Sustainable Hydrogen and Electrical Energy Storage
03-06-2013

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Hydrogen storage requirements

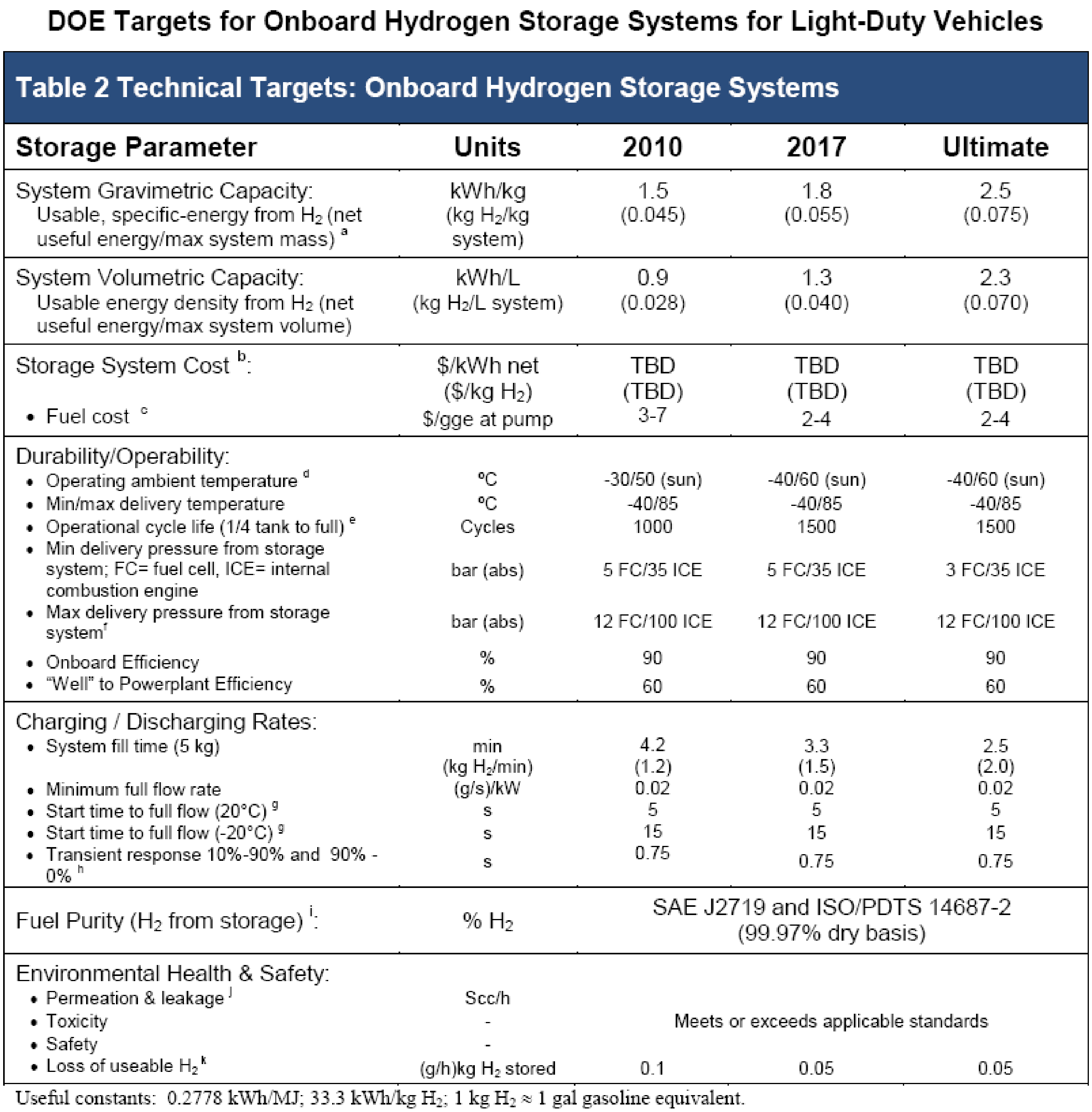
Often the targets of the Department of Energy of the USA are quoted

U.S. DEPARTMENT OF ENERGY

www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html

Last week we saw hydrogen storage requirements

- High capacity expressed in wt.% H_2 of the system
- High capacity in kg H_2/L of the system
- Practical operating conditions (T and P ‘close’ to RT and 1 Bar)
- Energy efficient (compared to energy content)
- Fast in loading and unloading
- Safe
- Cheap
- Reloadable for many cycles
- Environmentally sound
- no leaking of hydrogen



DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles

Table 2 Technical Targets: Onboard Hydrogen Storage Systems

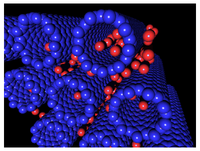
Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass) [a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost [b]:	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost [c]	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
• Operating ambient temperature [d]	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full) [e]	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system [f]	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
• System fill time (5 kg)	min (kg H_2/min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C) [g]	s	5	5	5
• Start time to full flow (-20°C) [g]	s	15	15	15
• Transient response 10%-90% and 90% - 0% [h]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage) [i]:	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety:				
• Permeation & leakage [j]	Scc/h	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H_2 [k]	(g/h)kg H_2 stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh/MJ; 33.3 kWh/kg H_2; 1 kg H_2 $\approx$ 1 gal gasoline equivalent.

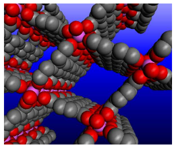
gasoline gallon equivalent

Hydrogen surface adsorption; towards stronger bonding

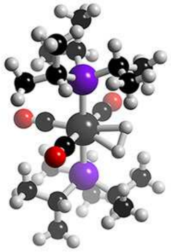
Nanocarbons



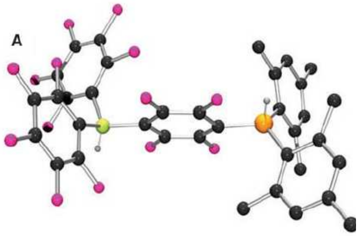
Metal organic frameworks



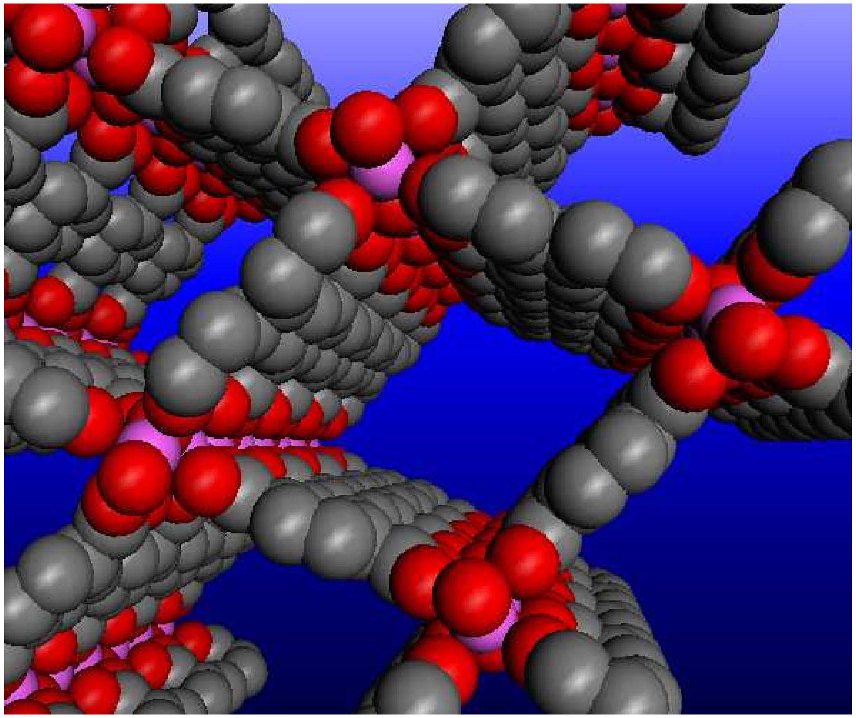
Kubas compounds



Electrophilic activation



A ‘breathing’ MOF: ‘MIL-53’



Adsorption up to 3 – 3.5 wt % in MIL53 at 77 K

Some H_2 seems
to get stuck here

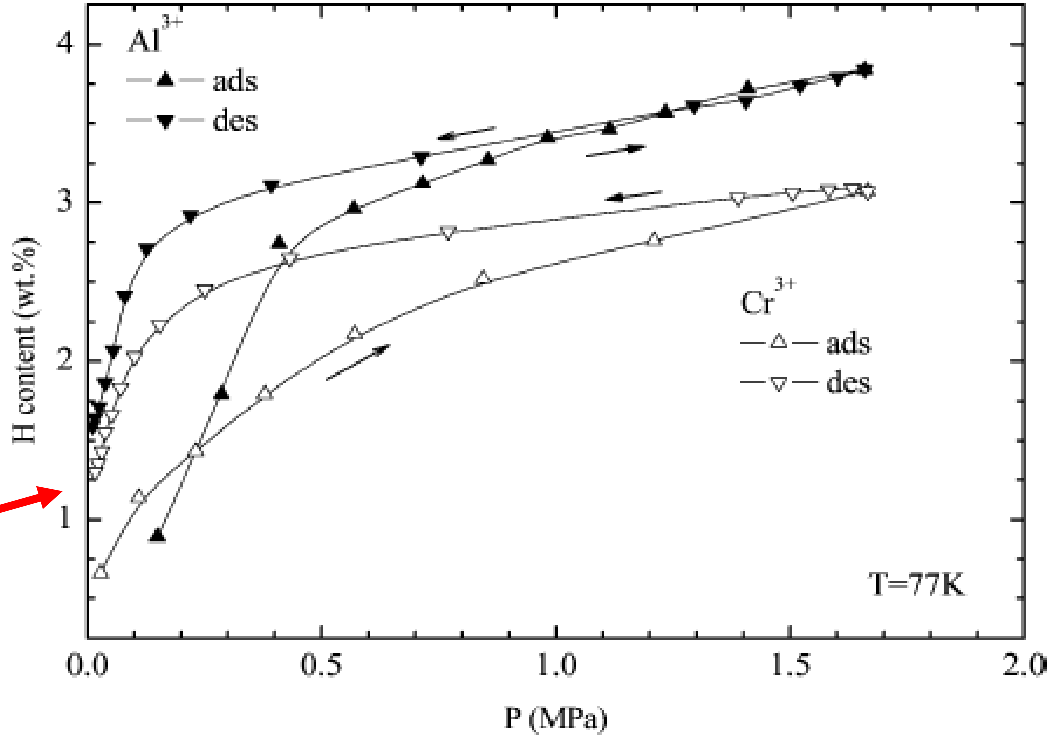
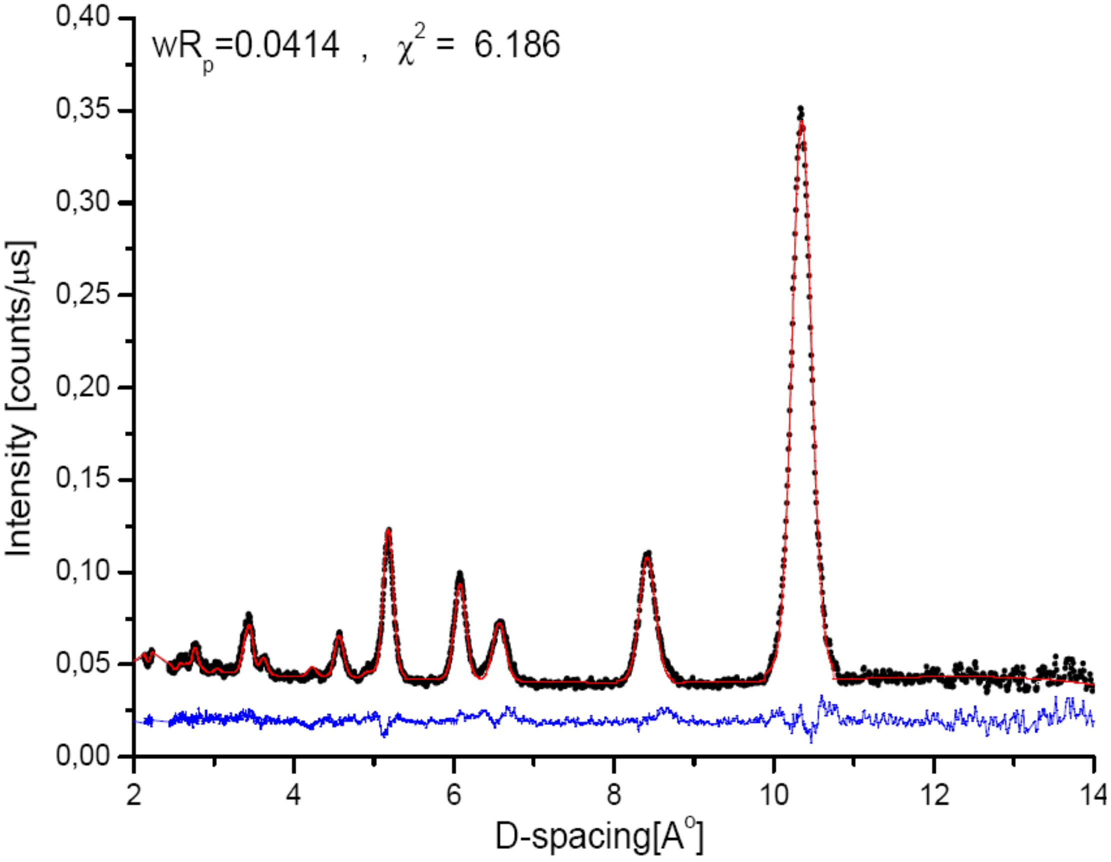
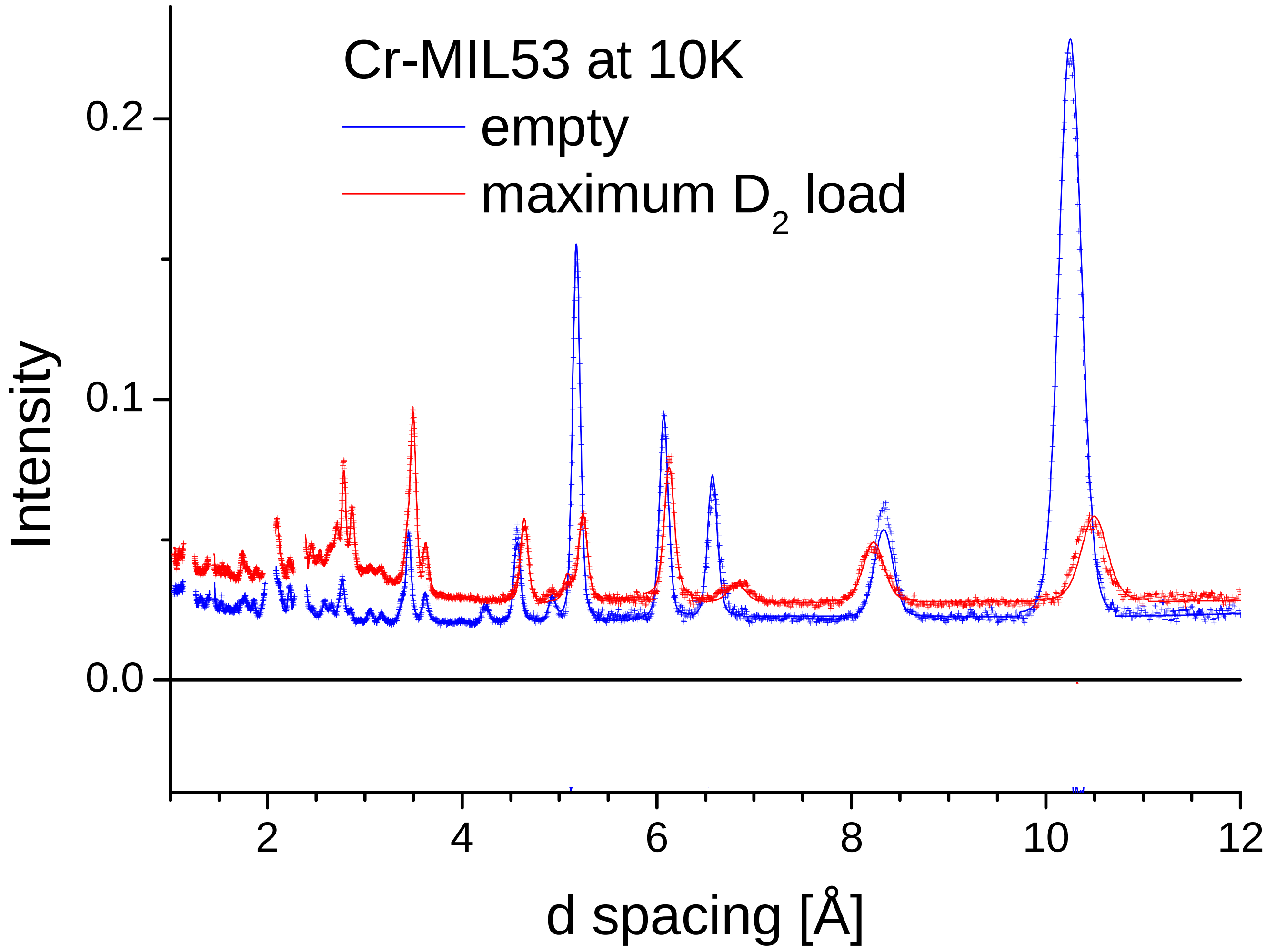


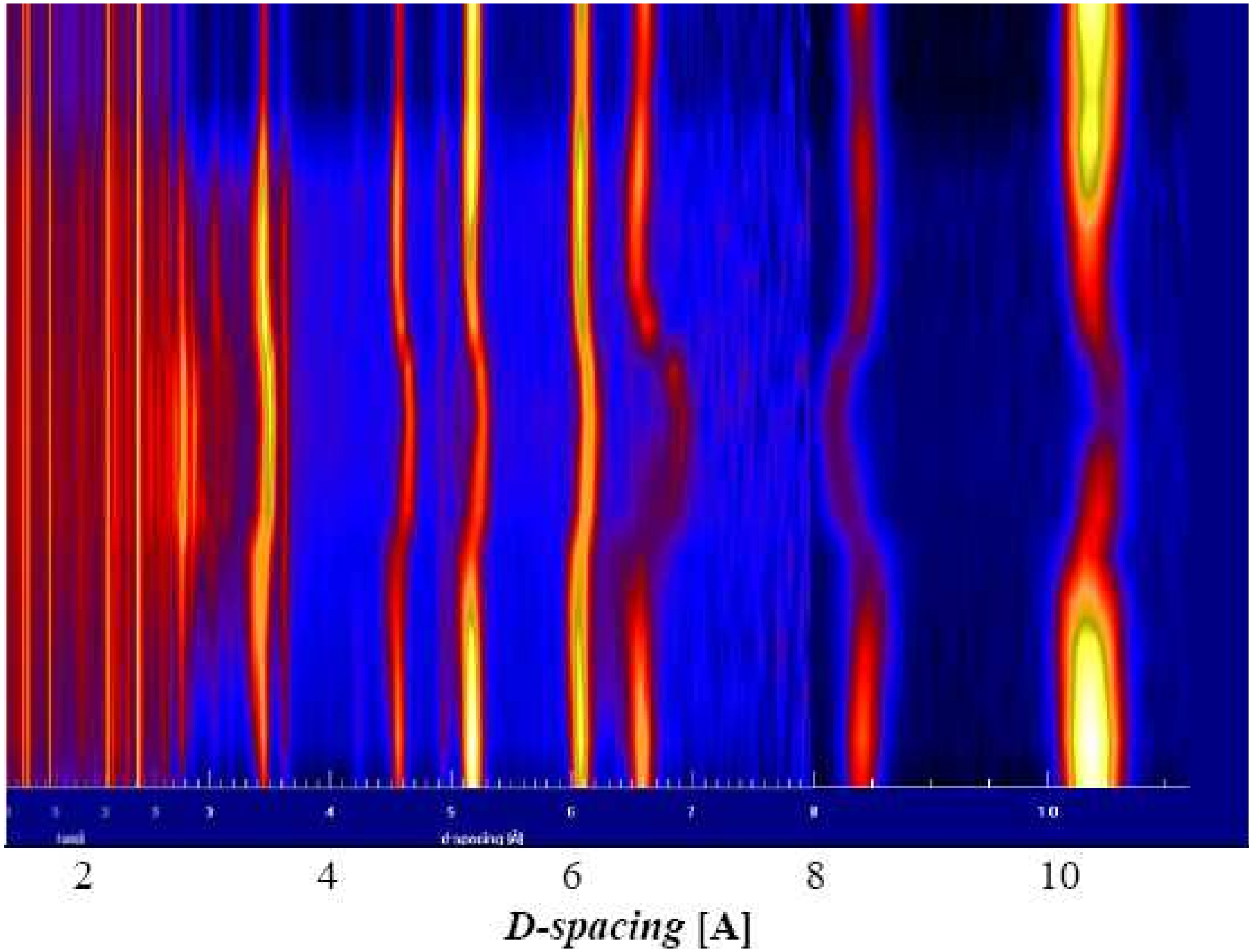
Fig. 2 PCI curves (▲: adsorption; ▼: desorption) measured at 77 K up to 1.6 MPa of hydrogen pressure for the MIL-53 samples with M = Cr^{3+} (open symbol) and M = Al^{3+} (full symbol).

