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School on Pulsed Neutrons: Characterization of Materials

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Hydrogen in Metals and Hydrogen Storage

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22. October 2007

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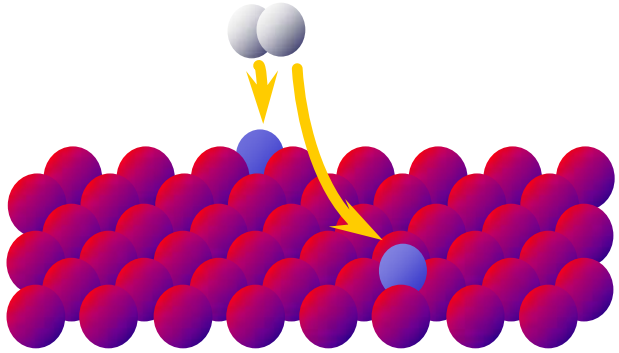
Content

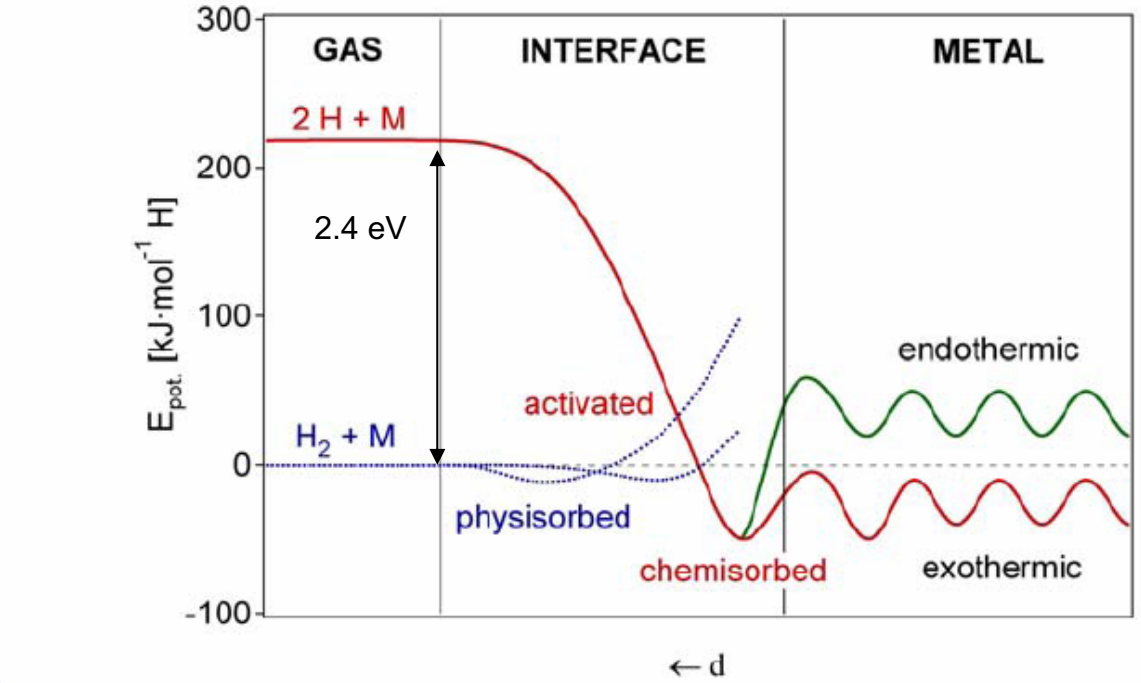
1. Primer for hydrogen in metals
2. A deeper insight
3. Neutron studies
4. Hydrogen economy
5. Hydrogen storage materials

1. Primer
for hydrogen in metals

1. Step:
Dissociation, Physisorption, Chemisorption

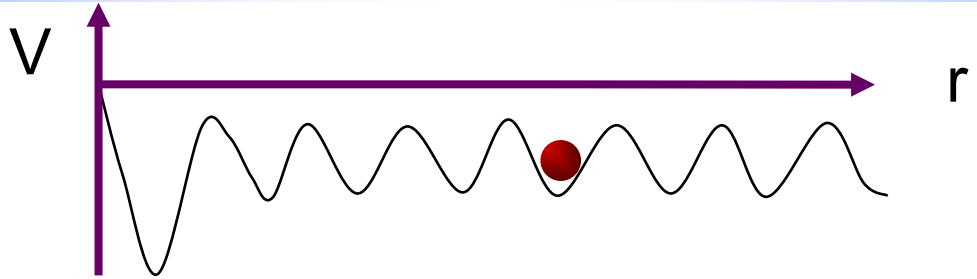


$$M + \frac{1}{2} x H_2 \leftrightarrow MH_x$$



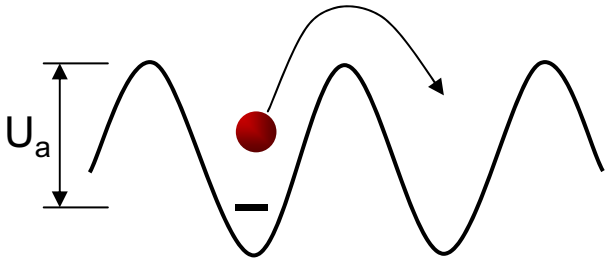
Ref.: J. E. Lennard-Jones, Trans. Faraday Soc. 28 (1932), pp. 333.
L. Schlapbach, Chapter 1, L. Schlapbach (Ed.) in Intermetallic Compounds I, Springer Series Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 10.

2. Step: Diffusion into the metal

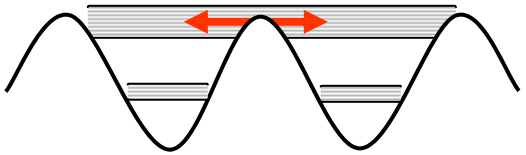


Three diffusion types:

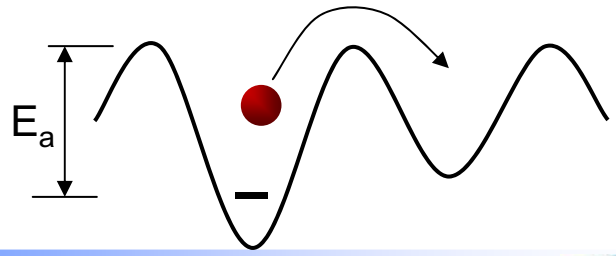
1. Classical jump diffusion:



2. Thermally activated tunneling:



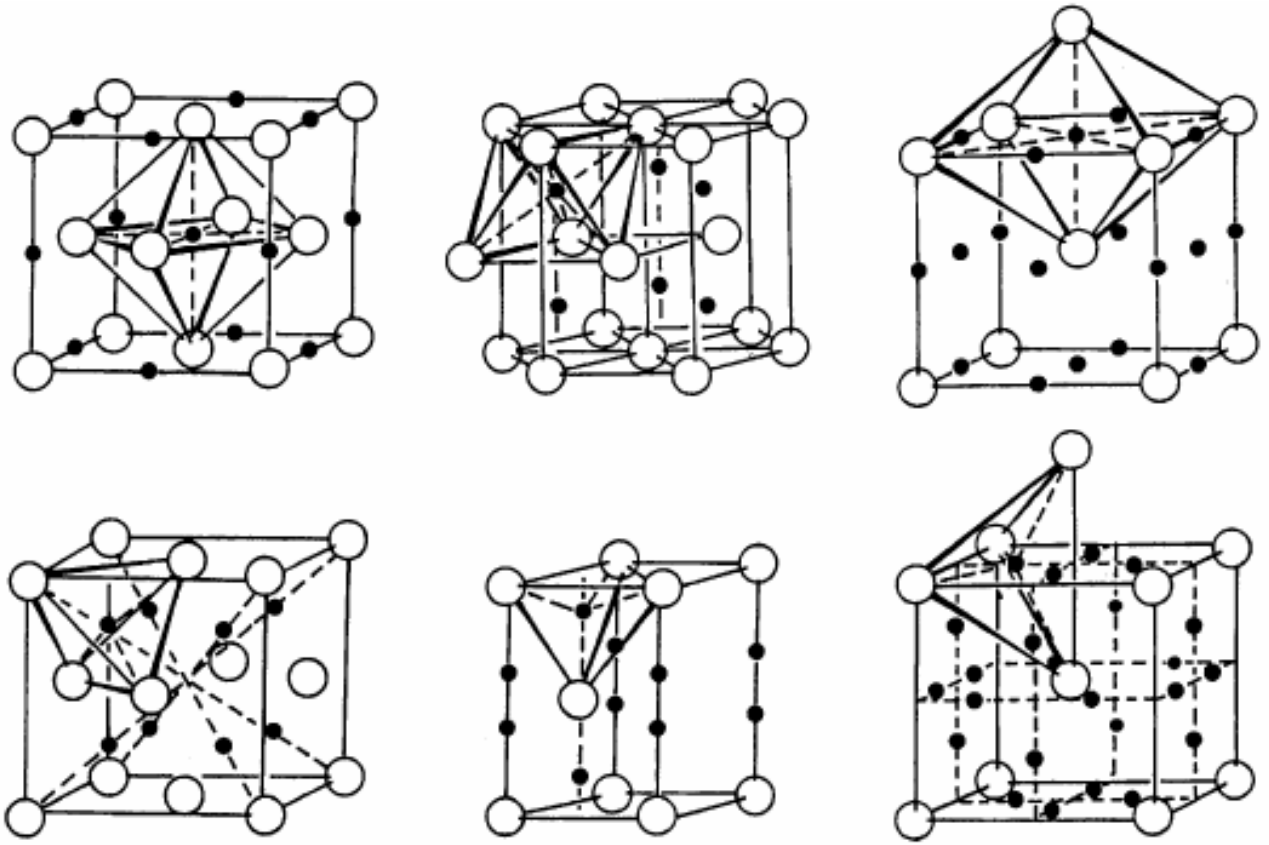
3. Self trapping through lattice relaxation:



3. Step: Occupation of interstitial sites in metals

octahedral

tetrahedral



fcc hcp bcc

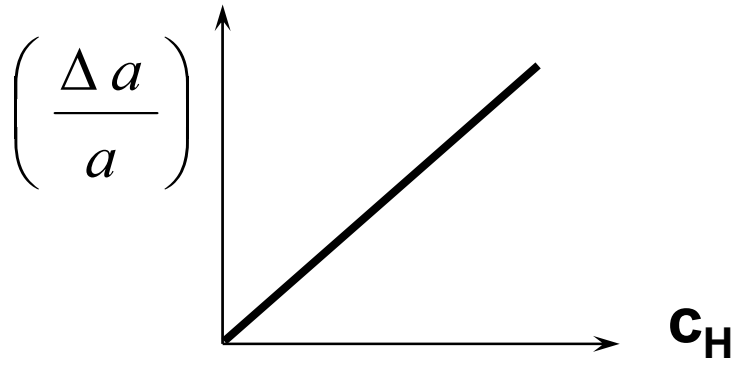
4. Step: Volume change

Lattice parameter change due to point defects:

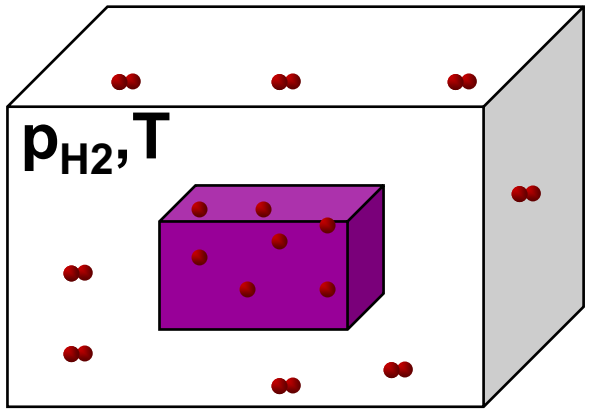
$$\frac{\Delta a}{a} = \frac{1}{3}\frac{\Delta V}{V} = \frac{1}{3}\frac{\Delta v}{\Omega} c_H$$

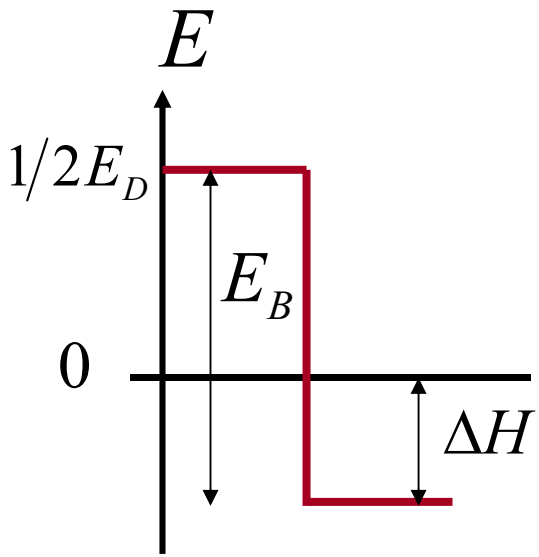
$\Delta v = \Delta V / N_D =$ defekt strength

$\Omega = V/N_H = a^3/2 =$ volume of hostatom



5. Step: Chemical equilibrium





Equilibrium condition between external H_2 - pressure and dissolved H in metal:

$$\frac{1}{2}\mu_{H_2}(gas) = \mu_H(metal)$$

$$\ln\sqrt{\frac{p_{H_2}}{p_0}} = \frac{\Delta H}{RT} + \ln\left(\frac{c_H}{1-c_H}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

