightarrow \frac{1}{n}M(\mathrm{BH}_4),$$

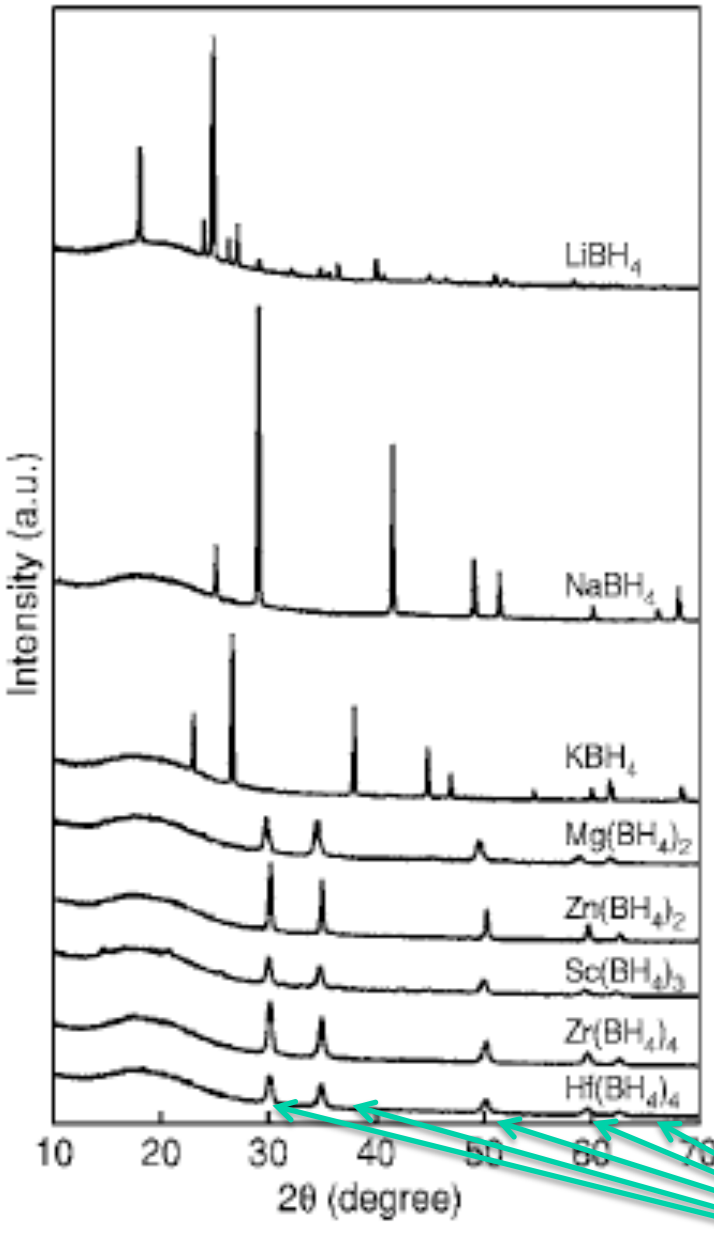
$Mg(BH_4)_2$ = - 71

$Zn(BH_4)_2$ = 15

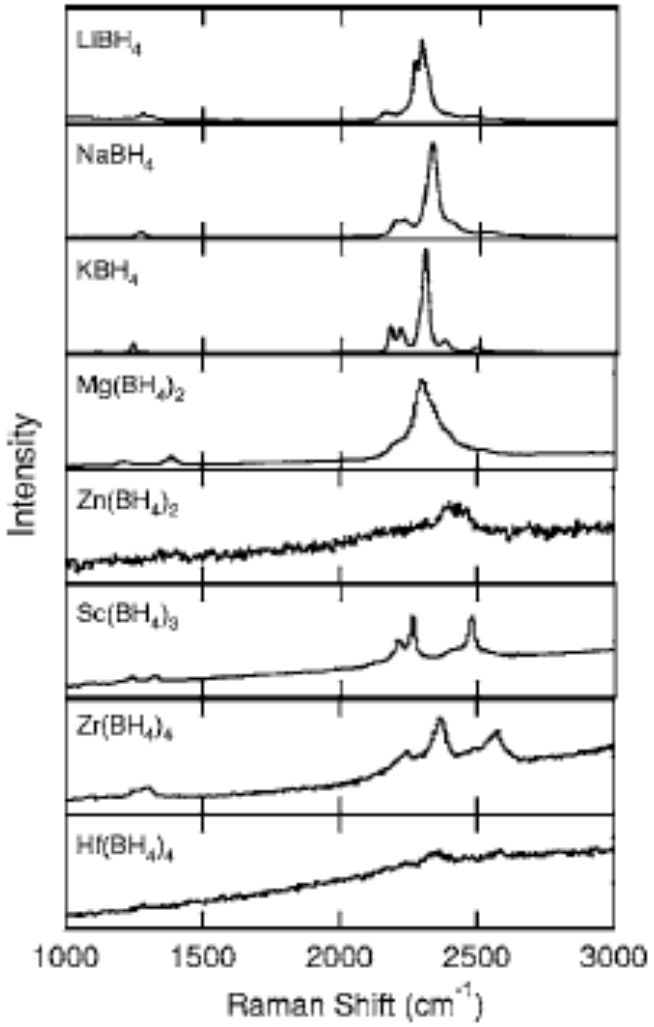