Neutron diffraction: a technique which is sensitive to hydrogen





Large change of neutron diffraction pattern when D_2 is loaded.
This tells you that this technique is sensitive to D_2.



unload

Load

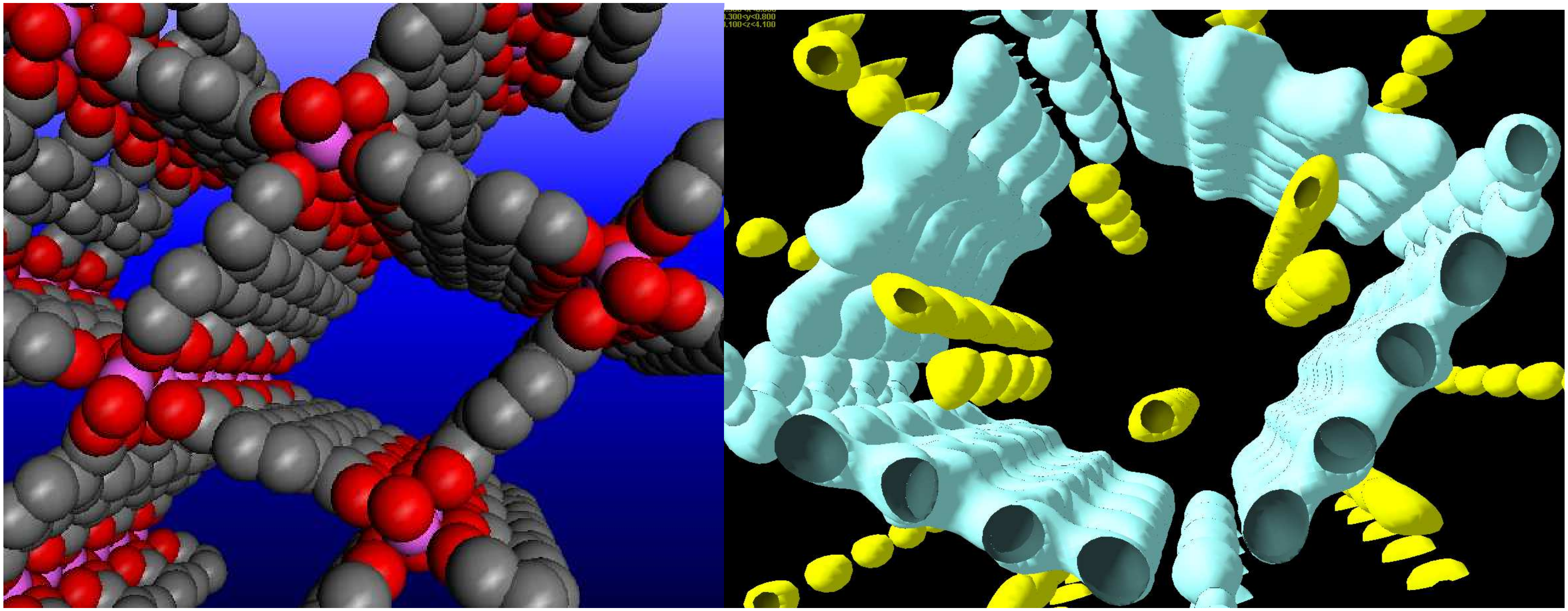
2Bar, 150K,
0.2 wt.%

2Bar, 25K,
7.5 wt. %

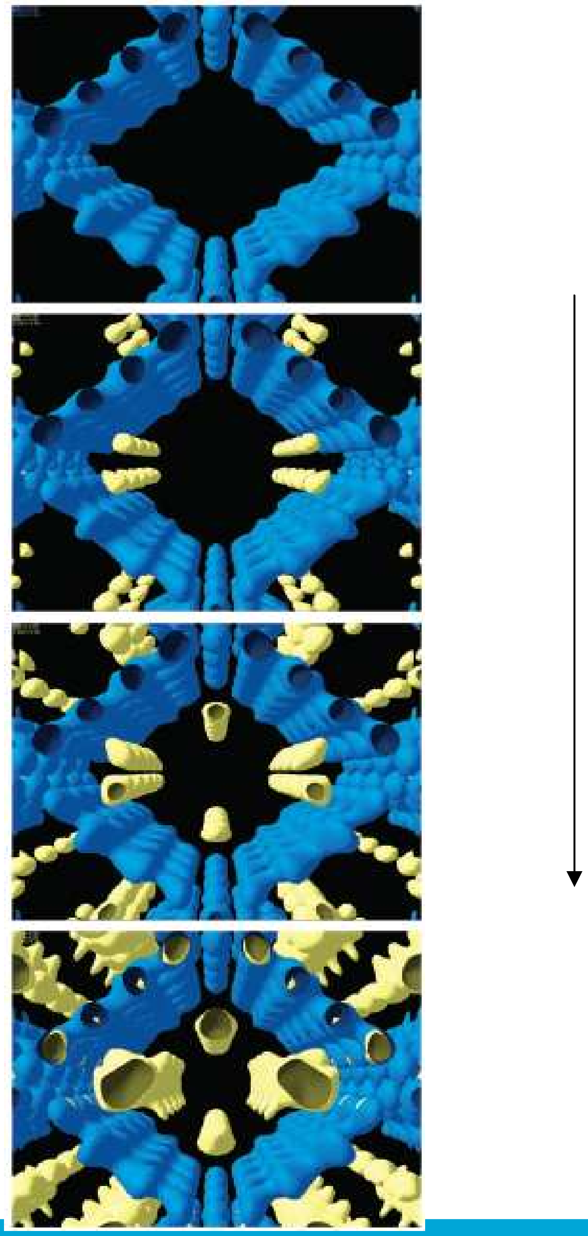
0Bar, 25K

Neutron diffraction on MIL53 (GEM, ISIS, Oxfordshire)

Mulder *et al.* J. Phys. Chem. C, 114 (2010) 10648

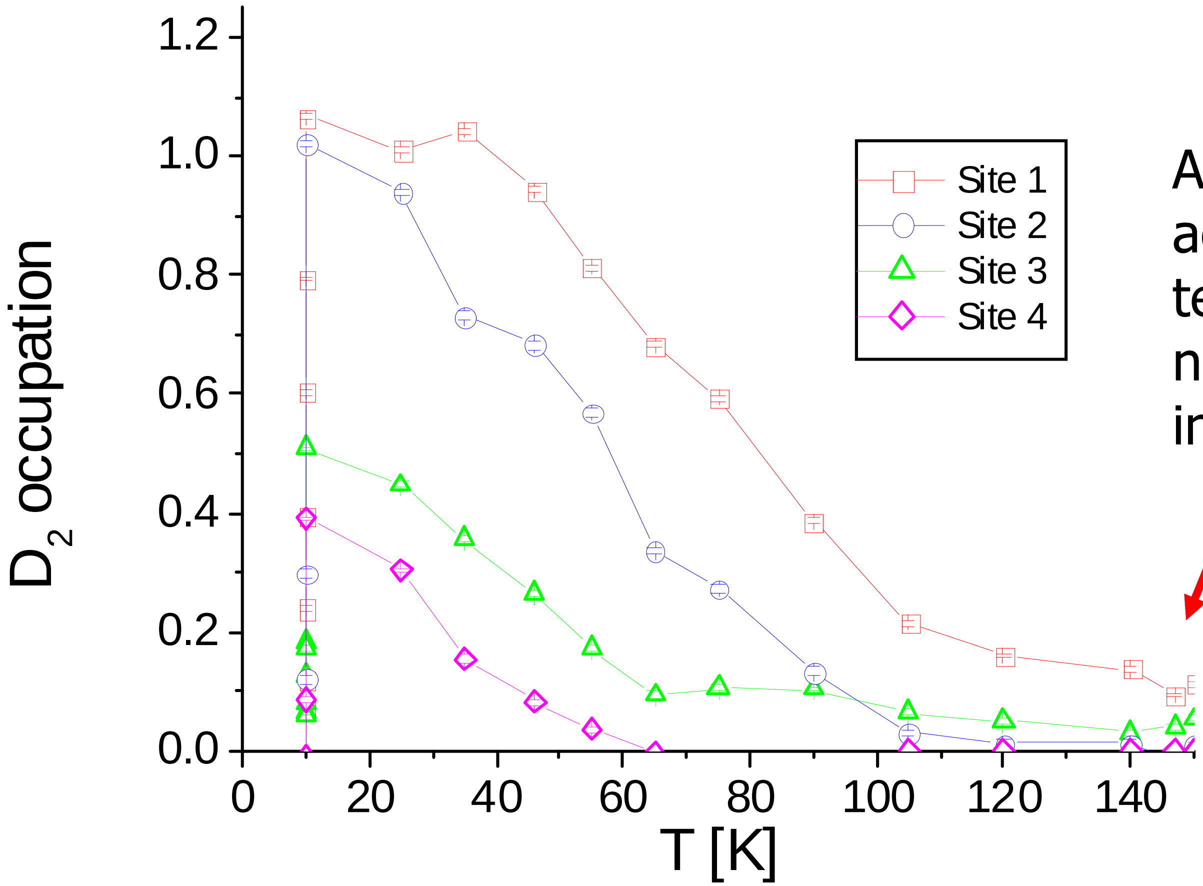


‘Fourier maps’ of the diffraction data show where the hydrogen (or rather deuterium) is located:
Right picture: in blue the MIL structure, yellow: the loaded D_2

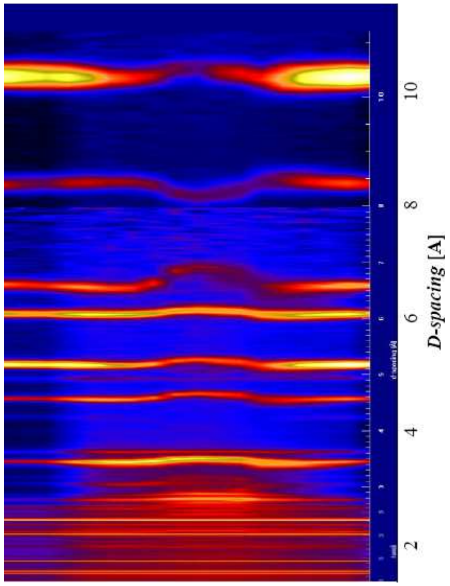


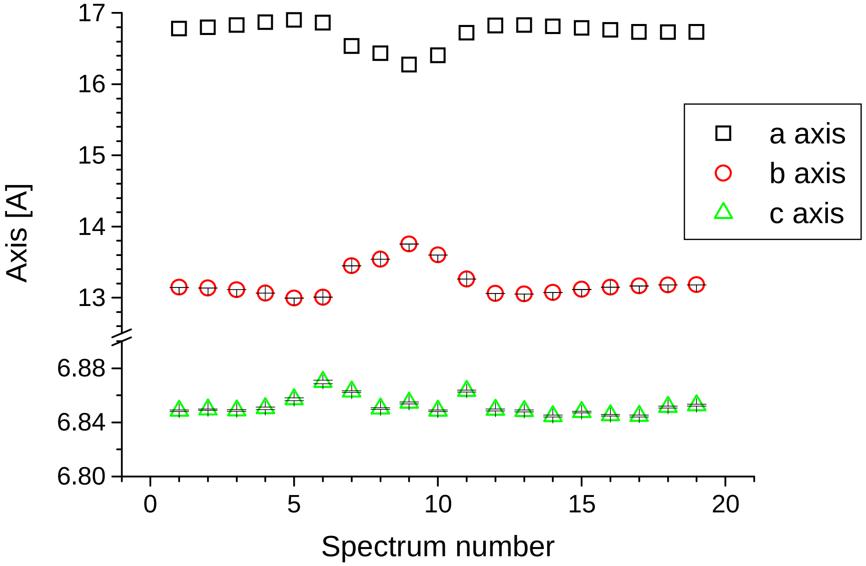
Increasing D_2 load

‘Rietveld refinements’ give site occupations as a function of: load, pressure, temperature.



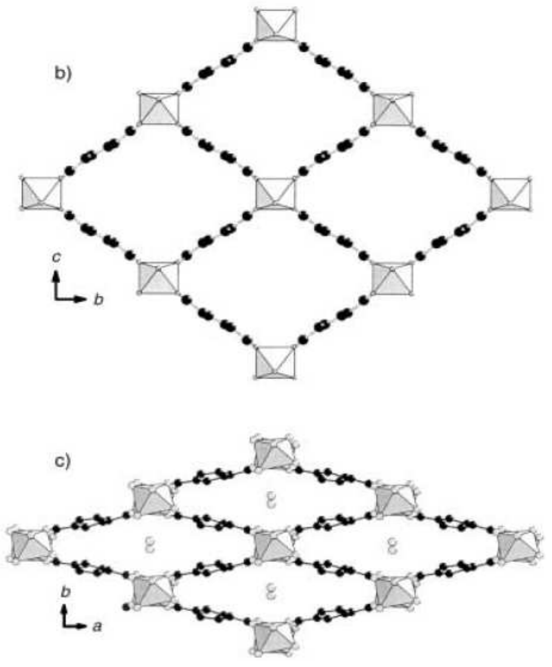
All hydrogen gets out again, but higher temperatures are needed: stronger interactions





Most remarkable result: the loading with hydrogen causes the lattice Parameters to change a lot, up to 7%. This was not observed before for Hydrogen.

However, for strongly interacting solvents this has already been observed.



MIL53 ‘breathing modes’
upon water uptake

Chem. Eur. J. 10 (2004) 1373

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9. C. Troadec *et al.*, *Nanotechnology* 15, 1818 (2004).
10. R. M. Feenstra, J. A. Stroscio, J. Tersoff, A. P. Fein, *Phys. Rev. Lett.* 58, 1192 (1987).
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17. S. R. Forrest, *Chem. Rev.* 97, 1793 (1997).

gently contact the metallic bismuth layer. To conduct BEEM, we chose tunneling currents between 10 and 50 pA as a compromise between the threshold for damaging the molecular layer and a reasonable signal-to-noise ratio for the current of ballistic electrons. At a tunneling current of 50 pA, the BEEM current typically amounted to 4 pA on the clean bismuth surface, 0.5 pA for most of the C_{60} molecules, and 3 pA for the PTCDA molecules.

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40. We thank H. Nienhaus and A. Lorke for fruitful discussions. Supported by the German Research Council within Sonderforschungsbereich 616, “Energy Dissipation at Surfaces.”

Supporting Online Material
www.sciencemag.org/cgi/content/full/315/5820/1824/DC1
Figs. S1 to S5

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Role of Solvent-Host Interactions That Lead to Very Large Swelling of Hybrid Frameworks

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An unusually large expansion upon solvent adsorption occurs without apparent bond breaking in the network of a series of isoreticular chromium(III) or iron(III) diarboxylates labeled MIL-88A to D [dicarbox = fumarate (88A); terephthalate (1,4-BDC) (88B); 2,6-naphthalenedicarboxylate (2,6-NDC) (88C); and 4-4′-biphenyldicarboxylate (4-4′-BPDC) (88D)]. This reversible “breathing” motion was analyzed in terms of cell dimensions (extent of breathing), movements within the framework (mechanism of transformation), and the interactions between the guests and the skeleton. In situ techniques show that these flexible solids are highly selective absorbents and that this selectivity is strongly dependent on the nature of the organic linker.

Crystalline solids are normally quite rigid, but a reversible feature of some large-pore, hybrid, inorganic-organic crystalline solids is an unexpected swelling under external stimuli (such as pressure, temperature, light, or gas or solvent adsorption), sometimes with large magnitude (~5 Å) (*1*, *2*) in the variation of cell parameters. Such large volume variations suggest that these solids might have useful applications because of their selective adsorption, increased storage, and facile delivery (*3*, *4*).

The flexibility of hybrid organic-inorganic porous frameworks that enables these volume changes is governed by their host-guest interactions. Kitagawa (*3*, *5*) recently classified the different known behaviors of flexibility into six classes according to these interactions and the dimensions of the inorganic subnetwork, with the highest “breathing” amplitude so far being 40% (*2*). However, most of the studies reported have been limited to the structures of the frameworks at the initial and final stages of breathing but have not revealed the geometric changes and locations of the guests during the swelling that would provide insight into the mechanism of breathing. These necessary structural data are not always easy to obtain, because the swelling often breaks the crystals into powders, which are sometimes poorly crystallized.

We recently overcame these limitations by implementing a strategy based on a combination of targeted chemistry that controls the nature of the inorganic building block (*6*) and computer simulation (*7*). The structure of hybrid frameworks with giant cells [~380,000 Å^3 (*8*) and ~700,000 Å^3 (*9*)] can be determined for powdered samples by means of a direct space-computational strategy, by pushing the limits of conventional ab initio structure-determination methods of nonmolecular solids from synchrotron data. Moreover, when the crystal structure of a parent hybrid framework is known, lattice energy minimizations can be used to anticipate the series of related crystal structures experimentally obtained with linkers of greater size, with a simple ligand-replacement strategy in which the observed cell parameters of the series are used as target values. The simulations then provide the most likely atomic coordinates for the new framework (*10*), which may be directly used for further Rietveld refinements. The same combined approach was used successfully in the case study of the atypical iron(III) fumarate

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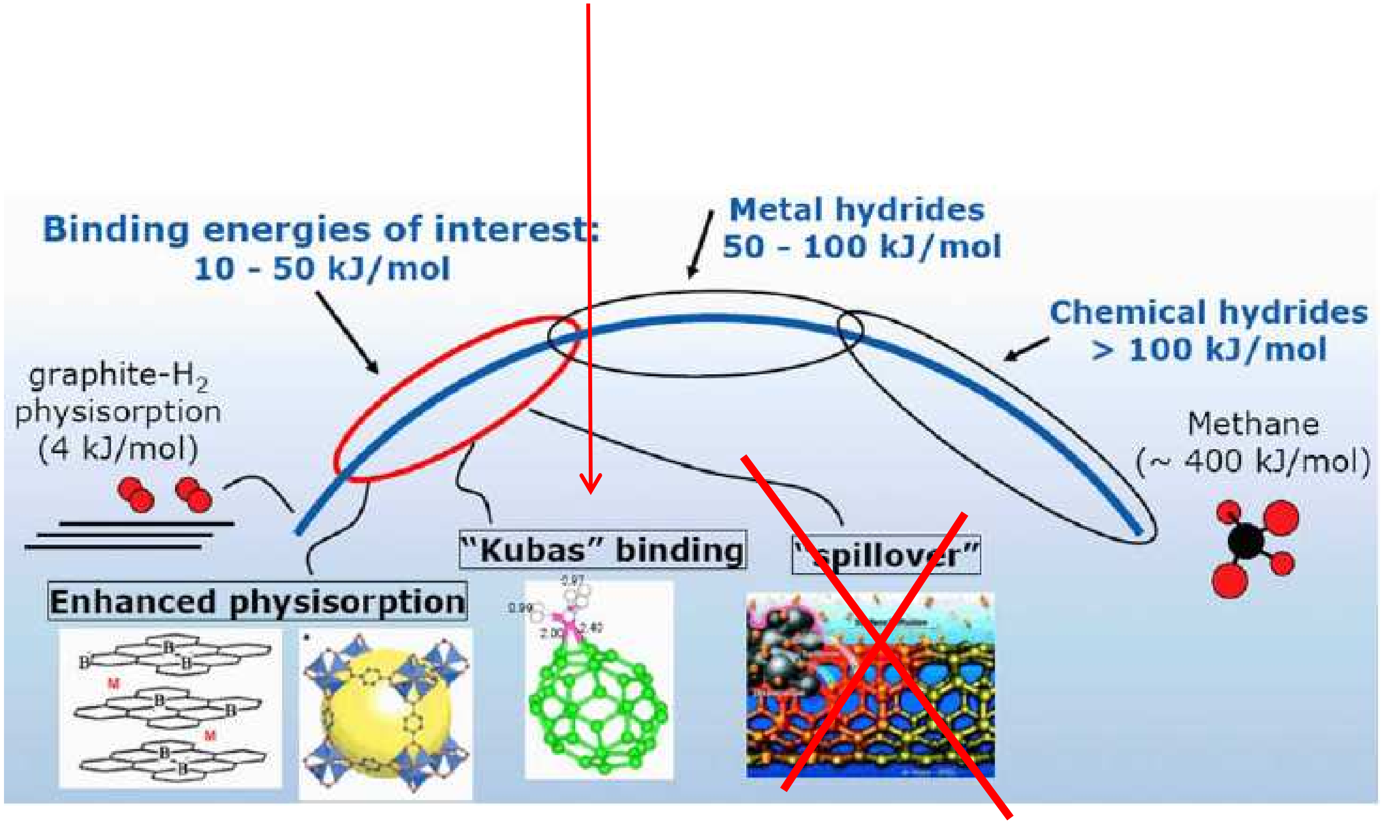
Basic results MOF’s

- adsorption capacities up to ~11.5 wt. % can be obtained at 77K and 120 Bar
- adsorption takes place at low T
- hydrogen can be loaded and unloaded in a fast way
- different adsorption sites are present:
  - -next to metal clusters
  - -next to organic spacer molecules
  - -on a second ‘layer’ in the pores
- adsorption energies are largest near the metal cluster:
  - ~ 800K maximum next to Zn of MOF5,
  - ~ 500K next to organic spacers
- surprising changes in the lattice can occur.

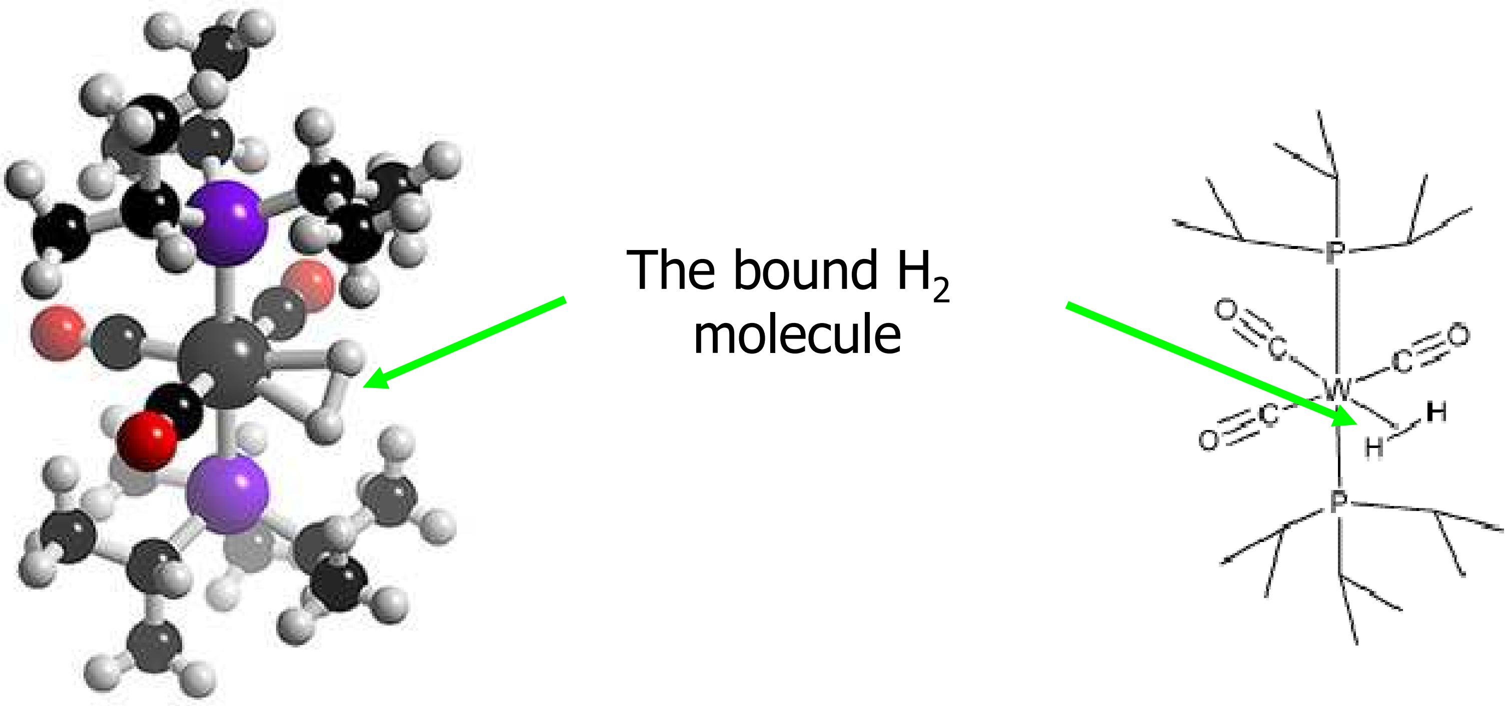
So far we looked into surface adsorption materials

Now stronger interactions



Increasing the interaction strength: From surface adsorption towards chemical bonding of H_2 *molecules* in 'Kubas complexes'

In Kubas complexes: the H_2 molecule does not jet split in separate H atoms, but still remains intact.