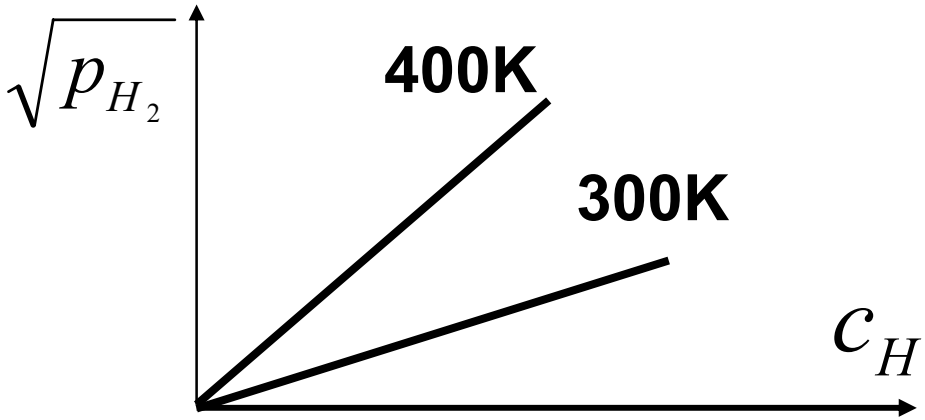
Solution enthalpy:

$$\Delta H = E_B - \frac{1}{2}E_D < 0$$

Solubility isotherms for hydrogen in metals

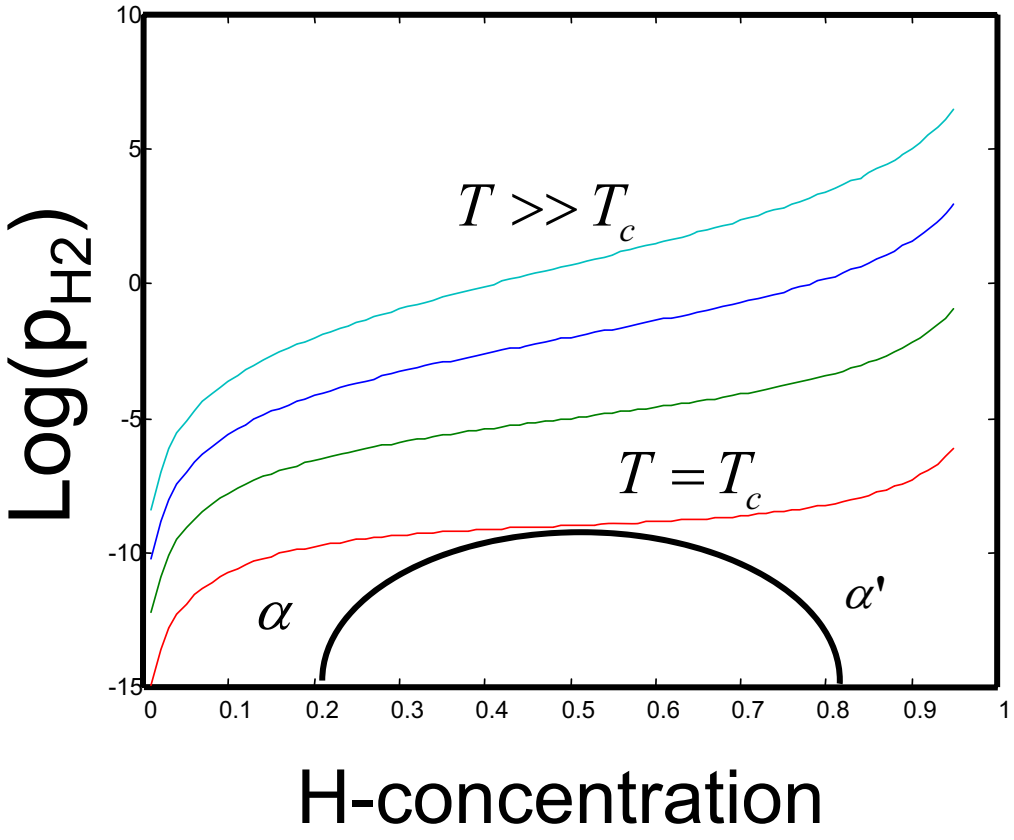
$$\ln\sqrt{\frac{p_{H_2}}{p_0}} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Sieverts law : $\sqrt{p_{H_2}} \propto c_H$



The linear dependence $(p_{H2})^{1/2} \sim c_H$ is a direct consequence of hydrogen dissociation in the metal.

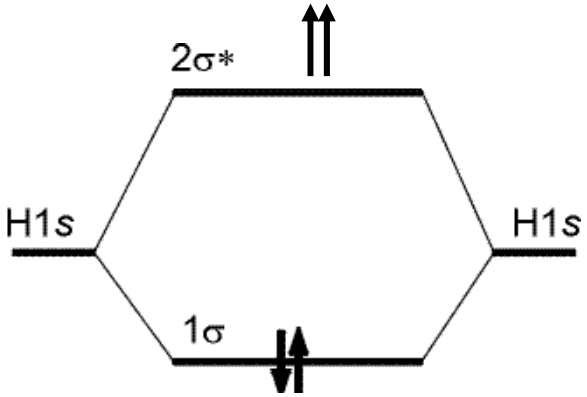
Solubility isotherms and phase transition



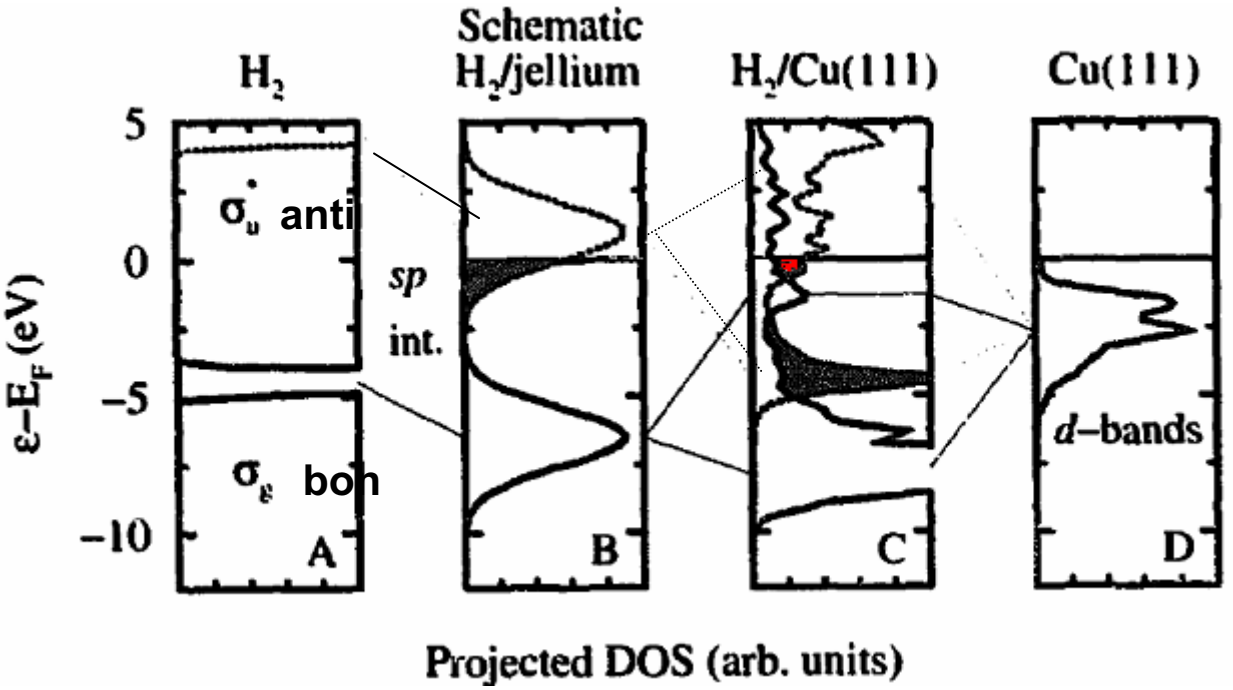
2. A deeper insight

Dissociation at the surface

H_2-molecule bonding and antibonding states



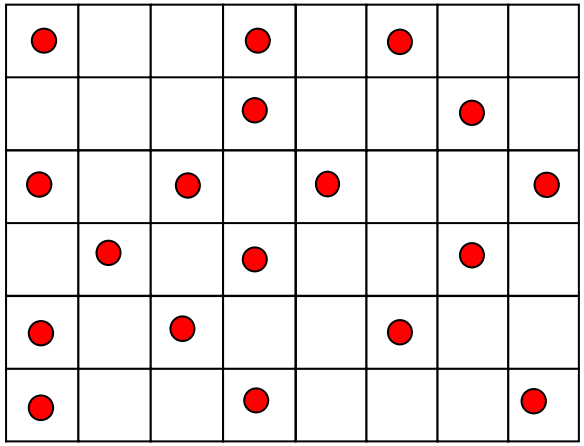
Orbital broadening, overlap and orthogonalization with metal d-bands



1. H_2 – molecule bonding and antibonding state relative to the metal d-band
2. Coupling matrix element between molecular orbitals in metal d-band
3. Filling of the molecule – surface antibonding state

B. Hammer and J.K. Nørskov, Surface Science 343 (1995) 211

Hydrogen in Metals: Lattice gas with interaction



Lacher's Ansatz for the free energy (1937):

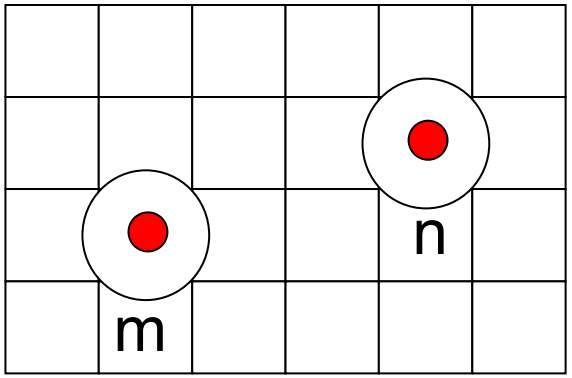
$$F = -\frac{1}{2} J \tau_H^2 N_0 - k_B T \, ln \frac{N_0!}{(N - N_0)! N!}$$

$$\mu_H = \Delta H + k_B T \, ln\left(\frac{\tau_H}{1-\tau_H}\right),$$

$$\Delta H = \underbrace{\underbrace{E_B - 1/2 E_D}_{\text{H–Metal}} - \underbrace{J \tau_H}_{\text{H–H}}}_{\text{interaction}}$$

What is the binding energy E_B and the interaction energy J due to?

H-H elastic interaction



H-H interaction is mediated by long range strain fields = elastic interaction.

$$E_{el} = \frac{1}{2}\sum_{m,n} u_m J_{mn} u_n$$

Strain field: $\vec{u}_m(\vec{r}) = \frac{\Delta v}{4\pi C_{11}\kappa_T}\frac{\vec{r}}{r^3}$ For J follows: $J = \eta B \frac{(\Delta v)^2}{\Omega} c_{\max}$

Δv = volume change per hydrogen atom.
Ω = volume per host metal atom
B = bulk modulus
η =short range electronic parameter
c_{max} = maximum hydrogen concentration

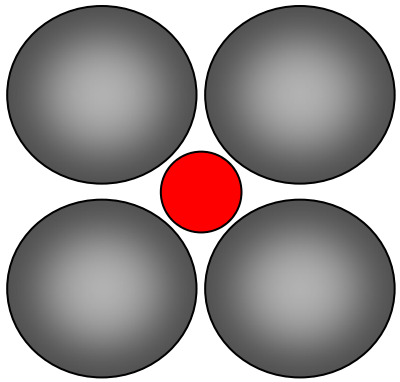
The H-H interaction is only attractive, if the system is finite and has free surfaces.

Energetics

Westlake criterion:

Size for hydrogen site: r > 0.37Å

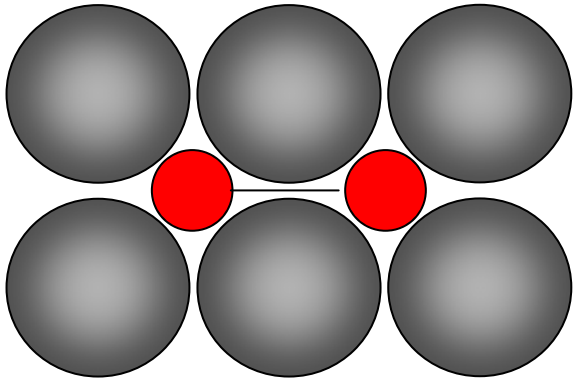
D. G. Westlake, J. Less-Common Metals **91** (1983) 275



Switendick criterium:

Minimum distance between two hydrogen atoms d > 2.1 Å

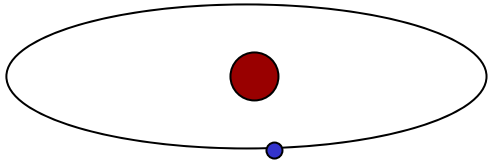
A. C. Switendick, Z. Phys. Chem. N.F. 117 (1979) 89



Maximum hydrogen density in metals is then ~ 200 kg/m^3 as compared to 70 kg/m^3 in the liquid state.

