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Basics of metal hydrides

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Basics of metal hydrides

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History

- T. Graham (1866)
  - Metal palladium absorbs hydrogen
  - Hydrogen can permeate Pd-membranes
- Reilly and Wiswall (1968)
  - Mg_2Ni, FeTi
- Van Vucht, Kuijpers and Bruning (1970)
  - $LaNi_5$

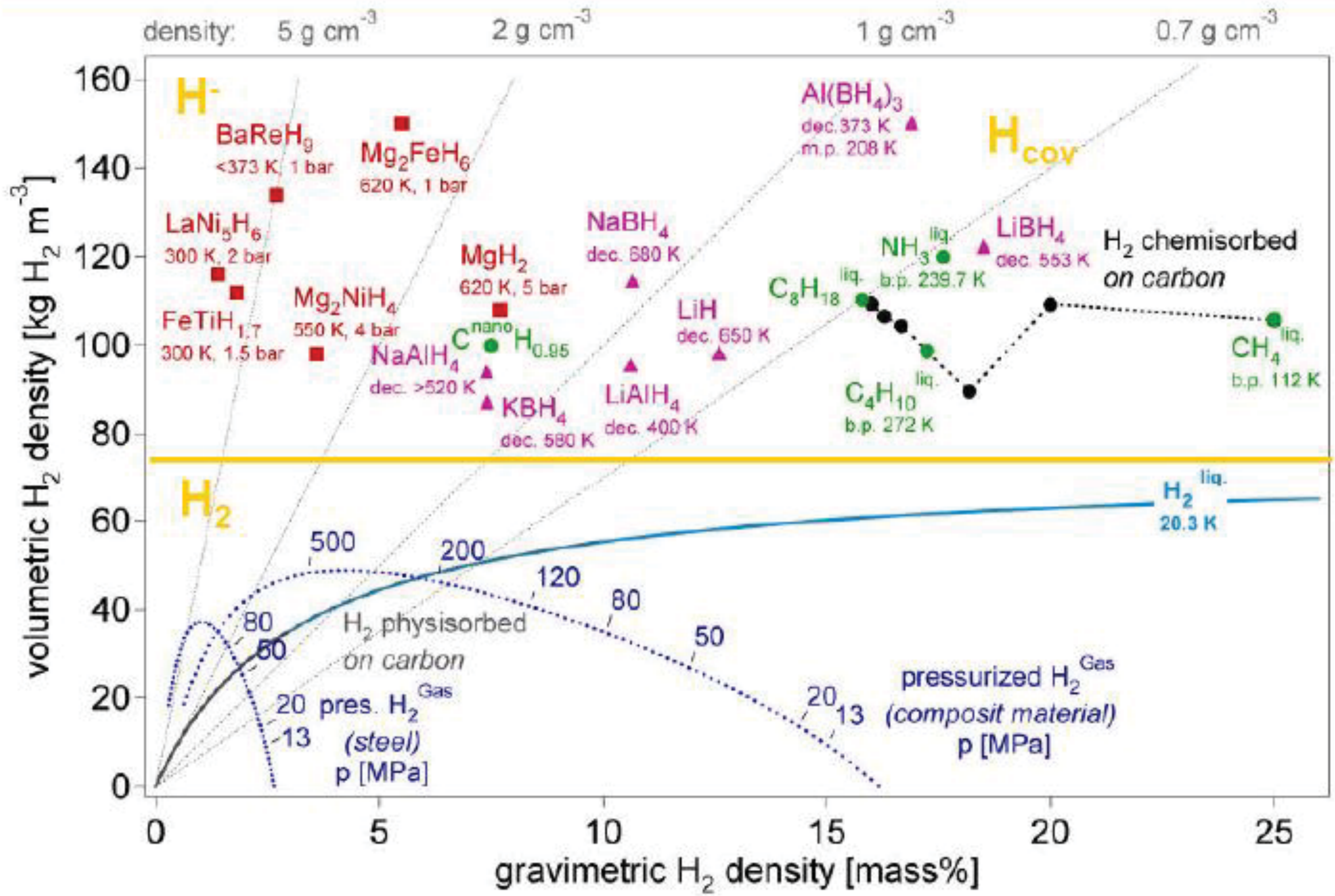
Applications of MH

- Hydrogen storage
- Purification/separation
- Isotope separation
- Hydrogen getters
- Hydrogen compression
- Heat storage
- Heat pumps and refrigerators
- Temperature sensors and actuators
- Liquid H_2 (boil-off losses)
- Batteries electrodes
- Permanent magnet production
- Neutron moderators
- Switchable Mirrors

Hydrogen storage

System	Hydrogen mol H_2 dm^{-3}	Hydrogen wt.%
Gas (273K, 1 bar)	0.045	100
pressure (150 bar)	6.7	1.2
LH_2 (20K)	35	100
MgH_2	55	7.7
$LaNi_5H_6$	52	1.4

HYDROGEN DENSITY



Ref: A. Züttel, "Materials for hydrogen storage", materialstoday, Septemper (2003), pp. 18-27

Metal Hydrides

- Advantages
  - ➢ High volumetric density
  - ➢ Low pressure
  - ➢ Endothermic reaction (desorption)

- Disavantages
  - ➢ Temperature of operation
  - ➢ Hydrogen sorption kinetic
  - ➢ Cost
  - ➢ Pyrophoricity

Classes of hydrides

Ionic or saline hydrides

- Formed by alkali and alkaline earth metals.
- hydrogen is a negatively charged ion (H-)
- Typical binary ionic hydrides are sodium hydride NaH and calcium hydride CaH_2.
- high conductivities just below or at the melting point.
- Complex ionic hydrides $LiAlH_4$, $NaAlH_4$

Covalent hydrides

- compounds of hydrogen and nonmetals.
- atoms of similar electronegativities share electron pairs.
- low melting and boiling points. (most of them are liquid or gaseous at room temperature)
- weak van der Waals forces.
- water (H2O), hydrogen sulfide (H2S), silane (SiH4), aluminum borohydride Al(BH4)3, methane (CH4) and other hydrocarbons.
- Complex chemical reactions should be used to synthesize them

Classes of hydrides

Metallic hydrides

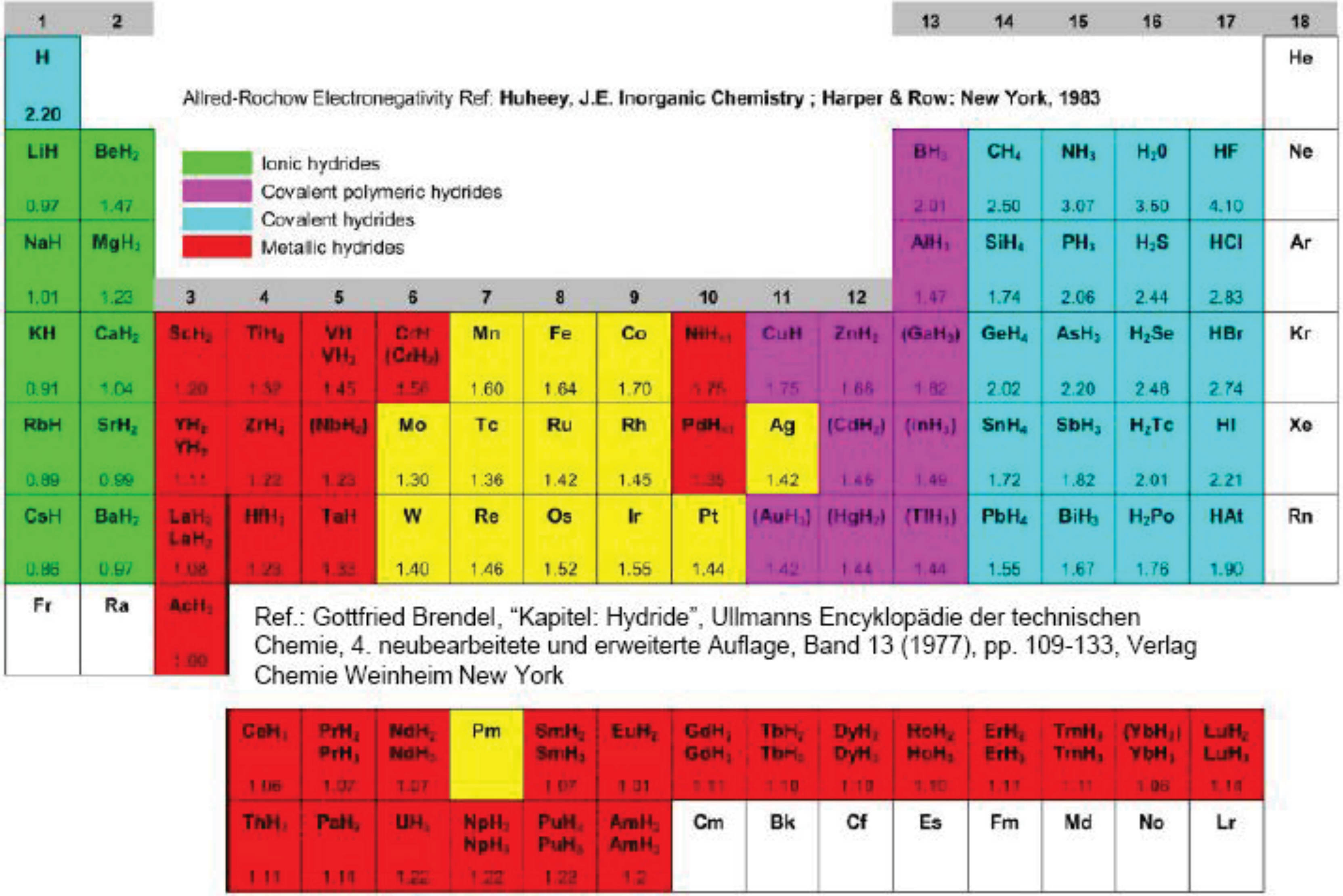
- Formed by transition metals including rare earth and actinide series.
- hydrogen acts as a metal and forms a metallic bond.
- wide variety stoichiometric and nonstoichiometric compounds.
- formed by direct reaction of hydrogen with the metal or by electrochemical reaction.
- TiH_2 and ThH_2.
- $LaNi_5H_6$, $FeTiH_2$

Note

this division should not be taken too literally. Most hydrides are a mixture of different bonding.

Example: LiH mainly ionic but partly covalent.

