

## Lecture notes

# Hydrogen absorption properties and activation methods

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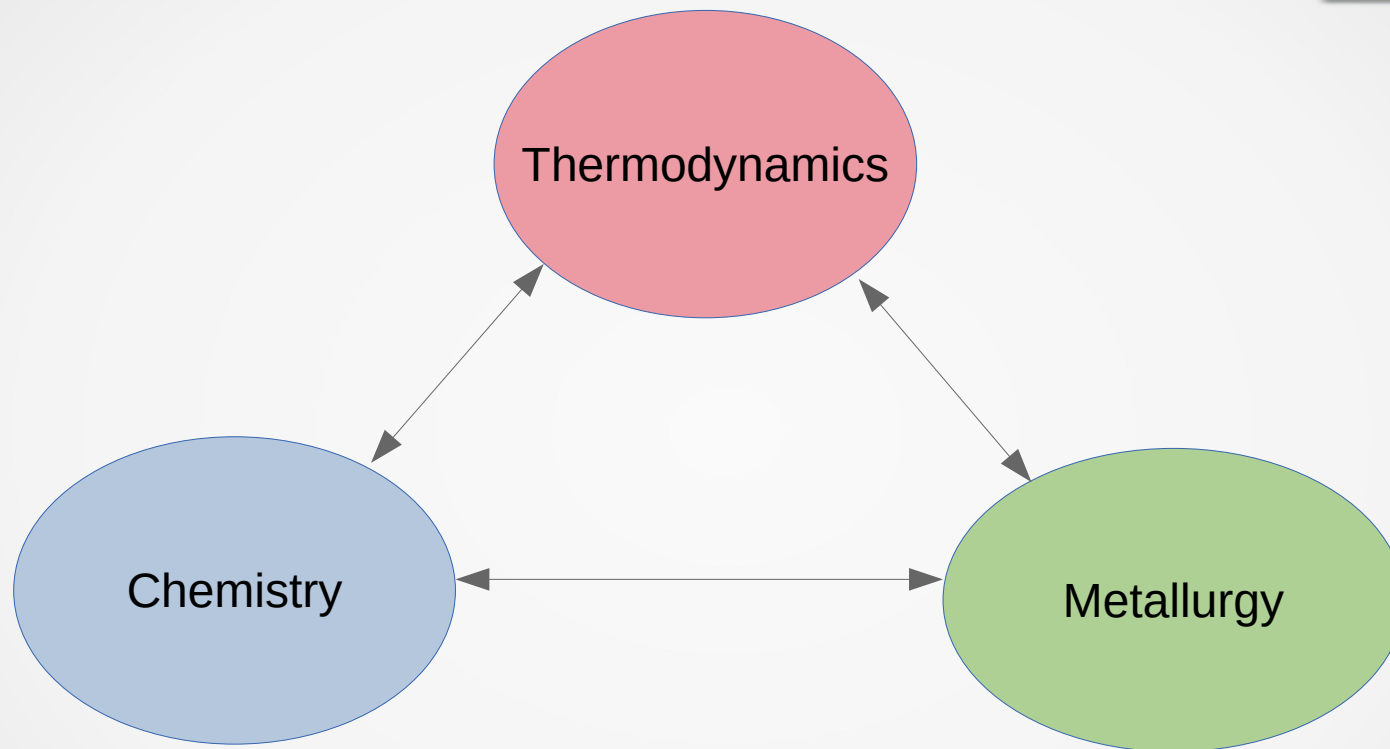
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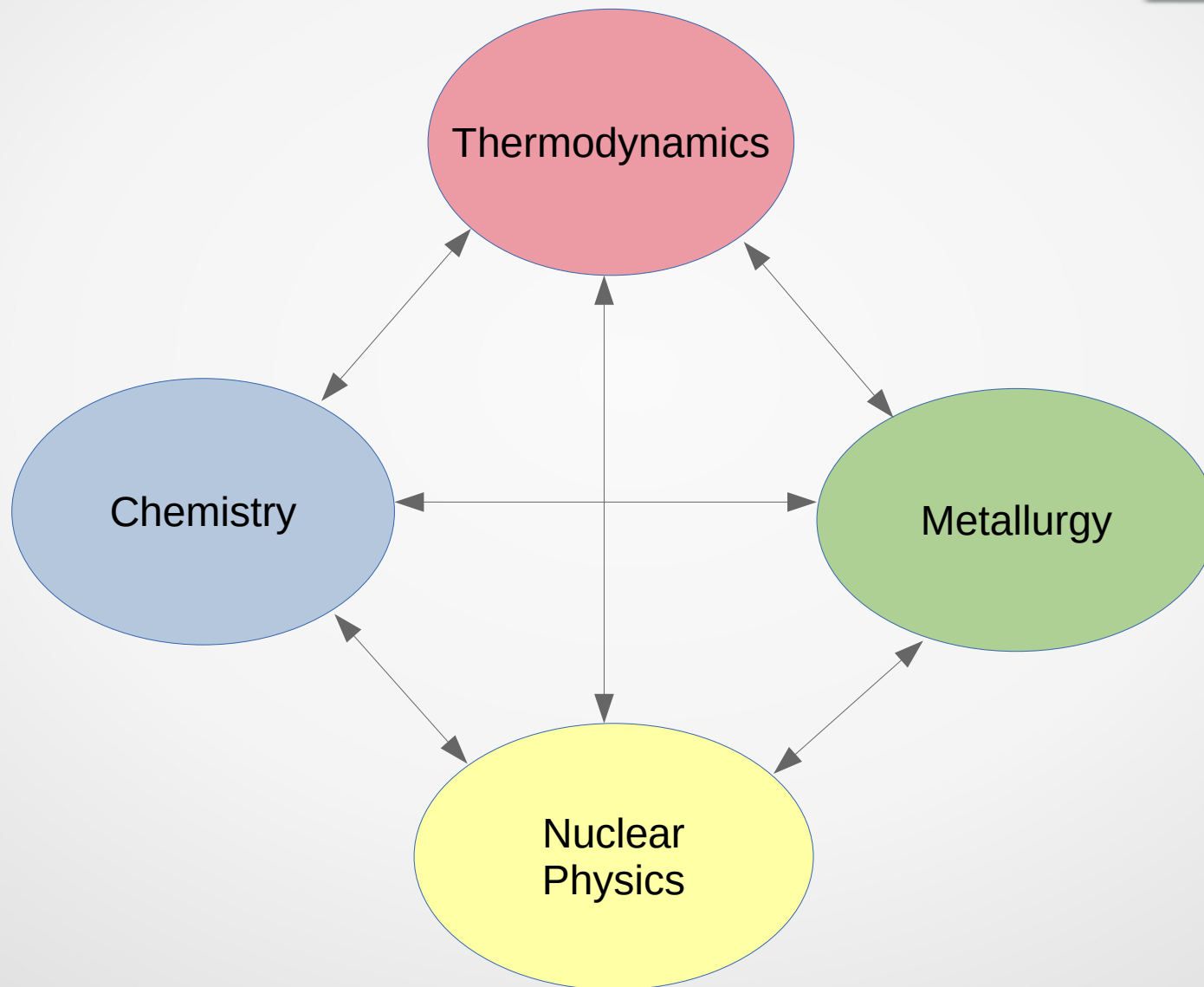
# Outline