$Sc(BH_4)_3$ = - 72



Y. Nakamori et al., Phys. Rev. B 2006



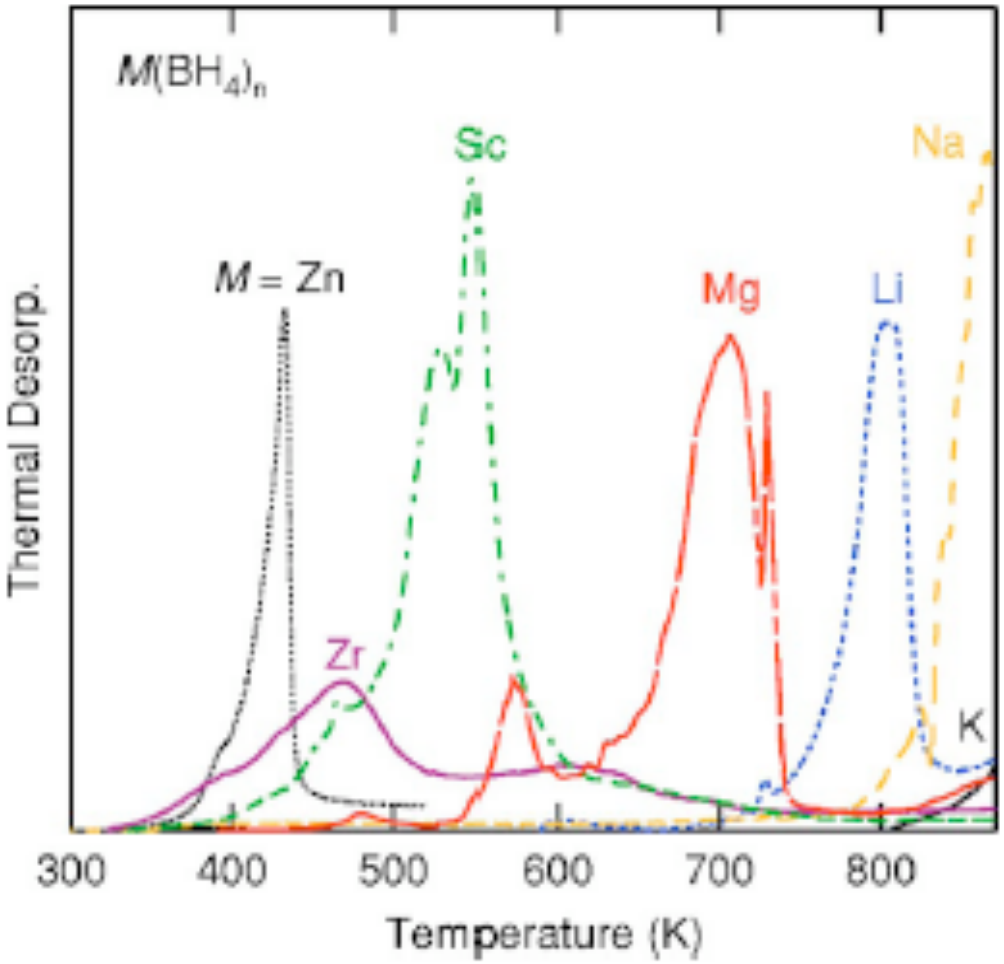
$$n\ LiBH_4 + MCl_n \rightarrow M(BH_4)_n + n\ LiCl$$