BINARY HYDRIDES



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

🟩 Ionic hydrides
🟪 Covalent polymeric hydrides
🟦 Covalent hydrides
🟥 Metallic hydrides

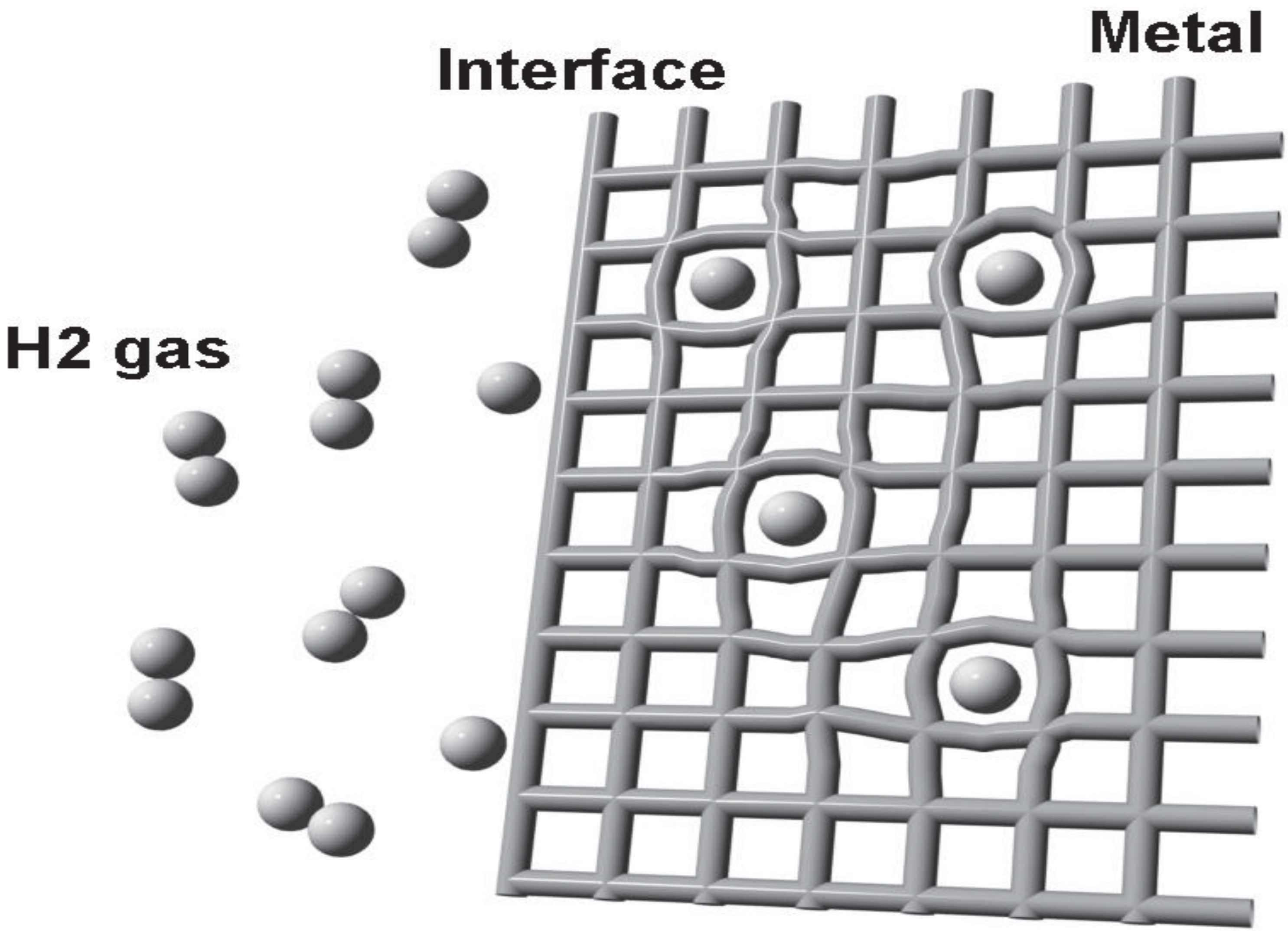
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
LiH 0.97	BeH_2 1.47											BH_3 2.01	CH_4 2.50	NH_3 3.07	H_2O 3.50	HF 4.10	Ne
NaH 1.01	MgH_2 1.23											AlH_3 1.47	SiH_4 1.74	PH_3 2.06	H_2S 2.44	HCl 2.83	Ar
KH 0.91	CaH_2 1.04	ScH_2 1.20	TiH_2 1.32	VH VH_2 1.45	CrH (CrH_2) 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_2Te 2.01	HI 2.21	Xe
CsH 0.86	BaH_2 0.97	LaH_2 LaH_3 1.08	HfH_2 1.23	TaH 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

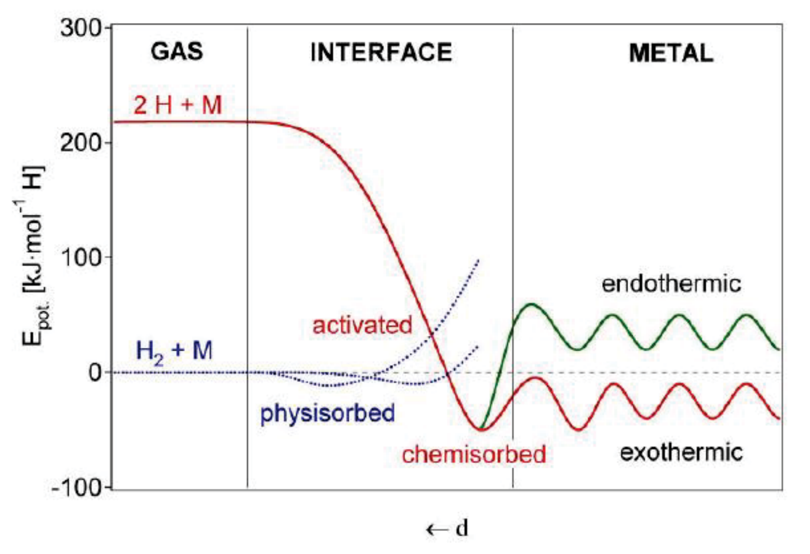
Ref.: Gottfried Brendel, “Kapitel: Hydride”, Ullmanns Encyklopädie der technischen Chemie, 4. neubearbeitete und erweiterte Auflage, Band 13 (1977), pp. 109-133, Verlag Chemie Weinheim New York

A. Züttel (2004)

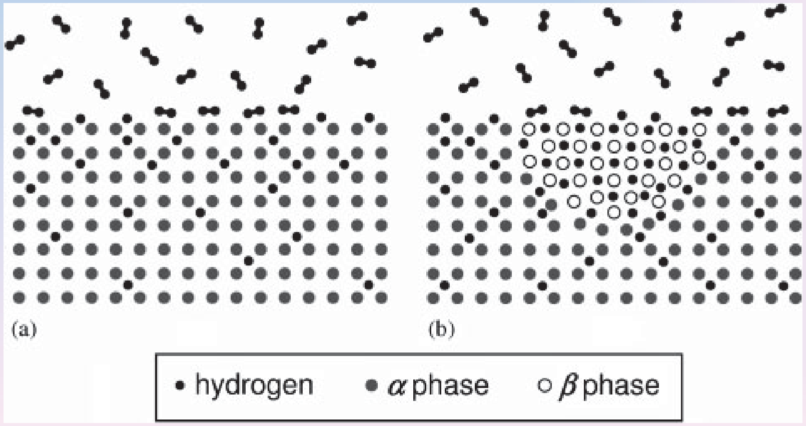
Schematic of formation



Formation



- $H_2 \rightarrow 2H$
- Oxide layer
- Solid solution
- $P_{H2}\uparrow \Rightarrow$ H concentration $\uparrow$
- Nucleation of β phase (hydride)
- H on octahedral or tetrahedral site
- Lattice expansion
- Symmetry reduction



Int. J. Energy Res. 2007; 31:637–663

Thermodynamics

Reaction

$$M+\frac{x}{2}H_2 \Leftrightarrow MH_x+Q$$

***Q* is the heat of reaction**

Low concentration (*x*<<1) : α phase

Hydride : β phase

Thermodynamics

Phase rule (Gibbs)

$F = C - P + 2$

Components = 2 (H + Metal)

Phases: $(x \ll 1) \Rightarrow 2\ (\alpha, H_2)$

when nucleation of $\beta \Rightarrow 3\ (\alpha, \beta, H_2)$

Degree of freedom:

$(x \ll 1) \Rightarrow F = 2$ (P and c varies)

when nucleation of $\beta \Rightarrow F = 1$ (plateau)

Pressure-Composition Isotherm (PCT)

Low concentration

- hydrogen randomly distributed in the metal host lattice
- concentration varies slowly with temperature.

Condition for thermodynamic equilibrium.

$$\frac{1}{2}\mu_{H_2}(p,T)=\mu_H(p,T,c_H)$$

Ideal gas:

$$\mu_{H_2}=H^0_{H_2}-TS^0_{H_2}+RT\ln p_{H_2}$$

Chemical potential of a dissolved H atom:

$$\mu_H=H_H-TS^{id}_H+RT\ln\left(\frac{c}{b-c}\right)$$

H_H : enthalpy

S_h^{id} : non-configurational part of entropy

b: number of interstitial sites per atom

Ln(c/b-c): configurational part of entropy

Low concentration ⇒ Seivert law

$$p_{H_2}^{1/2} = K_S$$

- H_2 is an ideal gas
- H_2 is dissociated

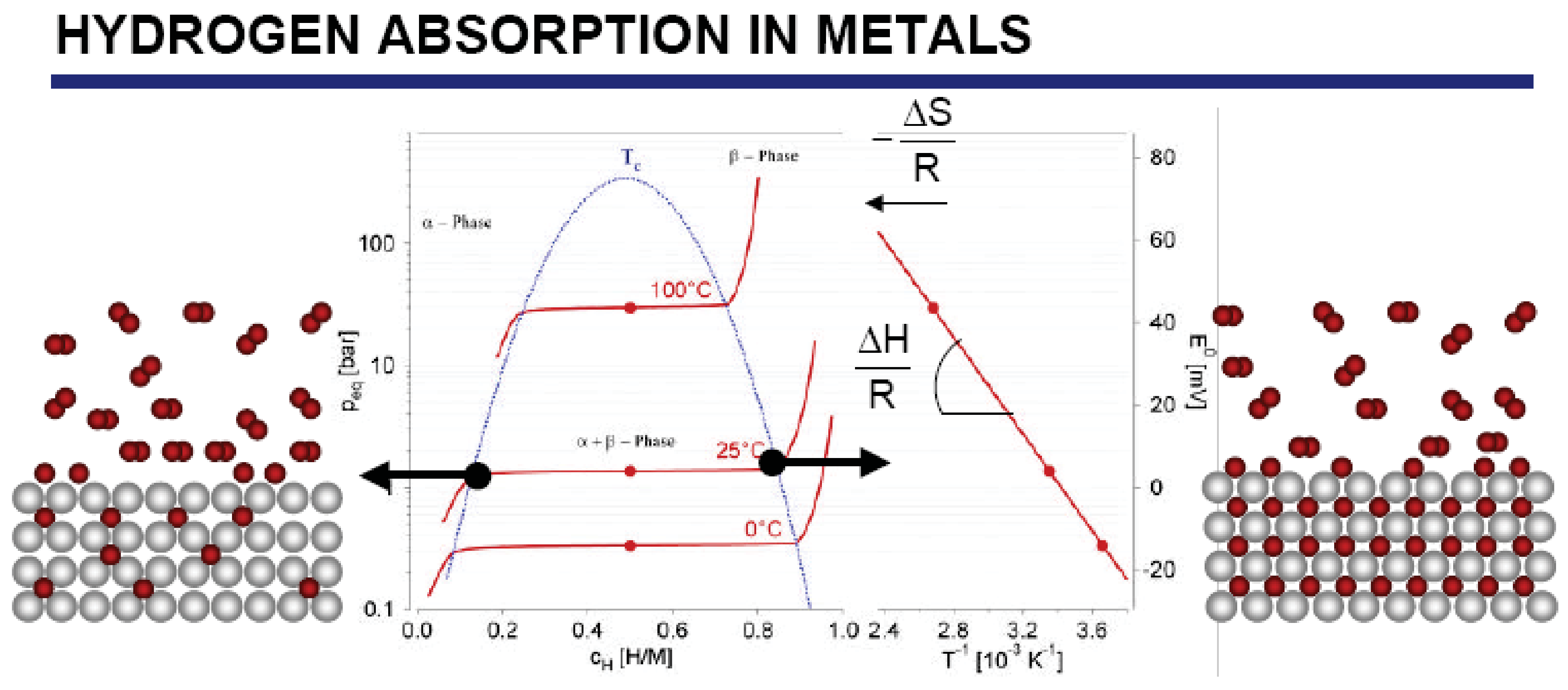
$$LnP = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

- Higher concentration

  $\alpha \rightarrow \beta$ transition

  ΔH: enthalpy

  ΔS: entropy ≈ constant



A. Züttel (2004)

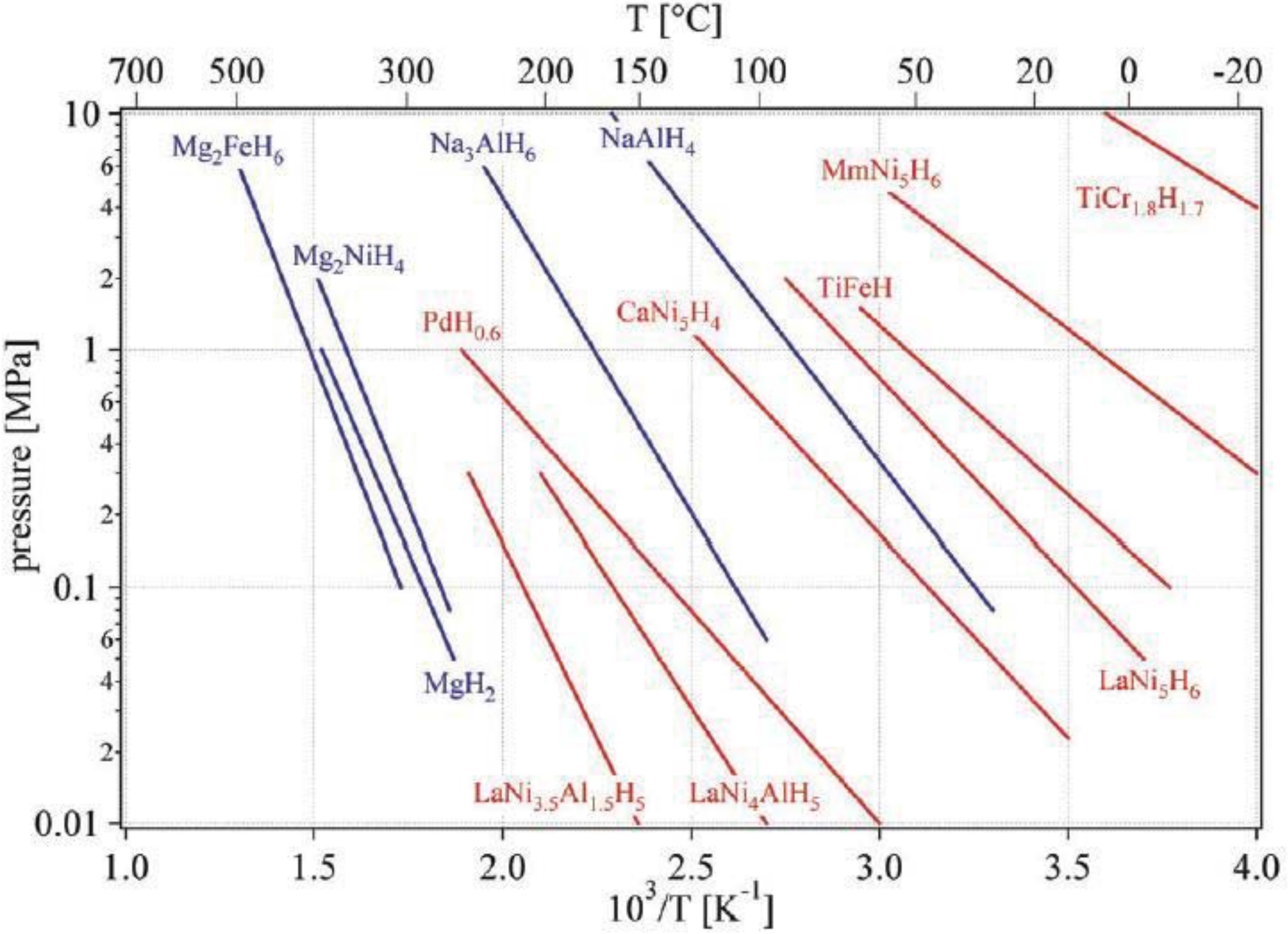


Fig. 6 Van't Hoff plots of some selected hydrides. The stabilization of the hydride of $LaNi_5$ *by the partial substitution of Ni with Al in* $LaNi_5$ *is shown, as well as the substitution of La with mischmetal (e.g. 51% La, 33% Ce, 12% Nd, 4% Pr).*

Züttel, A., *Materials for hydrogen storage.* Materials Today, 2003. **6**(9): p. 24-33.

Dependence of ΔH on concentration

H-H interactions

$$\frac{\partial \Delta H}{\partial x} = \underbrace{\left(\frac{\partial \Delta H}{\partial V}\right)_x \frac{\partial V}{\partial x}}_{\text{Elastic}} + \underbrace{\left(\frac{\partial \Delta H}{\partial x}\right)_V}_{\text{‘Electronic’}}$$

Elastic contribution

$$\left(\frac{\partial \Delta H}{\partial V}\right)_x \frac{\partial V}{\partial x} \cong -K_0 \frac{v_H^2}{v_0} \equiv -u_{els}$$

v_0 : **Atomic volume**

v_H^2 : **Volume increases/H**

K_0 : **Bulk modulus ≈ constant**

⇒ **Elastic contribution ≈ constant**

- Elastic contributions ≈ electronic contribution
- Elastic = attractive
- Energy ~ few hundredths of eV
- long range

Electronic contribution

Expansion of lattice ⇒ modification of the symmetry of electronic states and reduction of the width of the bands

Appearance of a metal-hydrogen bonding band below the metal d-band.

New attributes in the lower portion of the density of states due to H-H interaction.