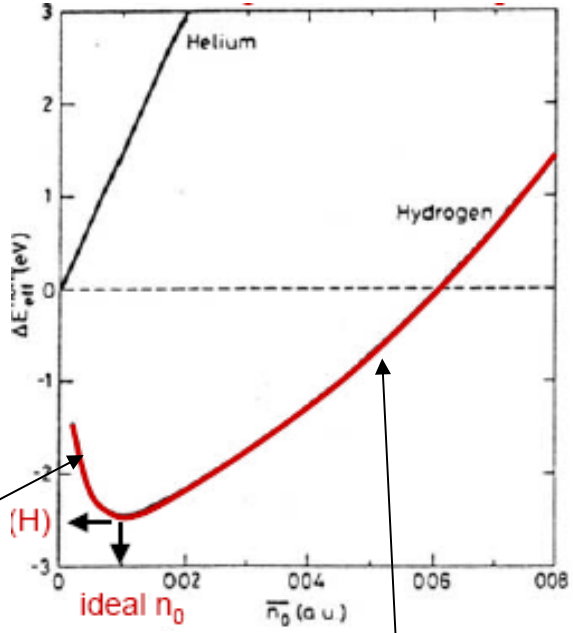
Effective embedding theory

Homogeneous
free electron density n_0



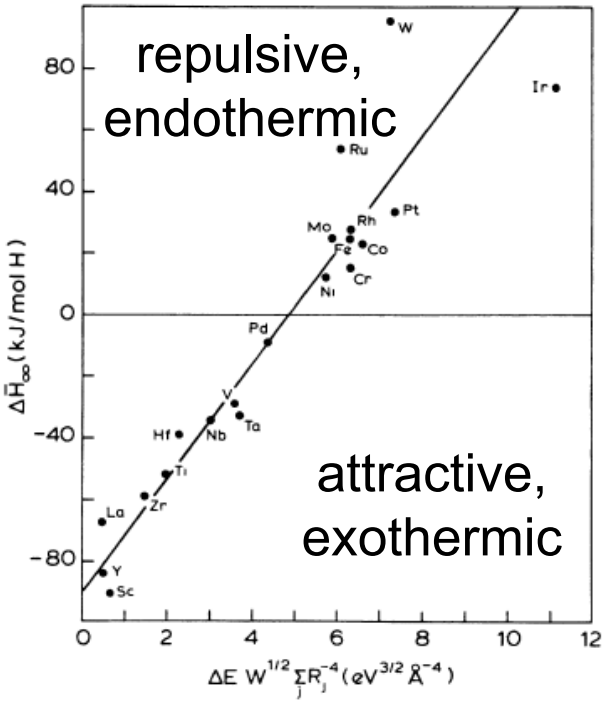
Filling of 1s state

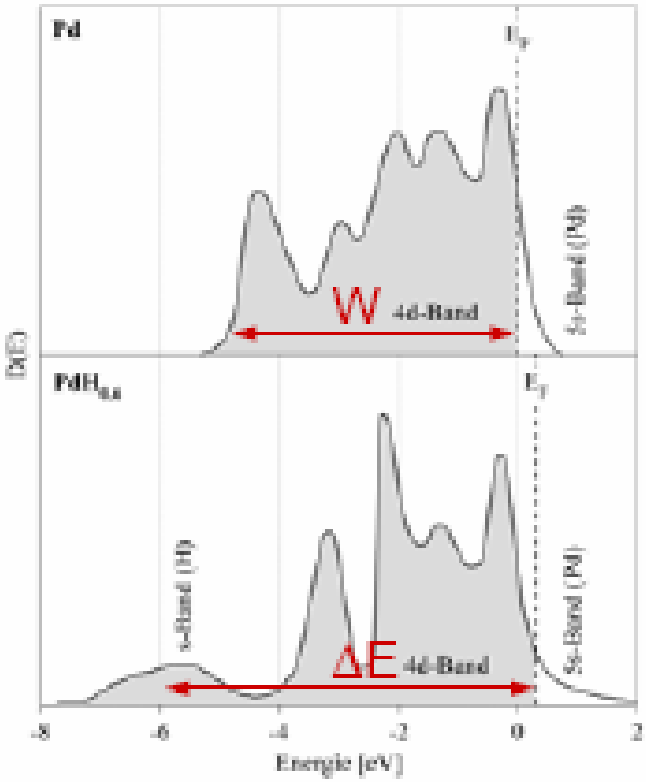
Effective embedding
energy of H



Repulsion due to
orthogonalization

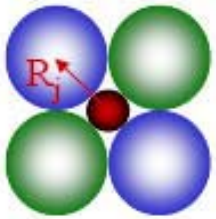
Local band structure semiempirical model





$$\Delta\overline{H}_\infty = a \cdot \Delta E \cdot \sqrt{W} \cdot \sum_i R_j^{-4} + b$$

a,b = fit parameters,
R_j = n.n. H-M distance



R Griessen, Phys. Rev. B **38**, 3690 (1988)

BINARY HYDRIDES

1	2											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	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															

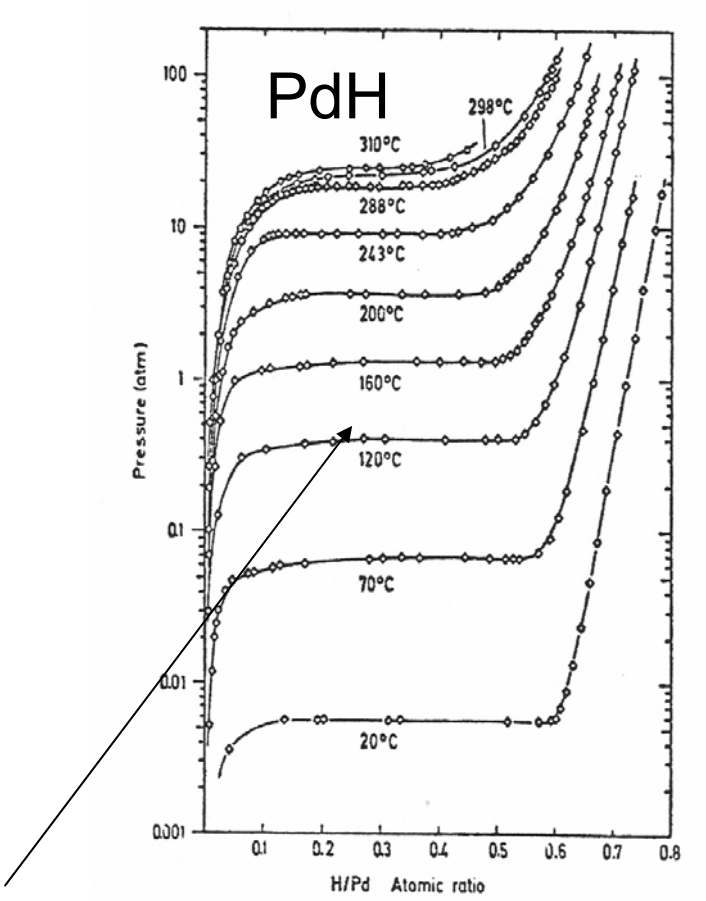
Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

- Ionic hydrides
- Covalent polymeric hydrides
- Covalent hydrides
- Metallic hydrides

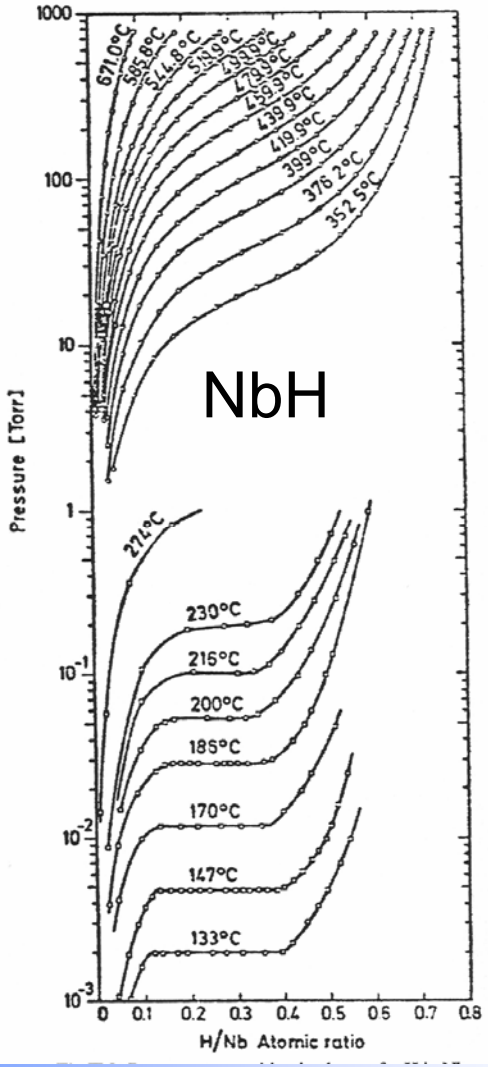
Ref.: Gottfried Brendel, “Kapitel: Hydride”, Ullmanns Encyklopädie der technischen Chemie, 4. neubearbeitete und erweiterte Auflage, Band 13 (1977), pp. 109-133, Verlag Chemie Weinheim New York

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_2 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

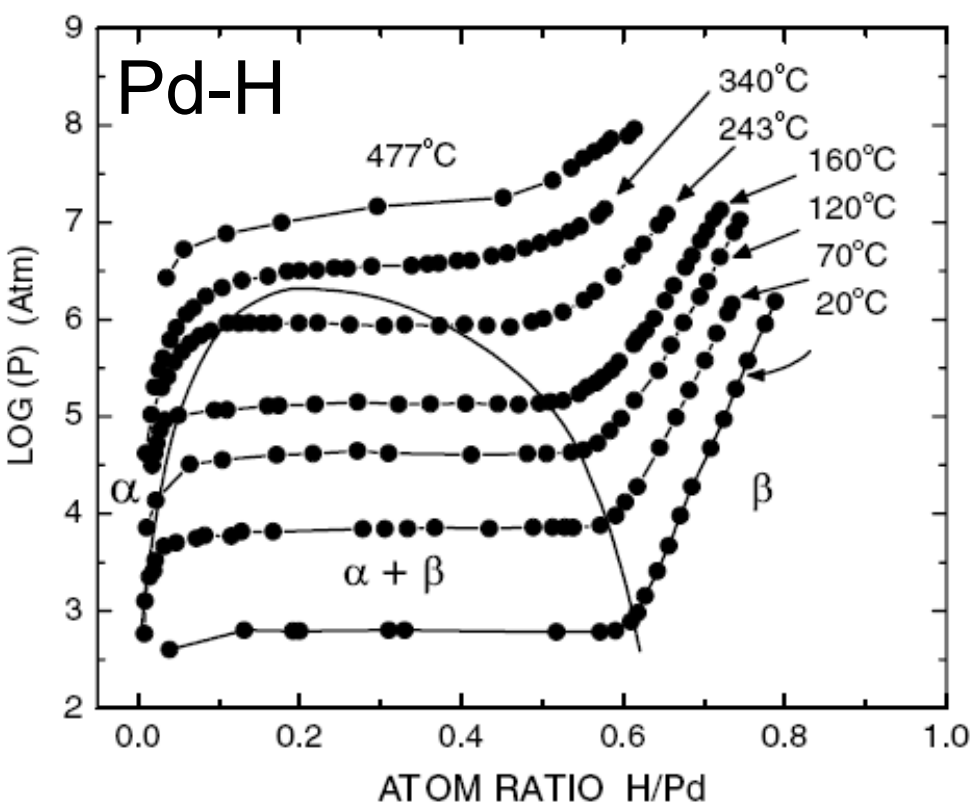
Pressure-composition isotherms for the determination of phase diagrams and solution enthalpies