The bound H_2 molecule

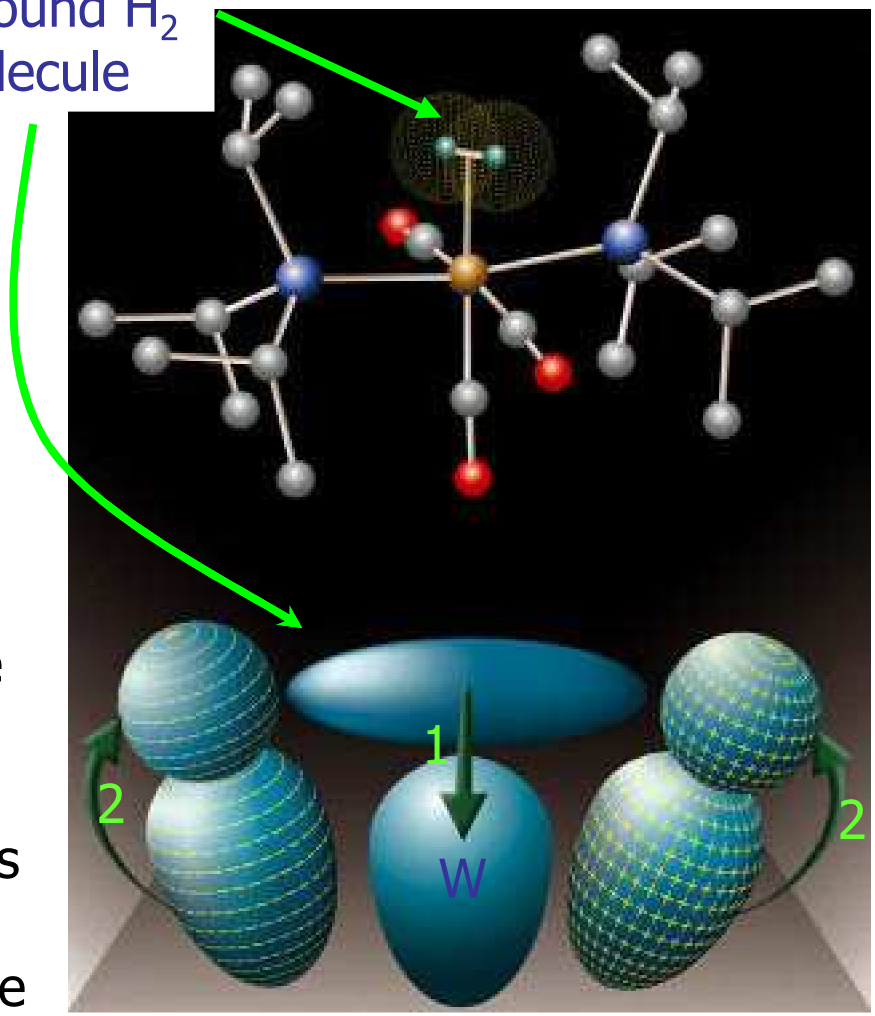
G.J. Kubas, Acc Chem. Res. 21 (1988) 120.

How does it work?

- The electrons in a hydrogen molecule are forming a normal sigma bond.
- The complex has an empty d orbital of its metal ion
- Some electronic density is transferred from the H_2 sigma bond to the empty d orbital (1).

-Some electronic density of another –occupied- d orbital is donated back to the unoccupied s orbitals of the H_2 (2).

-because the bond is not broken, mixtures of D_2 and H_2 do not form H-D by interacting with the complex (unlike above a Pd surface where H_2 / D_2 is split and recombined to form H_2, D_2, *and* HD)



The bound H_2 molecule

The Kubas Complex
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$

Kubas complexes; properties

- the hydrogen molecules can be added under mild hydrogen pressures at temperatures close to room temperature.

- typical interaction enthalpies are ~ 15 kJ/mol ~ 1800 K/ H_2 molecule: indeed just what we needed for the surface adsorption to occur at RT

- hydrogen can be added in solid state (slow) or when the complex is in solution (fast) in some solvents (e.g. THF)

- hundreds of different complexes have been identified.

- all complexes need a transition metal like W, Cr, Fe, Ru, Ir

- typical hydrogen storage capacities are low: 1 H_2 on e.g. 15 atoms that are heavier than C

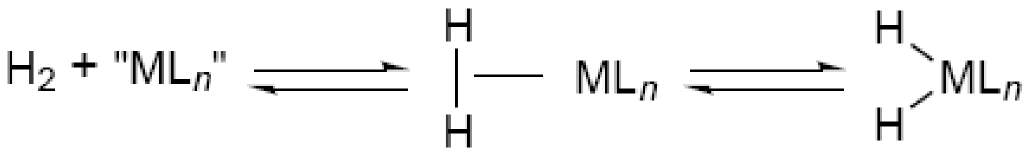
Kubas complexes; properties continued

- the hydrogen molecule has a weakened H-H bond that is also lengthened somewhat from 0.74 Å in free H_2 to e.g. 0.9 Å. This can be observed in Infra Red (IR) absorption spectroscopy as a lowering of H-H stretch frequencies (weaker bond), and in neutron diffraction as a larger separation between the H atoms.

- In various complexes the H-H bonds appear to vary between 0.82 Å to the limit of 1.6 Å, the point at which the bond is considered to be broken in order to form a normal hydride.

- the H-metal bonds are longer and weaker than a normal H-metal bond. In the W complex shown: 1.89 Å instead of ~1.7 Å for a normal W-H bond.

- the complex is viewed as an intermediate along the reaction pathway of H_2 ‘oxidative addition’



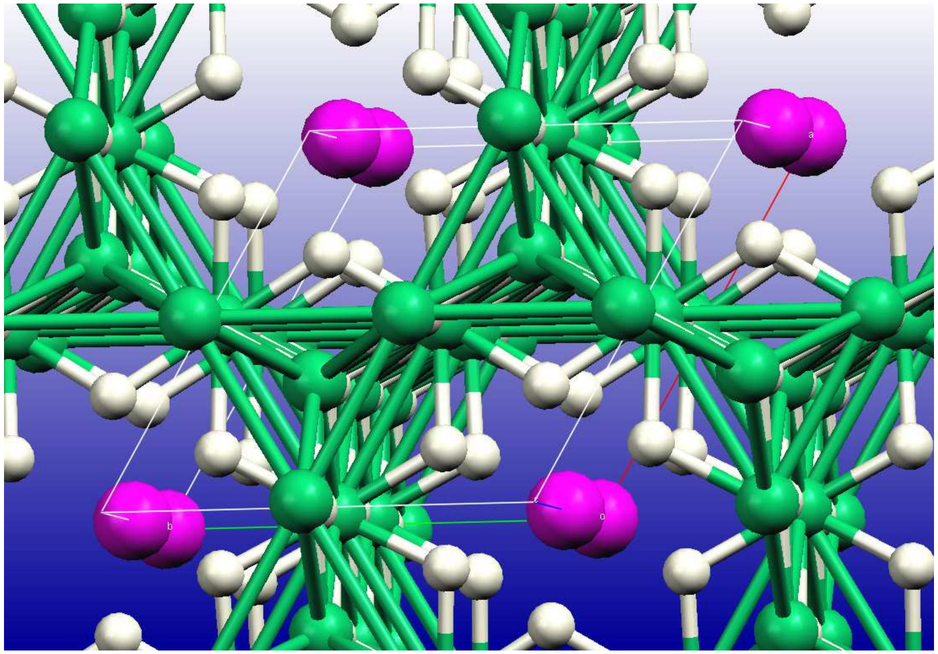
Relevance of Kubas compounds and such electrophilic activation compounds?

- they reversibly bind hydrogen at ~RT and moderate pressure

- however: low capacity (wt.%) due to large number of other atoms.

To become useful, new materials are required that contain many of these binding sites. One might e.g. think of MOF's with Kubas binding sites.

Metal hydrides see also Gupta Ch 11.

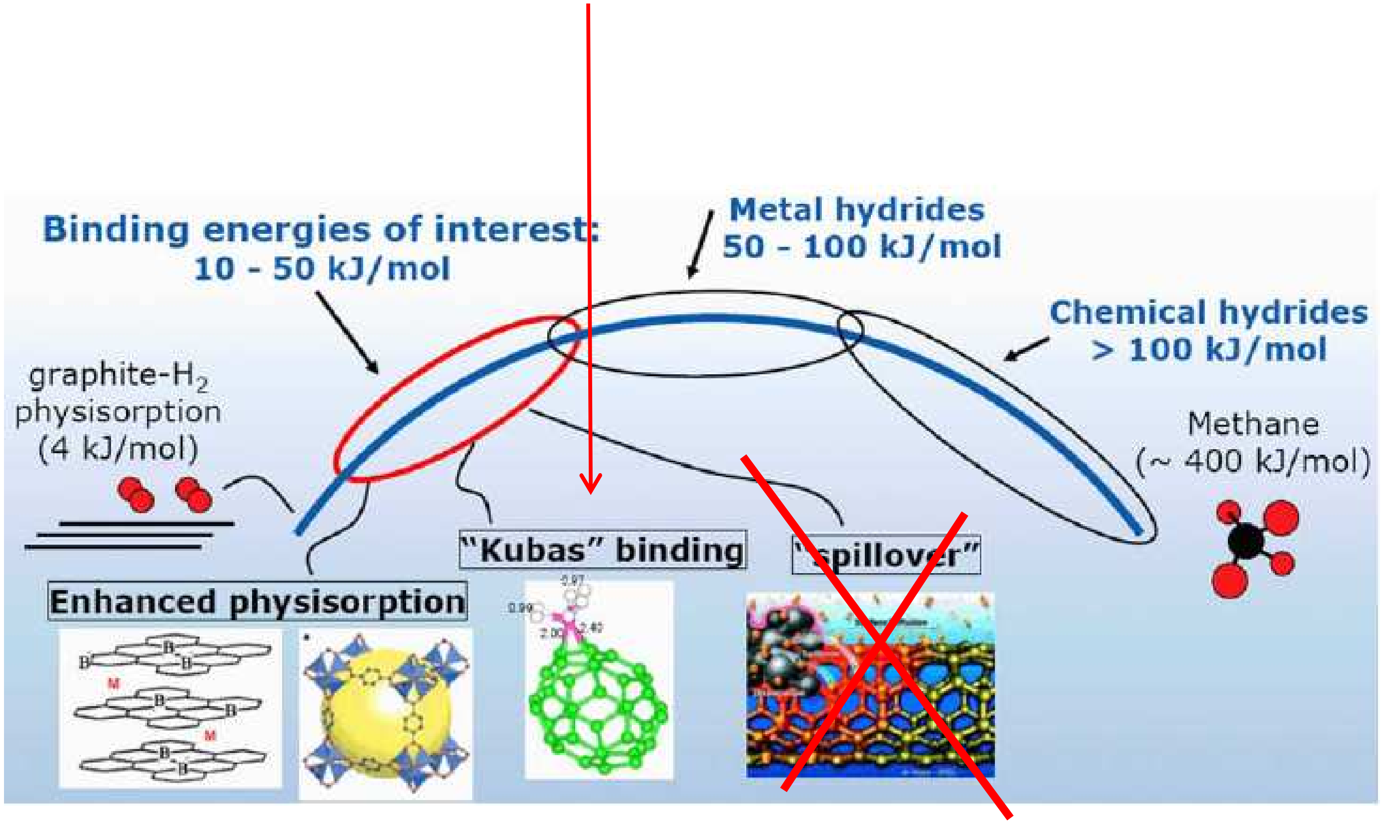


Example of ‘classic’ metal hydrides:

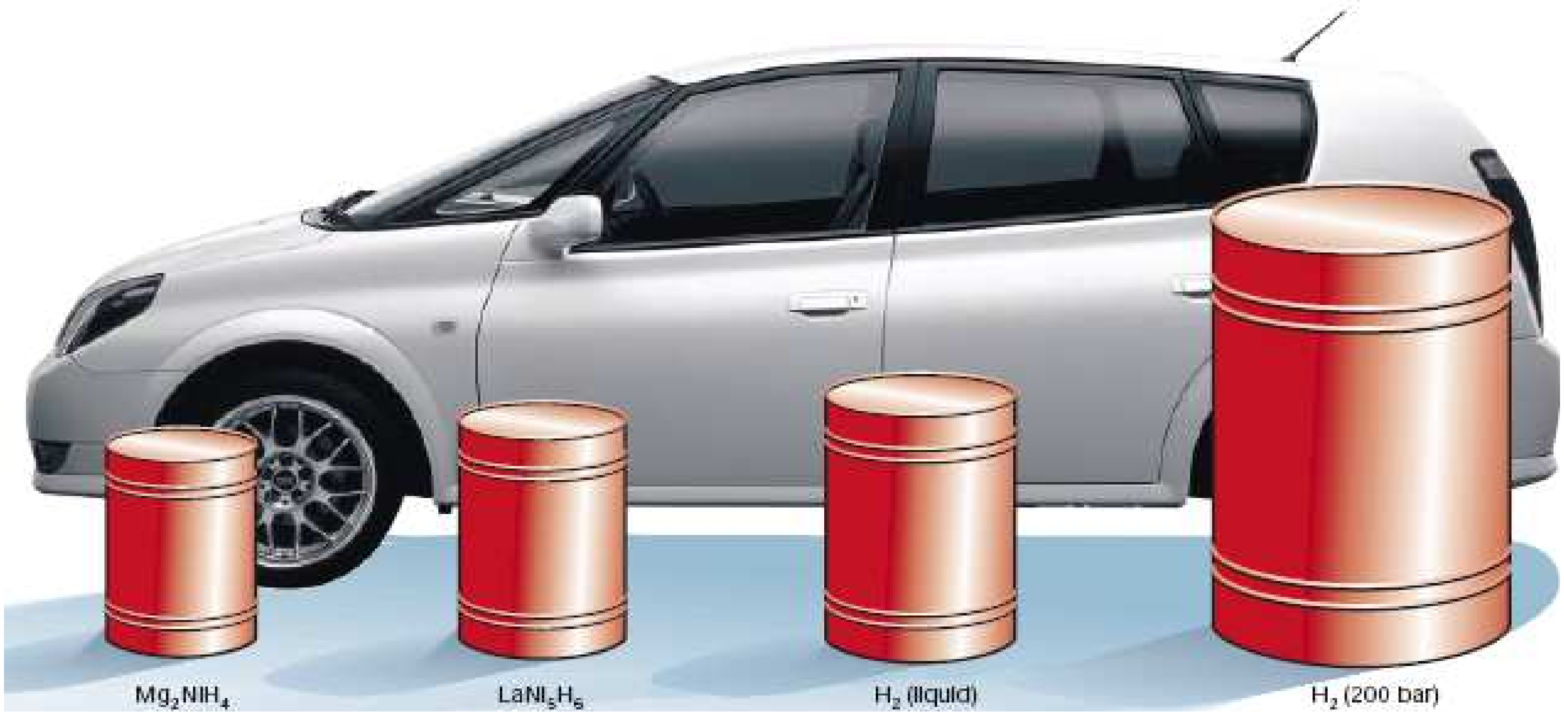
$LaNi_5 + 3H_2 \rightarrow LaNi_5H_6$

So far we looked into surface adsorption materials

Now stronger interactions

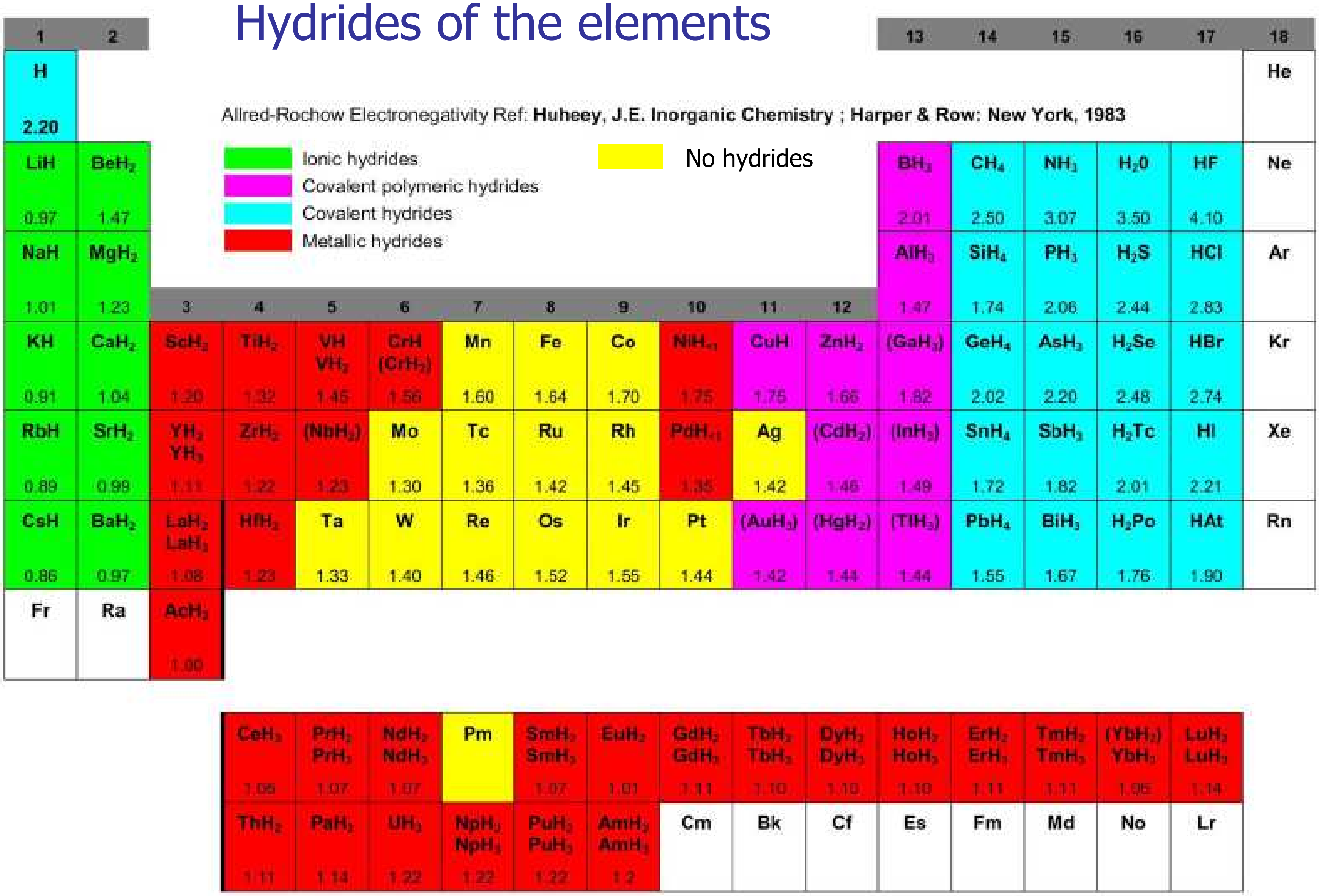


Metal hydrides: chemically bound hydrogen, strong interactions



Metal hydrides can have higher volumetric H densities than liquid H_2

Hydrides of the elements



Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

- 🟩 Ionic hydrides
- 🟪 Covalent polymeric hydrides
- 🟦 Covalent hydrides
- 🟥 Metallic hydrides
- 🟨 No hydrides

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
LiH 0.97	BeH_2 1.47											BH_3 2.01	CH_4 2.50	NH_3 3.07	H_20 3.50	HF 4.10	Ne
NaH 1.01	MgH_2 1.23											AlH_3 1.47	SiH_4 1.74	PH_3 2.06	H_2S 2.44	HCl 2.83	Ar
KH 0.91	CaH_2 1.04	ScH_2 1.20	TiH_2 1.32	VH VH_2 1.45	CrH (CrH_2) 1.56	Mn 1.60	Fe 1.64	Co 1.70	$NiH_{<1}$ 1.75	CuH 1.75	ZnH_2 1.66	(GaH_3) 1.82	GeH_4 2.02	AsH_3 2.20	H_2Se 2.48	HBr 2.74	Kr
RbH 0.89	SrH_2 0.99	YH_2 YH_3 1.11	ZrH_2 1.22	(NbH_2) 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	$PdH_{<1}$ 1.35	Ag 1.42	(CdH_2) 1.46	(InH_3) 1.49	SnH_4 1.72	SbH_3 1.82	H_2Tc 2.01	HI 2.21	Xe
CsH 0.86	BaH_2 0.97	LaH_2 LaH_3 1.08	HfH_2 1.23	Ta 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	(AuH_3) 1.42	(HgH_2) 1.44	(TlH_3) 1.44	PbH_4 1.55	BiH_3 1.67	H_2Po 1.76	HAt 1.90	Rn
Fr	Ra	AcH_2 1.00															

CeH_3 1.06	PrH_2 PrH_3 1.07	NdH_2 NdH_3 1.07	Pm	SmH_2 SmH_3 1.07	EuH_2 1.01	GdH_2 GdH_3 1.11	TbH_2 TbH_3 1.10	DyH_2 DyH_3 1.10	HoH_2 HoH_3 1.10	ErH_2 ErH_3 1.11	TmH_2 TmH_3 1.11	(YbH_2) YbH_3 1.06	LuH_2 LuH_3 1.14
ThH_2 1.11	PaH_3 1.14	UH_3 1.22	NpH_2 NpH_3 1.22	PuH_2 PuH_3 1.22	AmH_2 AmH_3 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Some metal hydrides and ‘complex hydrides’

Compound	N_H 10^{22} at./ml	H wt.%
Liq. H_2	4.2	100
TiH_2	9.2	4
ZrH_2	7.3	2.1
LaH_3	6.5	2.1
$LaNi_5H_6$	5.3	1.4
$TiFeH_{1.95}$	6.2	1.85
AlH_3	8.9	10
$LiBH_4$	7.5	18.3
$PdH_{0.7}$	4.3	0.7
MgH_2	6.6	7.6
$NaAlH_4$	6.5	7.5