Palladium

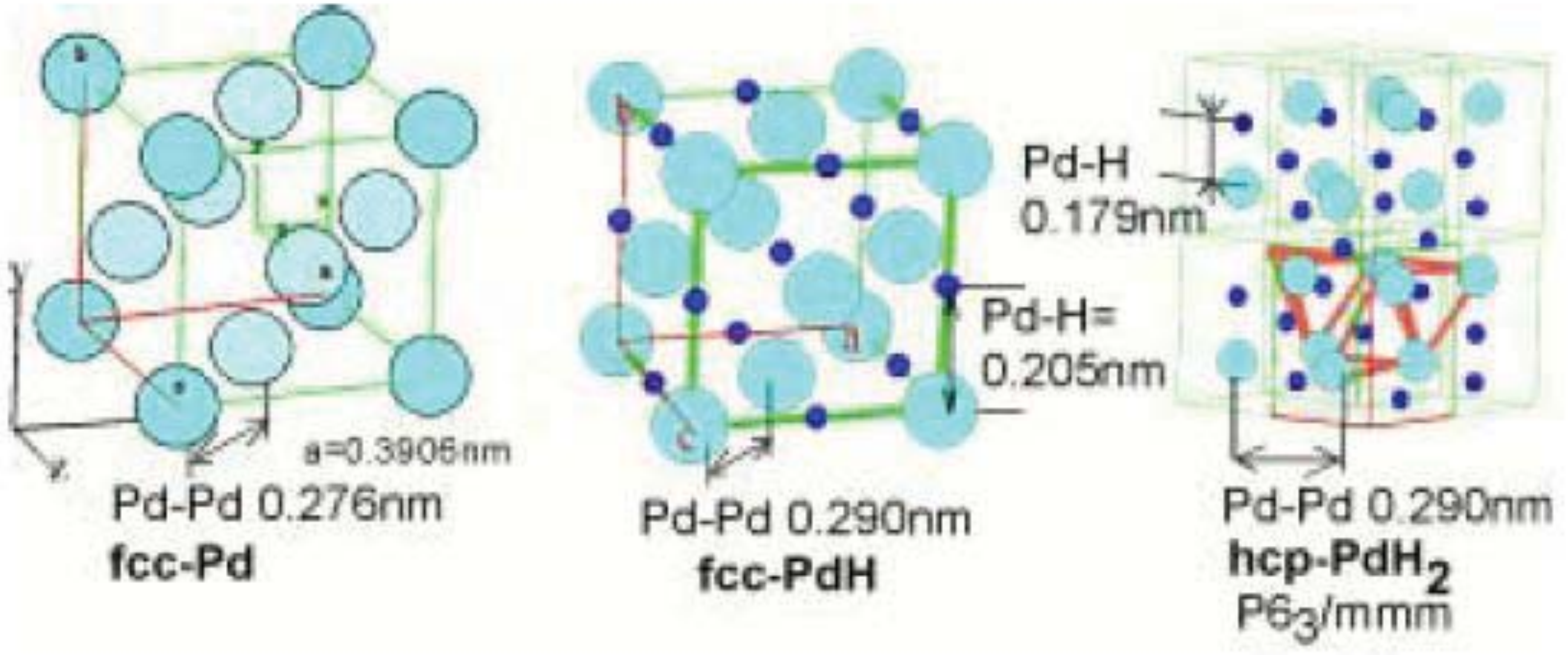
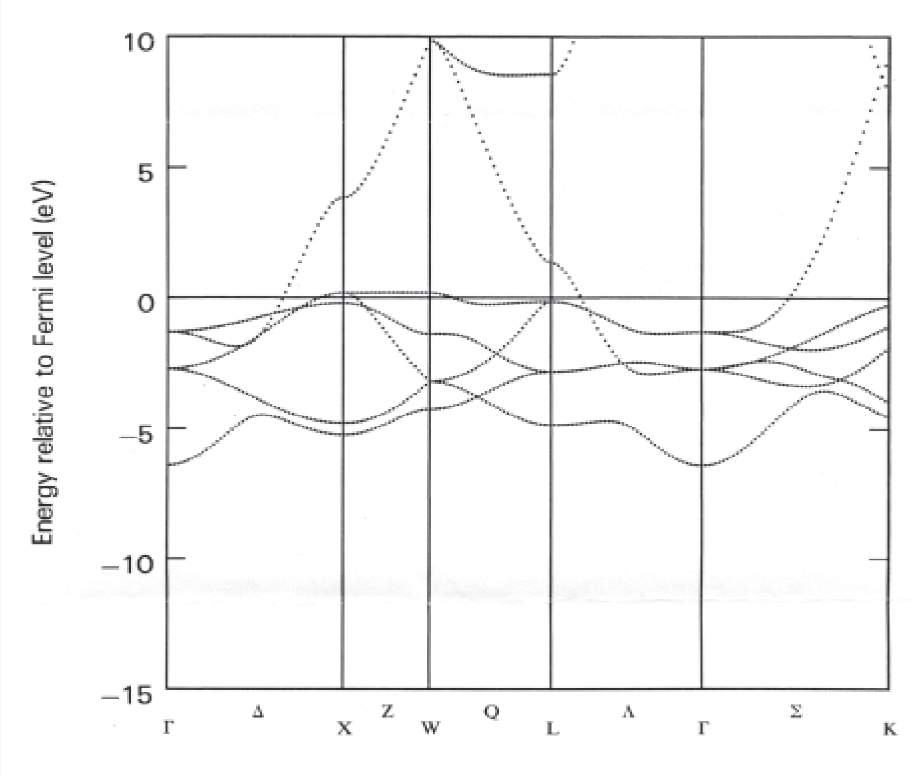
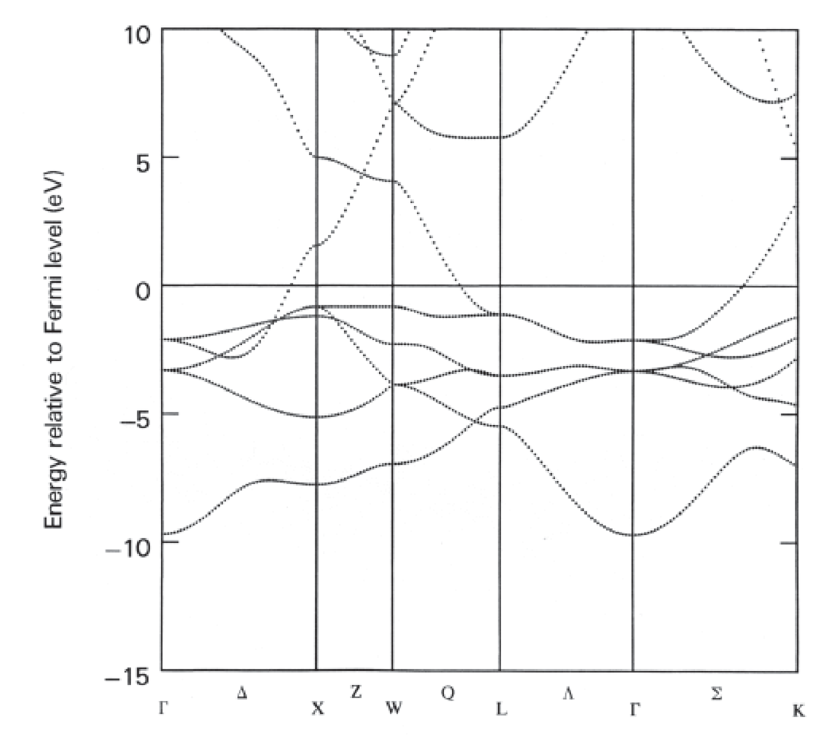


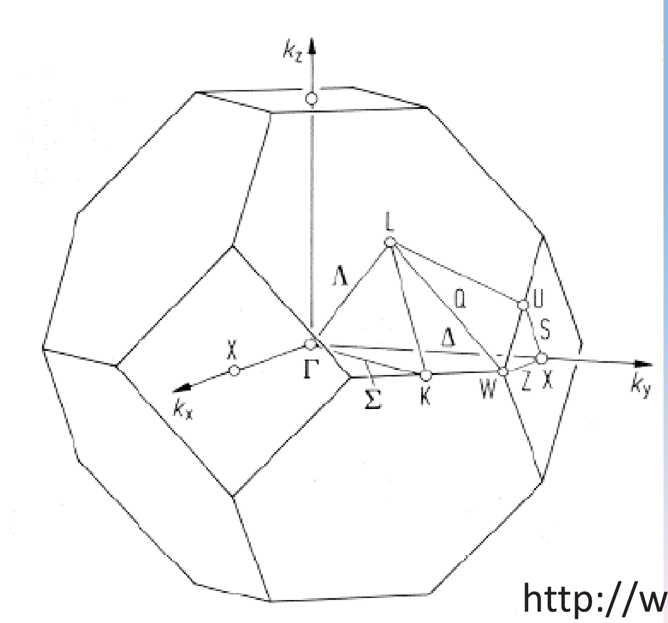
Fig.5 Crystal structure of a) fcc-Pd, b) fcc-PdH and c) hcp-PdH_2

http://arxiv.org/ftp/cond-mat/papers/0304/0304307.pdf



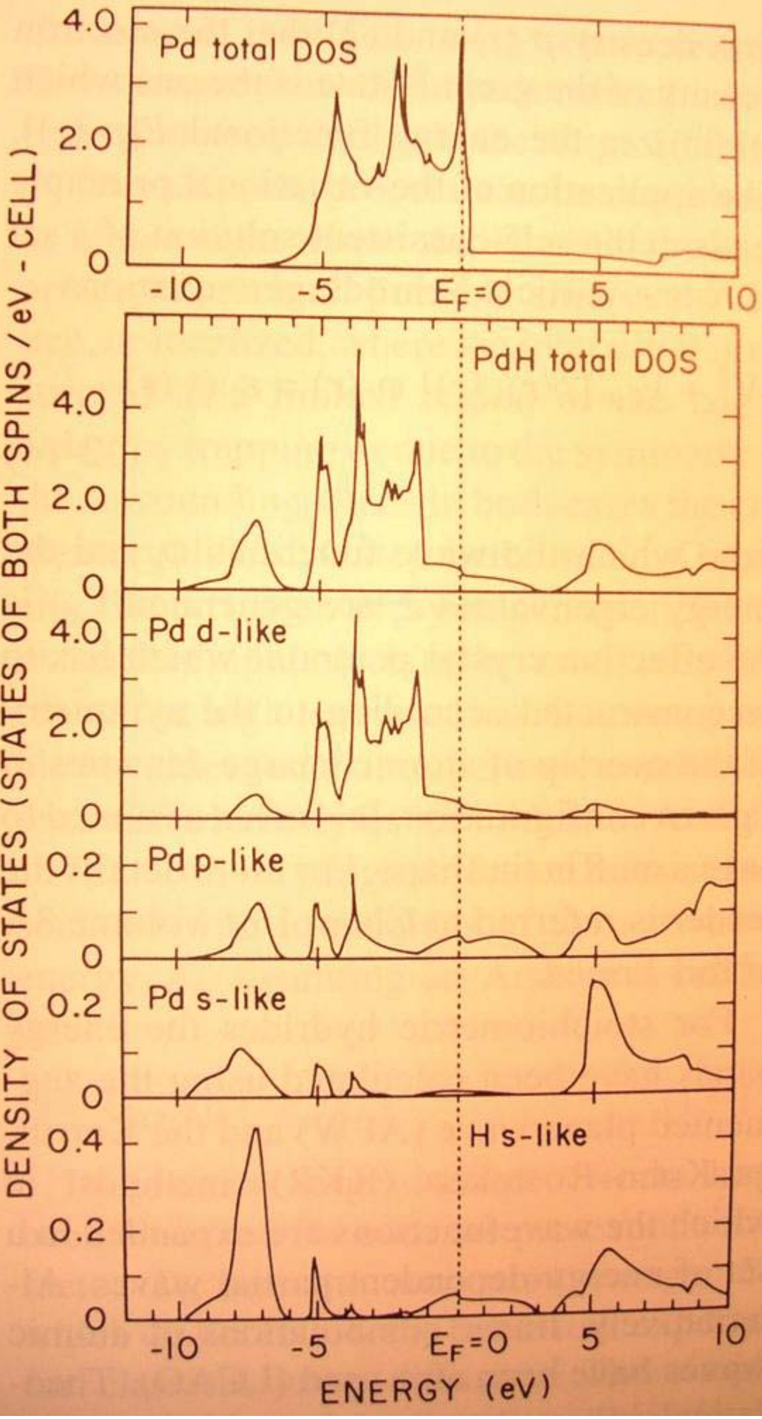


Pd



PdH

http://www.nat.vu.nl/CondMat/griessen/



Pd total DOS
PdH total DOS
Pd d-like
Pd p-like
Pd s-like
H s-like
DENSITY OF STATES (STATES OF BOTH SPINS / eV - CELL)
4.0
2.0
0
0.2
0.4
-10
-5
E_F=0
5
10
ENERGY (eV)