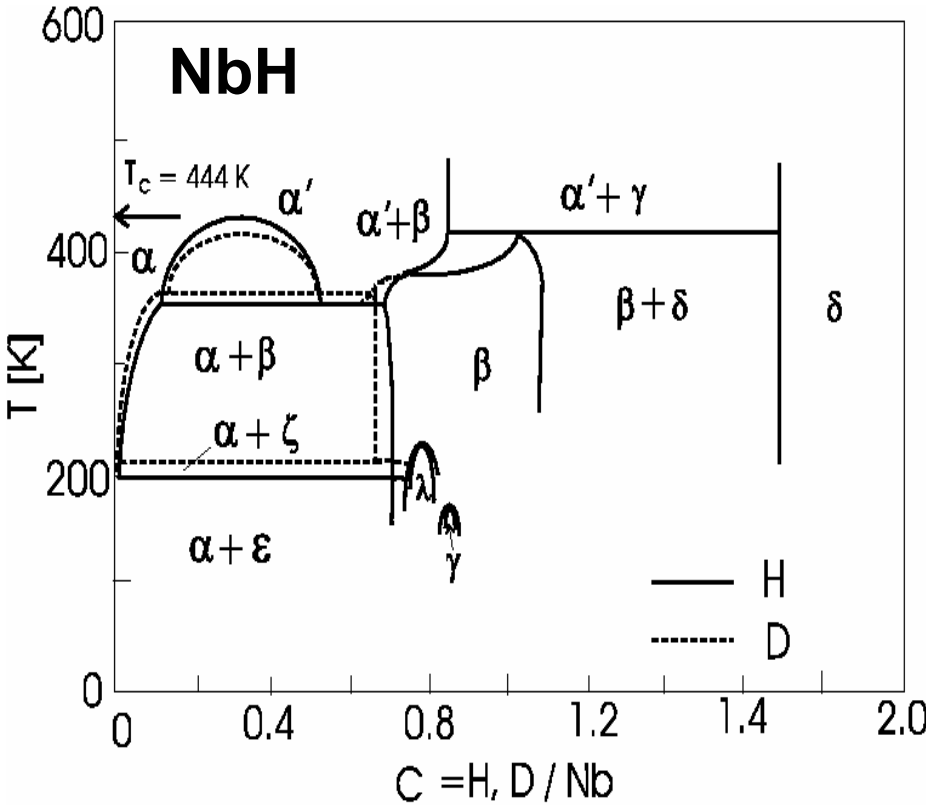


Equilibirium or dissociation pressure

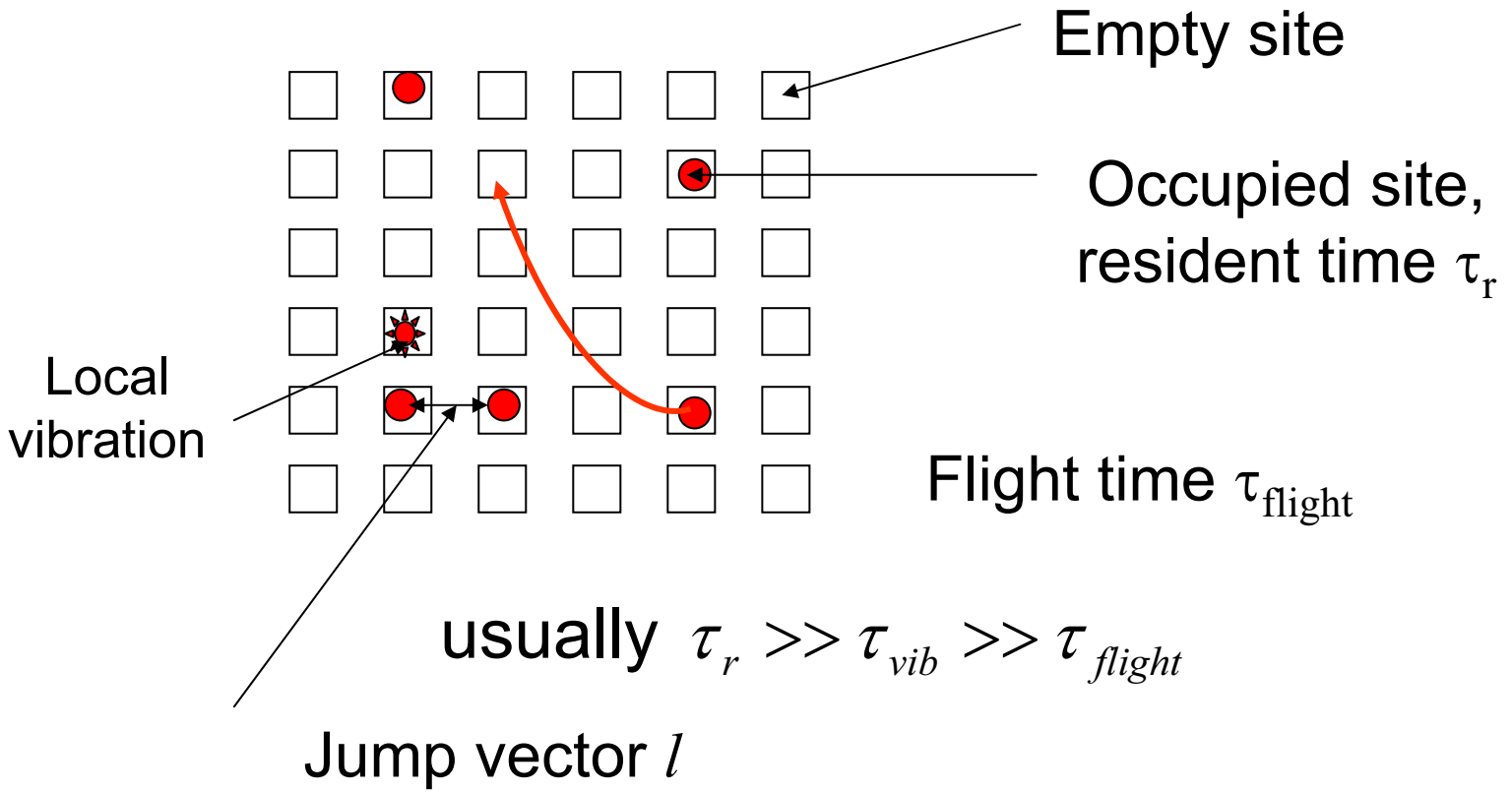


Metal-hydrogen phase diagram

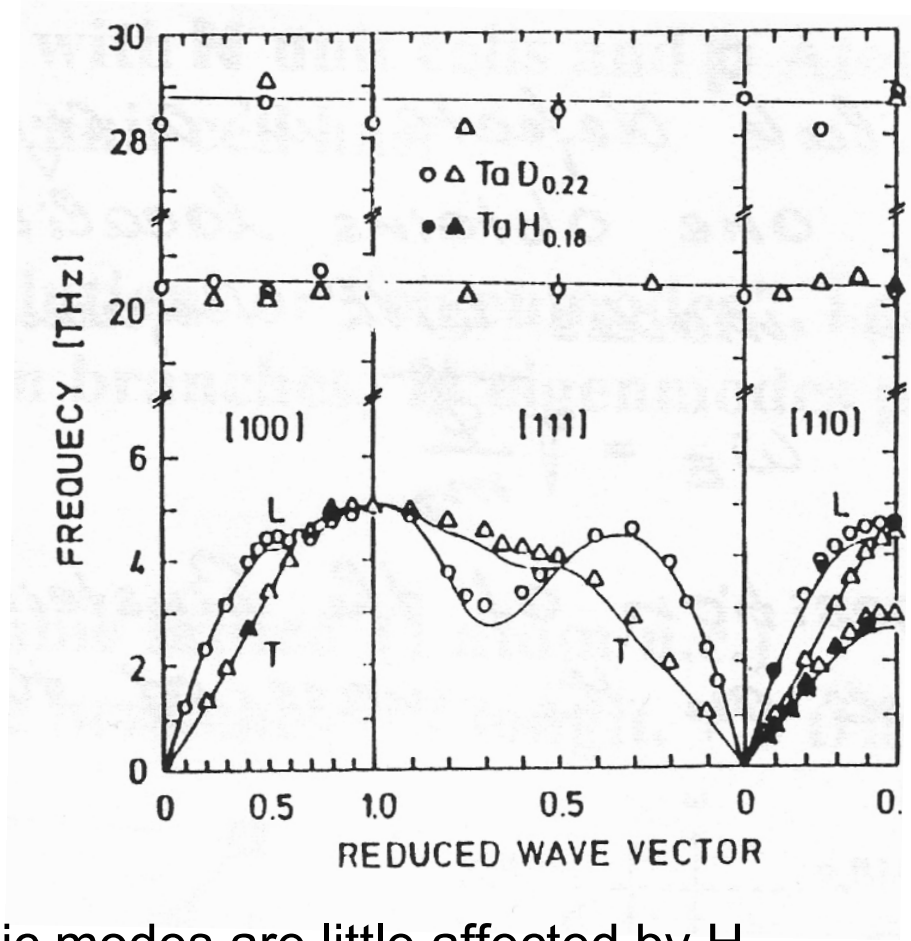




Dynamics and diffusion of a lattice gas



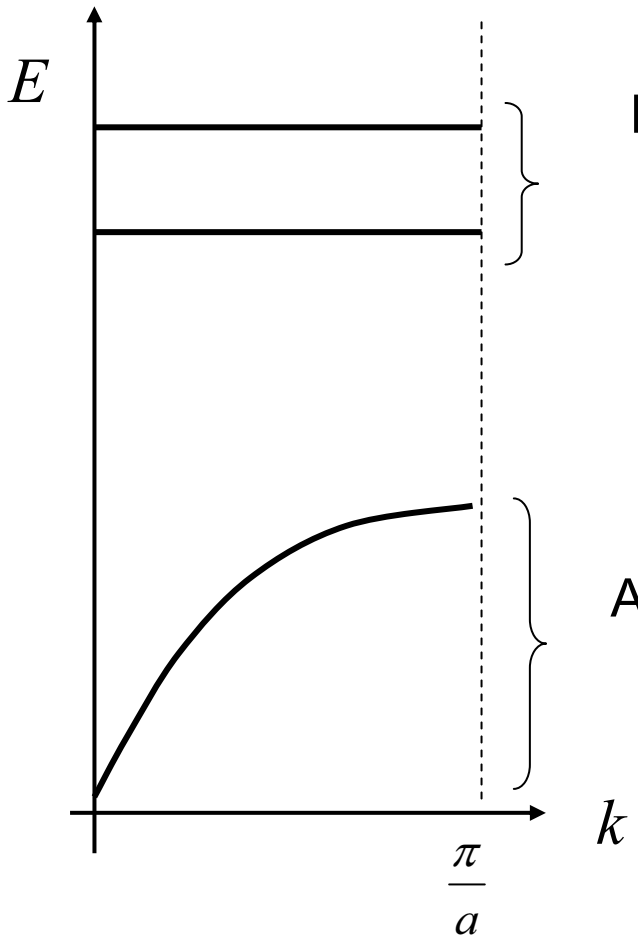
Phonon dispersion of Ta with H



Acoustic modes are little affected by H
New optic modes due to local hydrogen vibration.

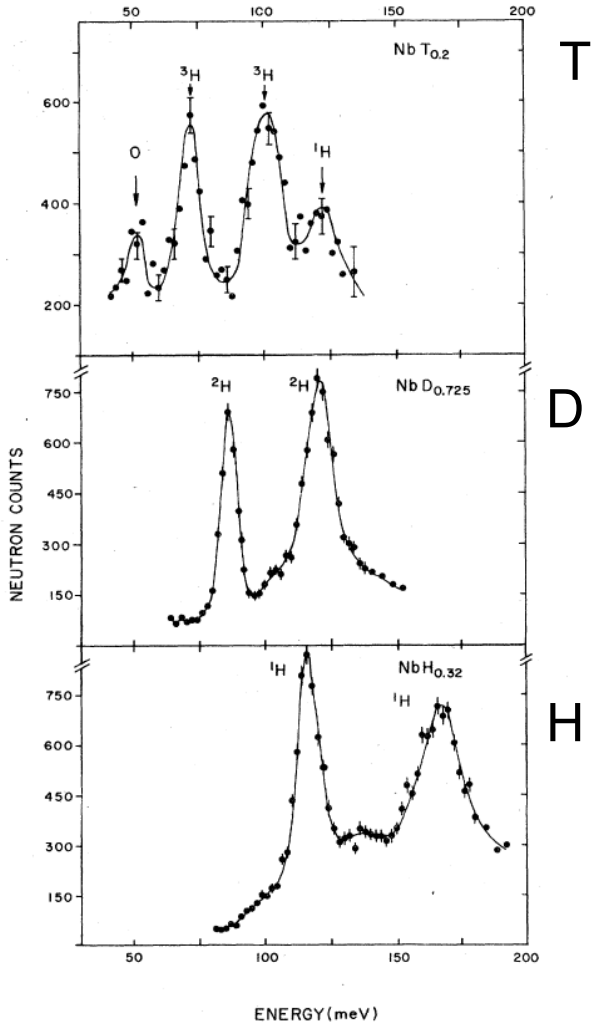
A. Magerl et al. J. Phys. C 10 (1977) 2783

Local hydrogen vibration



Einstein modes with tetragonal symmetry

Acoustic modes of host lattice



J. Rush et al. PRB **24**, 4903 (1981)

Local hydrogen vibrational potential

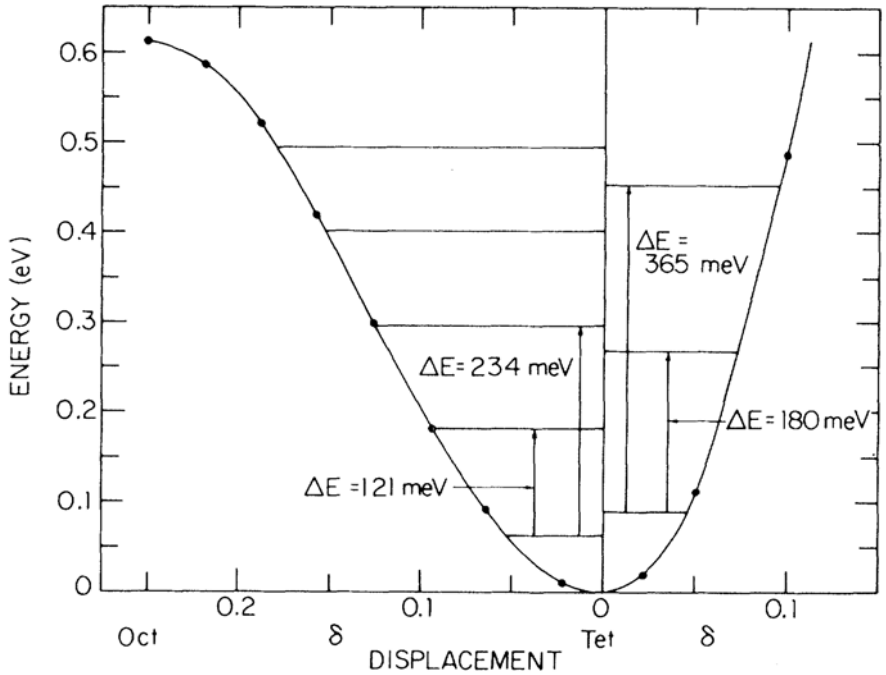
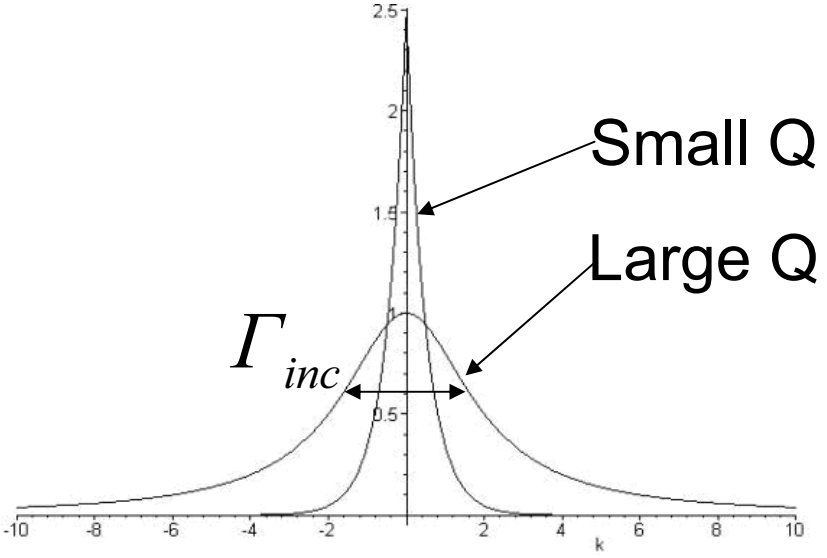


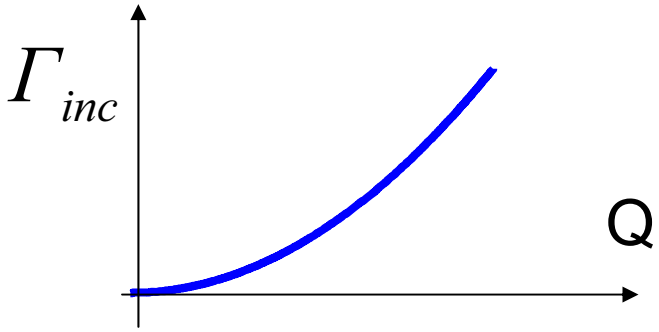
FIG. 2. Calculated energy vs displacement curves for hydrogen in Nb. The displacements of the hydrogen for the tetrahedral site are $(0,0,a)$ [*t-o* in Fig. 1(a)] for the left-hand portion of the curve and $(0,a,0)$ [*t-y* in Fig. 1(a)] for the right-hand portion.