- General view of Metal-Hydrogen and CMNS
- Generalities about Ni and Pd
  - Hydrogen adsorption
  - Hydrogen absorption
  - Ni and Pd main observational values
- Crystallography of hydrogen in FCC metals
- Intermetallics
- Loading kinetic
- Activation(s)
- How does it fit to our theory?
- Follow the essential steps

# General view of Metal-Hydrogen



# Condensed Matter Nuclear Science



# Hydrogen Adsorption

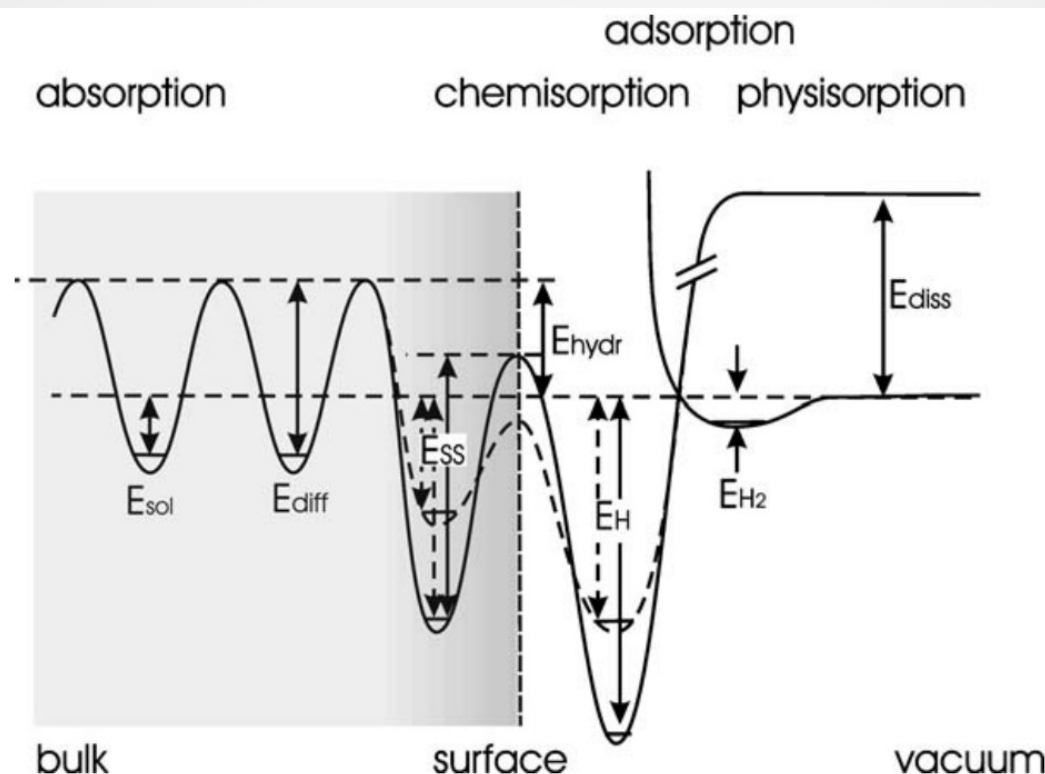
- Adsorption means interaction with the first layers of metals only.
- All kind of things happen in this first contact (physisorption, chemisorption, catalysis, etc...)
  - It also include the splitting of hydrogen, which require a lot of energy ( $\sim 230\text{kJ/mol/H} = 2.38\text{eV/H}$ )
- Energy to then reach the surface, form a proto-hydride and further penetrate is much lower.

=> The main gain we can expect in the necessary work of hydride formation is to facilitate atomisation of hydrogen.

# Hydrogen Absorption

- Thermodynamics
  - Ni absorption is endothermic  $\Delta H_{\text{Ni}} = 15.1 \text{ kJ/mol} = 156 \text{ meV/hydride}$
  - Pd absorption is exothermic  $\Delta H_{\text{Pd}} = -18.7 \text{ kJ/mol} = 193 \text{ meV/hydride}$
  - Ni absorb at high temperature (doubled at 1200°C)
  - Pd absorb at lower temperature ( $Q^{-1}_{\text{max}} = 110\text{K}$ )
- Lattice parameters:
  - Ni = 3.525 Å
  - $\text{Ni}_{\alpha \text{ max}} = 3.532 \text{ Å}$
  - $\text{Ni}_{\beta \text{ min}} = 3.735 \text{ Å}$  ( $\Delta a = +5.5\%$ ,  $\Delta a^3 = 8.3\%$  in volume !!!)
  - Pd = 3.89 Å
  - $\text{Pd}_{\alpha \text{ max}} = 3.984 \text{ Å}$
  - $\text{Pd}_{\beta \text{ min}} = 4.025 \text{ Å}$  ( $\Delta a = 3.5\%$ ,  $\Delta a^3 = 6.34\%$ )

# Thermodynamics



**Figure 3** Schematic of the potential energy of a hydrogen atom at the (110) surface of Pd (*left side*) and the immediate vacuum (*right side*). The energy is scaled to that of the hydrogen molecule  $H_2$  ( $E_{H_2}$ ) far away from the surface. The various energy levels in the figure correspond to the expected values of the heat of solution ( $E_{sol}$ ), the activation energy for diffusion ( $E_{diff}$ ), the activation energy for hydrogen absorption ( $E_{hydr}$ ), the desorption energy from a subsurface site ( $E_{SS}$ ), and the desorption energy from a chemisorbed site ( $E_H$ ), both for the original and reconstructed surfaces. Adapted from Behm et al. (105). The energy level for hydrogen molecule dissociation ( $E_{diss}$ ) is also implemented. Note the broken energy scale.