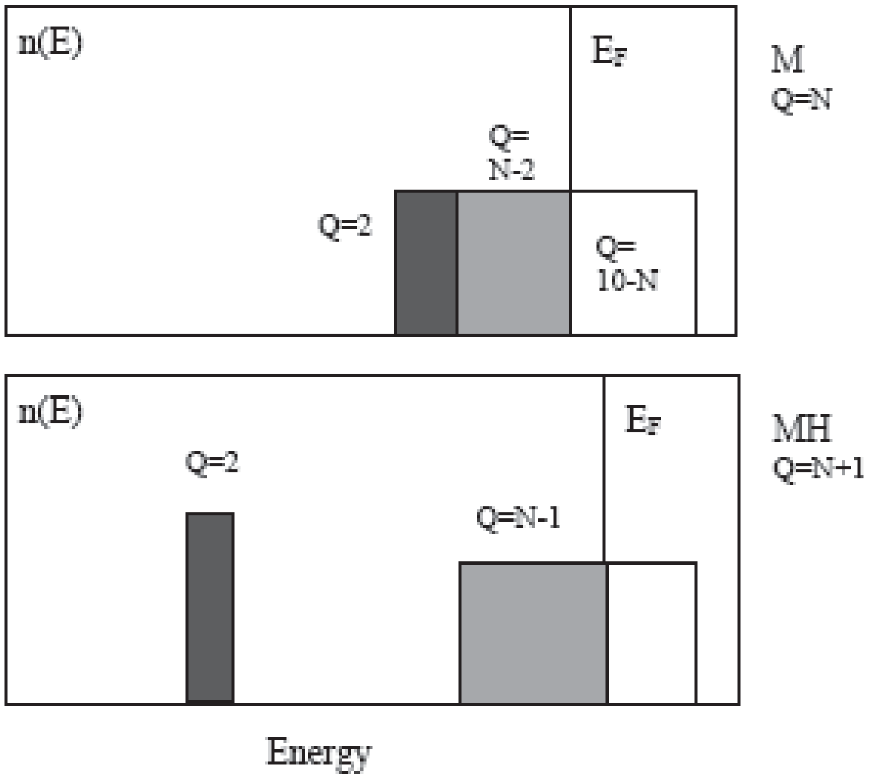


Fig.V.25: Schematic representation of the changes in the electronic structure of a metal M induced by the introduction of hydrogen in M to form a metal-hydride MH.

http://www.nat.vu.nl/CondMat/griessen/

Hydrogen in alloys

Practical applications ⇒ specific properties

Intermetallic hydrides have a wider range of hydride stability

Alloys of:

- A: hydride forming
- B: non-hydride forming

Types

AB_5 ($LaNi_5$, $CaNi_5$), AB_2 ($ZrMn_2$, ZrV_2), AB (FeTi) and A_2B (Mg_2Ni).

Stability

$$A + (x/2)H_2 \leftrightarrow AH_x$$

$$(P', \Delta G_A)$$

The alloy AB_n reacts with hydrogen as

$$AB_n + (x/2)H_2 \leftrightarrow AH_x + nB$$

$$\boldsymbol{P} = \boldsymbol{P}' \exp\left(\frac{-2\Delta \boldsymbol{G}_A}{\boldsymbol{xRT}} \right)$$

P>P’

Destabilization

Stability

Heat of formation

$$\Delta H(AB_nH_{2x}) = \Delta H(AH_x) + \Delta H(B_nH_x) - \Delta H(AB_n)$$

Miedema's *rule of reversed stability*

<u>Less stable alloys form more stable hydrides</u>

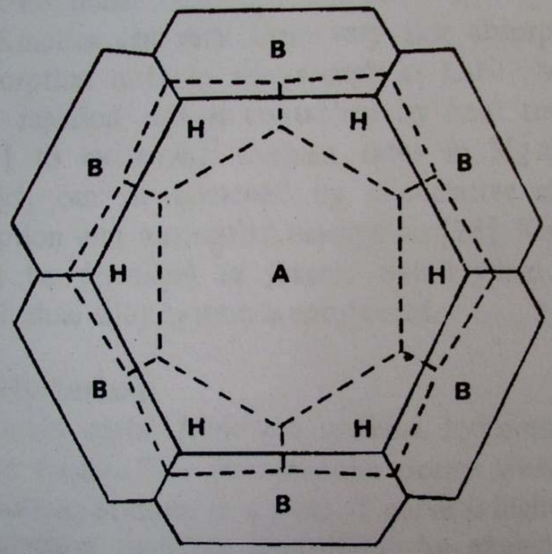


Figure 5 Atomic cells in an intermetallic compound of two metals, A and B, with and without hydrogen present. The atomic cells of hydrogen are indicated by broken lines. Upon hydrogen absorption the lattice is increased, which is not shown here [22].

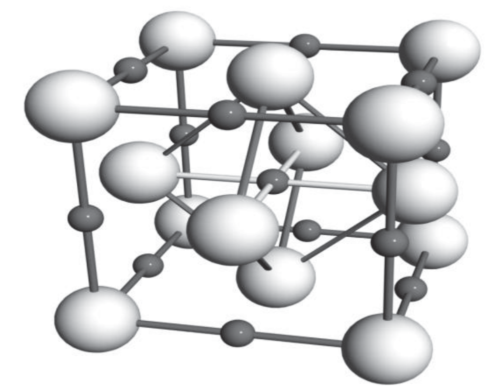
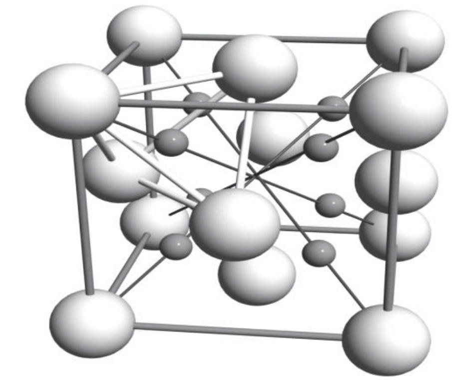
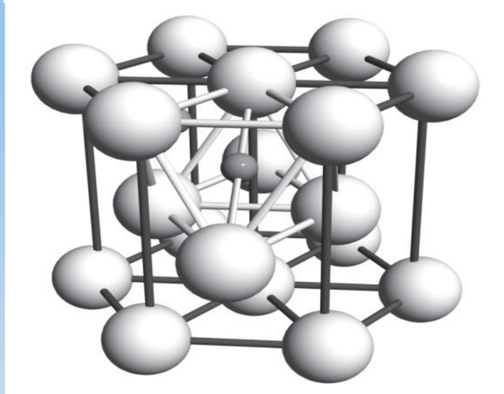
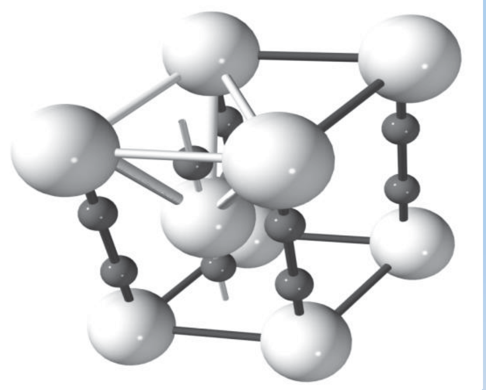
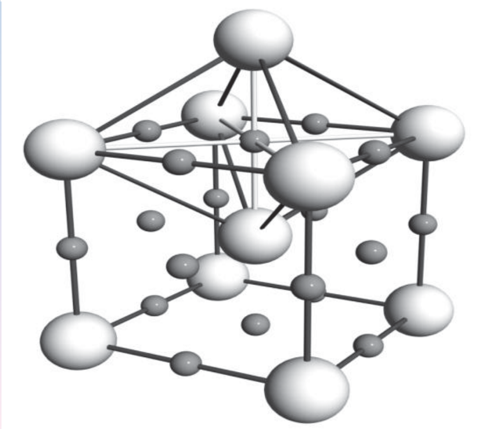
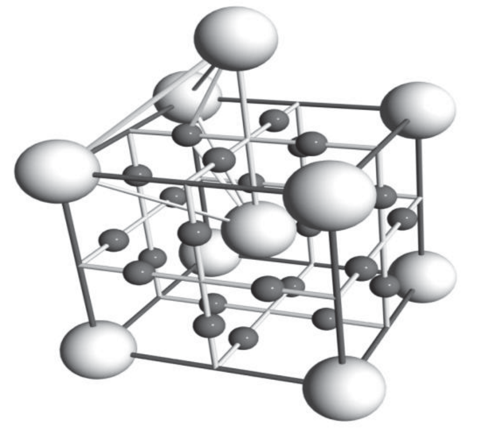
Crystal structure

Formation of hydride

- Expansion of the lattice (2-3 Å^3)
- Volume expansion (30vol.%)
- Reduction of symmetry
- Hydrogen occupy specific sites
- Octahedral (O), Tetrahedral (T)

- fcc low concentration O site
- hcp T and O sites distorted
- bcc T and O sites greatly distorted