Quasi-elastic neutron scattering:
Scattering function for continuous diffusion in a liquid

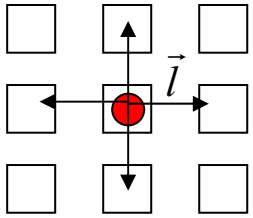
$$S_{inc}\left(\vec{Q},\omega\right)=\frac{1}{\pi\hbar}\frac{DQ^2}{\left(DQ^2\right)^2+\omega^2}$$



$$\Gamma_{inc}=2\hbar DQ^2$$



Quasi-elastic neutron scattering: Scattering function for jump diffusion



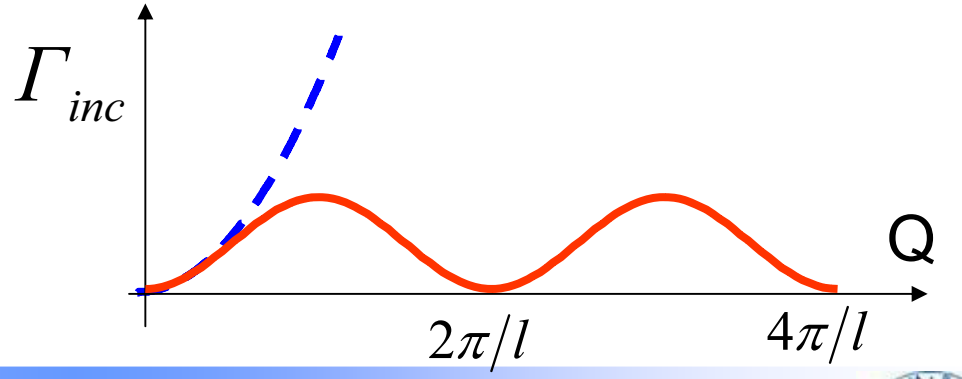
$$S_{inc}(\vec{Q},\omega)=\frac{1}{\pi\hbar}\frac{f(Q)/\tau}{(f(Q)/\tau)^2+\omega^2};\quad \Gamma_{inc}=2\hbar\, f(Q)/\tau$$

$f(Q)$ is an oscillatory structure factor:

$$f(Q)=\frac{1}{n}\sum_{i=1}^{n}\left(1-\exp\left(-i\vec{Q}\cdot\vec{l}_i\right)\right)$$

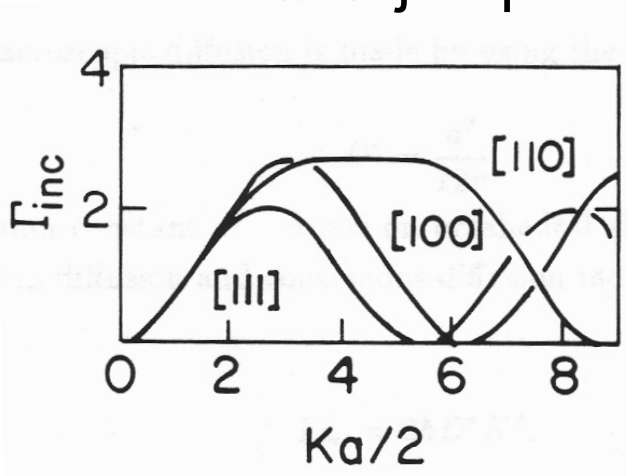
The incoherent line width oscillates in case of jump diffusion, and for a Bravais lattice is:

$$\Gamma_{inc}=\frac{8\hbar}{n\tau}\sum_{i=1}^{n/2}\sin\left(\frac{\vec{Q}\cdot\vec{l}}{2}\right)$$

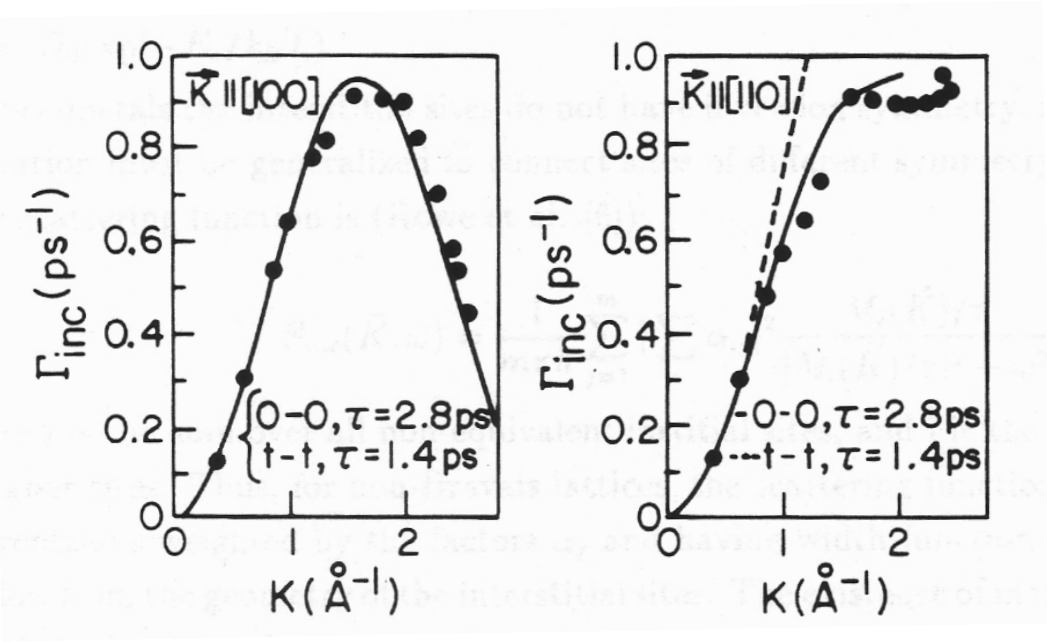


Hydrogen diffusivity in Pd single crystals

Calculated widths for O-O jumps



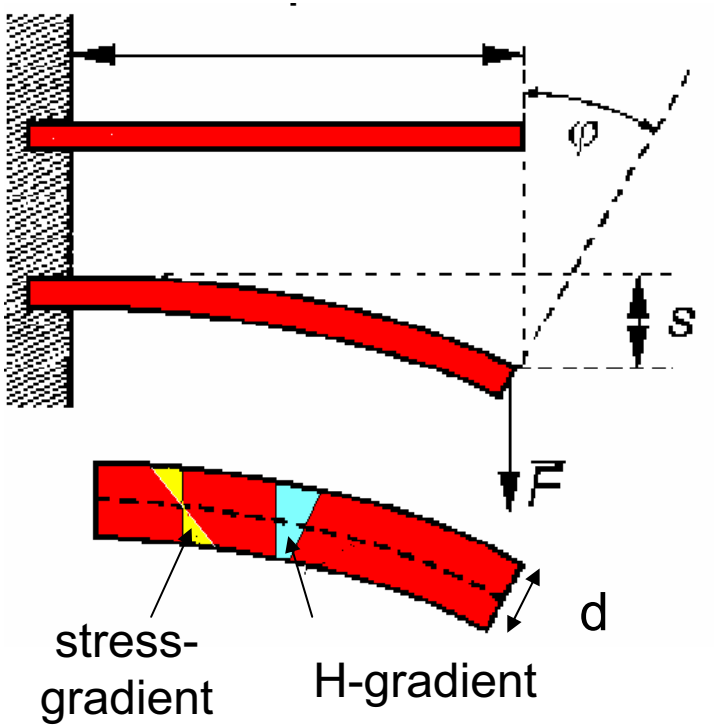
Measured line widths

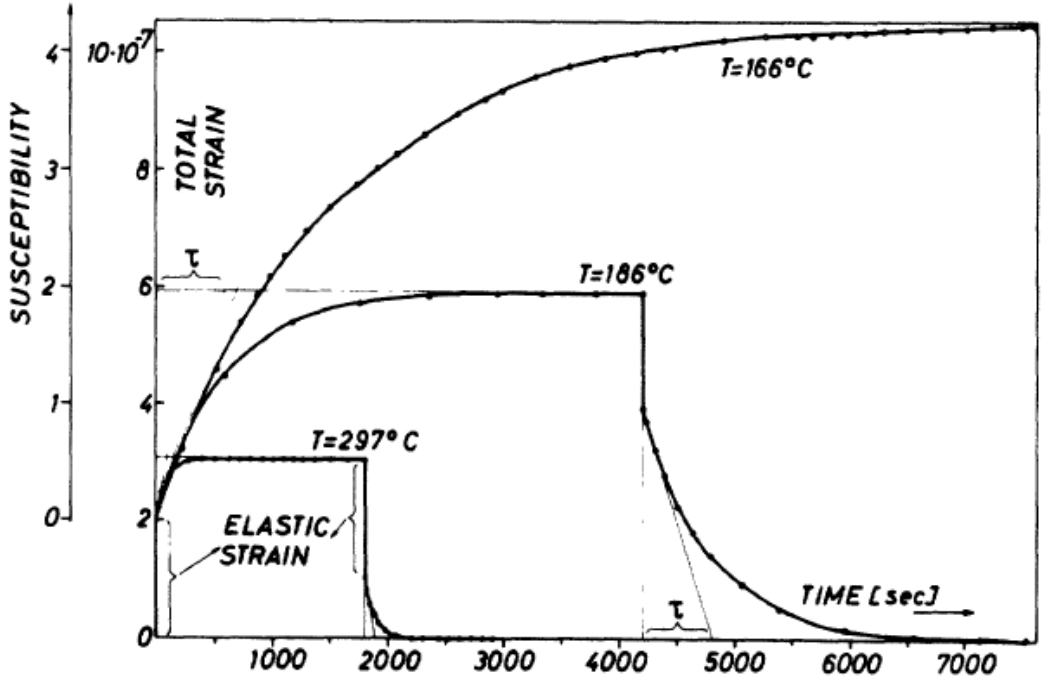


Only O-O jumps are consistent with measurements

QENS allows to determine self-diffusivity and geometry of jump vectors

Gorsky effect or anelastic relaxation for the study of diffusion in solids





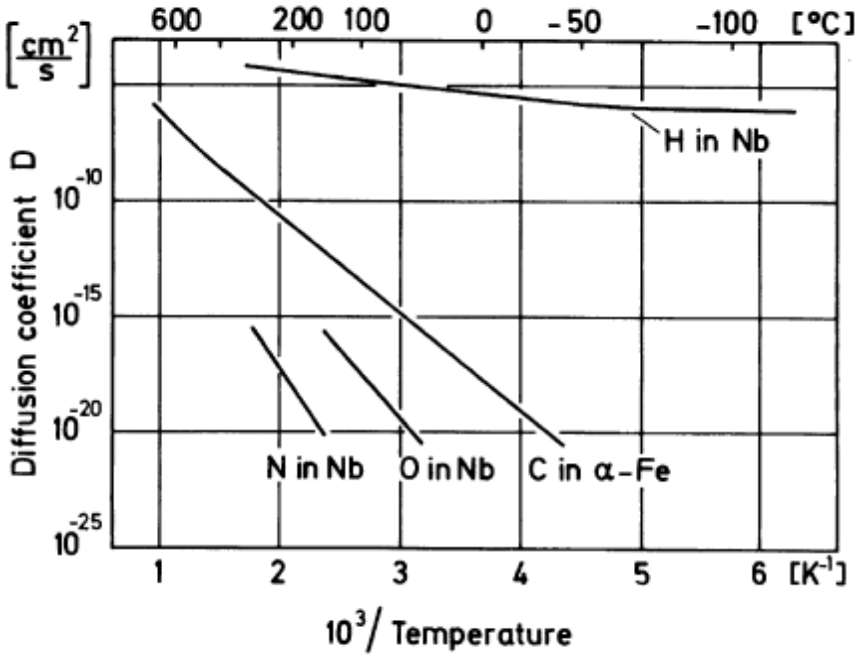
Relaxatíon time and diffusion constant:

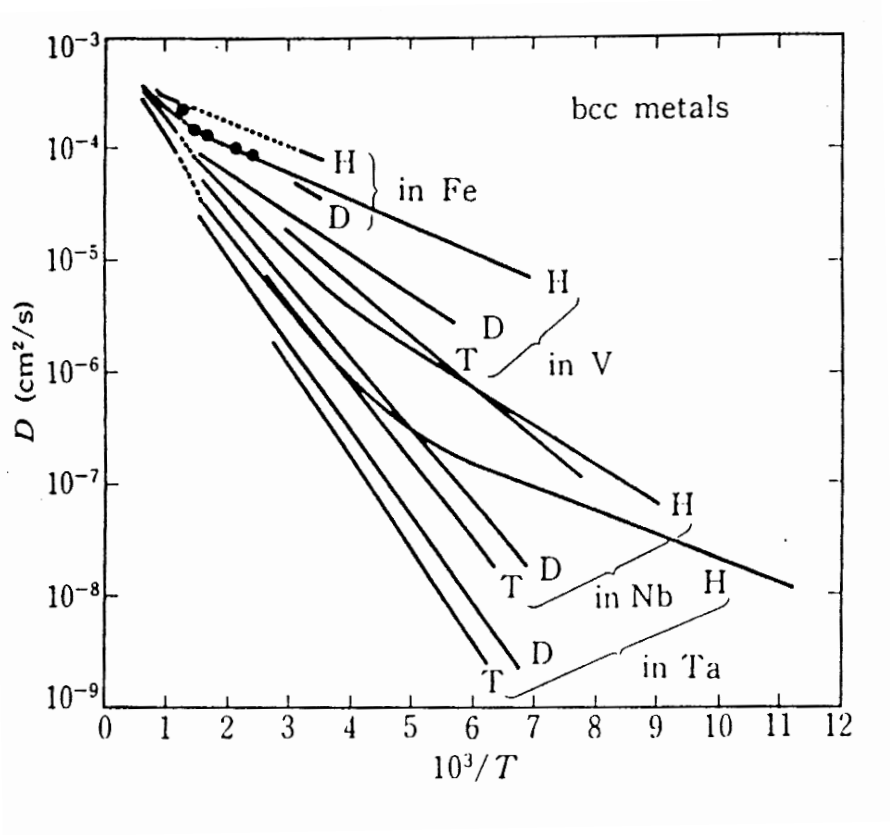
$$\tau_{anel} = \tau_{0,anel} \exp\left(U_D / k_B T\right)$$

$$\tau_{0,anel} = d^2 / \pi^2 D_0 ; \quad D = D_0 \exp\left(-U_D / k_B T\right)$$

G. Alefeld et al. PRL **22**, 697 (1969)

Hydrogen diffusivity





$D_0 = 5 \times 10^{-4}$ cm^2/s; U = 0.106 eV for H in Nb and T > 300K

4. Hydrogen economy:

1. Production
2. Storage
3. Transport
4. Uses of hydrogen

1. Production of Hydrogen

- Water vapor over hot coal
- Thermal Dissociation of carbon hydrides (Steam-reforming of oil and natural gas produces 9M tons H_2/yr)
- Electrolysis of water
- Separation of acid with metals
- Photovoltaic dissociation
- Photobiological production

2. Storage of hydrogen

- Liquid hydrogen at temperatures $\leq$ 20K
- High pressure gas tanks, 1 – 20 MPa (10 –200 bar)
- Storage in solids or liquids:
  - ♦ metal alloys and compounds
  - ♦ carbon nanotubes
  - ♦ glass micropores, polymers, etc.
  - ♦ iron sponges
  - ♦FeTi – nanophase material with high grain boundary density
  - ♦ methanol (CH_3OH)

Requirements of hydrogen storage materials identified by DOE panel

- High gravimetric and volumetric density (10 wt %)
- Fast kinetics
- Favorable thermodynamics
- Reversible and recyclable
- Safe, material integrity
- Cost effective
- Minimal lattice expansion
- Absence of embrittlement

Further requirements

- Ambient temperature for charge and discharge
- Low hysteretic losses
- Sensitivity to impurity gases
- Multi-cycle stability
- Activation procedure
- Large-scale production possibility at low cost

Some classical metal-hydrides for storage

Alloy	Weigth % H_2	Rel. Volume density	Dissociation temperature (°C)
LH_2		1	
MgH_2	7.6	1.8	290
Mg_2NiH_4	3.6		250
$TiFeH_{1.9}$	1.8	1.8	50

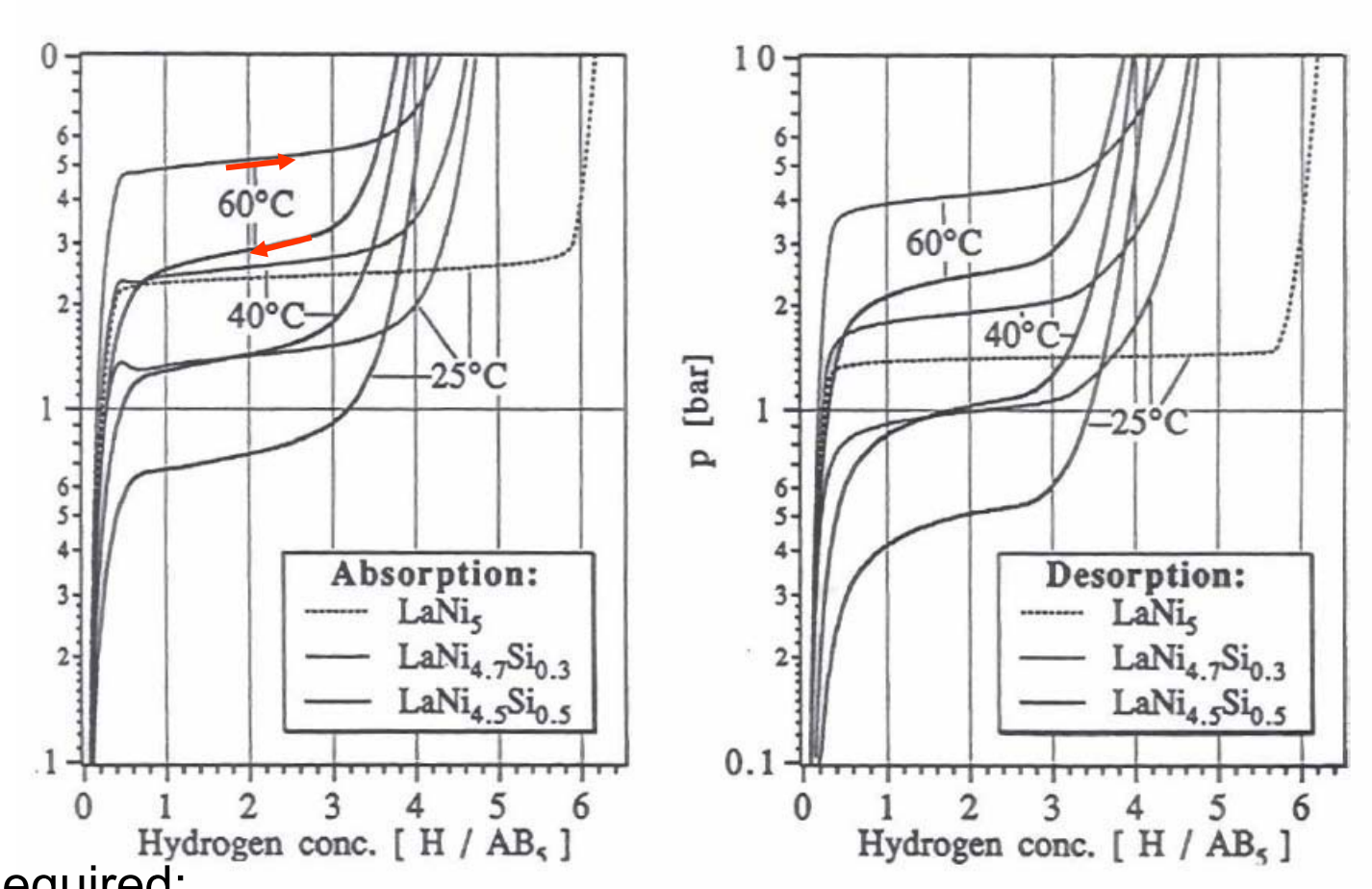
Target of International Energy Association (IEA):

- ≥ 5% hydrogen capacity
- Desorption temperature ≤ 80°C at 1 bar

$LaNi_5$-based intermetallic Alloys

- Produced by high-energy mechanical alloying
- $LaNi_{5-y}Sn_y$
  - Sn:
    - to reduce the plateau pressures for absorption and desorption
    - to decrease the hysteresis between the pressure for hydride formation and decomposition (side effect: decreases the hydrogen storage capacity)
  - An activation cycle is not necessary for the powders to absorb H.
  - Nanocrystalline powder are less affected by the volume change variation due to H charging.

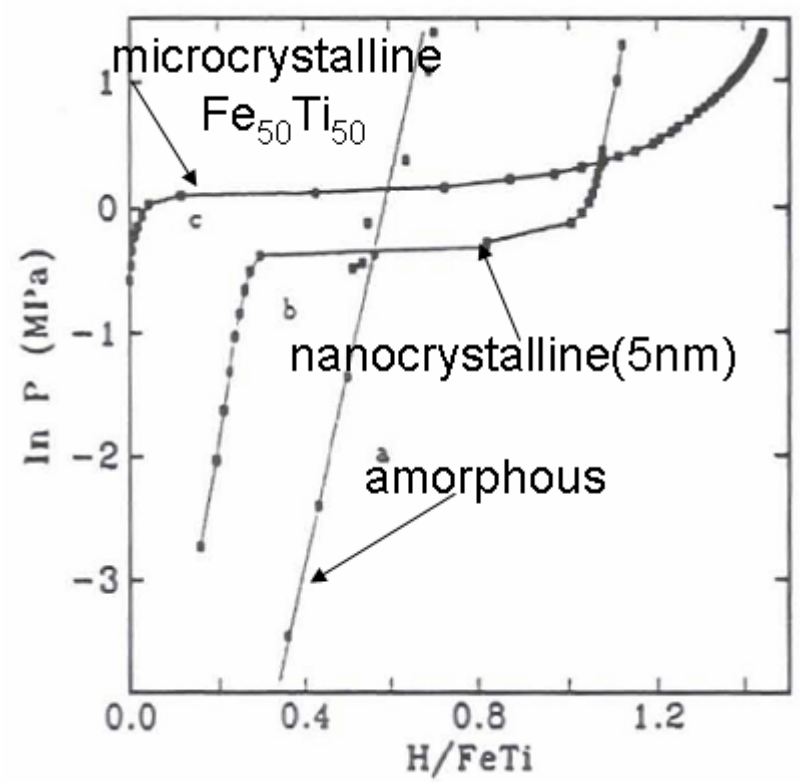
Typical hydrogen absorption-desorption curves



Required:

absorption-desorption cycle around 300°C with rapid rates.

Pressure-composition isotherms for micro- and nanocrystalline FeTi Alloys



Nanocrystalline $Fe_{50}Ti_{50}$ has:

- a lower pressure plateau
- a reduced capacity
- a much easier activation
- Pd addition: enhance the adsorption kinetics

Mg-based Alloys

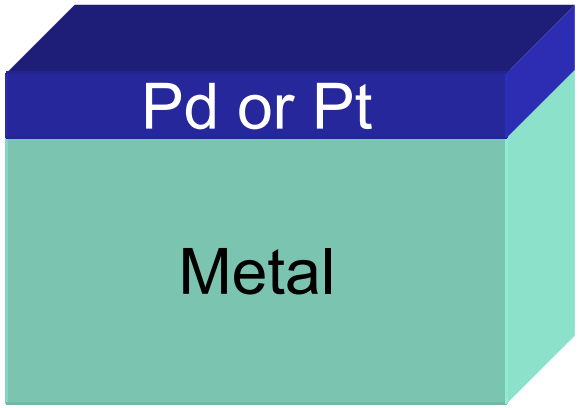
- Advantages:
  - Light weight
  - High hydrogen capacity

- Mg_2Ni, 20-30nm by mechanical alloying, adsorb H without activation at temperature <250˚C (Mg_2NiH_4)
  - Pd addition: enhance the adsorption kinetics

- Mg_2Ni-H system, by milling in a hydrogen atmosphere
  - much higher absorption capacity (1.6wt%) at ambient temperature
  - much lower dehydriding temperature (440K) (Mg_2NiH_4 520K)

Surface coating for faster hydrogen charging

Inactive surface
Diffusion barrier

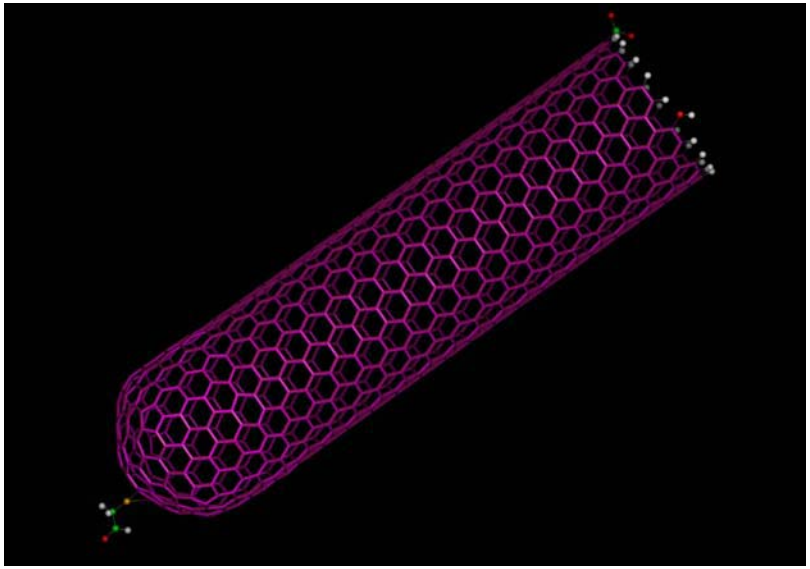


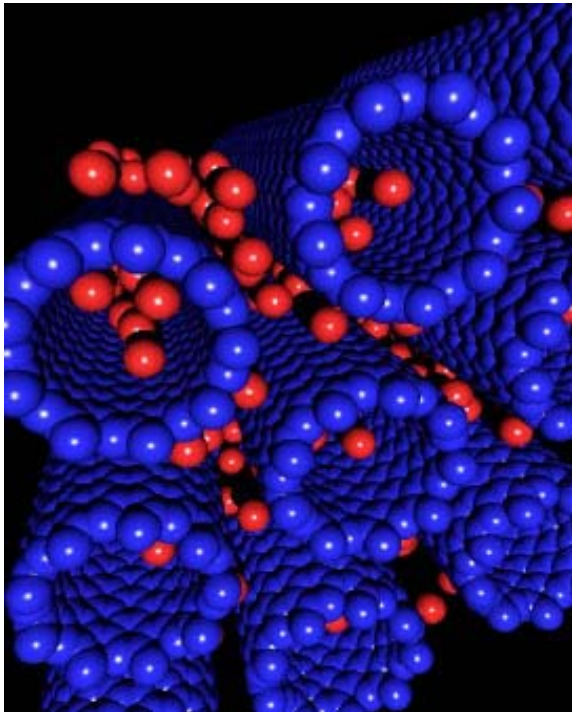
catalytic H_2 dissociation,
oxidation protection,
hinders poisening of surface