High wt% capacities
only for light
elements in hydride

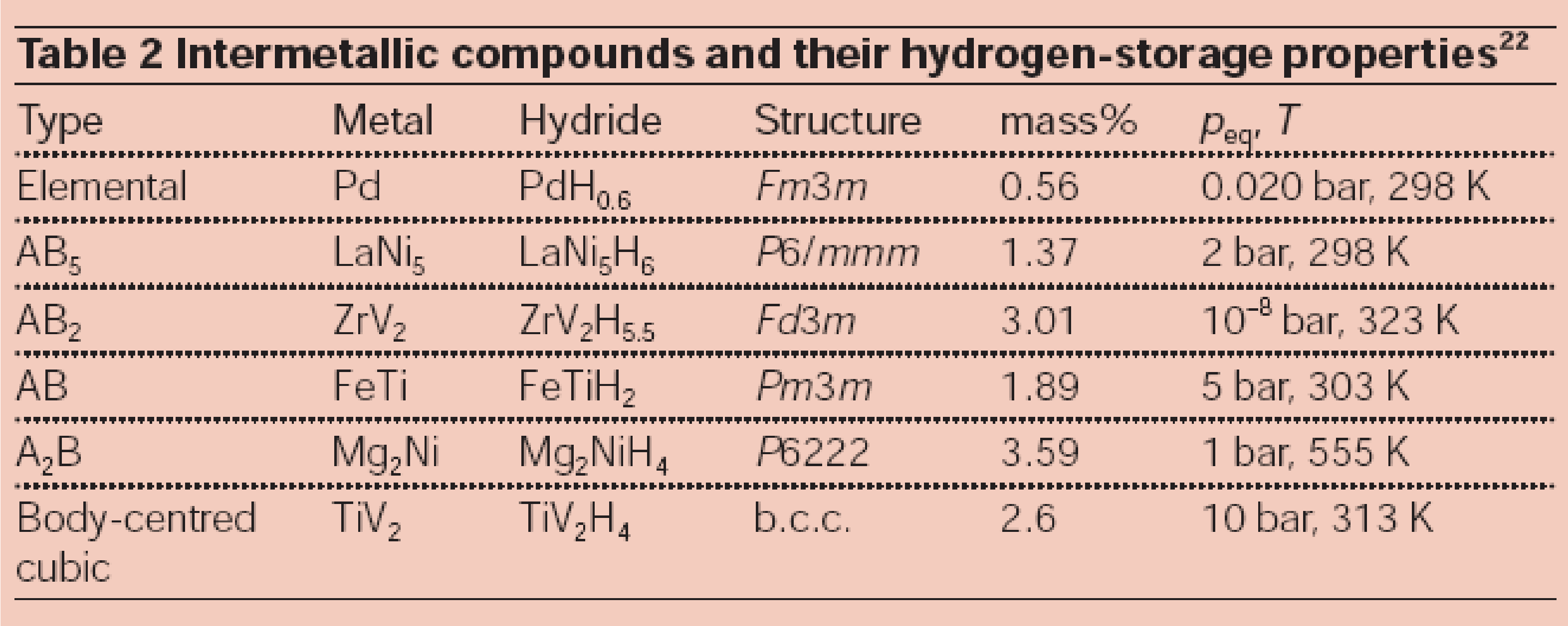
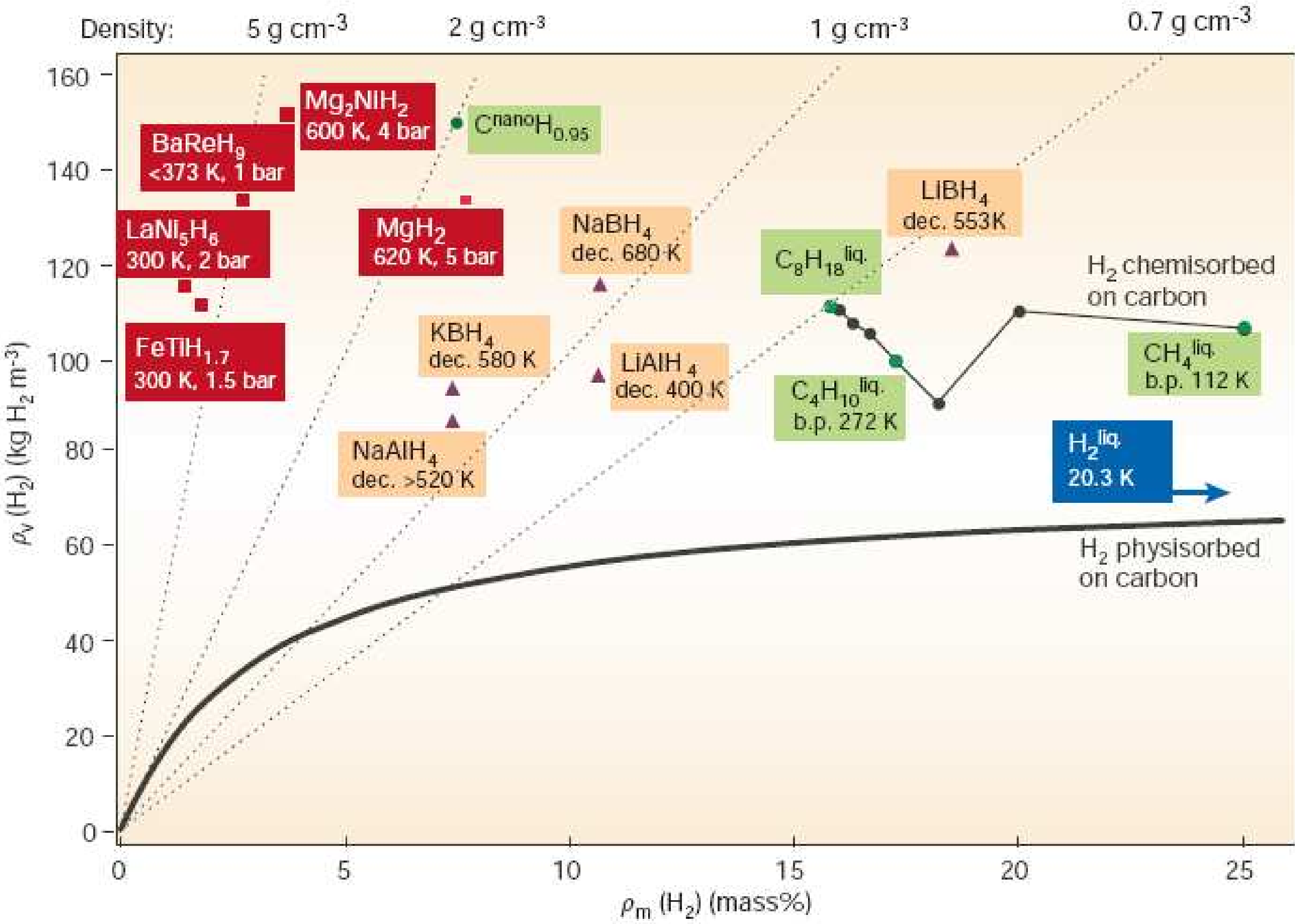
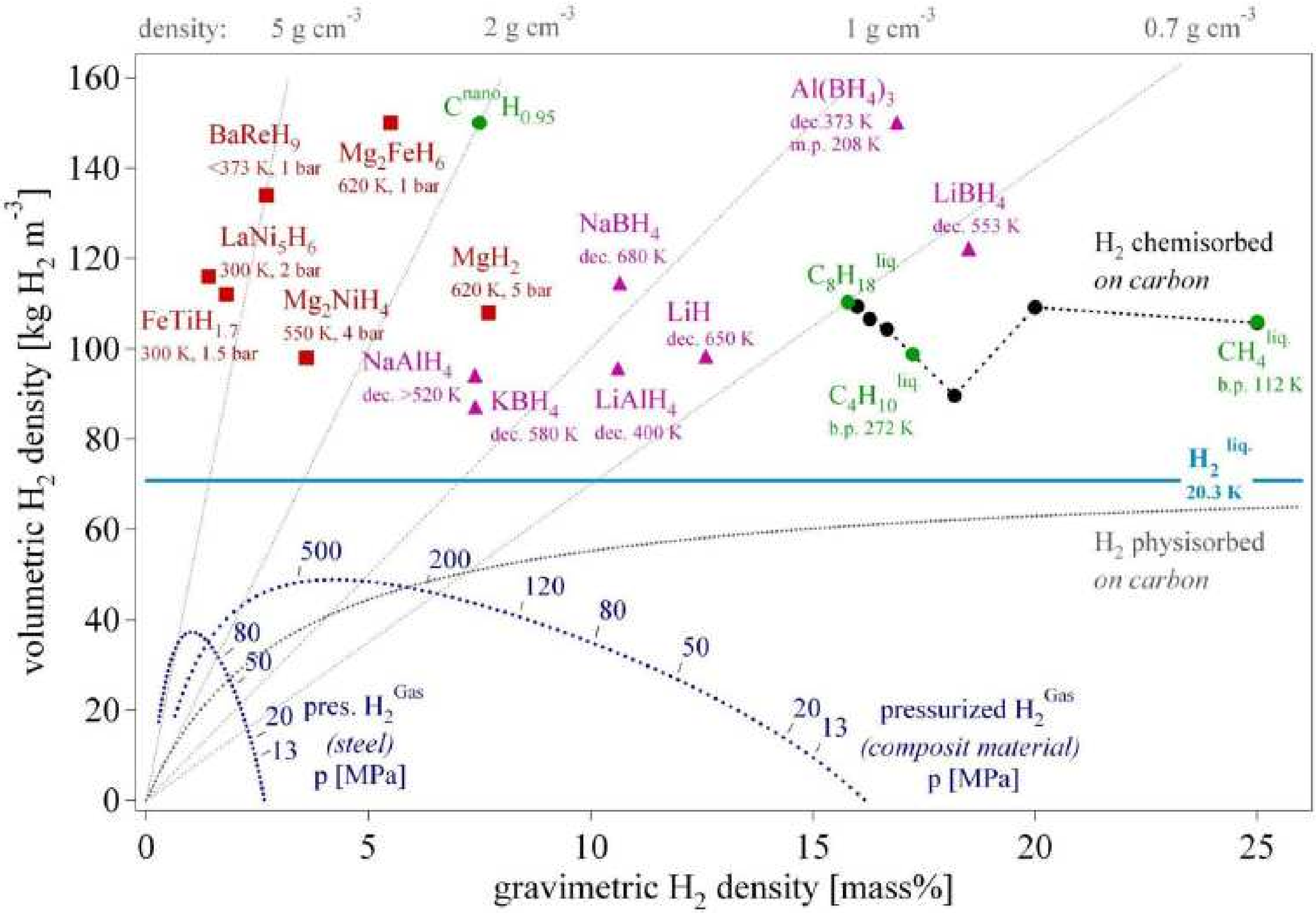


Table 2 Intermetallic compounds and their hydrogen-storage properties[22]

Type	Metal	Hydride	Structure	mass%	p_{eq}, T
Elemental	Pd	$PdH_{0.6}$	*Fm3m*	0.56	0.020 bar, 298 K
AB_5	$LaNi_5$	$LaNi_5H_6$	*P6/mmm*	1.37	2 bar, 298 K
AB_2	ZrV_2	$ZrV_2H_{5.5}$	*Fd3m*	3.01	10^{-8} bar, 323 K
AB	FeTi	$FeTiH_2$	*Pm3m*	1.89	5 bar, 303 K
A_2B	Mg_2Ni	Mg_2NiH_4	*P6222*	3.59	1 bar, 555 K
Body-centred cubic	TiV_2	TiV_2H_4	b.c.c.	2.6	10 bar, 313 K

Varying operating conditions

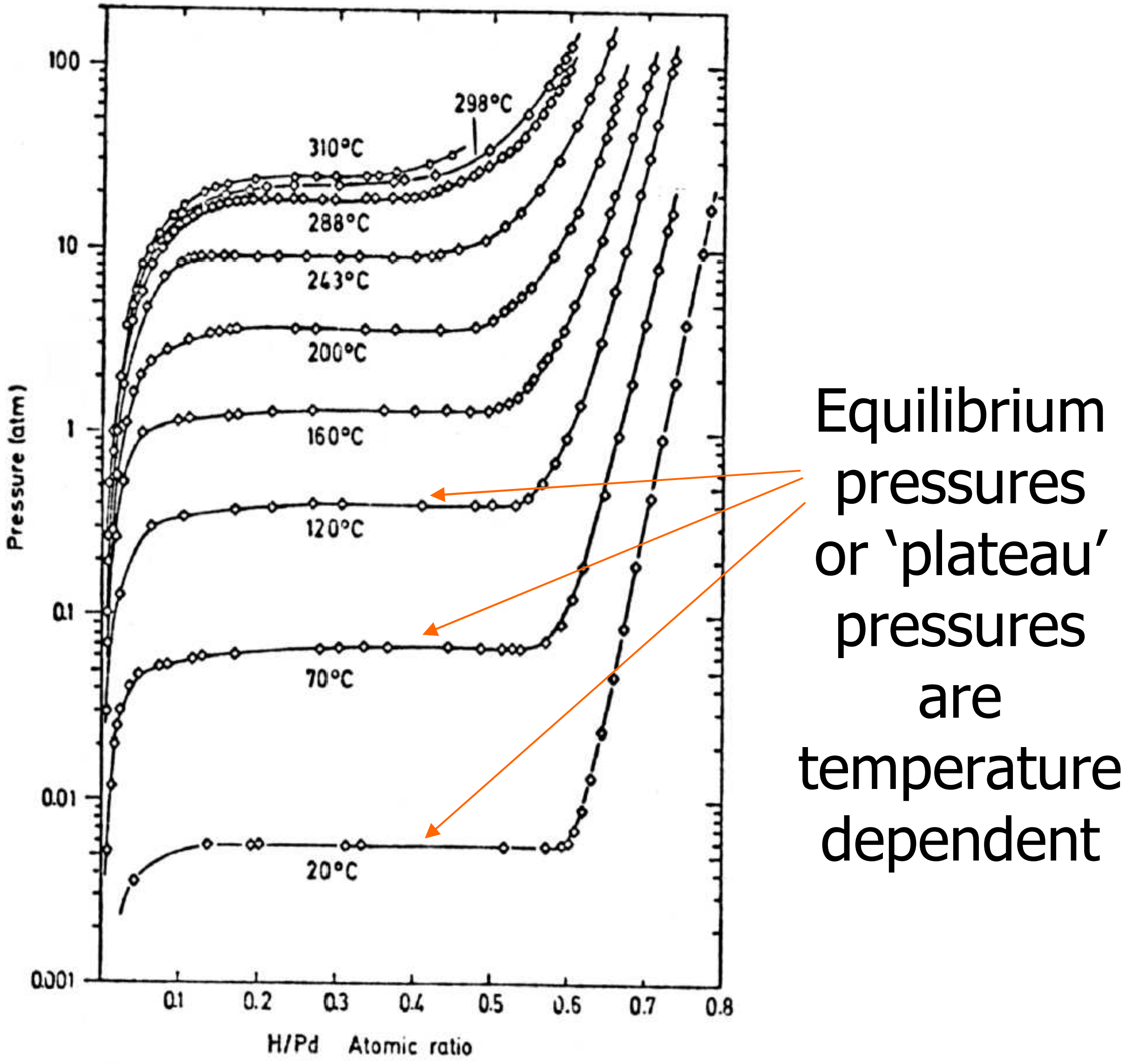

Density:
5 g cm-3
2 g cm-3
1 g cm-3
0.7 g cm-3
Mg_2NiH_2 600 K, 4 bar
$C^{nano}H_{0.95}$
$BaReH_9$ <373 K, 1 bar
$LaNi_5H_6$ 300 K, 2 bar
MgH_2 620 K, 5 bar
$NaBH_4$ dec. 680 K
$LiBH_4$ dec. 553K
C_8H_{18} liq.
H_2 chemisorbed on carbon
$FeTiH_{1.7}$ 300 K, 1.5 bar
KBH_4 dec. 580 K
$LiAlH_4$ dec. 400 K
CH_4 liq. b.p. 112 K
C_4H_{10} liq. b.p. 272 K
$NaAlH_4$ dec. >520 K
H_2 liq. 20.3 K
H_2 physisorbed on carbon
ρ_v (H_2) (kg H_2 m^{-3})
ρ_m (H_2) (mass%)
0
20
40
60
80
100
120
140
160
0
5
10
15
20
25



Comparison with pressurized gas cylinders

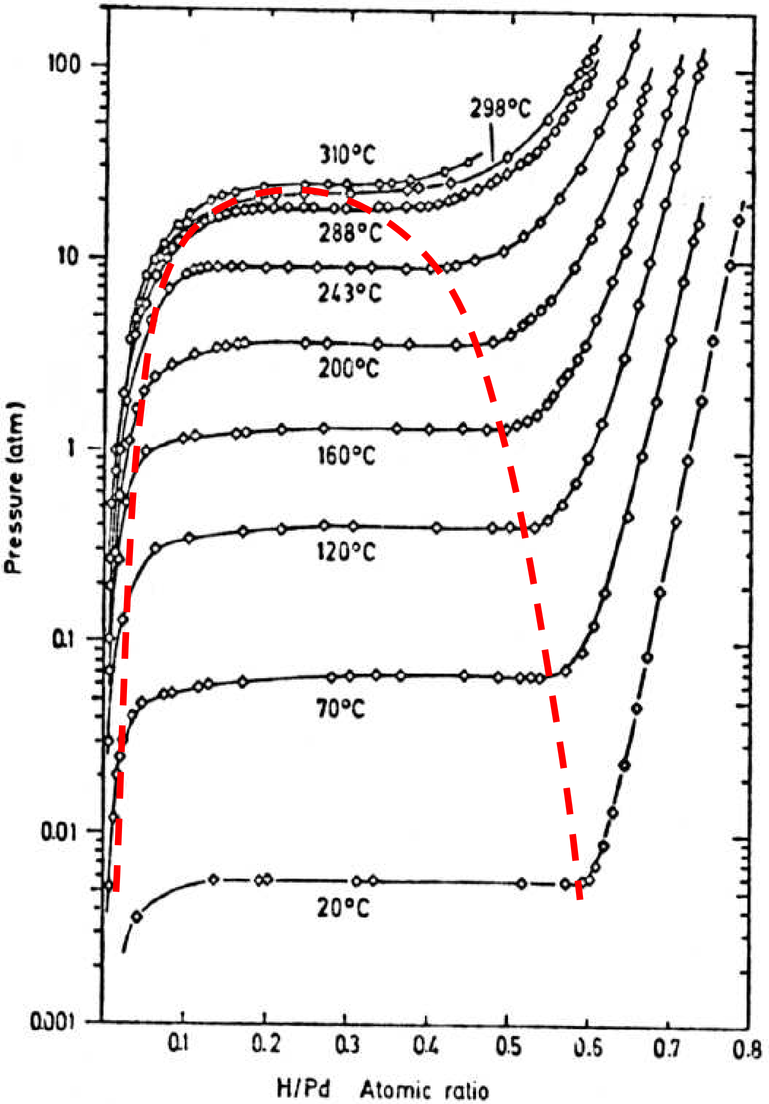
H in Pd metal

Loading does not
occur with continuously
increasing pressure,
but with steps during
which the pressure can
remain constant.
This is caused by the
occurrence of specific
crystalline phases
that are in equilibrium
with each other.
For Pd there is one such
step/plateau.

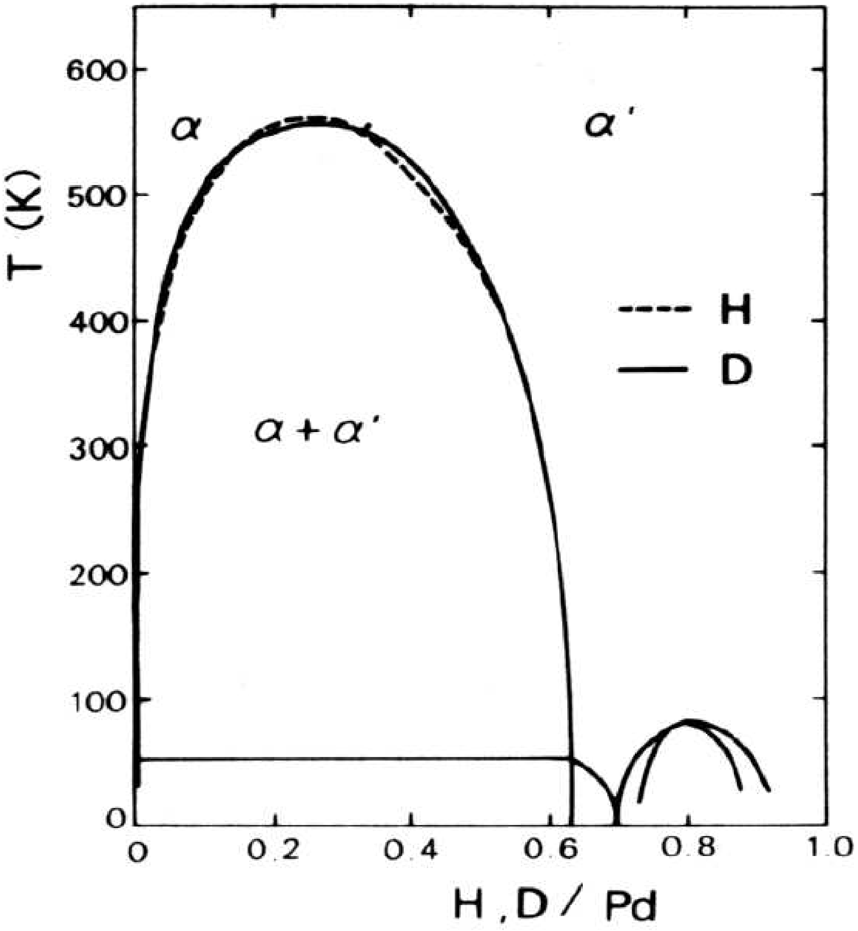


Equilibrium
pressures
or ‘plateau’
pressures
are
temperature
dependent

H in Pd metal



α is a H-poor phase, α′ a H rich phase. Below the parabola they occur next to each other.



The reason for the phase separation into 2 phases is the same as for Li-insertion compounds (see batteries)

The enthalpy and entropy of metal hydride formation; van 't Hoff equation

Hydrogen that reacts with a metal has the reaction:

$\frac{1}{2}H_2$ (in gas phase) $\rightarrow$ H (in metal hydride)

General Gibbs free energy change upon reaction:

$\Delta G = \Delta H - T\Delta S$

Now upon adding hydrogen atoms to the metal hydride the chemical potential of the added atoms is defined as:

$$\mu_H = \left(\frac{\partial G}{\partial n_H} \right)_{n_M, P, T}$$

Where n_H, n_M, are the number of hydrogen and metal ions involved.

At equilibrium between the gas phase and metal hydride phase, there is no difference for a hydrogen atom to enter the gas or the hydride phase so:

It costs less energy to put 2H atoms in the gas because they react to H_2 producing E_{diss}

$$\mu_{H-in-gas} = \frac{1}{2}\mu_{H_2-in-gas} - E_{diss.}$$

$$\mu_{H-in-gas} = \mu_H$$ when gas and hydride are in equilibrium

Where μ_{H2} and μ_H are the chemical potential of the H_2 molecules in the gas phase and the H atoms in the hydride phase respectively. $E_{diss.}$ is the dissociation energy of the H_2 molecule in 2 H's.

$$\Delta\mu_H = \Delta\bar{H}_H - T\Delta\bar{S}_H$$

where $\Delta\bar{H}_H, \Delta\bar{S}_H$ are the partial molar enthalpy and entropy of the hydride formation. $\Delta\mu_H$ is the chemical potential of one mole H (not a single molecule)

In SHEES5 (p32) we saw that compressing the H_2 gas required an energy:

$$W = nRT \ln \frac{P_0}{P_1}$$

The chemical potential of the gas (per molecule now) equals: (with $N_A k_B = R$)

$$\mu_{H_2} = \mu_{H_2}^0 + k_B T \ln\left(\frac{P}{P_0}\right)$$

Where p_0, μ^0_{H2} equal respectively a reference pressure (e.g. 1Bar), and the chemical potential for adding a single molecule at p_0.