Interstitial sites

	Octahedral	**Tetrahedral**
fcc		
hcp		
bcc		

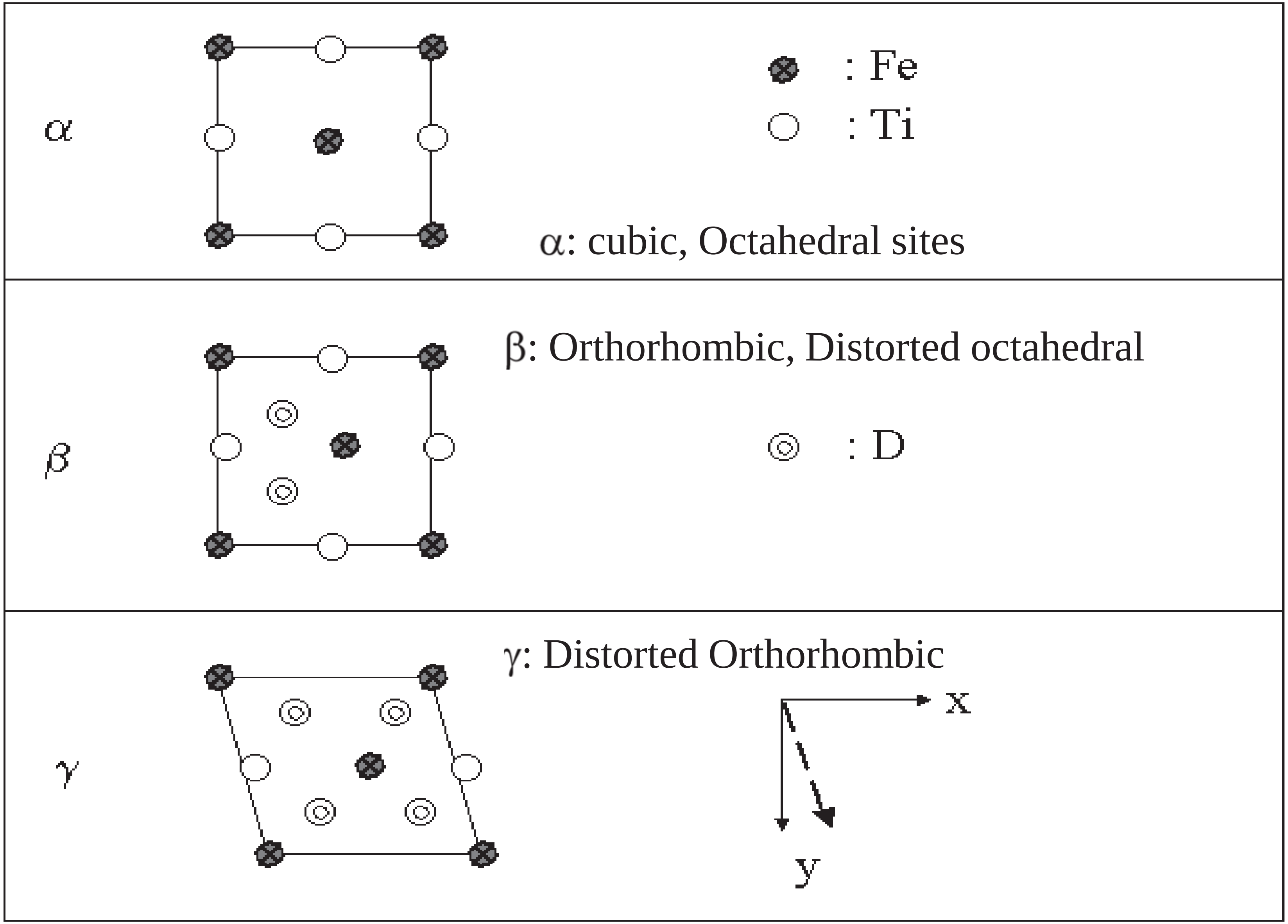
Crystal structure

Hydrogenation

- Lattice expansion, distortion
- Same crystal structure

Structure	Type
Cubic	Ti_2Ni, $MgCu_2$, CaF_2, Th_6Mn_{23}, CsCl, Cr_3Si
Hexagonal	$CaCu_5$, $MgZn_2$, Mg_2Ni, AlB_2, $PuNi_3$, $Pd_{15}P_2$
Tetragonal	TiCu, $CuAl_2$, $MoSi_2$, $Nd_2Fe_{14}B$
Orthorhombic	CrB, Fe_3C
Monoclinic	Pd_6P

TiFe



α: cubic, Octahedral sites

β: Orthorhombic, Distorted octahedral

γ: Distorted Orthorhombic

Geometry

- Minimum hole size: 0.4Å
- Minimum bond distance: 2.1Å

Stability of hydride increases with size of interstice.

Amorphous material

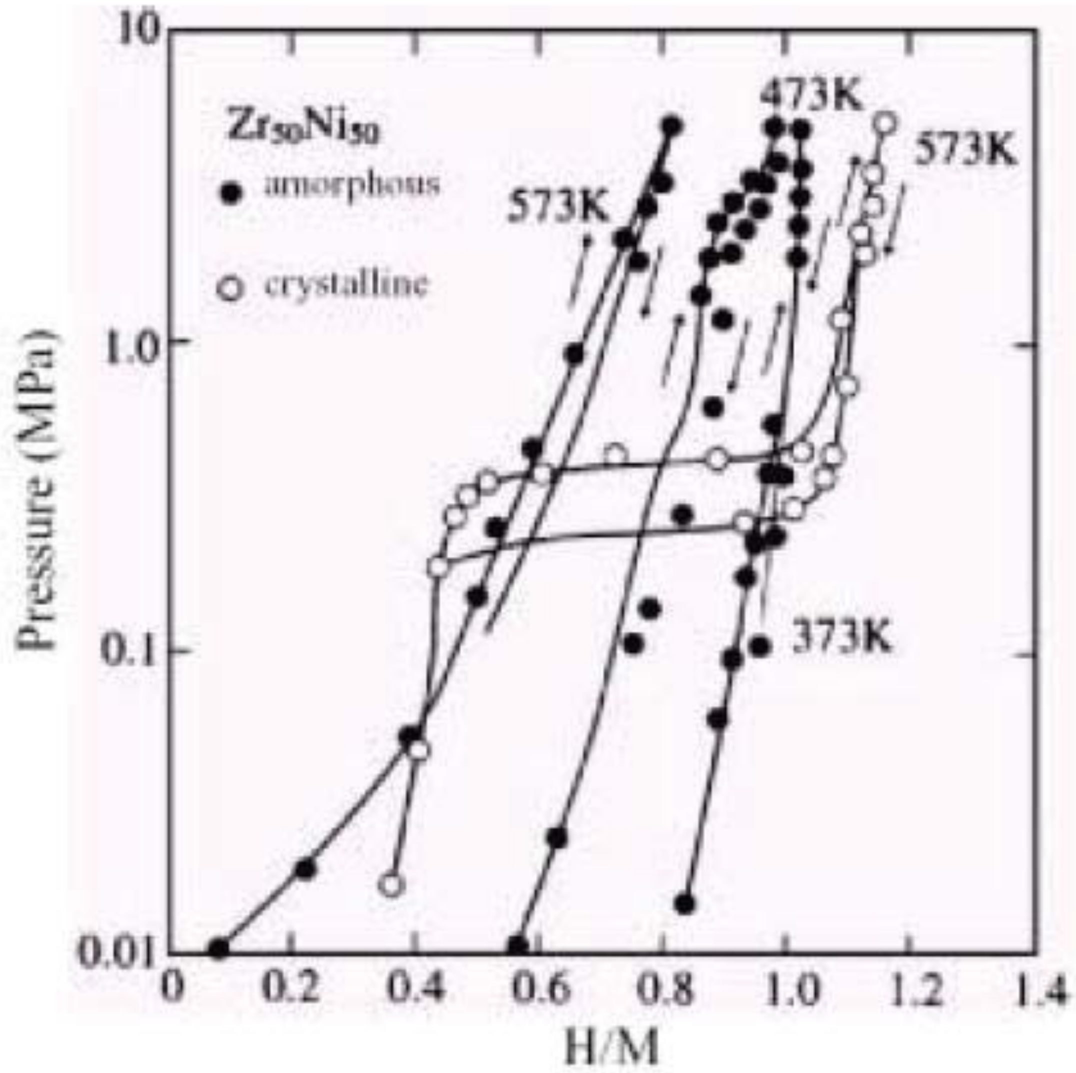
- Produced by:
  - Rapid quenching
  - Sputtering
  - Ball milling

- Hydrogen sites presents a distribution of energy states

- Hydrogen enters successively higher energy sites

- Hydrogen occupies distorted tetrahedral on fourfold coordinated sites

Amorphous material



Dynamics

- Proton vibrating on interstitial site (10^{14}Hz)
- Jump to neighbour site (10^{9}Hz)
- Rapid diffusion
- Diffuse faster in open structures (BCC) than in closed packed structures (FCC)
- Low activation energy (Arrhenius)

$$D = D_0 \exp(-E_a / kT)$$

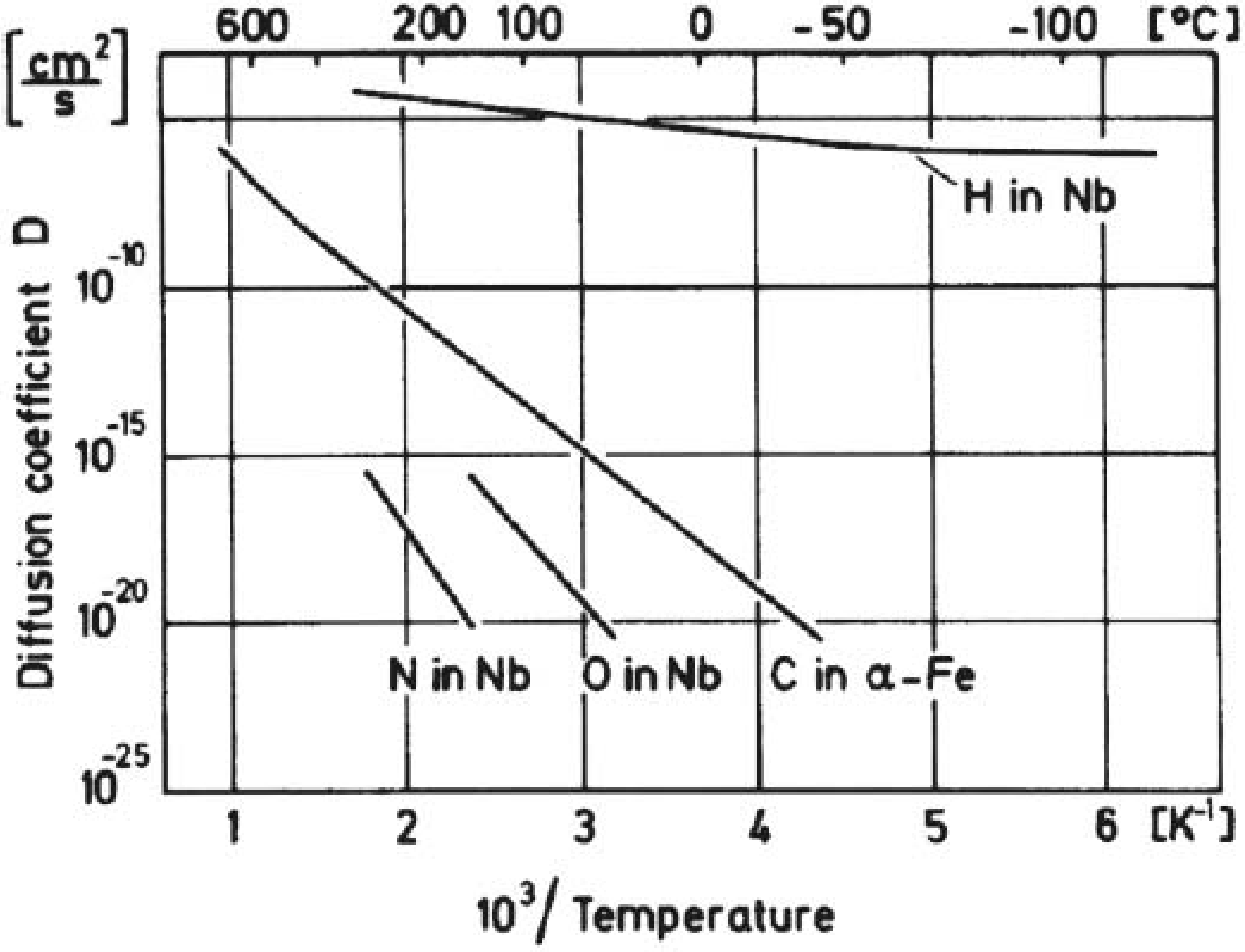


Fig. I.8: Diffusion coefficients of H (Schaumann et al.[5]), N and O (Powers and Doyle[6]) in Nb and C in α-Fe (Lord and Beshers[7]) after Völkl and Alefeld[8].