Storage of hydrogen in metal alloys

Cylinder storing 20 liters of hydrogen at normal pressure in a metal alloy

Hydrogen storage in graphite nanotubes

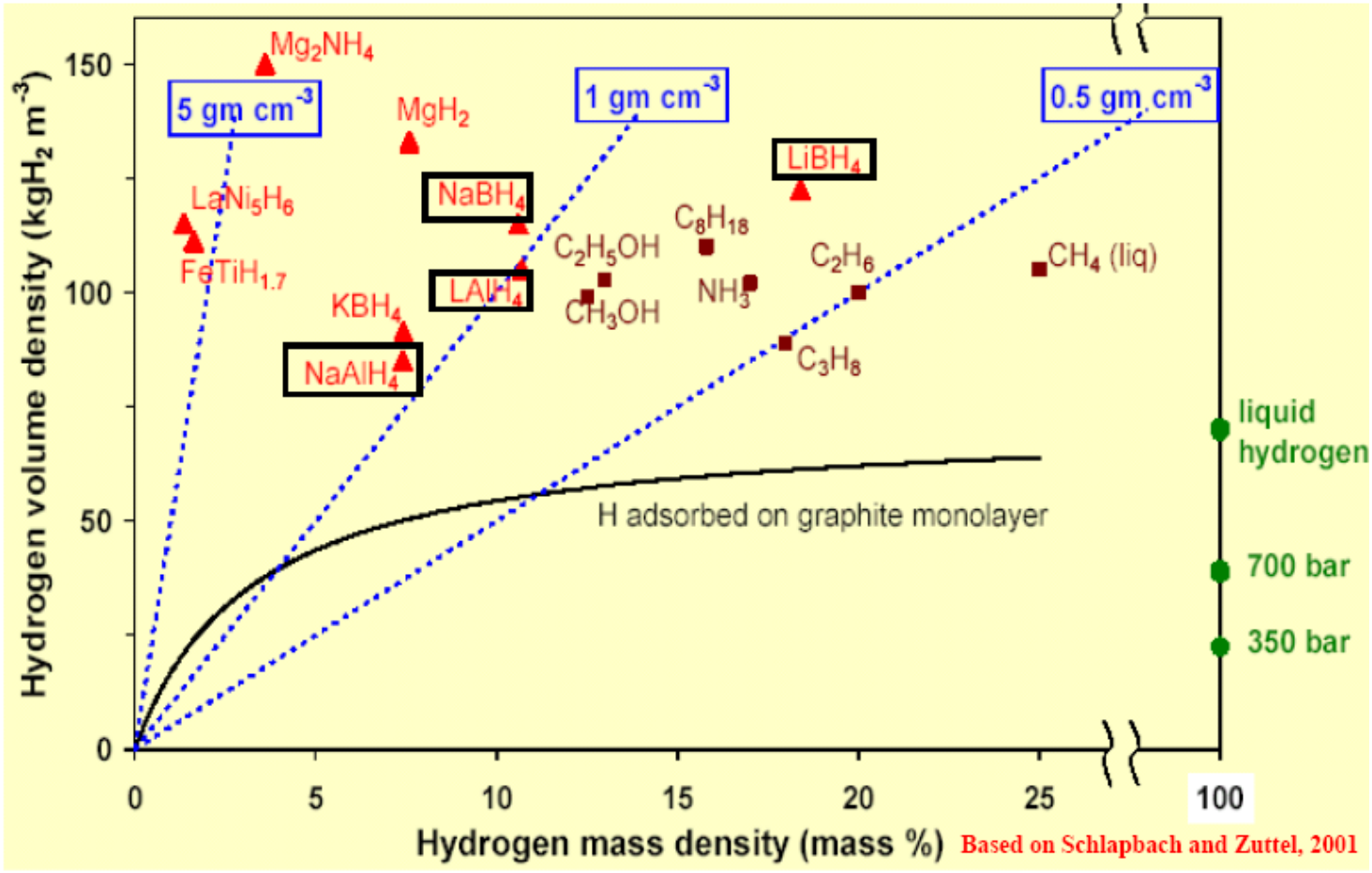




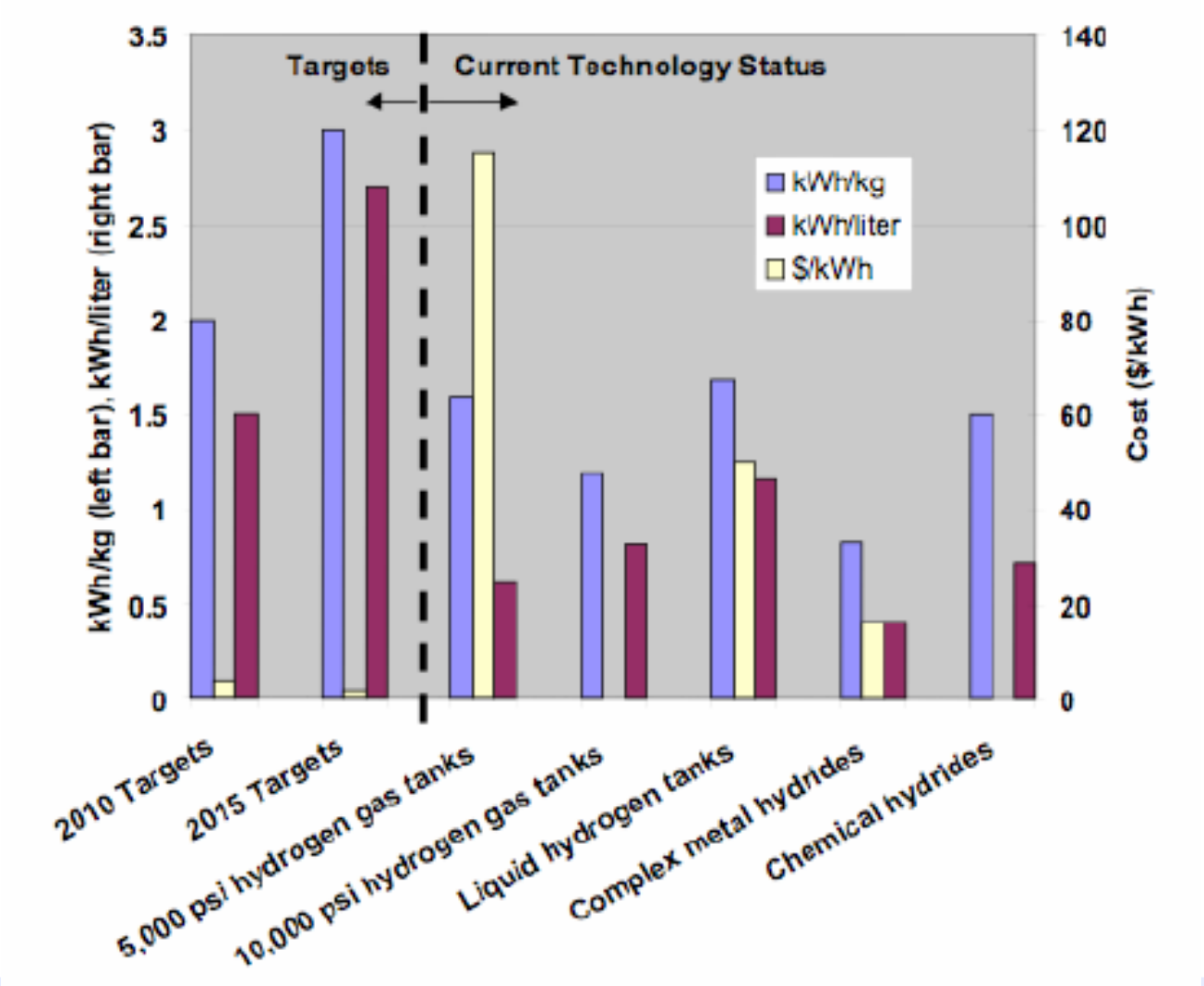
Volume comparison for storage

4kg hydrogen in/as	Mg_2NiH4	$LaNi_5H_6$	liquid H_2	H_2 at 100atm

Volumetric and gravimetric H_2 storage capacity



U. S. DOE Goals and Current Status of Hydrogen Storage Technologies (Milliken, June 2003)



3. Hydrogen Transport

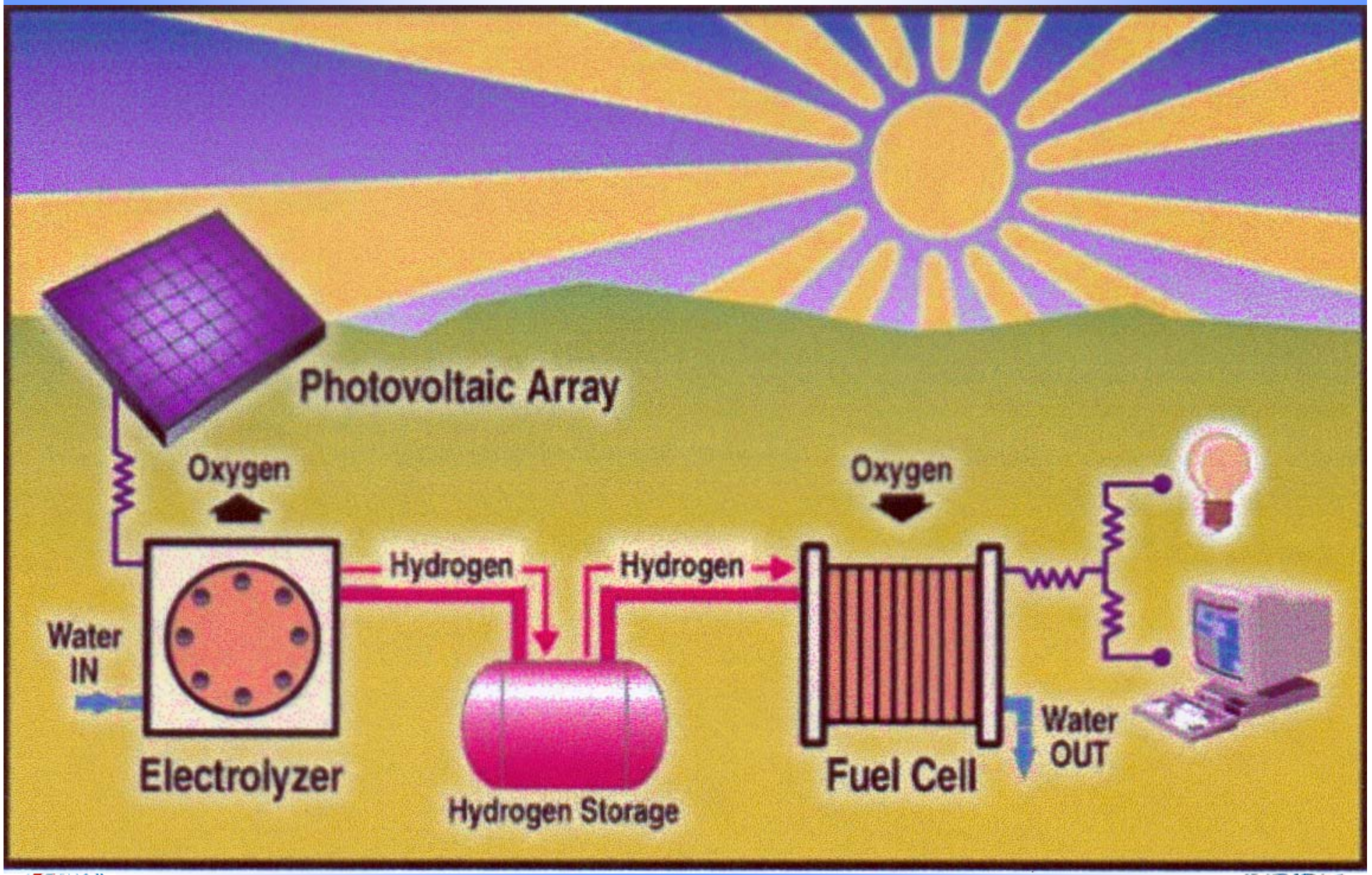
- Pipelines for gas or liquid
- Tanks
  - on trucks,
  - on ships,
  - or trains