# Ni-H Metallurgy vs. Thermodynamics

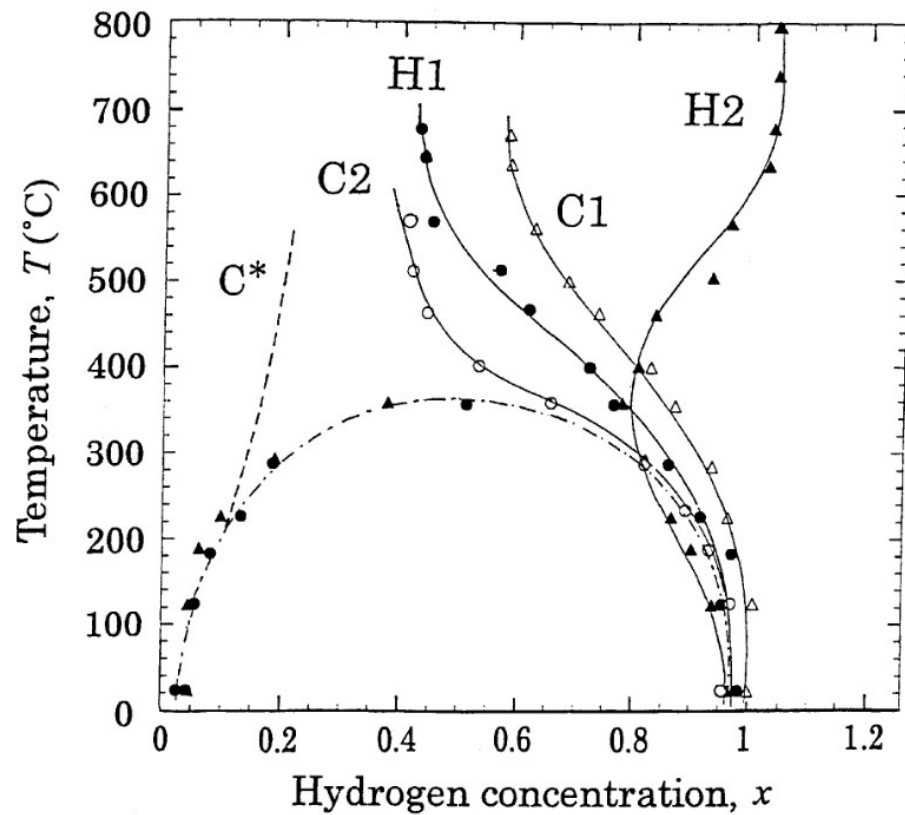
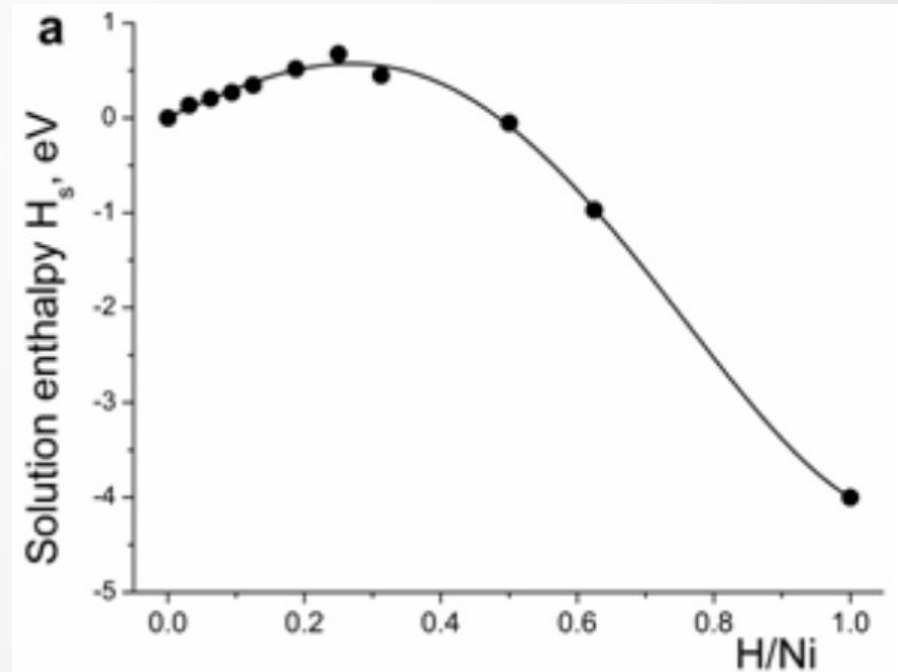