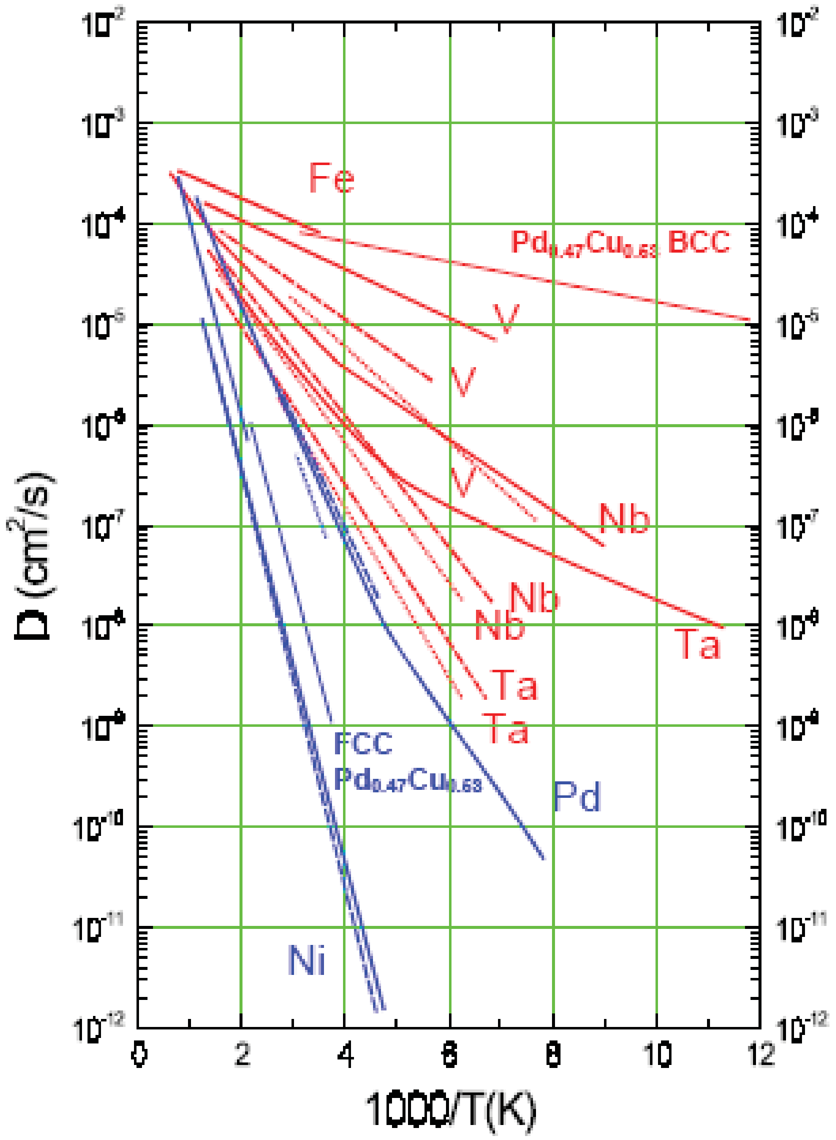


Fig. VIII.11: Temperature dependence of the diffusion coefficient for hydrogen (full line), deuterium (dashed line) and tritium (dotted line) in FCC metals (blue curves) and in BCC metals (red curves). The host metals are indicated by their symbols. Note the extreme influence of the crystal structure in the case of the PdCu alloy.

- Effect of structure PdCu alloy
- Reverse isotope effect for Pd

http://www.nat.vu.nl/CondMat/griessen/

Kinetics

- Must take into account nucleation and growth process.

$\Rightarrow$Johnson-Mehl-Avrami

$$-\ln\{\ln(1-f)\} = \ln(B) + m \ln(t)$$

f : reacted fraction

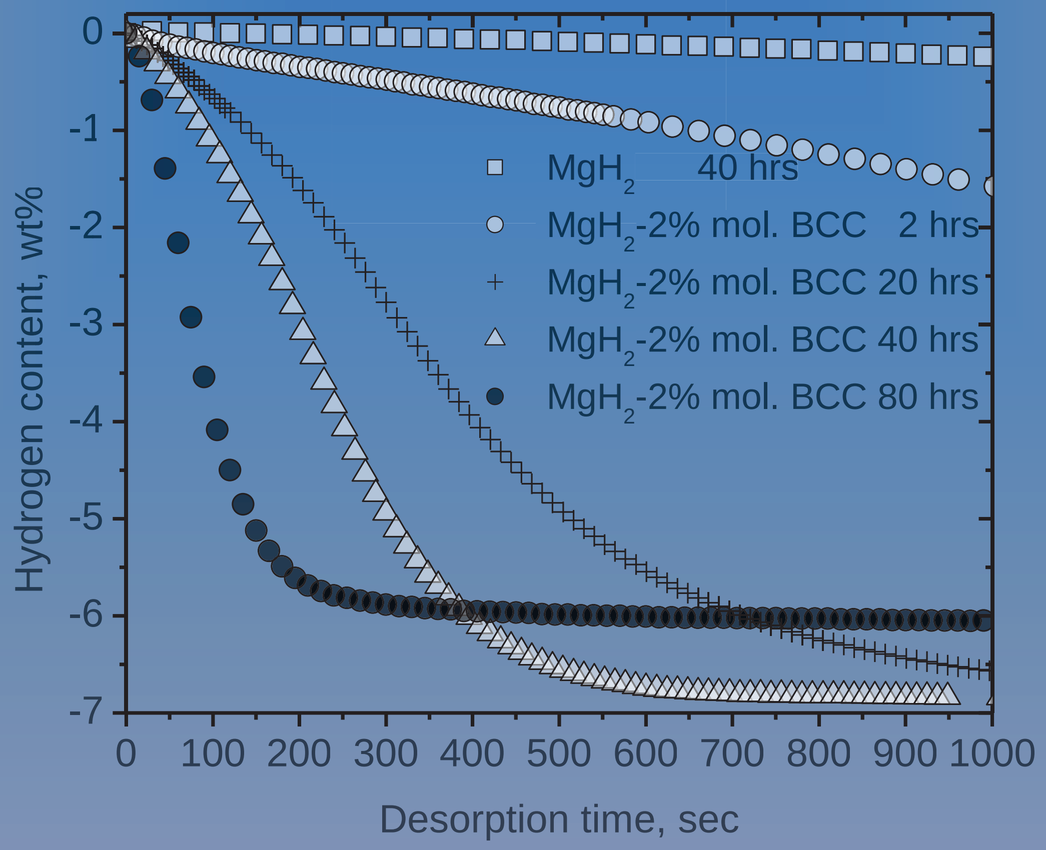
m : constant (rate-limiting step)

B = parameter that depends only on T and P

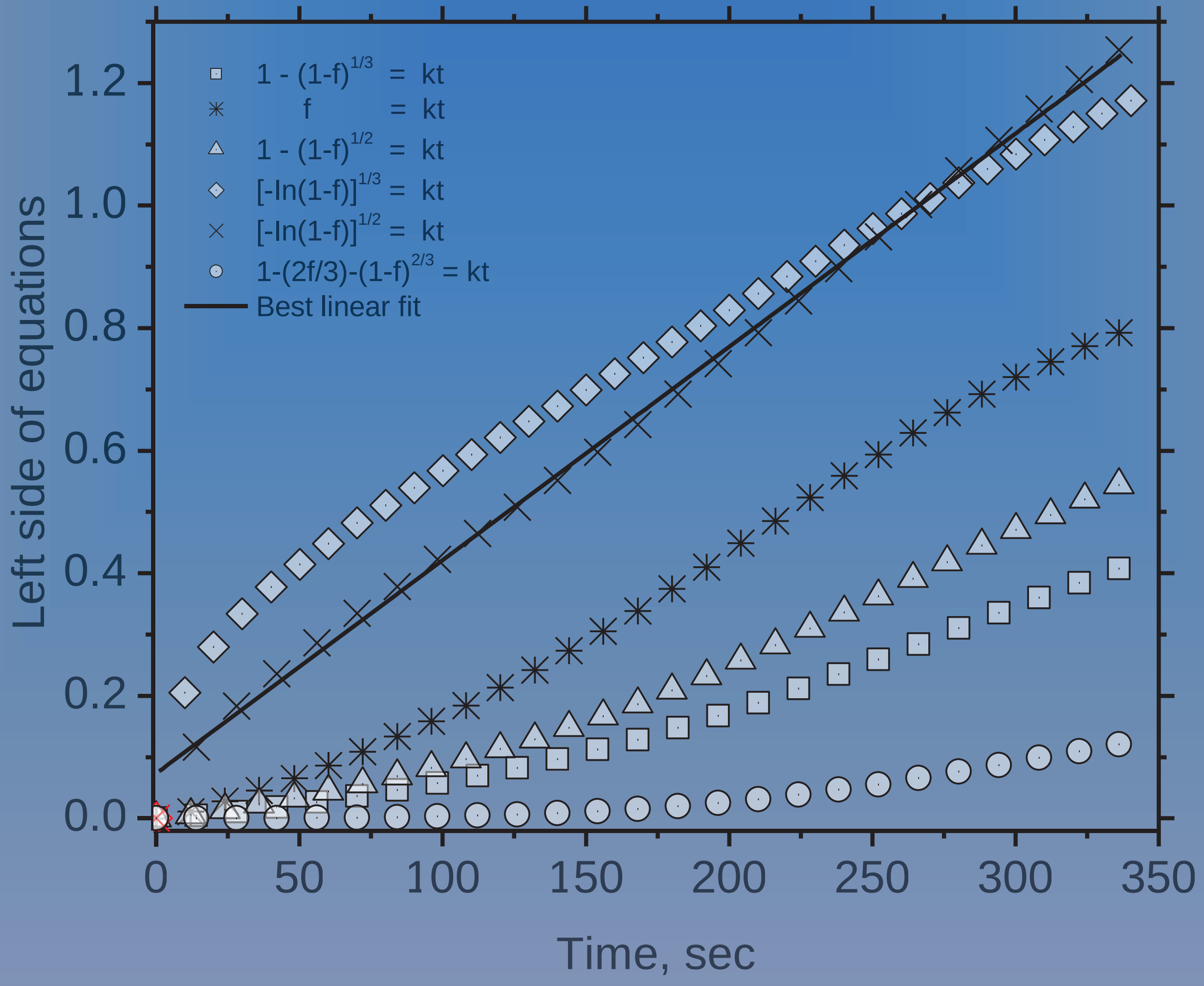
Rate-limiting step	Growth dimensionality	*m* constant nuclei sites	*m* constant nucleation rate
Diffusion	1	1/2	3/2
	2	1	2
	3	3/2	5/2
Interface transformation	1	1	2
	2	2	3
	3	3	4