LiCl

Y. Nakamori et al., Phys. Rev. B 2006

Exercise @ find relation desorption temperature vs Pauling electronegativity



Thermal desorption of M(BH4)n

ΔH_{des} indicator for serching the material with appropriate stability for hydrogen storage material

$$M(BH_4)_n \rightarrow MH_m + nB + \left(\frac{4n-m}{2}\right)H_2$$

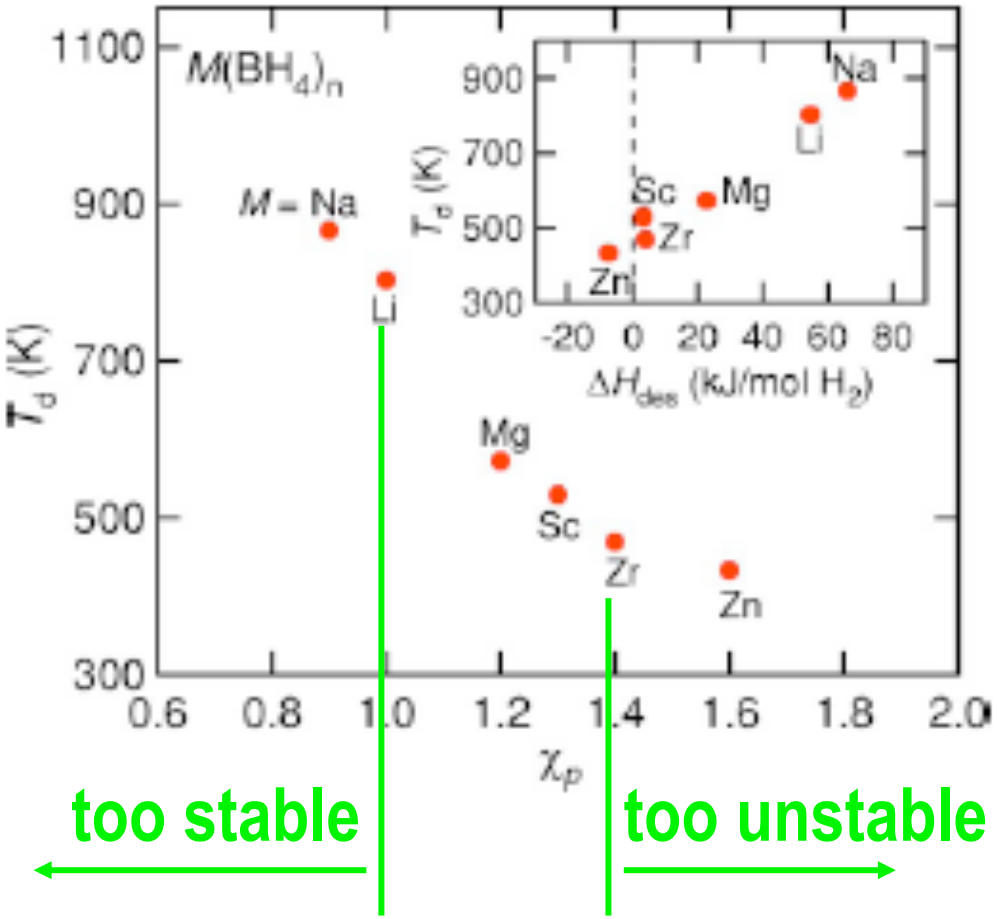
we can find relation between ΔH_{des} and T_d

Y. Nakamori et al., Phys. Rev. B 2006

Stability vs. electronegativity

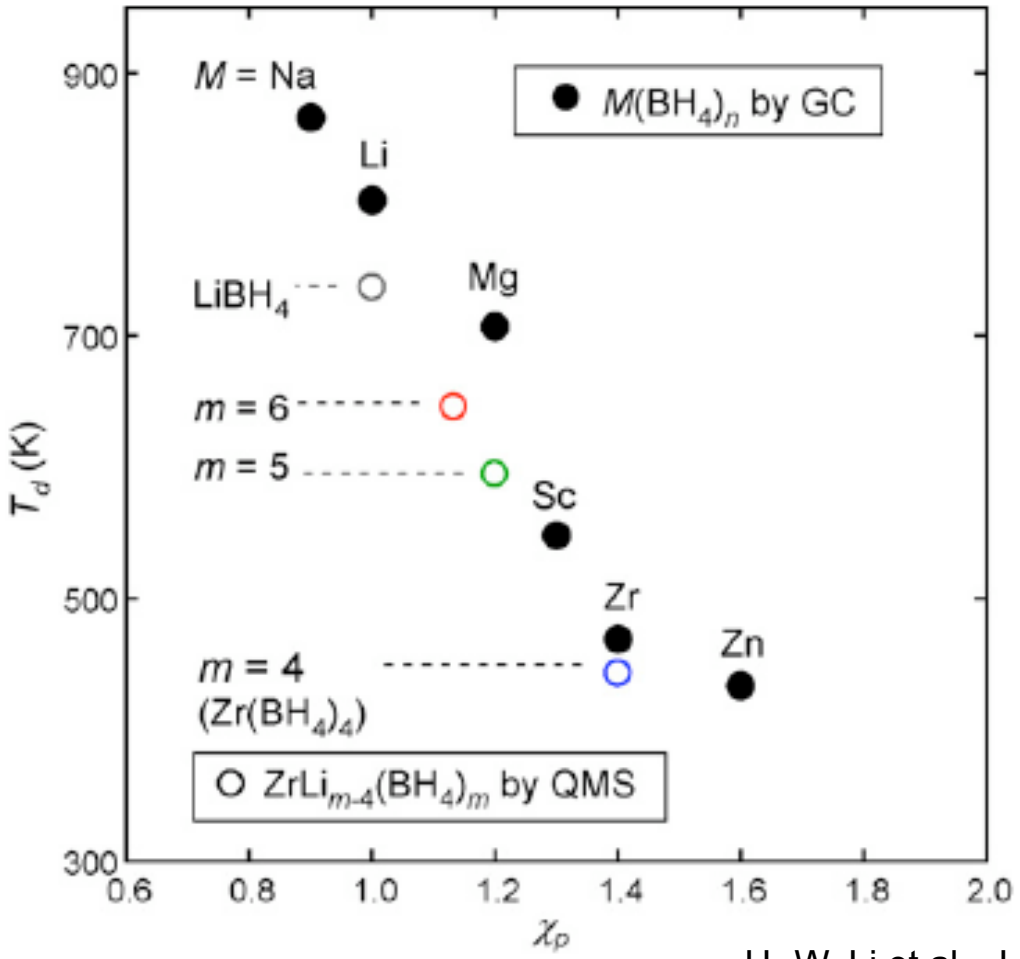
Charge compensation by M^{n+} is a key feature for the stability of $M(BH_4)_n$