The change in chemical potential in the metal - hydrogen reaction is:

$$\Delta\mu_H = \mu_H - \frac{1}{2}\mu^0_{H_2} + E_{diss.}$$

So

$$\Delta\mu_H = \mu_H - \frac{1}{2}(\mu_{H_2} - k_B T \ln\left(\frac{P}{P_0}\right)) + E_{diss.}$$

Because in equilibrium: $\frac{1}{2}\mu_{H_2} - E_{diss} = \mu_H$

This leads to: $\Delta\mu_H = \frac{1}{2}k_B T \ln\left(\frac{P}{P_0}\right)$

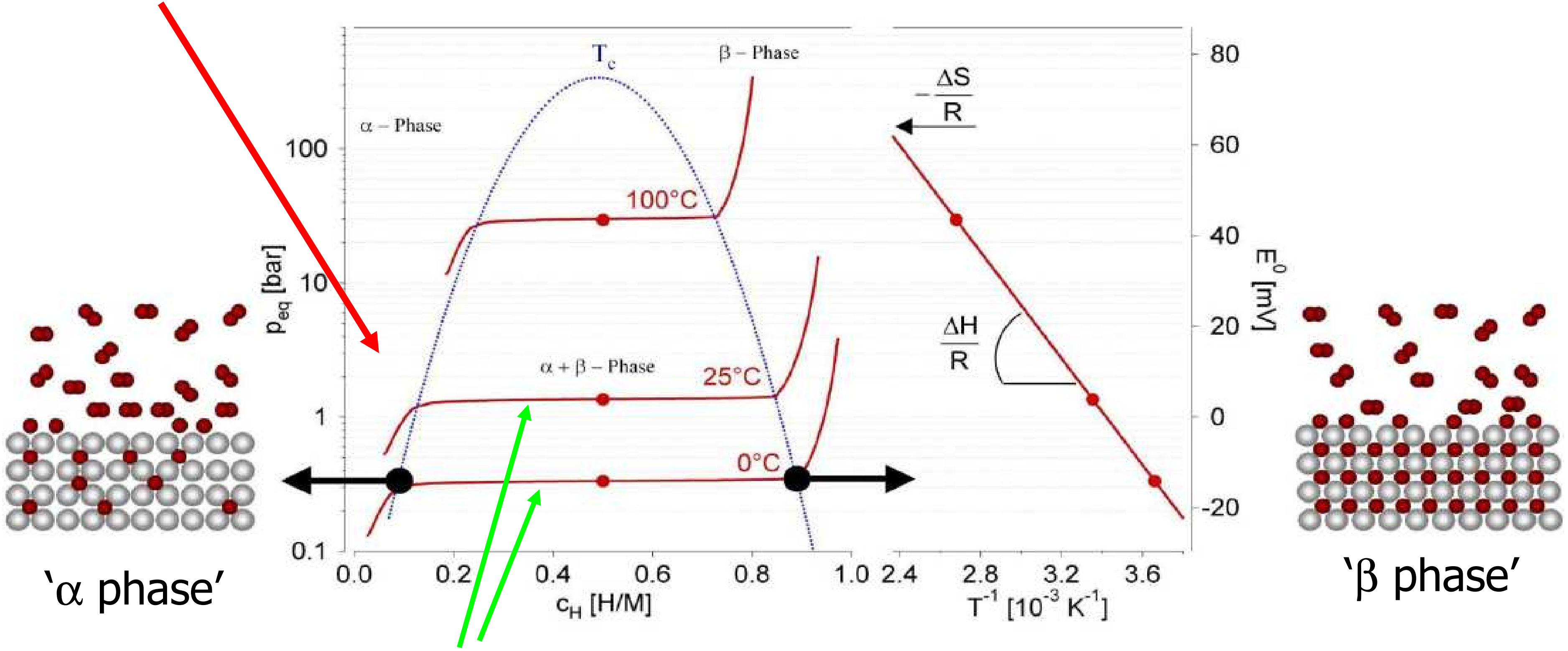
Using $\Delta\mu_H = \Delta\bar{H}_H - T\Delta\bar{S}_H$ we obtain the

Van ‘t Hoff equation $\frac{1}{2}\ln\left(\frac{P}{P_0}\right) = \frac{\Delta\bar{H}_H}{k_B T} - \frac{\Delta\bar{S}_H}{k_B}$

A graph of $ln(P/P_0)$ versus $1/T$ will show a line that has a slope related to the enthalpy of formation ΔH_H and an axis 1/T=0 intercept related to the entropy change ΔS_H upon hydride formation at pressure P_0.
Such graph is called van’t Hoff plot.

Van ‘t Hoff equation in practice

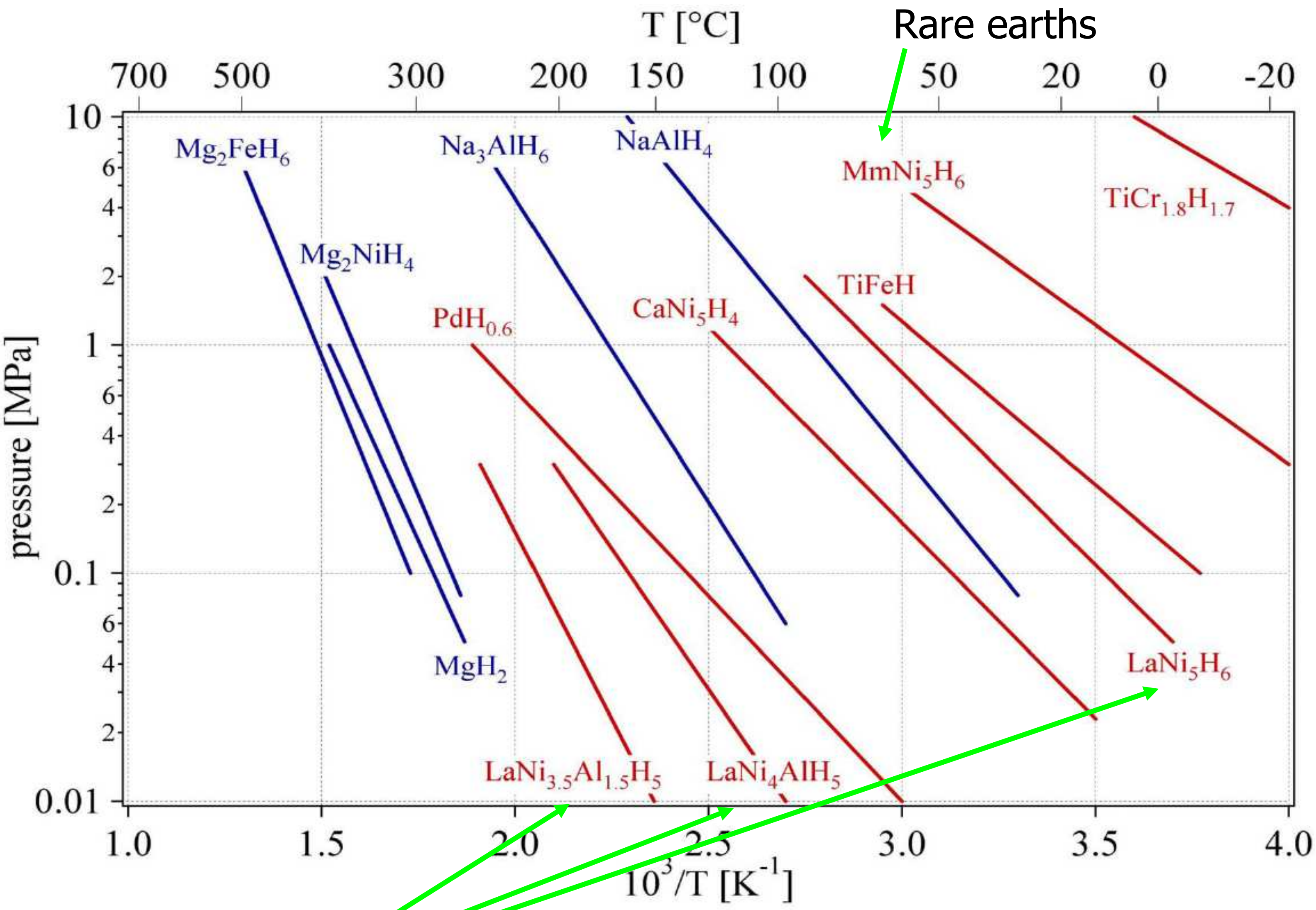
Left from the parabola the pressure is too low to reach the β phase



Here there is equilibrium between gas, α, and hydride β phase. The α phase corresponds to the normal metal with some dissolved H in it, but too little to form the real hydride.

Van 't Hoff plots for some metal hydrides

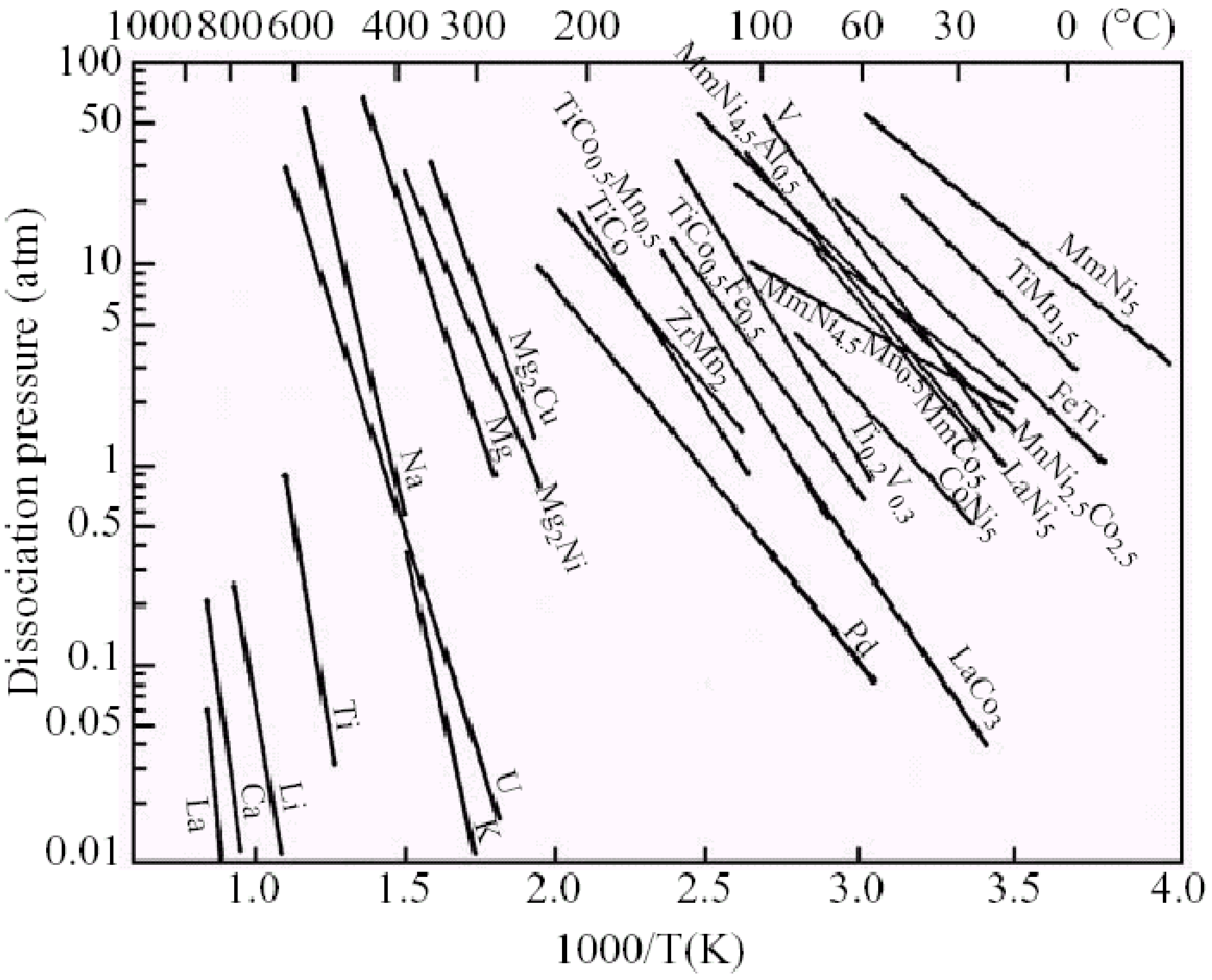
Misch metal: mixture of Rare earths



More Al leads to higher stability of hydride: lower P at same T

Some more van 't Hoff plots

The steeper the slope the higher the enthalpy of formation, the more stable the hydride



LiH: high capacity ~ 1/8 = 12.5 wt.%

However: very stable, equilibrium pressure of 0.1 Bar at 1000 K.

So unfortunately this is not a suitable storage material.

‘General’ phenomena during gas absorption and desorption in metal hydrides

- first: dissolving hydrogen in the α phase (H-poor)

- second: subsequent hydride formation: β phase, H-rich

- dumping/withdrawal of formation enthalpy causes heating/cooling, can be very significant. *This can directly limit the hydrogen uptake/release speeds.*

- swelling of the crystal lattice: about 3 Å^3 per H atom. For instance $LaNi_5$ swells 25% upon hydrogen uptake to $LaNi_5H_{\sim 6}$!!! To put this in perspective: one would require a pressure of ~200kBar to compress a solid like this by 25%: very high strains on the material

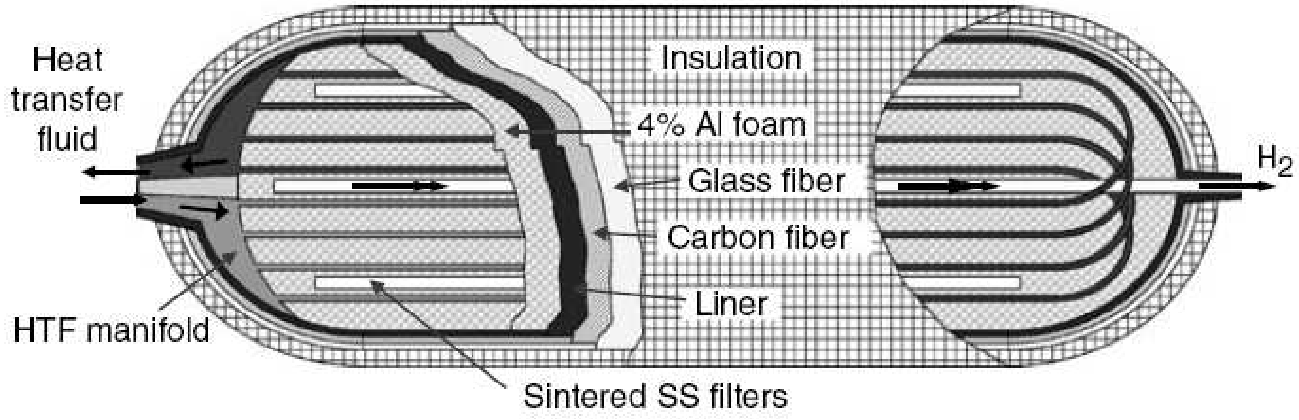
- the hydride phases and intermetallic compounds are often brittle. This together with the swelling can cause beak down of the crystallites in pieces.

- kinetics of hydrogen uptake/release can depend strongly on the type of metal hydride. It will depend on how fast H atoms can diffuse through the α and β phase.

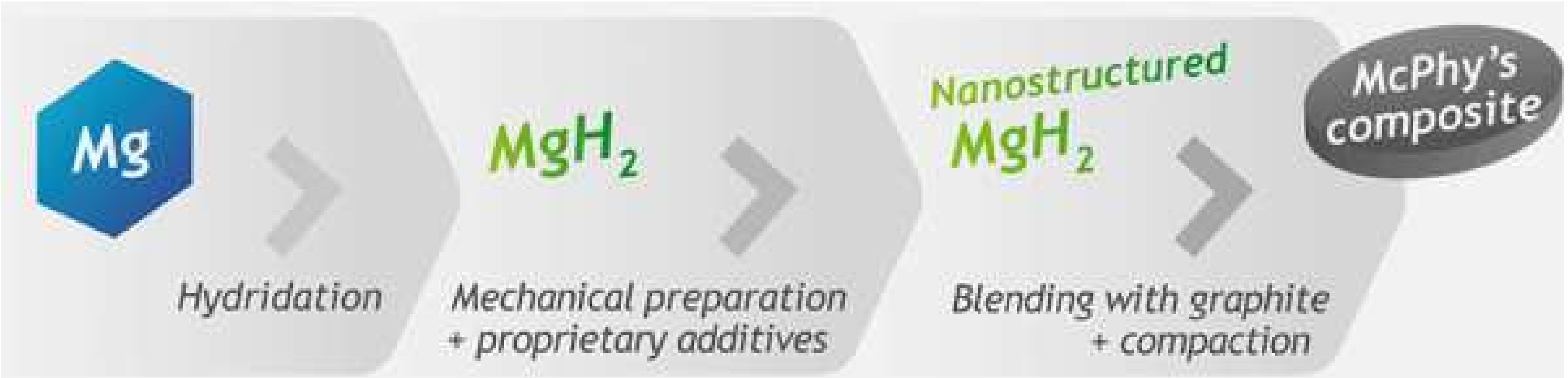
Strong interactions: negative ΔH and operating conditions

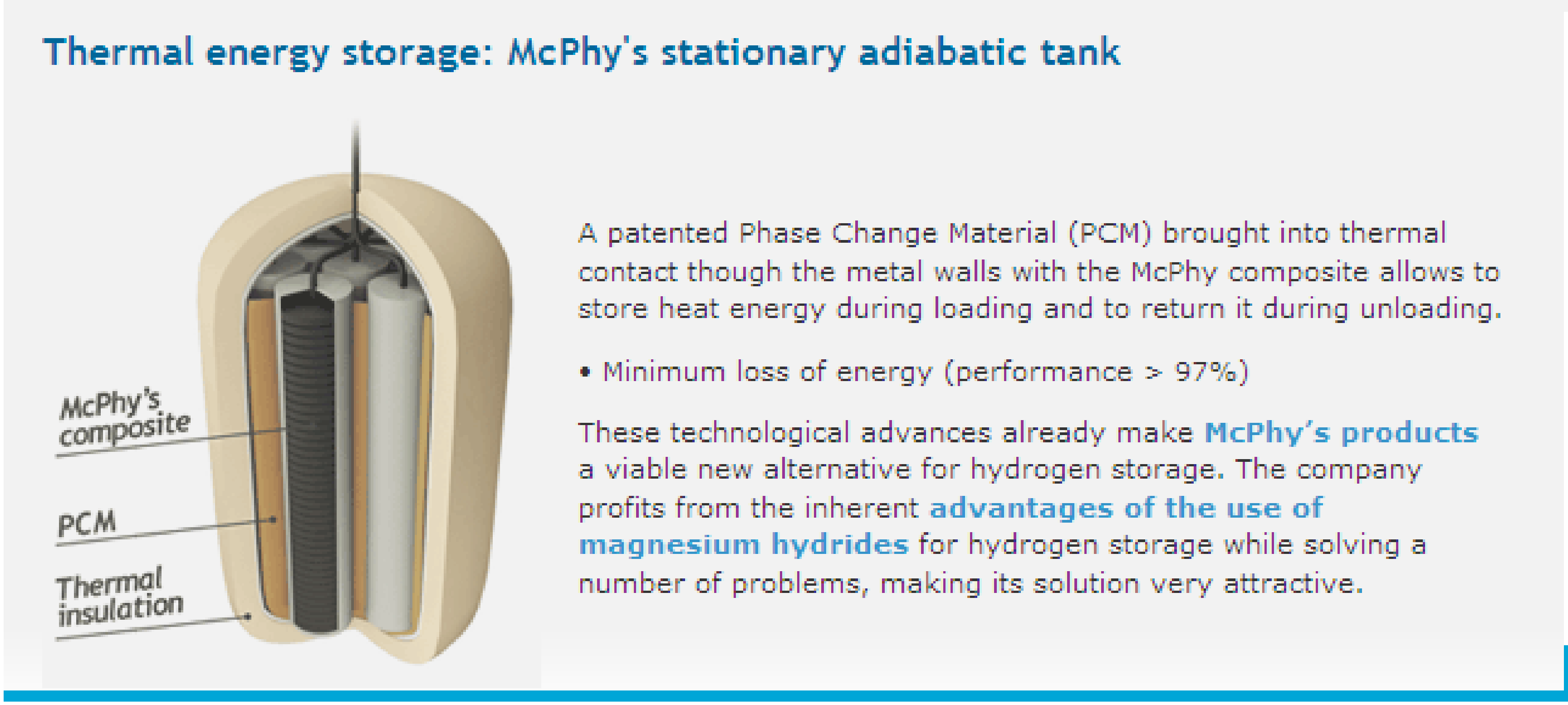
Observing the large negative ΔH for materials like MgH_2 (-77 kJ/mol H_2): Loading H_2 rapidly will cause heating effects since heat is released!

For coping with thermal heating effect during H loading: One incorporates heat exchangers in storage tanks. These exchangers can also supply heat during H release.



Store heat in additional heat storage material: then also available for later use





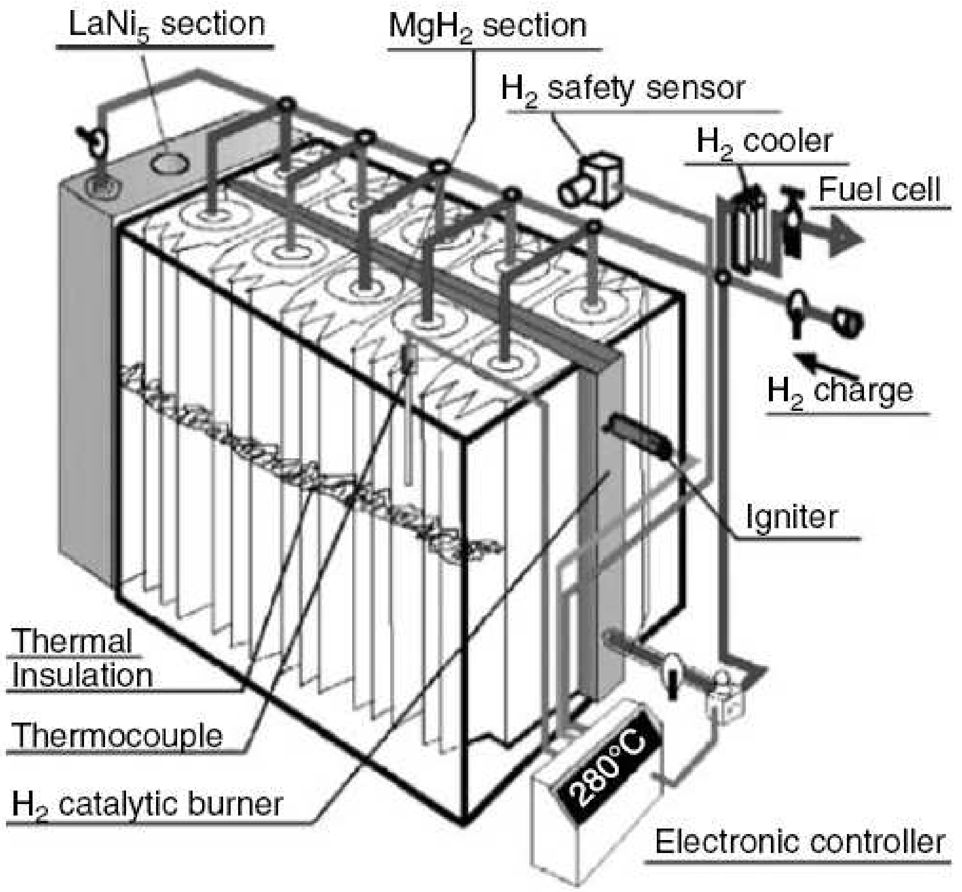
Thermal energy storage: McPhy's stationary adiabatic tank

A patented Phase Change Material (PCM) brought into thermal contact though the metal walls with the McPhy composite allows to store heat energy during loading and to return it during unloading.