MgH_2 + TiVMN bcc alloy

Hydrogen desorption 573 K



Rate limiting step

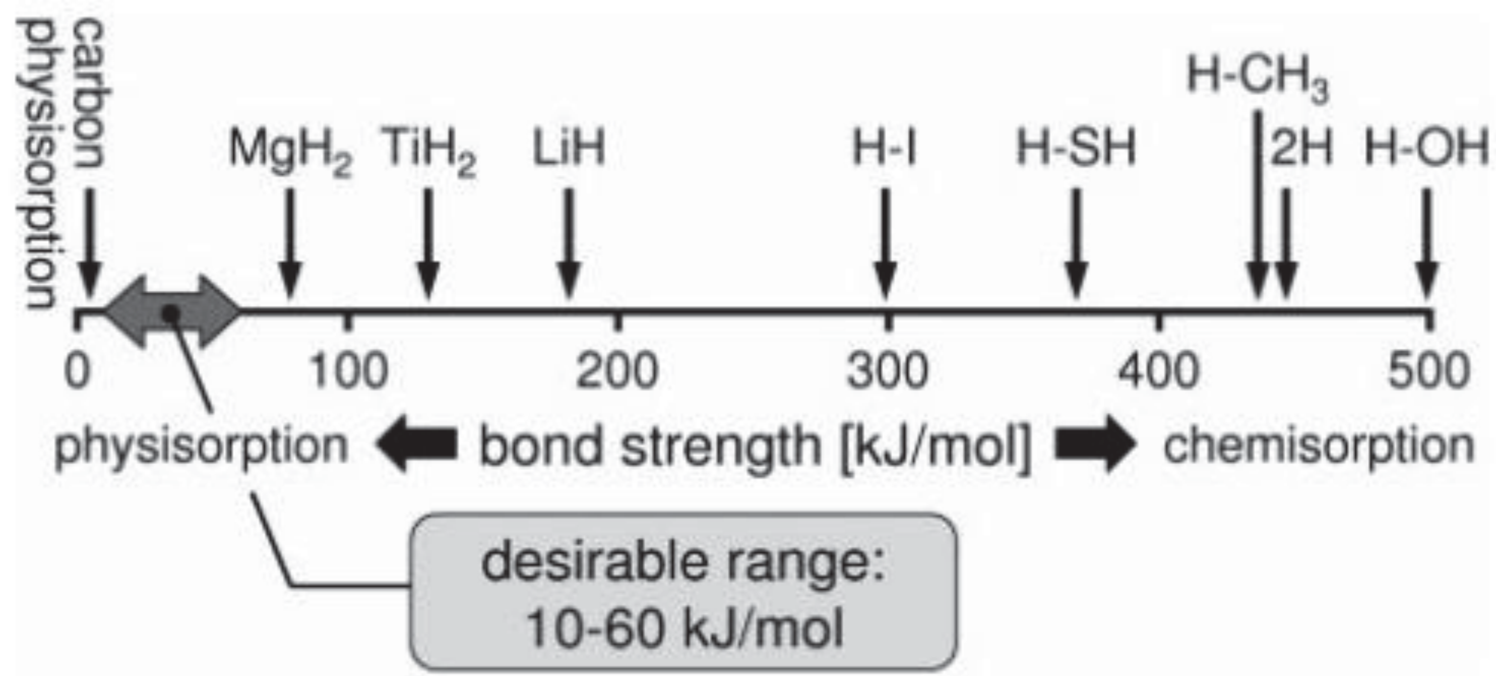


⇒ **Bulk nucleation and growth**

Destabilization

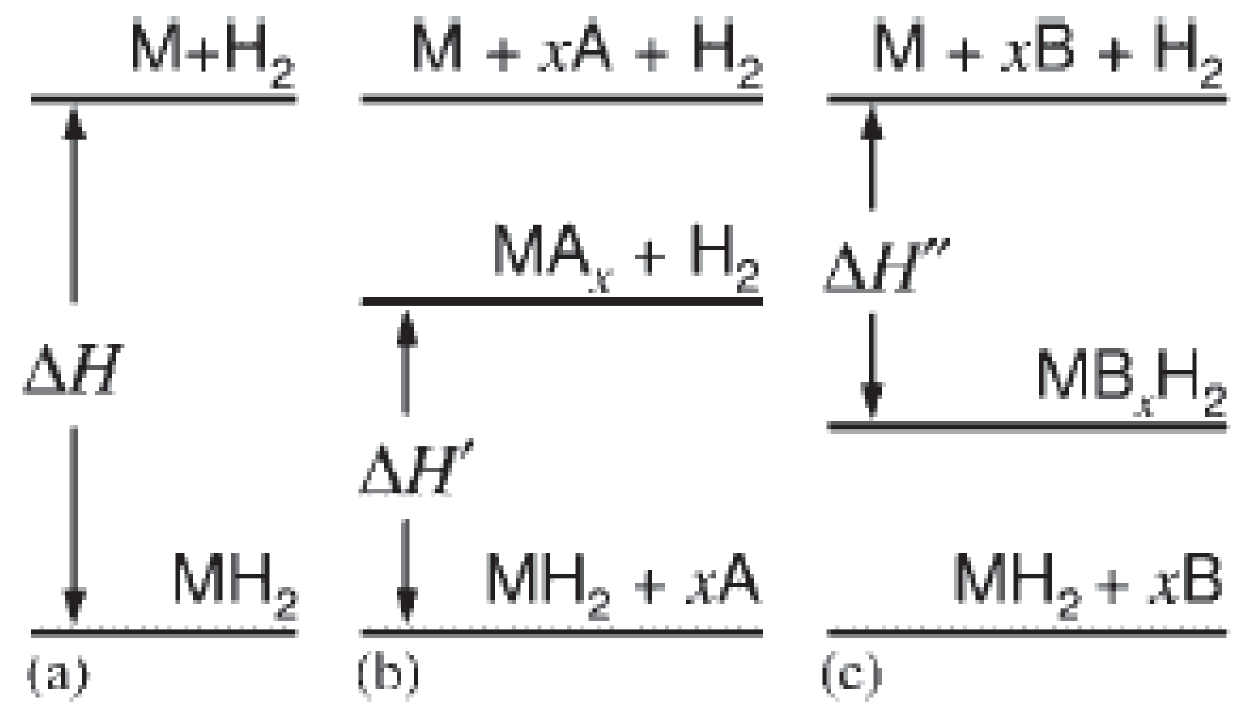
- Chemical
  - Formation of a new compound
- Size effect
- Excess enthalpy and strain at the grain boundary
- Recrystallization

Bond strength



Int. J. Energy Res. 2007; **31**:637–663

Chemical destabilization



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Effect of cluster size

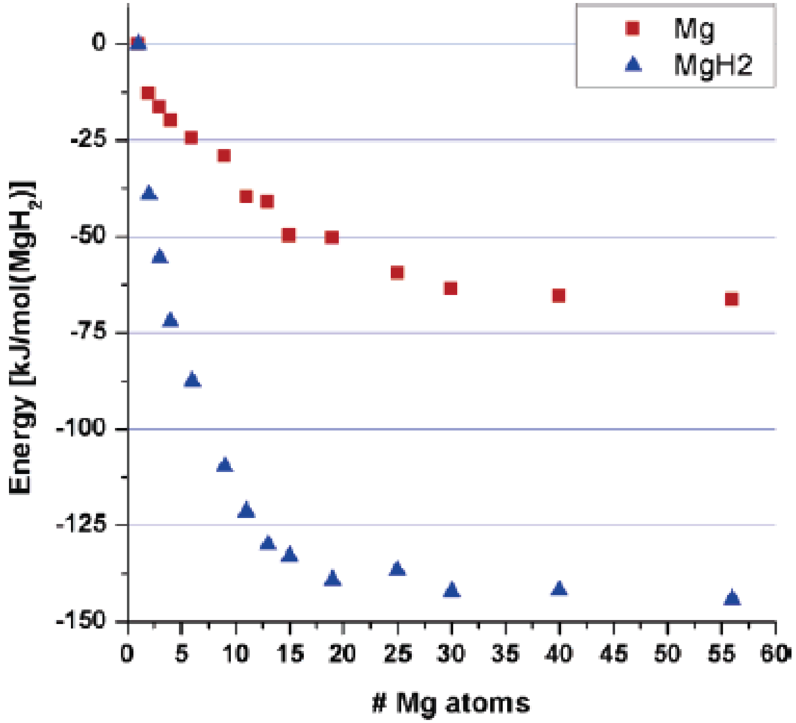

Figure 3. Energies for Mg and MgH_2 clusters as a function of cluster size, calculated with the DFT method (B97 functional). The energies are scaled to the Mg or MgH_2 cluster and normalized per Mg atom.

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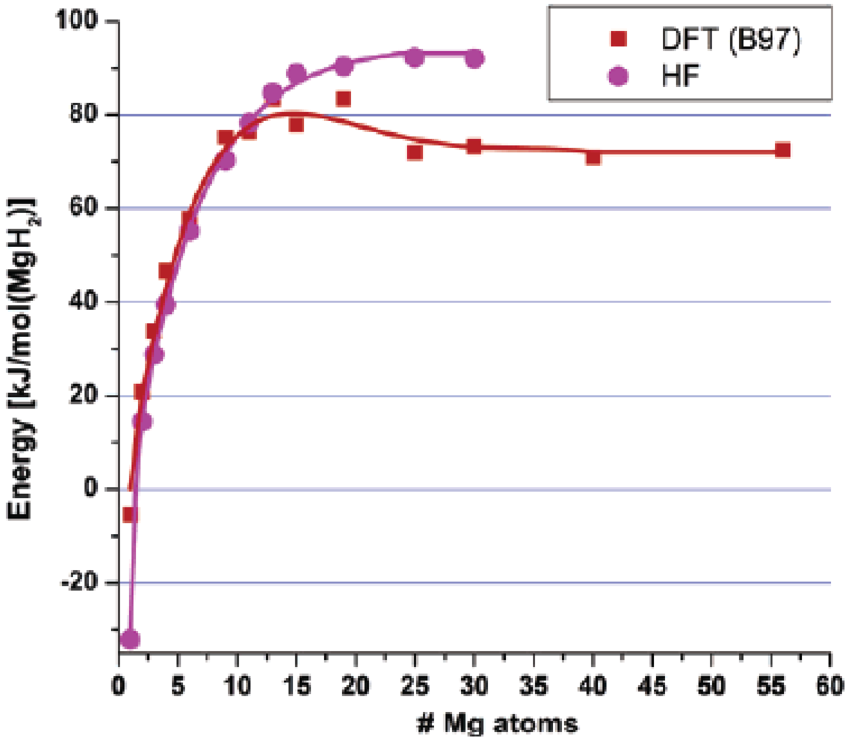

Figure 4. Calculated desorption energies for MgH_2 clusters with both the HF method and DFT method (B97 functional). The energies are normalized per mole of H_2 released.

J. AM. CHEM. SOC. ■ VOL. 127, NO. 47, 2005

Conclusion

MH have many practical applications and may be the solution for hydrogen storage problems

MH are also ideal systems for fundamental understanding of:

- Physics
- Chemistry
- Metallurgy
- Surface science
- Nanotechnology
- Clusters