and hydrogen **desorption temperature decreases with increasing of Pauling electronegativity χ_P of M**



Any solution?

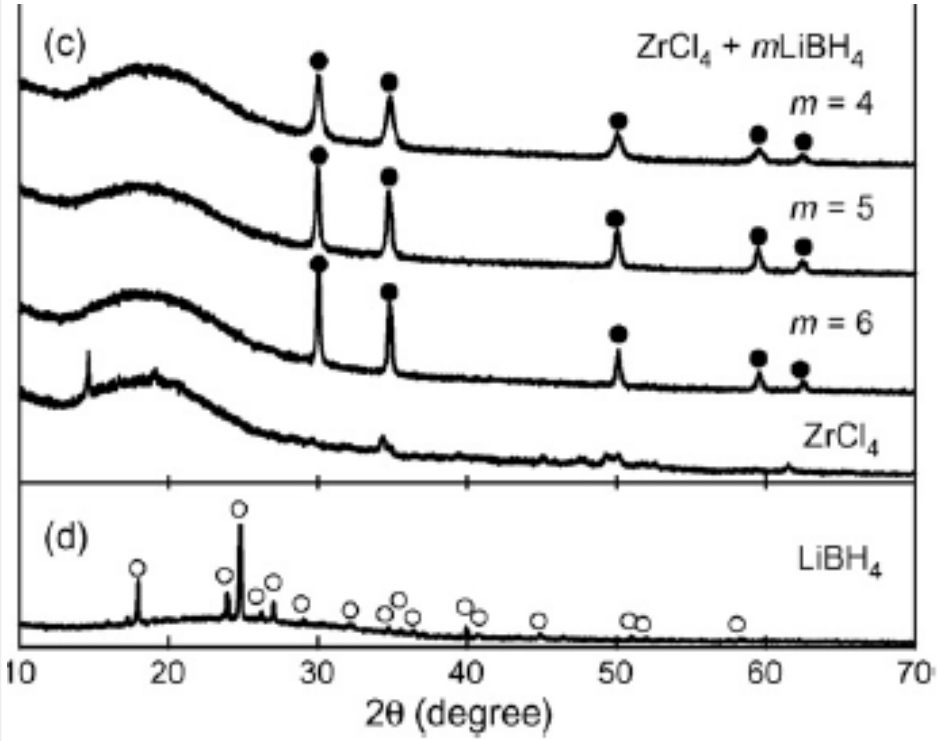
Double-cation borohydrides!