- Minimum loss of energy (performance > 97%)

These technological advances already make **McPhy's products** a viable new alternative for hydrogen storage. The company profits from the inherent **advantages of the use of magnesium hydrides** for hydrogen storage while solving a number of problems, making its solution very attractive.

$LaNi_5$ for 'cold start', MgH_2 for most H_2 release when heated up



Currently commercial relevant metal hydride for hydrogen storage:

$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}H_{5.18}$ as used in **nickel metal hydride batteries**:

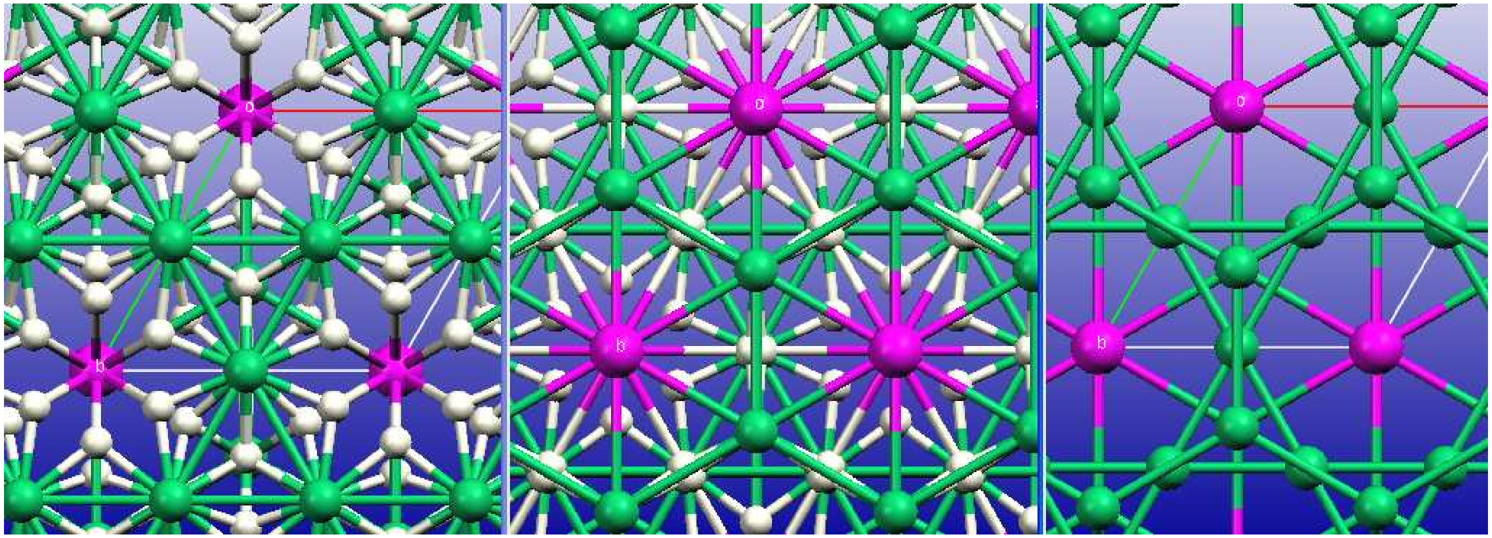
Drawbacks of the pure binary compound $LaNi_5$ for a battery:

- La is too expensive because it is always mined together with chemically similar (i.e. expensive to separate) other rare earths.
- has fairly low stability, i.e. at elevated T H_2 gas evolution (50 °C ~ 1Bar)
- it has a large lattice expansion upon H storage
- it corrodes heavily in a battery

Solutions:

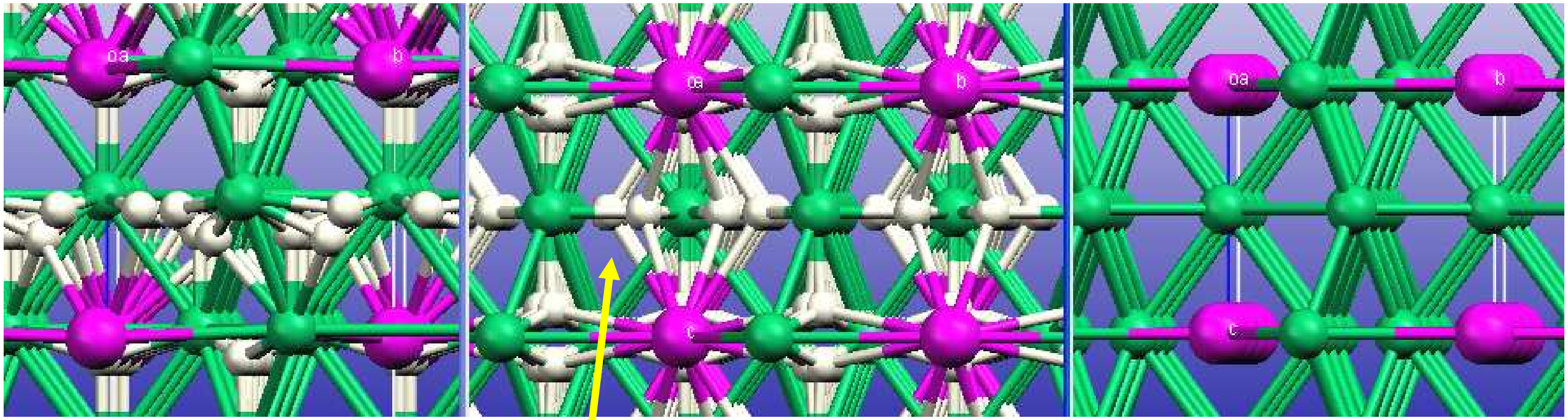
- use Misch metal (Mm), a cheap mixture of rare earths
- use Al substitution of Ni to strengthen H binding and reduce corrosion. Corrosion appears to be related to lattice expansion, i.e. the volume change upon H uptake. Also Al oxide at the surface reduces corrosion.
- exchange Ni with some transition metal, this reduces expansion somewhat
- Co appears to limit corrosion. Not too much Co because it is expensive
- H capacity reduced from $\sim H_{6.5}$ to $\sim H_{5.2}$

View
along
c-axis

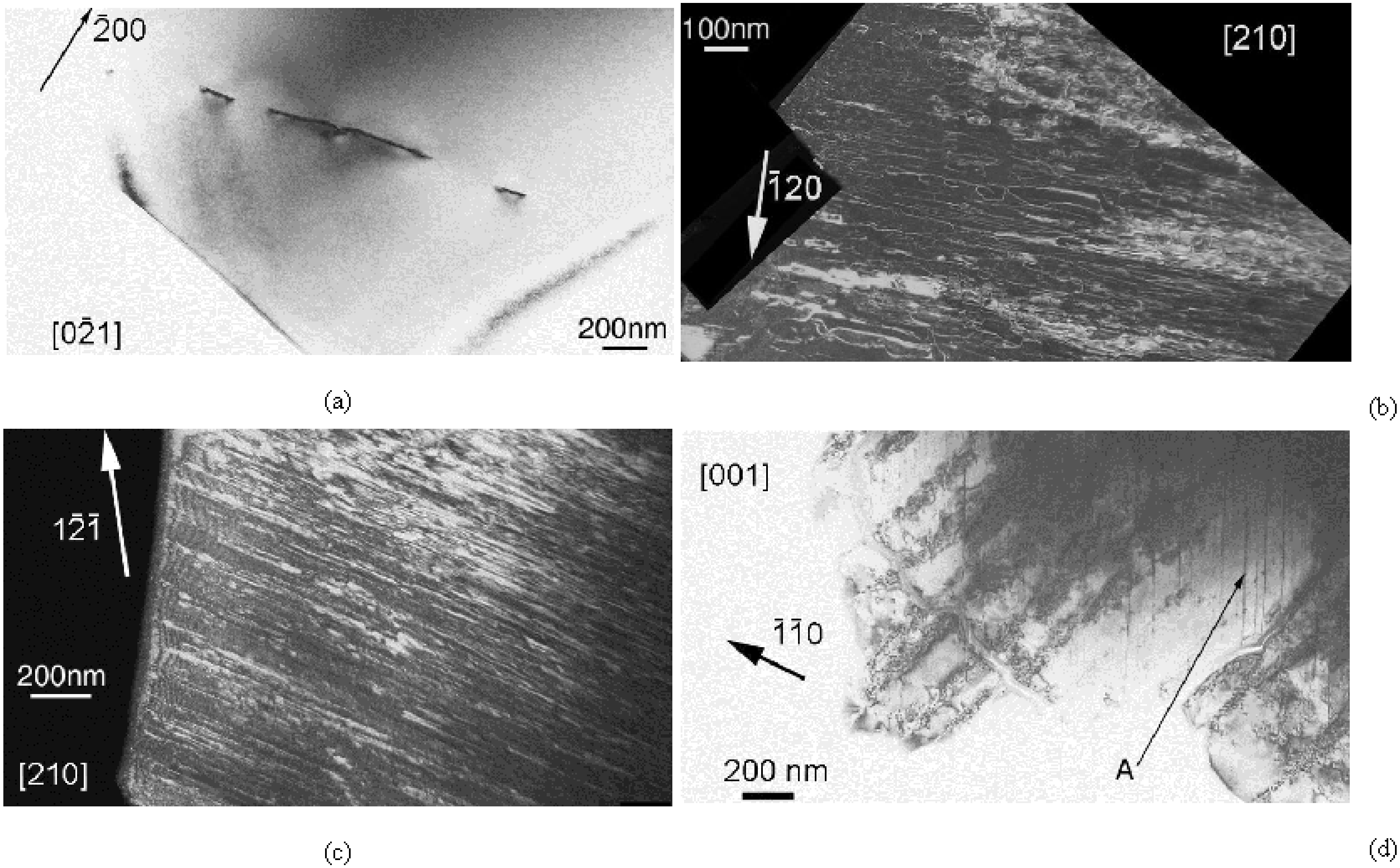


$LaNi_5H_{6.5}$ $LaNi_5H_{0.5}$ $LaNi_5$

View
along
a-axis



Looks like a lot of H atoms, but these
sites are only fractionally occupied



TEM pictures after cycling

(a) $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ (b)$LaNi_5$ (c) $LaNi_{4.25}Co_{0.75}$ (d) $LaNi_4Mn$

Surface activation of the hydride:

Many metal hydrides consist of corrosive materials where the surface can e.g. be oxidized. In $LaNi_5$ this is the case. Because of the large lattice expansion the material breaks in small pieces and clean surfaces are exposed to the gas. In that way the problem solves itself after the first difficult loading cycles: this is called ‘activation’.

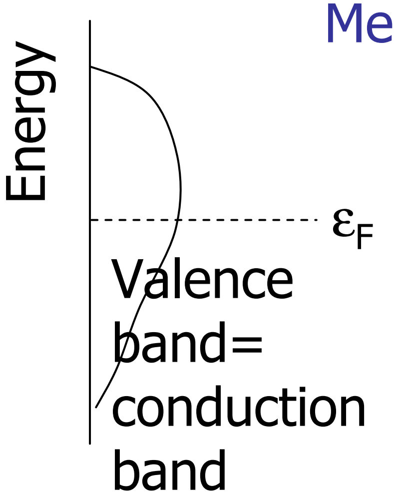
Some other materials can be loaded better by applying catalysts at the surface. Mg is an example. Here the idea is that the catalyst penetrates the MgO oxide layer and also splits hydrogen. Typical catalyst: V, Nb or Ti, i.e. hydride forming metals. Later more.

Electronic structure changes upon hydrogen absorption

The metals without hydrogen load are metallic. This means that the valence electrons are in a conduction band in which they are free to move. This leads to a high electrical conductivity. In addition metals reflect most if not all light that shines on it.

The hydrides can have a completely filled conduction band.
Examples are MgH_2 and YH_3. This leads to poor conductivity/ high resistivity, and it can also lead to a material which is transparent for light.

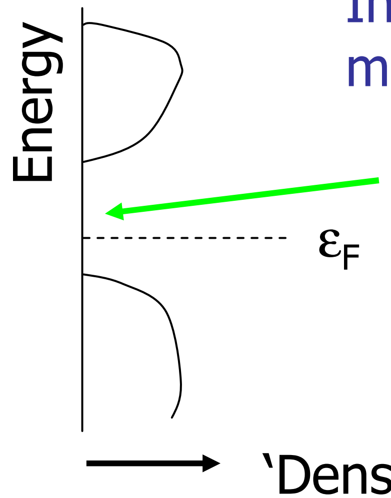
Metal



Valence band= conduction band

These electrons can easily be moved in applied field (low ‘excitations’ possible)

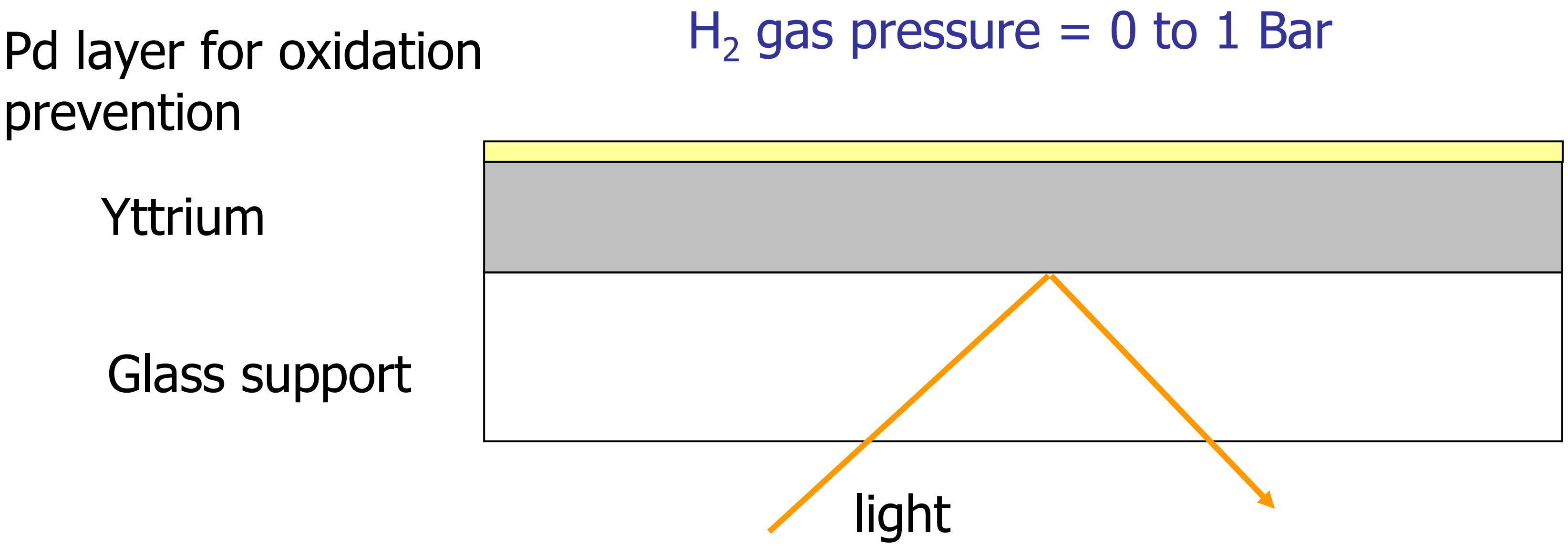
Insulating metal hydride



No electrons which can easily move in applied field

‘Density of states’, which indicates the number of electrons that have these energies

Example: Switchable mirrors as demonstrated by Huiberts et al. (Free University Amsterdam)



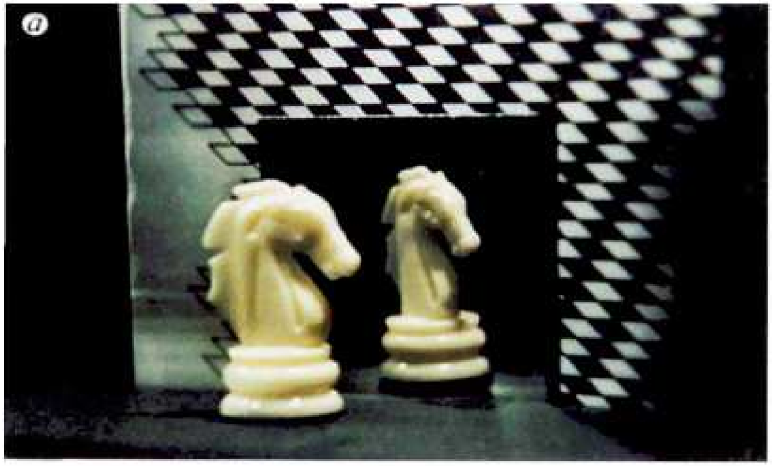
H_2 gas pressure = 0 to 1 Bar

Pd layer for oxidation prevention

Yttrium

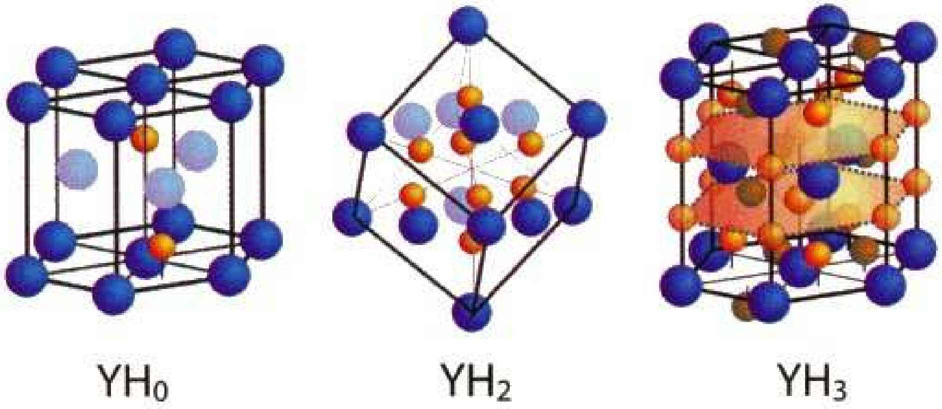
Glass support

light



Yttrium before H_2 admittance

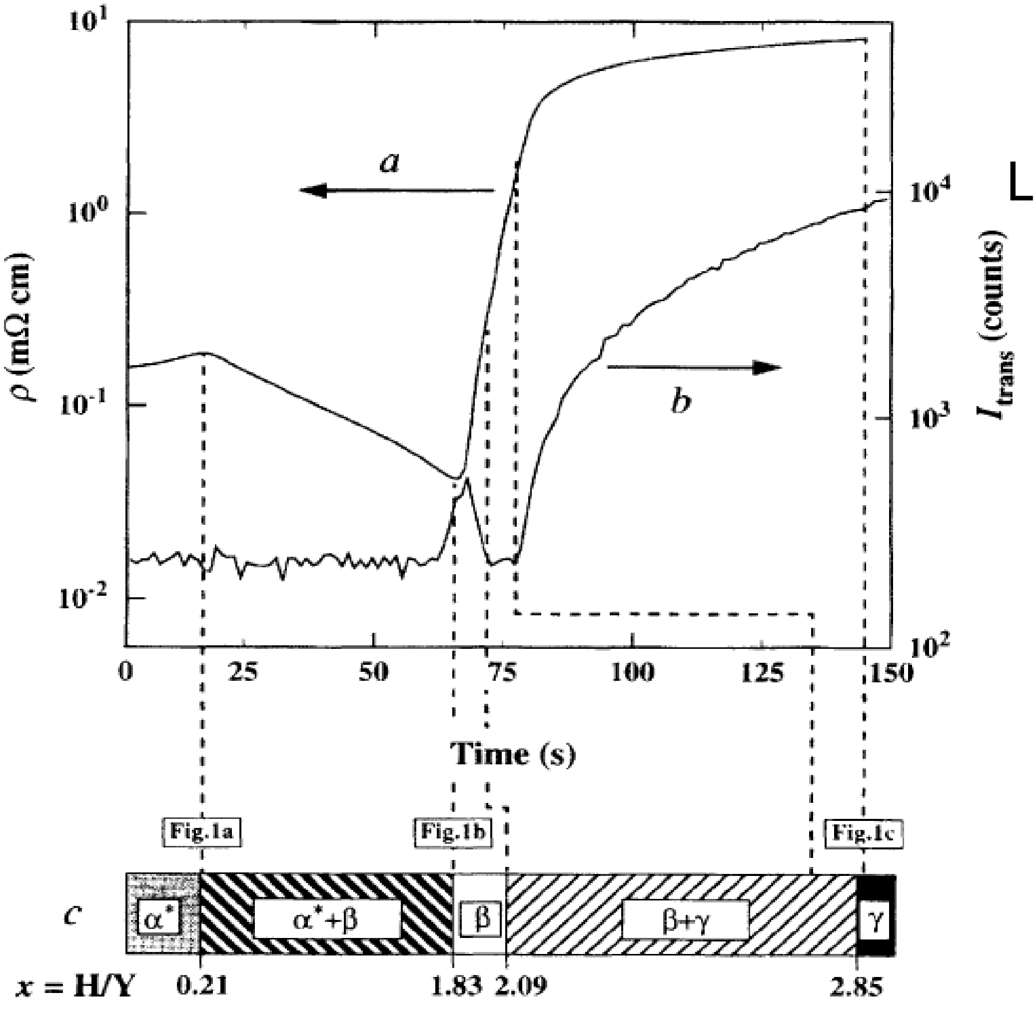
After partial loading $YH_{\sim 2}$, still metallic



YH_3 transparent insulator

Huiberts et al. Nature 380 (1996) 231.