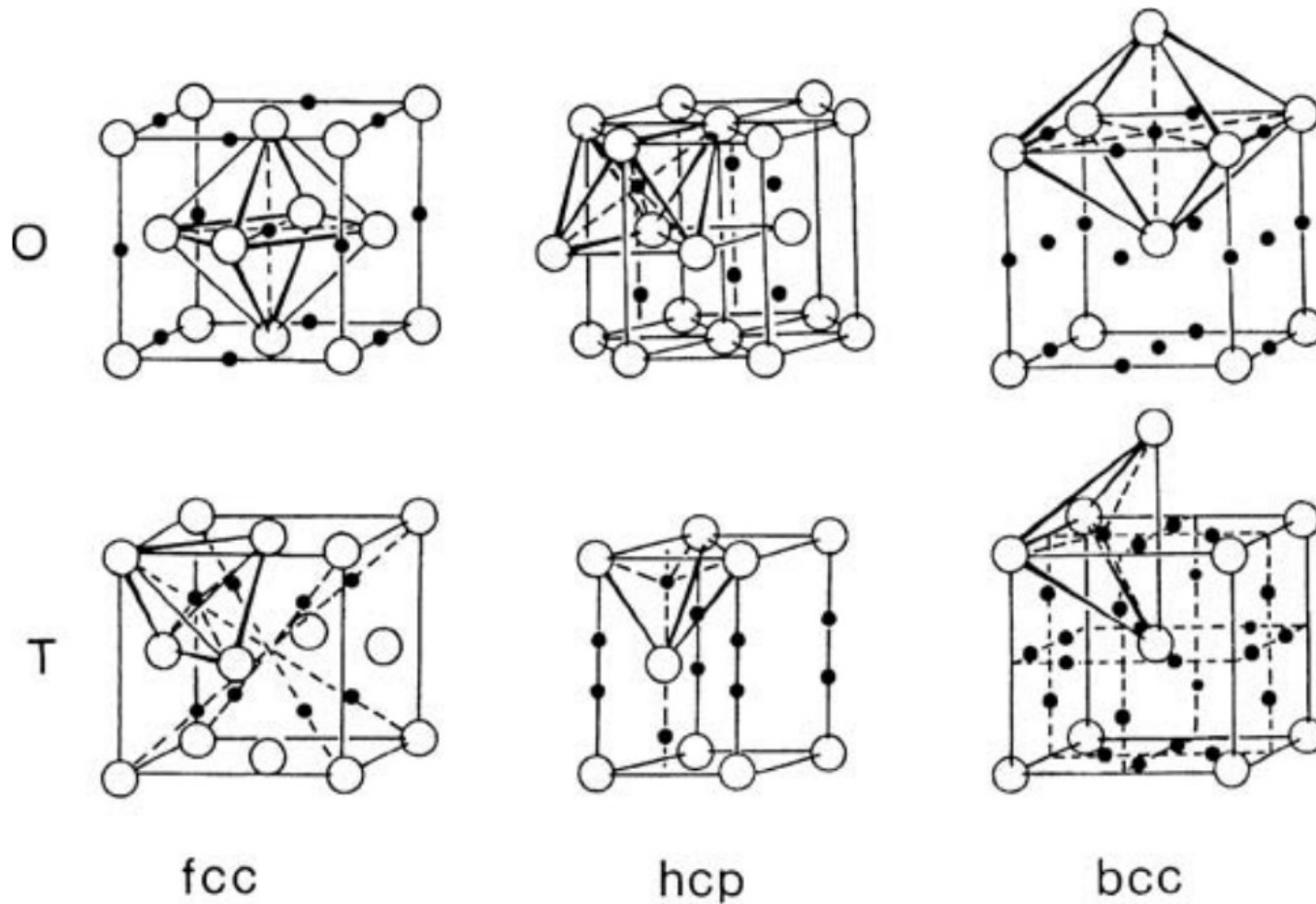
Fig. 1. Pressure-composition-temperature phase diagram of the Ni-H



# Crystallography of Hydrogen in Metals

- Site occupancy is very dependent on base pure vs. alloy metal crystalline structure and initial defect density,
- For Pd and Ni, the octahedral sites are occupied (FCC),
- Saturation of the octahedral site occupancy is seen as the limiting factor, preventing  $x = H/Pd \leq 1$  (Griessen 2015)
- The process influence crystal structure, for instance implantation tend to produce tetrahedral structures,
- Hence  $Pd/H = x > 1$  can be archived via other crystal structures.