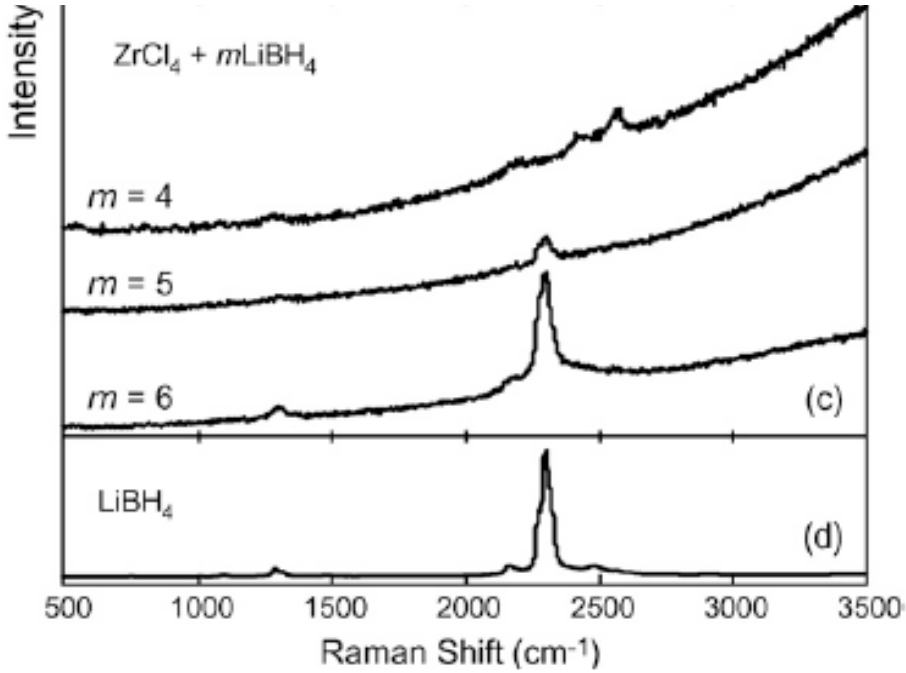


H.-W. Li et al., J. Alloys and Comp. 2007

Adjustment of thermodynamical stabilities by combination of two metals with differents electronegativities

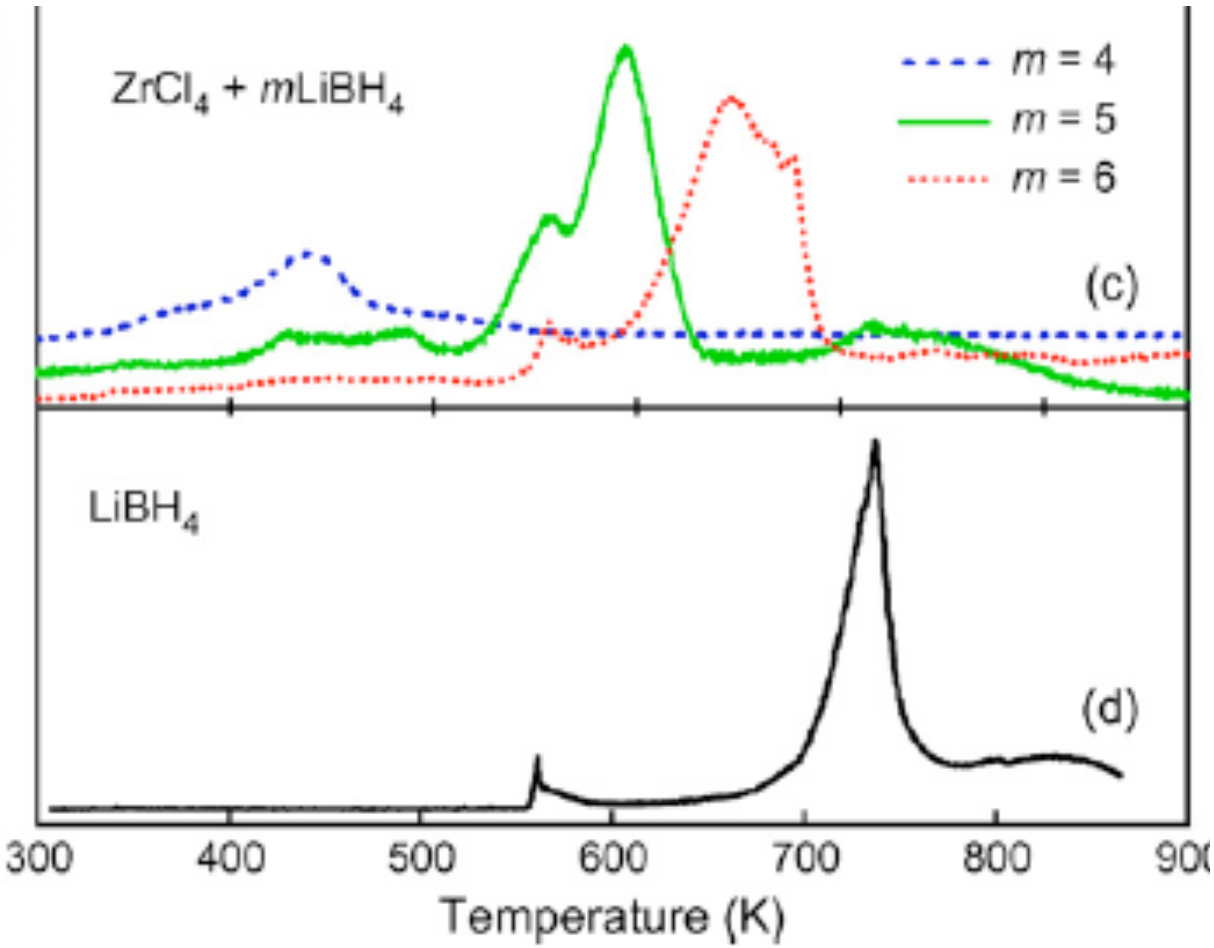
$$MCl_n + mLiBH_4 \rightarrow MLi_{m-n}(BH_4)_m + nLiC$$