resistivity

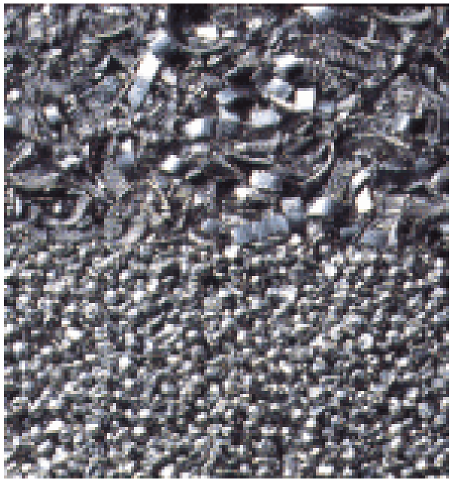


Light transmission

Y

$YH_{\sim 2}$

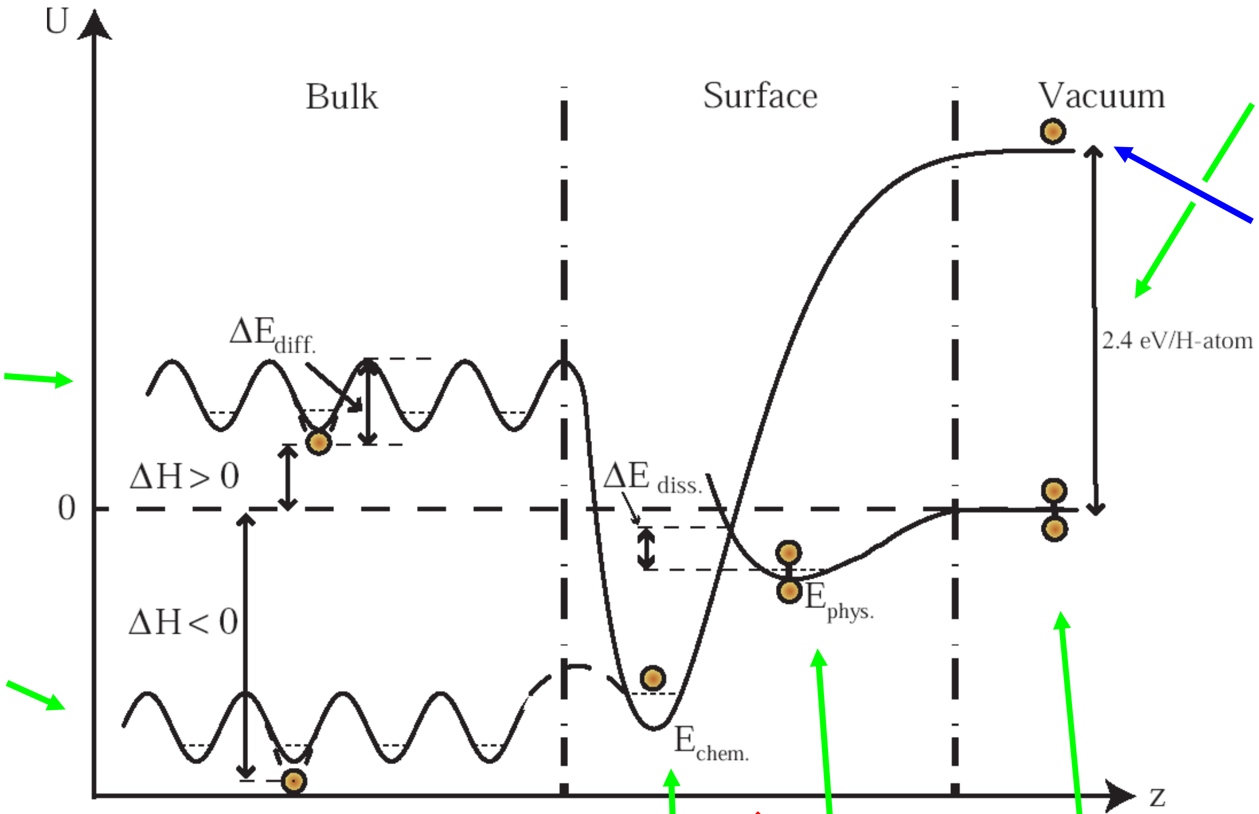
$YH_{\sim 3}$



Magnesium metal

whitish, transparent and insulating MgH_2

Energy landscape for adsorption, dissociation and binding of H_2 at a metal hydride surface



Unstable interstitial H atoms

Stable chemical hydride

Energy required to split H2 and release a single H atom from surface

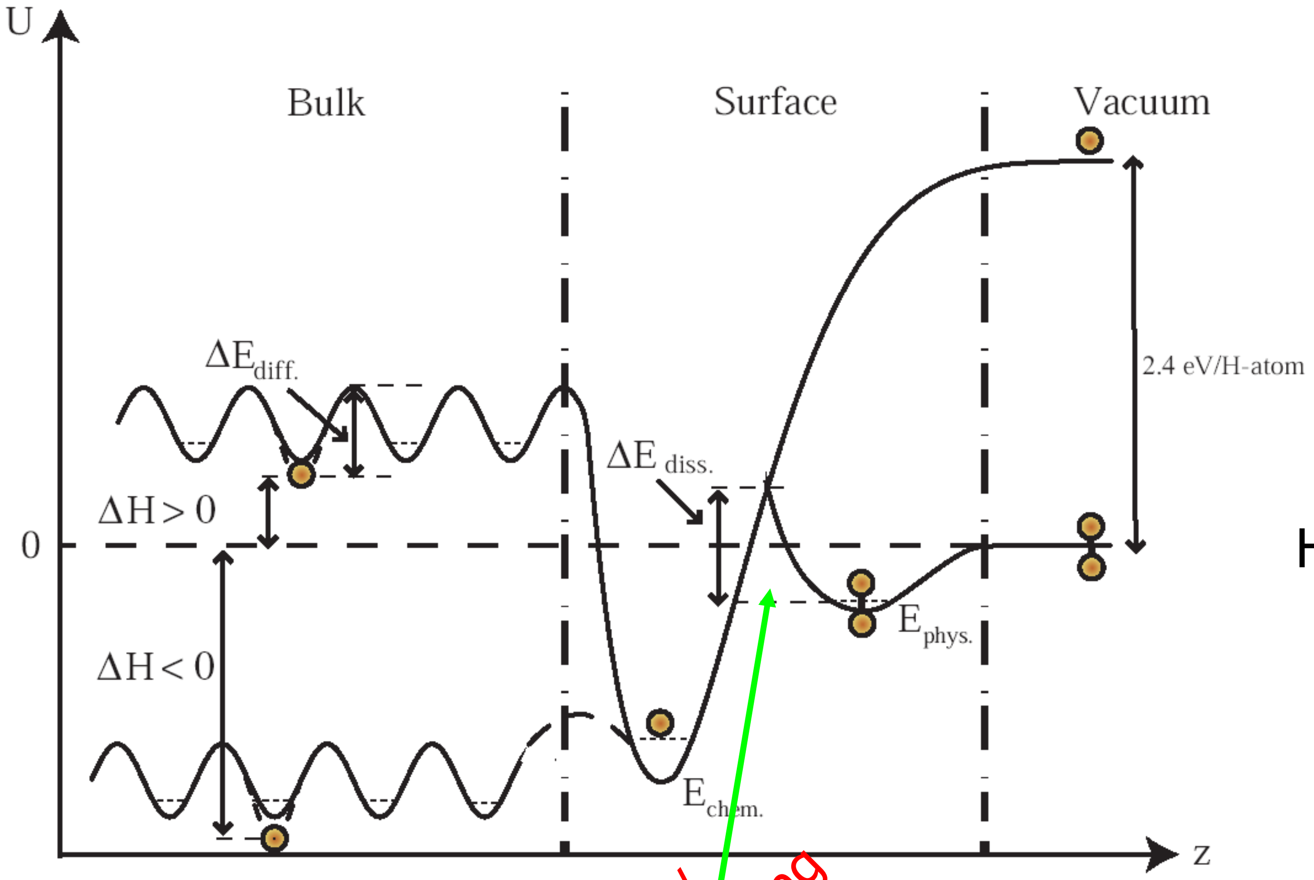
z = distance to surface

Dissociation/ Chemical binding

Adsorption

Gas phase

Same energy landscape but now with barrier for dissociation



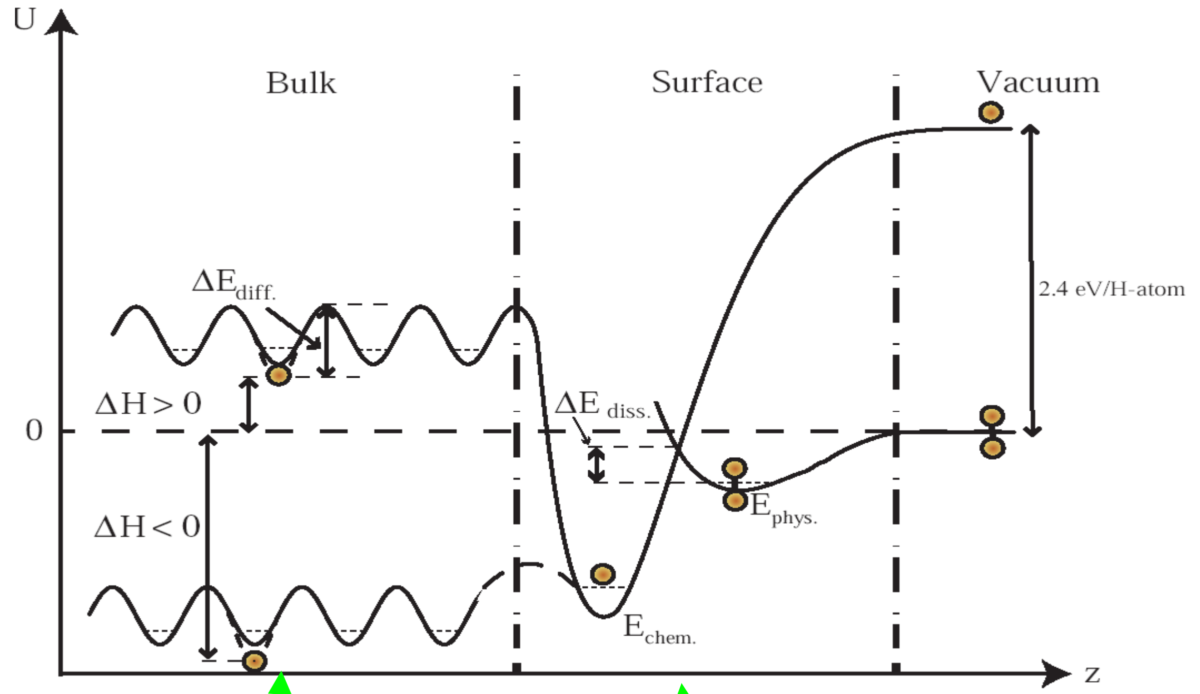
2 H atoms

H2 molecule

Dissociation/
Chemical binding

Here there is a barrier and in the previous graph not

H dynamics relevant for loading/unloading a metal hydride, rate limiting steps?



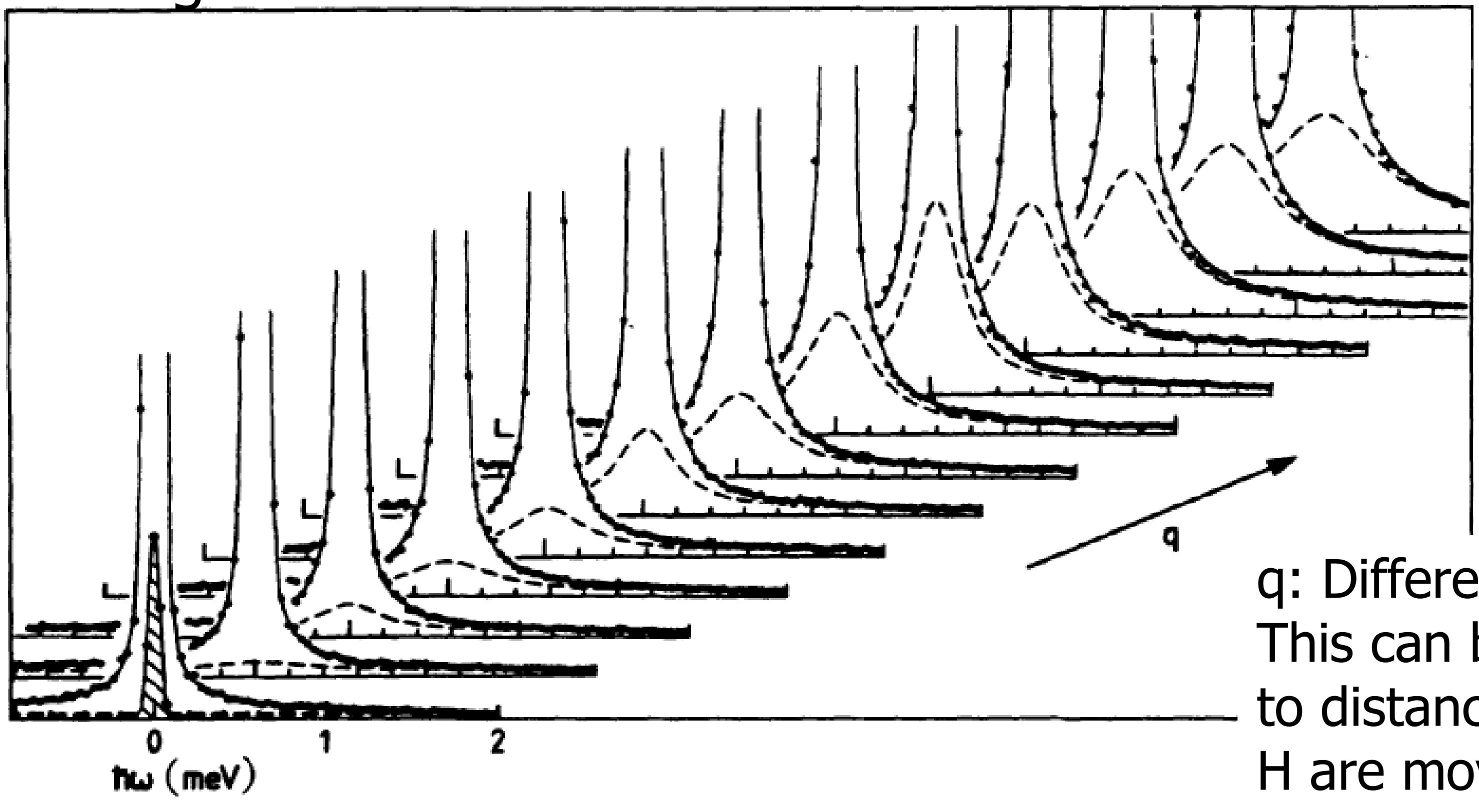
The potential energy landscape in the crystal determines the H diffusion rates

Surface ‘activation’ may be required to enhance splitting

Gas phase dynamics Will be fast

H dynamics relevant for loading/unloading inside the crystals

High hydrogen mobility in H diluted $LaNi_5H_{0.12}$. Hopping between sites on ps timescales. This is a 'quasi elastic neutron scattering measurement'



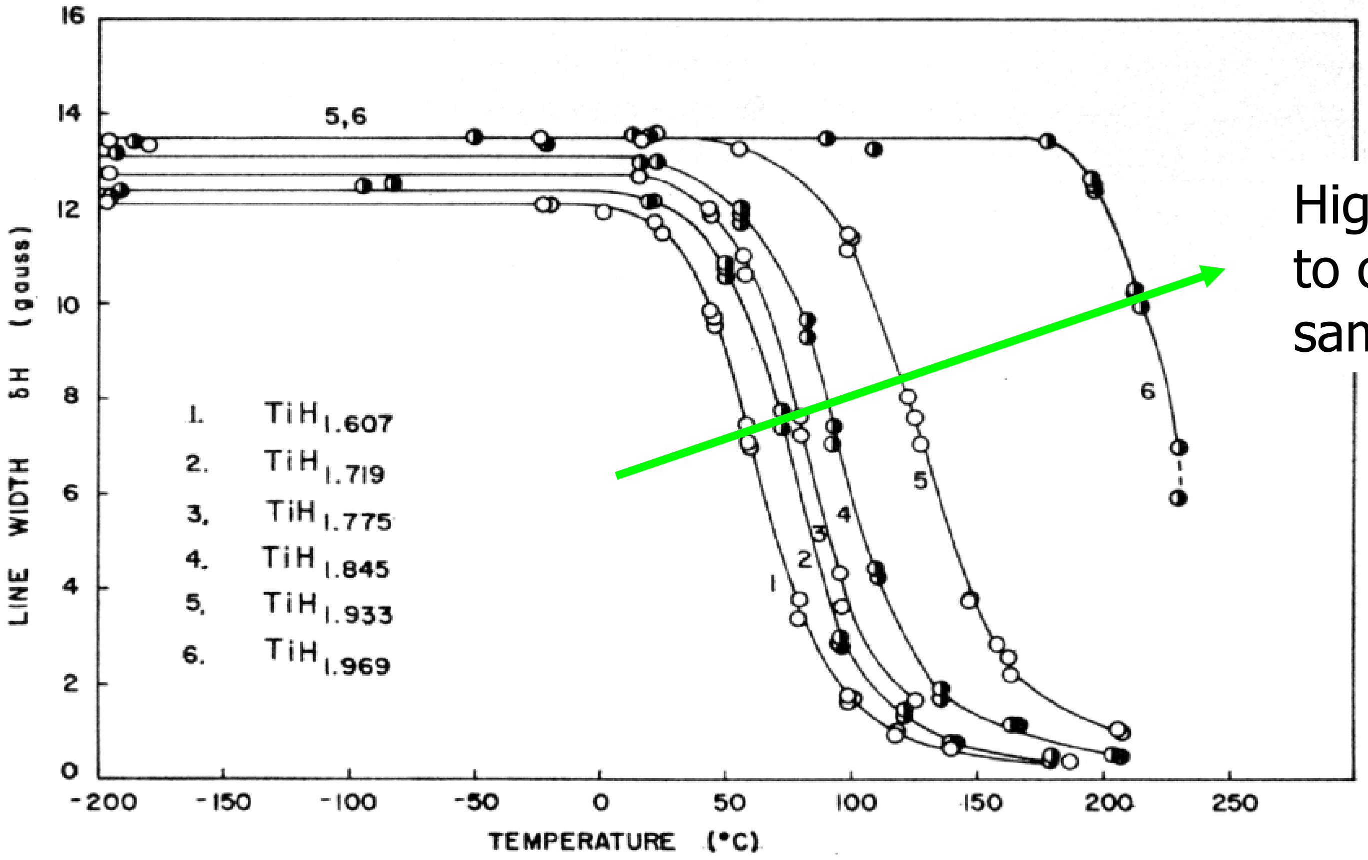
q: Different 'angles'. This can be translated to distances over which H are moving

ħω is the change of the neutron energy after collision with proton. It appears that because H are moving ħω can be different from 0 (H can give or take kinetic energy to/from neutrons).

Nuclear magnetic resonance

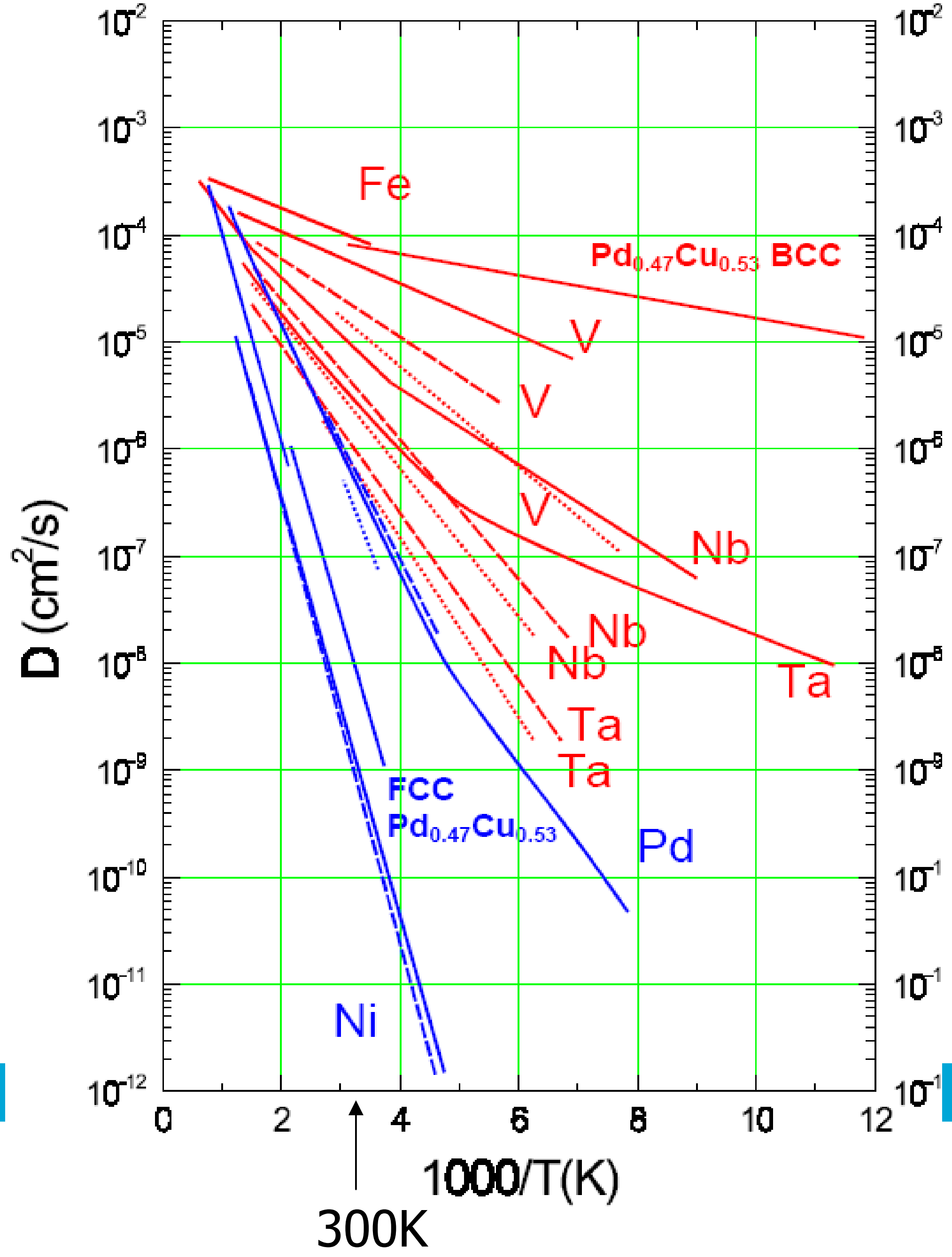
The linewidth of proton spectra becomes narrow when H start to diffuse.

For increasing H content higher T are needed because the crystal has fewer empty H sites.