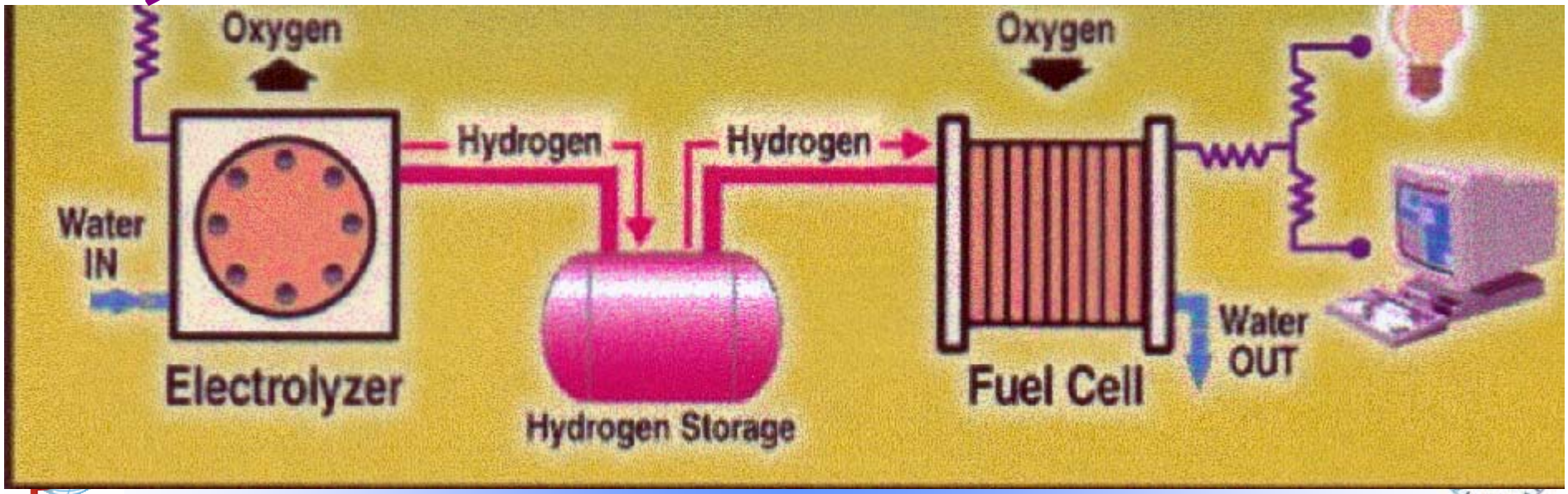
4. Uses of hydrogen

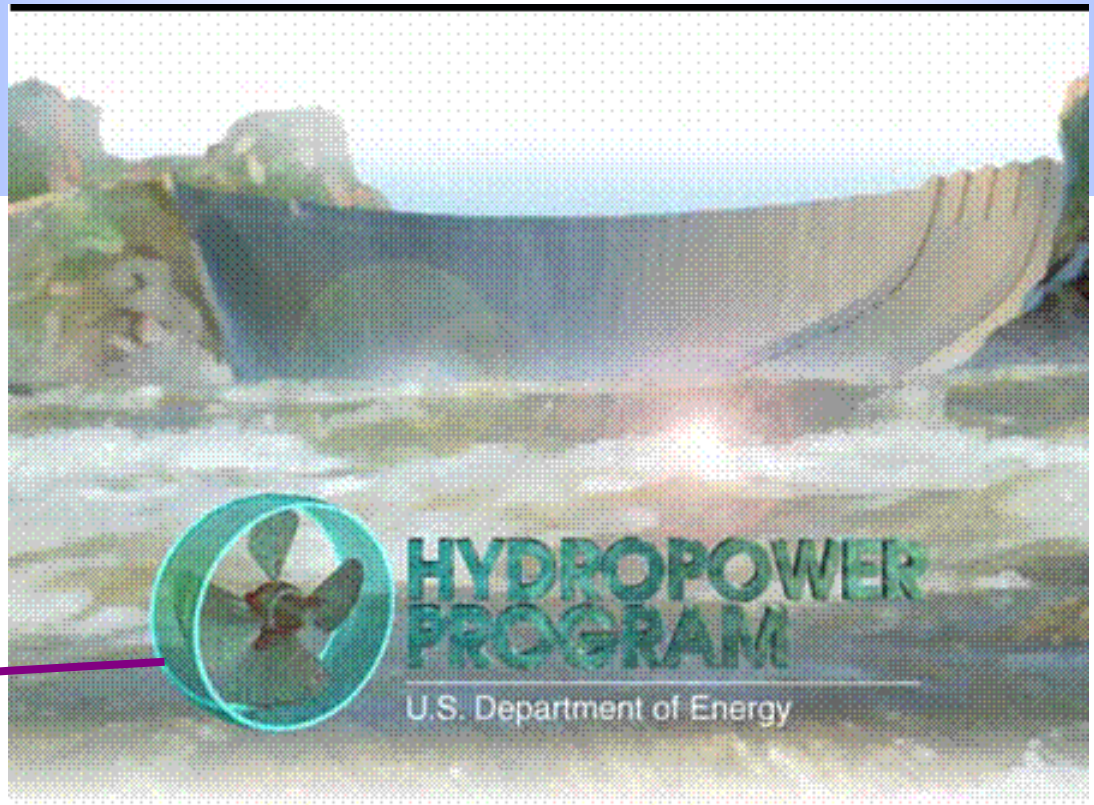
1. Fertilizers (presently largest use)
2. Fuel in combustion engines
3. Fuel cells for electrical power
4. Tuneable and switchable optical and magnetic materials
5. Sensors

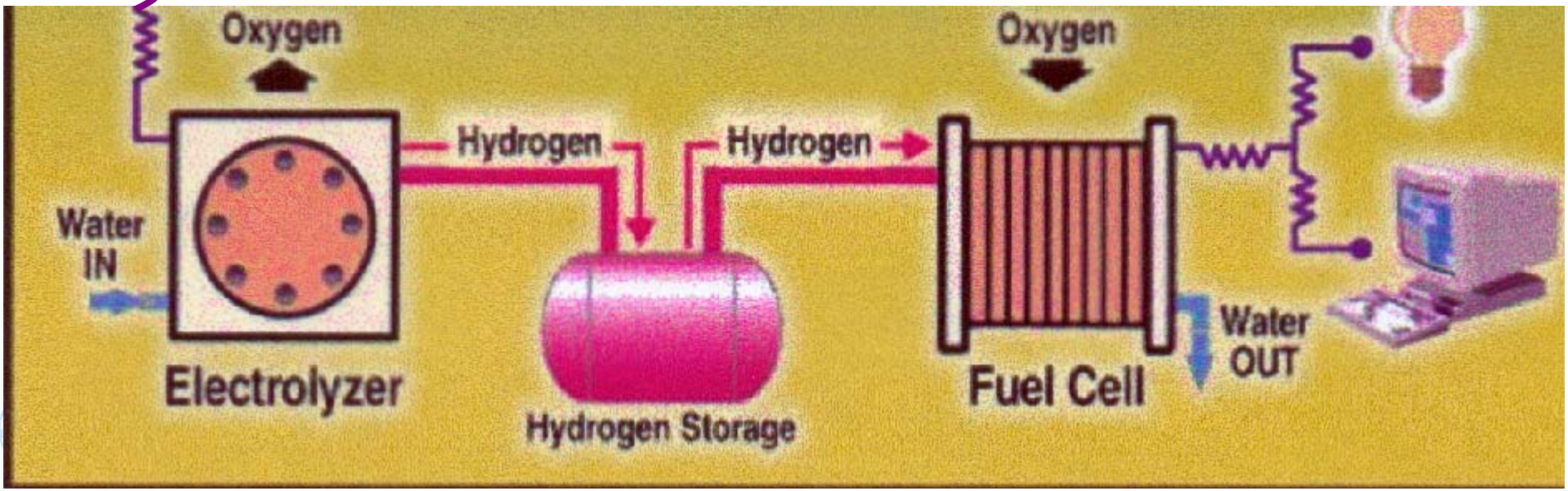
Hydrogen:

from production to use

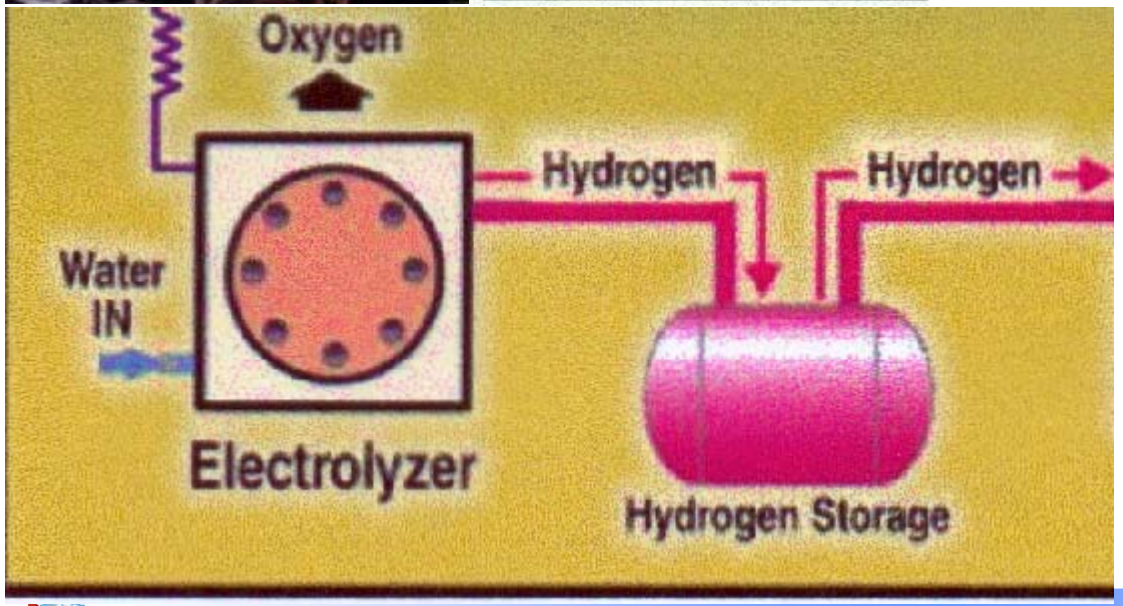

Photovoltaic Array
Oxygen
Oxygen
Hydrogen
Hydrogen
Water
IN
Electrolyzer
Hydrogen Storage
Fuel Cell
Water
OUT


Oxygen
Oxygen
Hydrogen
Hydrogen
Water
IN
Electrolyzer
Hydrogen Storage
Fuel Cell
Water
OUT


HYDROPOWER
PROGRAM
U.S. Department of Energy


Oxygen
Oxygen
Hydrogen
Hydrogen
Water
IN
Water
OUT
Electrolyzer
Hydrogen Storage
Fuel Cell

Production of hydrogen by wind or water and its use in internal combustion engines may be the most efficient hydrogen economy.....

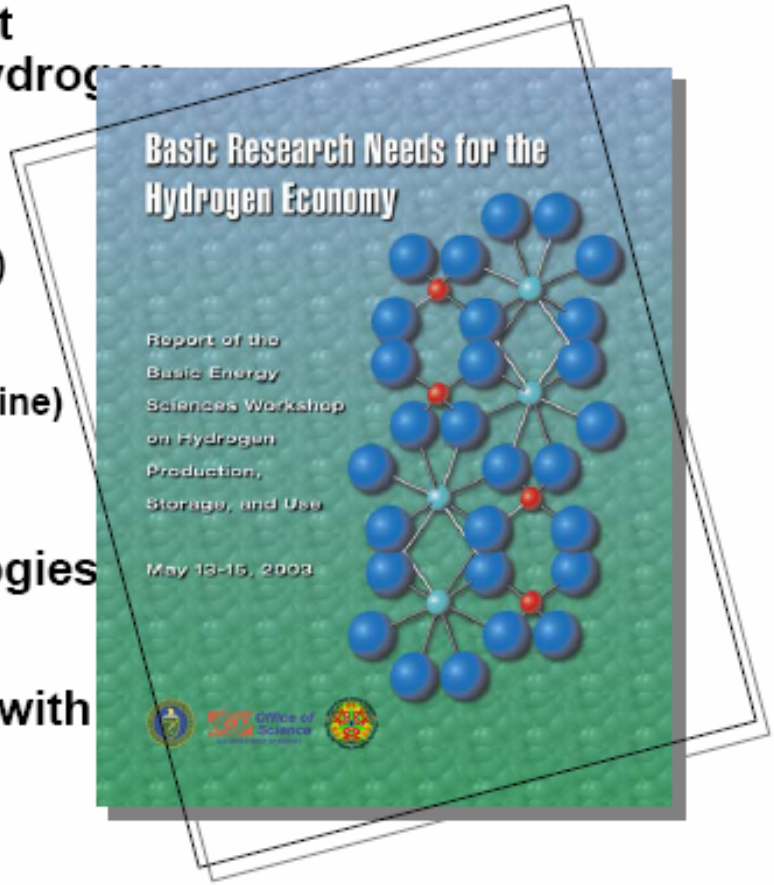


Comparison

	All electric economy	Hydrogen economy
Primary source	Oil, gas, coal, renewables	Wind, water, sun, renewables
Storage	Pumped reservoir, batteries	Pressurized tank, LH_2, metal hydrides
Transport	High voltage power lines	Tankers, pipelines
Advantages	Clean, safety standards established	Clean, good storage potential, use in combustion engines
Disadvantages	Firm supply, electrical road not applicable to aircraft, ships	Unfamiliar, danger of explosion, new infra-structure required

Messages

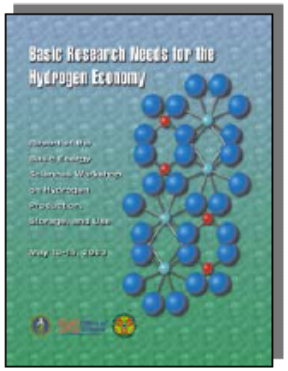
- Enormous gap between present state-of-the-art capabilities and requirements that will allow hydrog
  to be competitive with today's
  energy technologies
  - production: 9M tons ⇒ 40M tons (vehicles)
  - storage: 4.4 MJ/L (10K psi gas) ⇒ 9.72 MJ/L
  - fuel cells: $3000/kW ⇒ $35/kW (gasoline engine)
- Enormous R&D efforts will be required
  - Simple improvements of today's technologies will not meet requirements
  - Technical barriers can be overcome only with high risk/high payoff basic research
- Research is highly interdisciplinary, requiring chemistry, materials science, physics, biology, engineering, nanoscience, computational science
- Basic and applied research should couple seamlessly



http://www.sc.doe.gov/bes/hydrogen.pdf

The five priority research areas for the future identified by the DOE panel

- **Five high-priority research directions will be the focus of the solicitations:**



  - Novel Materials for Hydrogen Storage
  - Membranes for Separation, Purification, and Ion Transport
  - Design of Catalysts at the Nanoscale
  - Solar Hydrogen Production
  - Bio-Inspired Materials and Processes

http://www.sc.doe.gov/bes/hydrogen.pdf

Thank you for your attention