H.-W. Li et al., J. Alloys and Comp. 2007

Thermal desorption

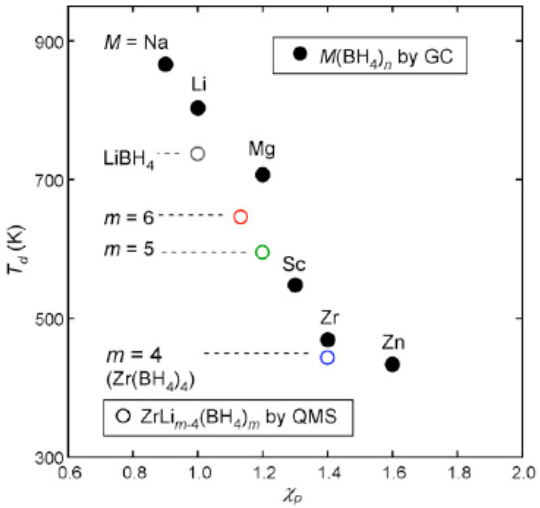


$Zr(BH_4)_4$

$ZrLi(BH_4)_5$

$ZrLi_2(BH_4)_6$

$$\chi_P = \frac{1.4 + 1.0(m-4)}{1 + (m-4)}$$



H.-W. Li et al., J. Alloys and Comp. 2007

The search for novel metal borohydrides

$LiK(BH_4)_2$, $LiMg(BH_4)_3$

Mixed metal borohydrides

$Li(BH_4)_{1-x}Cl_x$

Anion substitution

Mixed metal borohydrides

$LiSc(BH_4)_4$
$NaSc(BH_4)_4$
$KSc(BH_4)_4$

$LiZn_2(BH_4)_5$
$NaZn(BH_4)_3$
$NaZn_2(BH_4)_5$

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	ununnunium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]			

(Hummelshøj et al., 2008 CAMD Summer School, TDU)

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Local Coordination Screening (LCS) approach

CAMD 2008 Summer School
Center for **A**tomic Scale **M**aterials **D**esign
Technical University of Denmark, Kongens Lyngby, Denmark

Search for novel metal borohydrides

Systems with alloy composition

$M_1M_2(BH_4)_{2\text{-}5}$ ⟶ M1 = alkali metal
M2 = alkali, alkaline earth or 3d/4d transition metal

757 compositions have been simulated ⟶ **22** stable alloys with promising decomposition energies

Hummelshøj, J. Chem. Phys. 131 (2009)

The Approach

Configuration space and template structures ⟶ **Initial screening**

$M_1M_2(BH_4)_x$ M1 ∈ {Li,Na,K} x=2 M2 ∈ {Li,Na,K}
x=3,4 M2 ∈ {Li,Na,K,Mg,Al,Ca
Sc-Zn, Y-Mo, Ru-Cd}

exception: $Al(BH_4)_3$

literature search, structures reported ⟶ templates structures with tetrahedral (**T**) - for the smallest Li and Mg - and octahedral (**O**) - for the larger Na, K and Ca - **coordination of BH_4** groups **to** the **metal atoms** were used

For each alloy composition, 4 different template structures were used for the coordination of the BH_4:

M1	M2	M1	M2	M1	M2	M1	M2
T	T	O	O	T	O	O	T

Coordination polyhedra with either corner or edge-sharing or combination of both

Unit cell containing only ONE formula unit

Hummelshøj, J. Chem. Phys. 131 (2009)

Assessment of the stabilities for the 757 structures

Two selection criteria were used:

Phase separation into binary components:

$$\Delta E_{alloy} = E_{LiSc(BH_4)_4} - (E_{LiBH_4} + E_{Sc(BH_4)_3})$$

Decomposition:

Generic decomposition pathway, where the alloys decompose into alkali- and alkaline earth hydrides, transition metals, boron and hydrogen

$$\Delta E_{decomp} = E_{LiSc(BH_4)_4} - (E_{LiH} + E_{Sc} + 4E_B + 7.5E_{H_2})$$

stability range used to select:

$\Delta E_{alloy} \leq$ 0.0 eV/f.u. and $\Delta E_{decomp} \in$ {-0.5;0.0} ~ -0.2 eV/H_2 **TARGET**

$\Delta E_{alloy} \leq$ 0.2 eV/f.u. and/or $\Delta E_{decomp} \leq$ 0.2 eV/H_2 ***(alloys with only small instabilities)***

Hummelshøj, J. Chem. Phys. 131 (2009)

Calculation Procedure

Step 1:
Population of one of the four template structures with two supplied metal atoms followed by introduction of the necessary ($BH4^-$) groups. The ionic radii of the metals were taken from the 24 binary reference borohydrides; for $BH4^-$, the ionic radius was adjusted according to the coordination of the group to the metal ion (face,edge,corner)

INITIAL GUESS

Iteration process

(I) Relaxation of the Hydrogen positions
(II) Contraction/expansion of unit cell volume, keeping B-H distance fixed in order to find the optimum unit cell volume
(III) Relaxation of Hydrogen positions in optimized unit cell

Step 2:
After optimization of (M1,M2) templates, the most stable structure was relaxed without constraints in a two-stage process:

Relax atomic positions while keeping unit cell volume fixed
Relax unit cell volume while keeping atomic positions fixed

Hummelshøj, J. Chem. Phys. 131 (2009)

Results

Most of the alloys are stable against decomposition BUT the majority is found to be unstable against separation into the binary components

The stable alloys ($\Delta E_{alloy} \leq 0.0$ eV/f.u.) cluster around certain average electronegativities of 1.3-1.4 and 1.6. The cluster around 1.3-1.4 is highly promising and it contains alloys of the following elements: Mn, (Nb),Al, Zn and Fe

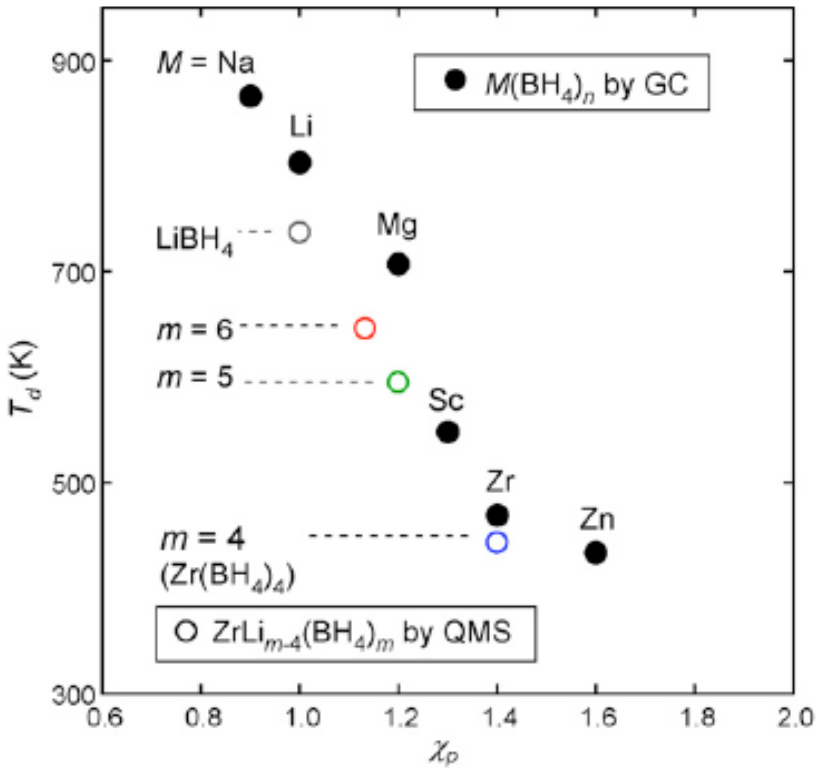
THE LIST

Composition	wt. %	ΔE_{alloy} [eV/f.u.]	ΔE_{decomp} [eV/H_2]
LiNa(BH4)2	13.5	-0.020	-0.581
KZn(BH4)3	8.1	-0.349	-0.423
KAl(BH4)4	12.9	-0.138	-0.416
KCd(BH4)3	6.2	-0.005	-0.352
NaZn(BH4)3	9.1	-0.358	-0.344
LiAl(BH4)4	17.3	-0.391	-0.311
KFe(BH4)3	8.7	-0.116	-0.282
LiZn(BH4)3	10.4	-0.362	-0.243
NaFe(BH4)3	9.8	-0.141	-0.206
KMn(BH4)4	10.5	-0.148	-0.174
NaNb(BH4)4	9.2	-0.128	-0.165
KCo(BH4)3	8.5	-0.089	-0.161
NaMn(BH4)4	11.7	-0.284	-0.131
KNi(BH4)3	8.5	-0.120	-0.116
LiFe(BH4)3	11.3	-0.141	-0.104
LiNb(BH4)4	10.1	-0.194	-0.097
NaCo(BH4)3	9.6	-0.143	-0.090
KRh(BH4)4	8.0	-0.058	-0.079
LiMn(BH4)4	13.3	-0.358	-0.063
NaNi(BH4)3	9.6	-0.164	-0.043
NaRh(BH4)4	8.7	-0.033	-0.016