Higher T required to obtain the same mobility

Measured diffusion constants D of H atoms in metals



Average distance r traveled by a proton during a time t can be estimated from:

$$r = \sqrt{\pi D t}$$

FCC structures

BCC structures

‘Classical’ metal hydrides: good but not good enough

Good:

- Favorable operating conditions possible: moderate pressures & temperatures
- Applicable in batteries (commercially available) and for gas phase storage
- Rapid loading and unloading possible
- Safe

Not good enough:

- Capacity in terms of wt.% lower than 2 wt.%
- Can be expensive
- Corrosion needs fine tuning
- Cooling and heating effects do play a role during sorption

New compounds are required: recently significant advances in light metal hydrides and complex hydrides

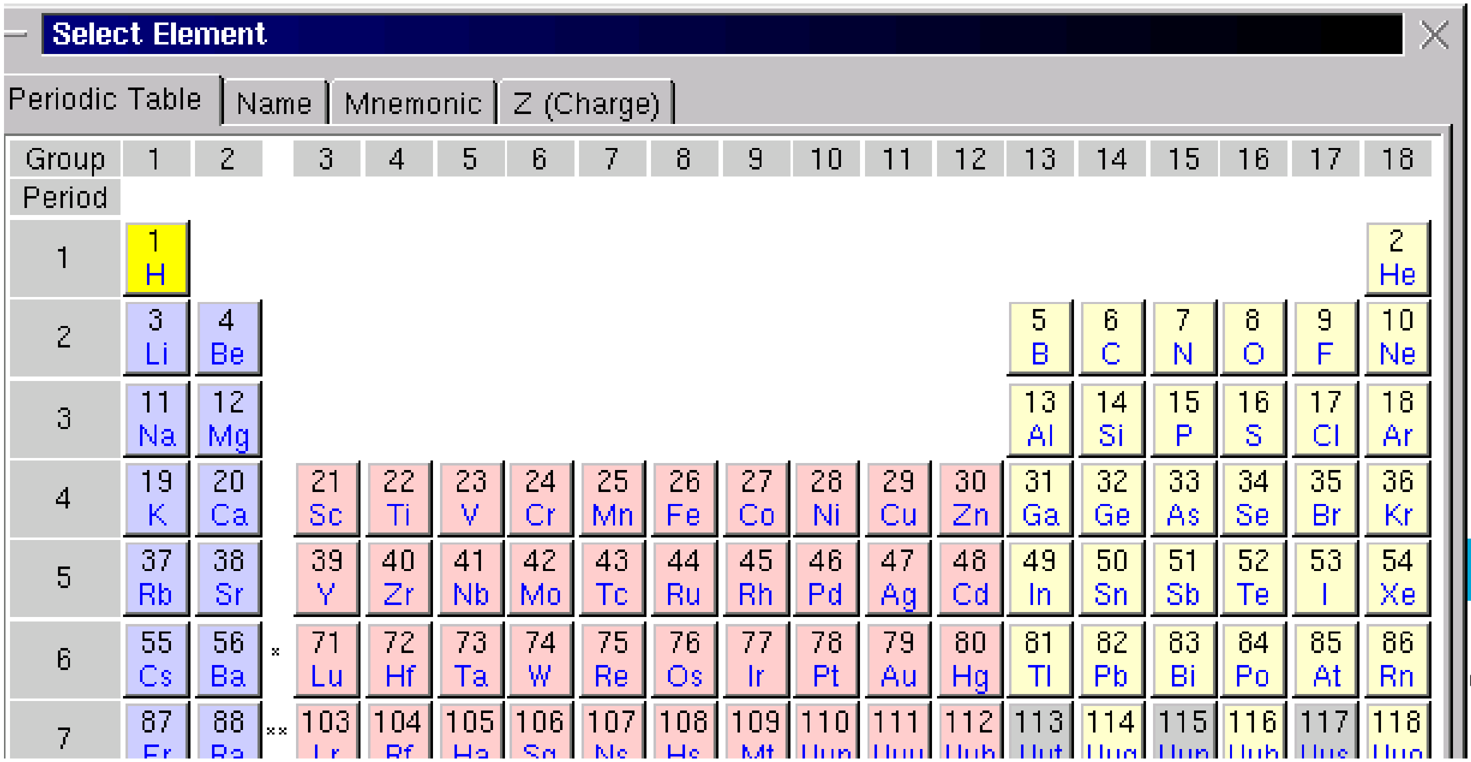
Light metal hydrides:

Elements to choose from, that are light enough:

Li, ~~Be~~, B, C, N, ~~O~~, ~~F~~, Na, Mg, Al

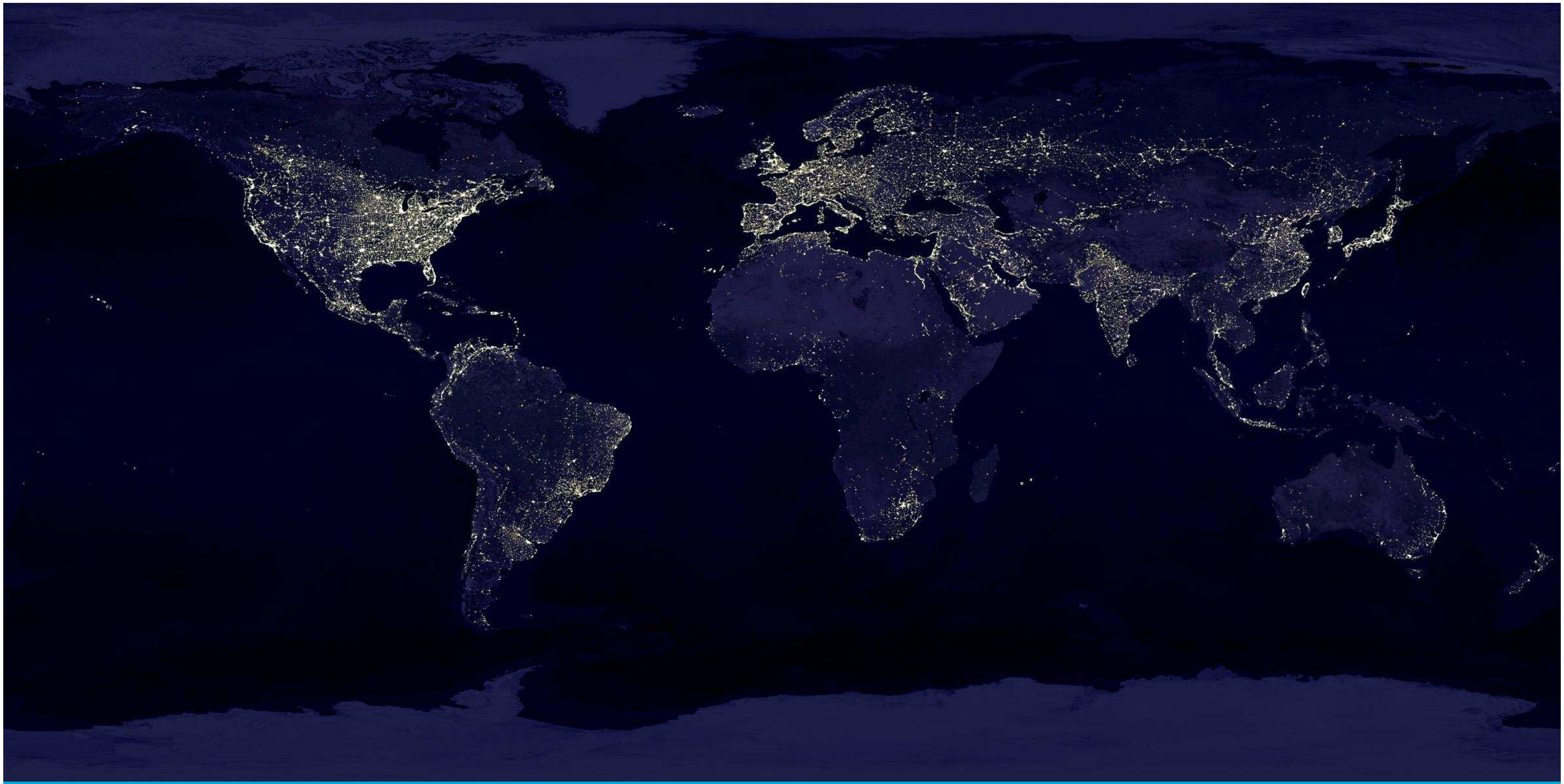
poisonous

Bind too strong



Group / Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87	88	**	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118

Sustainable Hydrogen and Electrical Energy Storage



Some extra slides

Structure determination of hydrides: neutron diffraction

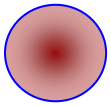
-the neutron behaves as a wave with a certain wavelength

- the wave is reflected under certain angles by atom planes in the crystal lattice

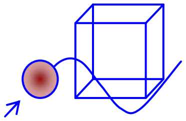
- analysis of the reflected intensity as a function of angle gives direct information about the crystal structure

- neutrons are sensitive to light elements like hydrogen and lithium (Röntgens, electron microscopy, … are not)

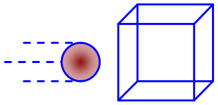
Properties of Neutrons - close to ideal for energy materials research



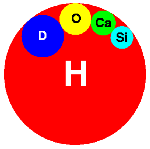
- no electric charge - can penetrate deep into a specimen (easy sample environment, unlike X-rays or electron microscopy)



- Thermal neutrons have wavelength similar to atomic spacing -can be used to determine the positions of atoms.



- Thermal neutrons move at a speed similar to that of atoms at room temperature (~800m/sec) - can investigate motion of atoms in a unique way.



- Isotopic sensitivity allows contrast variation: for hydrogen: ^{1}H and ^{2}D are visible in very different ways

Interaction strengths neutrons and X-rays with elements.

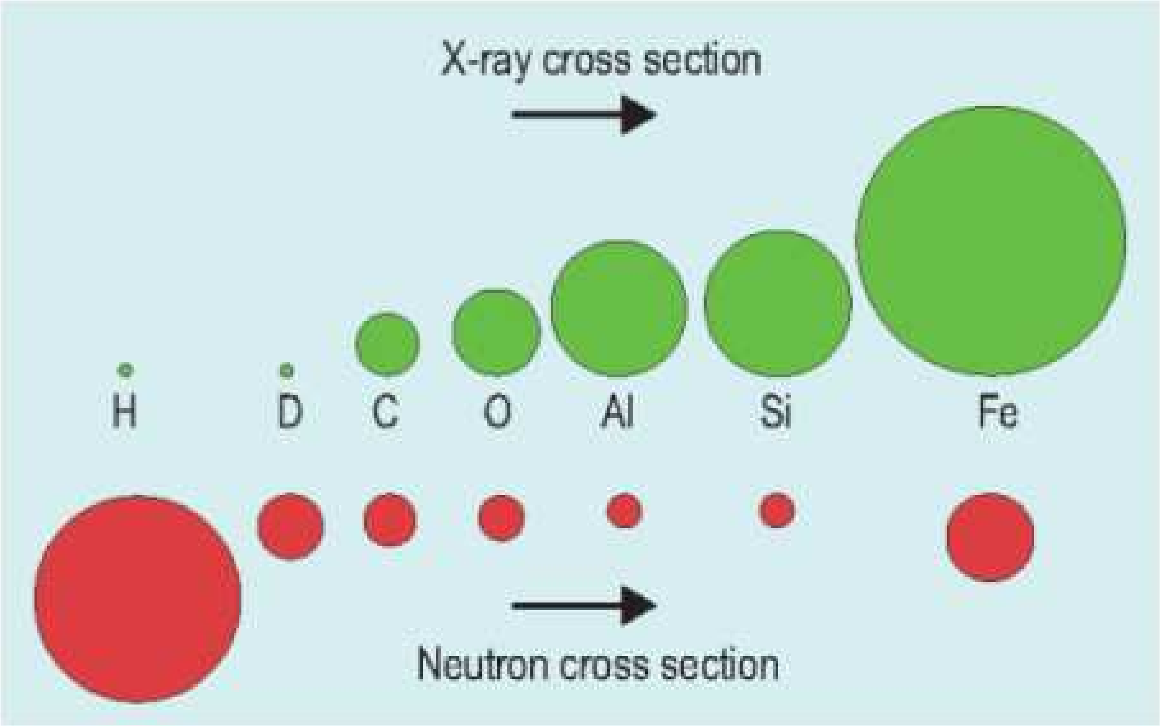
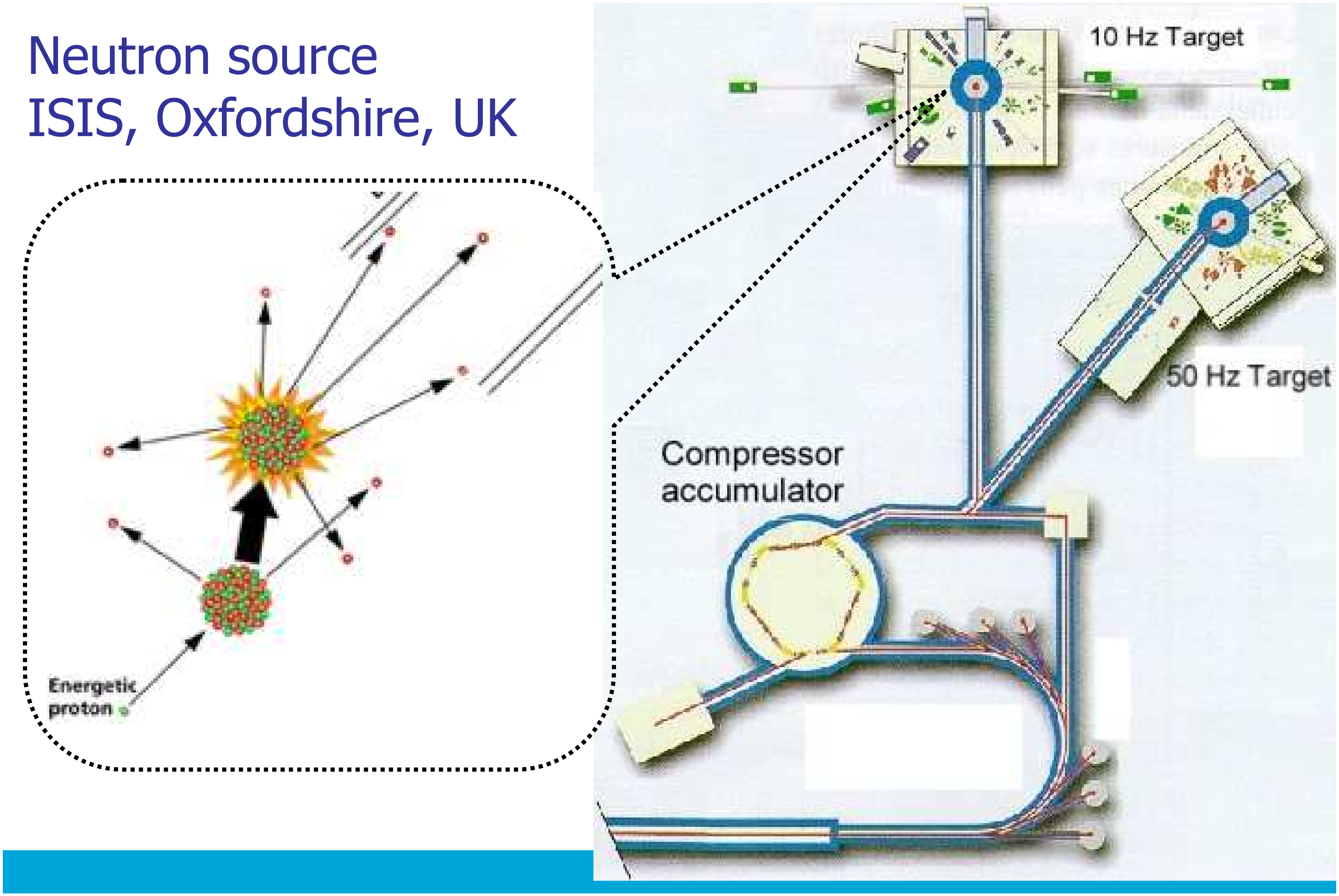


Fig. 2. Neutron and x-ray scattering cross-sections compared. Note that neutrons penetrate through Al much better than x rays do, yet are strongly scattered by hydrogen.

~ electron number

Rather random values, very sensitive to light elements H,Li

Neutron source
ISIS, Oxfordshire, UK

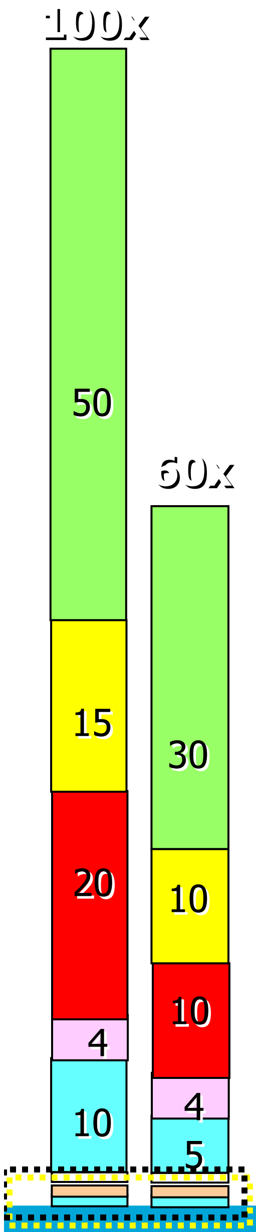


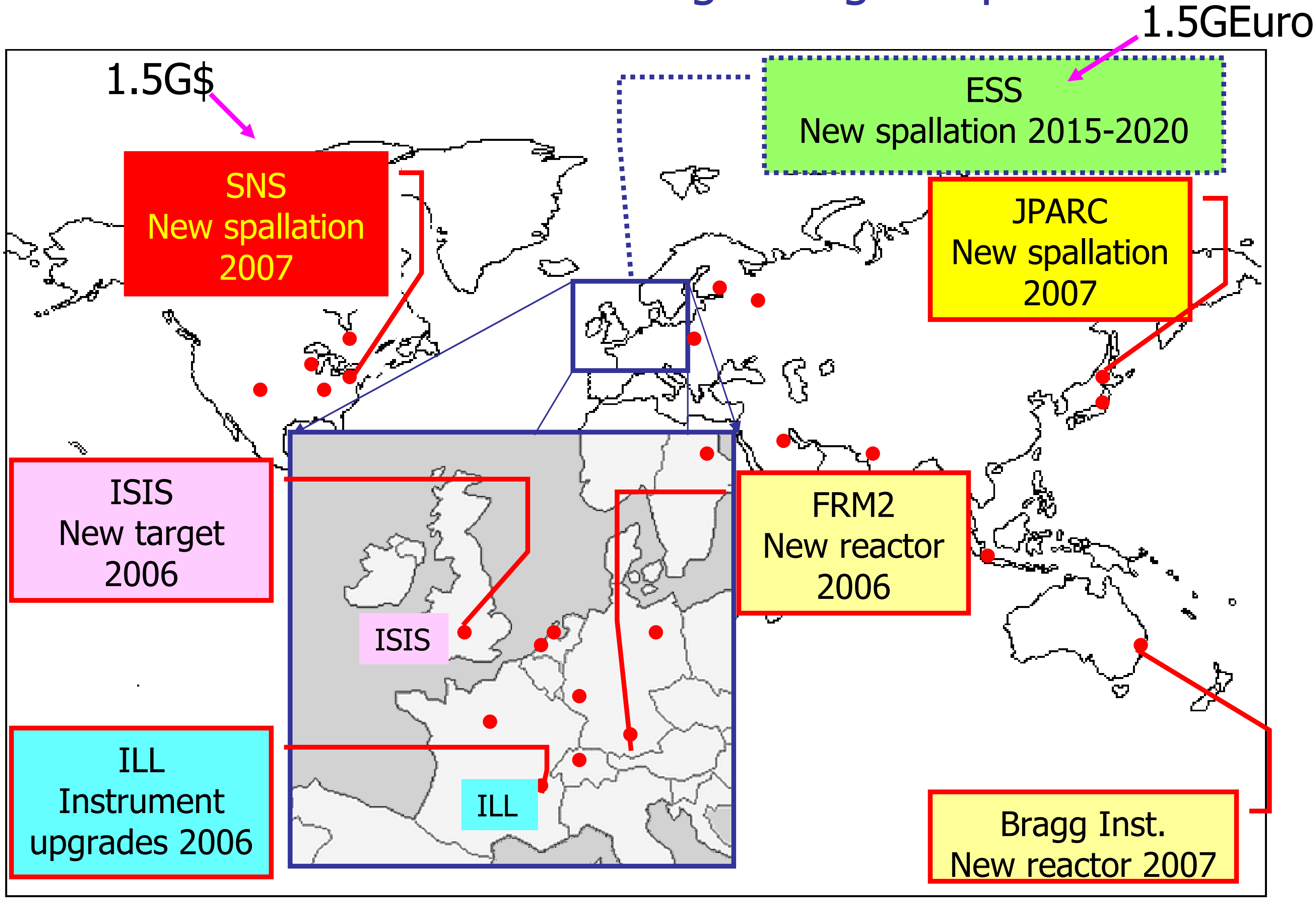
ISIS and ILL: Large scale facilities for neutron scattering
Diamond and ESRF: Large scale facilities for synchrotron X-rays

Oxfordshire, UK

Grenoble, France

Neutron facilities worldwide: growing competition





1.5G$

SNS
New spallation
2007

1.5GEuro

ESS
New spallation 2015-2020

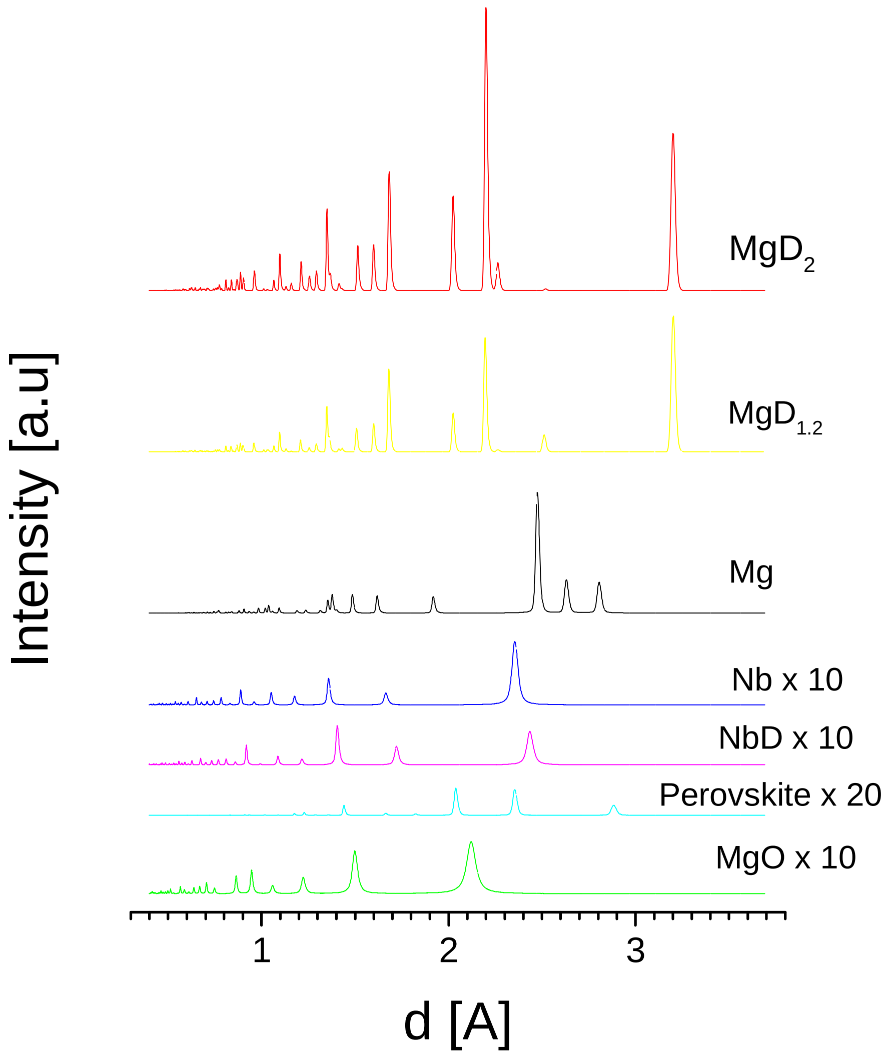
JPARC
New spallation
2007

ISIS
New target
2006

FRM2
New reactor
2006

ILL
Instrument
upgrades 2006

Bragg Inst.
New reactor 2007



- sensitivity to hydrogen (deuterium) results in changing intensities of diffraction peaks
- different materials have completely different diffraction spectrum