Further candidates with $0 < \Delta E_{alloy} < 0.2$ eV/f.u. and $\Delta E_{decomp} < 0.0$ eV/H2

Composition	wt. %	ΔE_{alloy} [eV/f.u.]	ΔE_{decomp} [eV/H_2]
K(Na(BH4)2	8.8	0.095	-0.825
NaY(BH4)4	9.4	0.115	-0.675
NaCa(BH4)3	11.2	0.129	-0.645
LiY(BH4)4	10.4	0.033	-0.609
LiCa(BH4)3	13.2	0.052	-0.556
LiSc(BH4)4	14.5	0.143	-0.534
NaCd(BH4)3	6.7	0.003	-0.271
KNb(BH4)4	8.4	0.016	-0.207
NaV(BH4)4	12.1	0.076	-0.188
NaAg(BH4)2	5.0	0.193	-0.177
LiCd(BH4)3	7.4	0.102	-0.152
KCr(BH4)4	10.7	0.199	-0.136
LiV(BH4)4	13.8	0.061	-0.113
NaCr(BH4)4	12.0	0.050	-0.095
KPd(BH4)3	6.4	0.047	-0.095
KMo(BH4)4	8.3	0.185	-0.079
KRu(BH4)3	6.5	0.168	-0.061
NaMo(BH4)4	9.0	0.056	-0.035
LiCr(BH4)4	13.6	0.029	-0.021
NaPd(BH4)3	7.0	0.052	-0.014
LiCo(BH4)3	11.0	-0.100	0.019
LiNi(BH4)3	11.0	-0.104	0.069

Double-Cation metal borohydrides



$MLi_{m-n}(BH_4)_m$ (Orimo, 2007)

M	n	
Zn	2	$LiZn(BH_4)_3$
Al	3	$LiAl(BH_4)_4$
Zr	4	$LiZr(BH_4)_5$

→ Disproportionate upon heating

$LiFe(BH_4)_3$	1961 ←
$(Li/Na)Mn(BH_4)_{3,4}$	2008
$(Li/Na)Zn(BH_4)_3$	1971 ←
$LiSc(BH_4)_4$	2008
$LiZn(BH_4)_3$	2006
$NaZn(BH_4)_3$	2008
$NaZn_2(BH_4)_5$	2008
$LiK(BH_4)_2$	2008
$LiZn_2(BH_4)_5$	2009
$NaZn_2(BH_4)_5$	2009
$NaZn(BH_4)_3$	2009
$NaSc(BH_4)_4$	2010
$KZn(BH_4)Cl_2$	2010

Aim

$$m\ NaBH_4 + TMCl_n \rightarrow Na_{m-n}TM(BH_4)_m + n\ NaCl$$

TM= Cd, Ti, V, Cu, Ni

Finding $Na(BH_4)_{1-x}Cl_x$

- **Synthesis**: ball milling in Ar, 3h, 100:1

Table 1 Refined unit cell parameters for NaCl-type phases and compositions estimated from Vegard's law

Sample	Unit cell parameter for NaCl-type phase (Å)	Composition from Vegards law, $Na(BH_4)_{1-x}Cl_x$
$3\ NaBH_4 + CuCl_2$	5.8103(2)	x = 0.65
$3\ NaBH_4 + NiCl_2$	5.80108(9)	x = 0.66
$3\ NaBH_4 + TiCl_2$	5.7851(2)	x = 0.69
$3\ NaBH_4 + CdCl_2$	5.7729(7)	x = 0.72
$4\ NaBH_4 + RhCl_3$	5.7281(5)	x = 0.80

Conclusion

- At present, no solid storage material fulfils the major targets for automotive applications;
- Up to now, storage densities of ~2 wt.% are achievable on system level with complex hydrides on alanate basis (capacity of the material 4 wt%);
- Further research for novel storage materials with improved storage densities, kinetics and thermodynamic behaviour as well as for advanced system components, e.g. heat exchanger, is still required;
- For on-board storage in fuel -cell-driven vehicles, the hydrogen in the alanates needs to be reversibly charged and discharged;
- To make the material reversible under practical conditions, it has to be added with a catalyst. Still not understood the effect of additives.