# Example of bulk crystallography



**Fig. 2.14.** Interstitial sites [octahedral (O) sites and tetrahedral (T) sites] in fcc, hcp, and bcc lattices

# The role of intermetallics (alloys)

- Intermetallics are of great interest for the following reasons
  - Allow to finely adjust the lattice parameter
  - Allow modification of lattice structure and crystallography
  - Allow management of defects diffusion
  - Can solve some single metal drawback properties
  - Can serve as a matrix for a LENR fertile material (NEDO materials:  $\text{ZrO}_2 + \text{Ni/Cu/Pd}$ )
  - Kirkendall effect: inter-diffusion producing defects (Clean Planet inc.).

# Intermetallics: example Ni-H vs. Ni-Cu-H

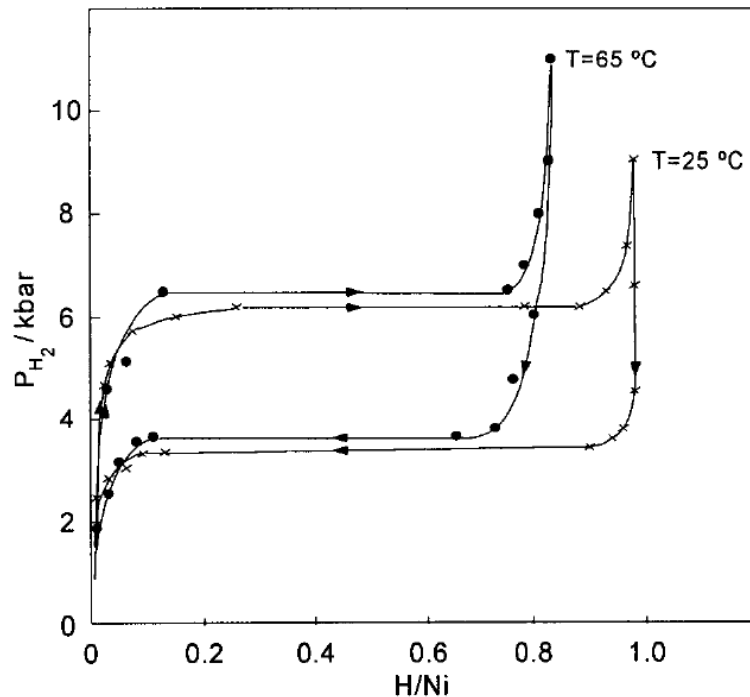


Fig. 9 Absorption and desorption isotherms of hydrogen in pure nickel

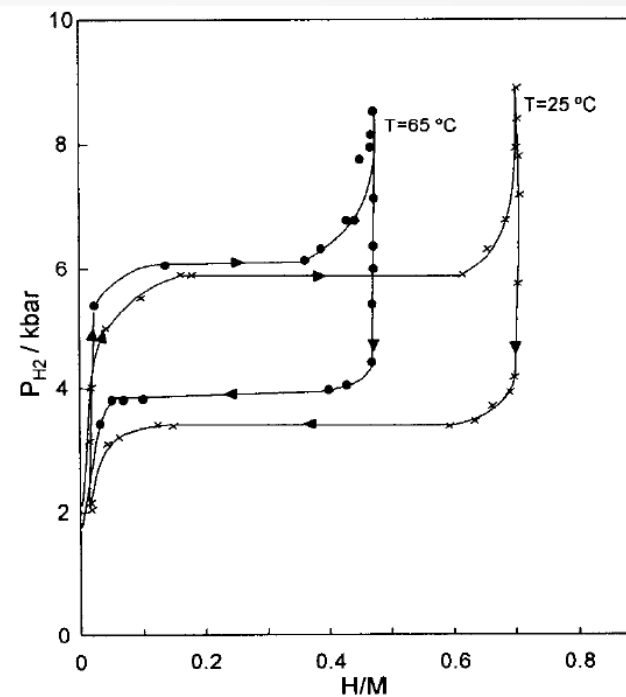


Fig. 10 Absorption and desorption isotherms of hydrogen in a Ni-10 at. % Cu alloy [25]

# Loading kinetic in M-H

- In M-H, no activation means the results will be inconsistent with previous publications
- Loading fast is almost never done, we deal with thermodynamicians, crystallographs, they are looking for equilibrium conditions
- Hydrogen remains in the lattice after the first loading
  - Decrease the energy of the following loadings
  - Increases the lattice parameter
  - Conforms the material
  - Produce defects

# Loading kinetic in CMNS

Fast loading is very different compared slow loading

- Fast loading will increase the density of defects in the materials.
- Because the defect density increases, the strain field will be increased and prevent diffusion, preventing the uniform distribution of hydrogen in the metal
- Slow loading will increase the loading density across the entire sample

# Activation an example

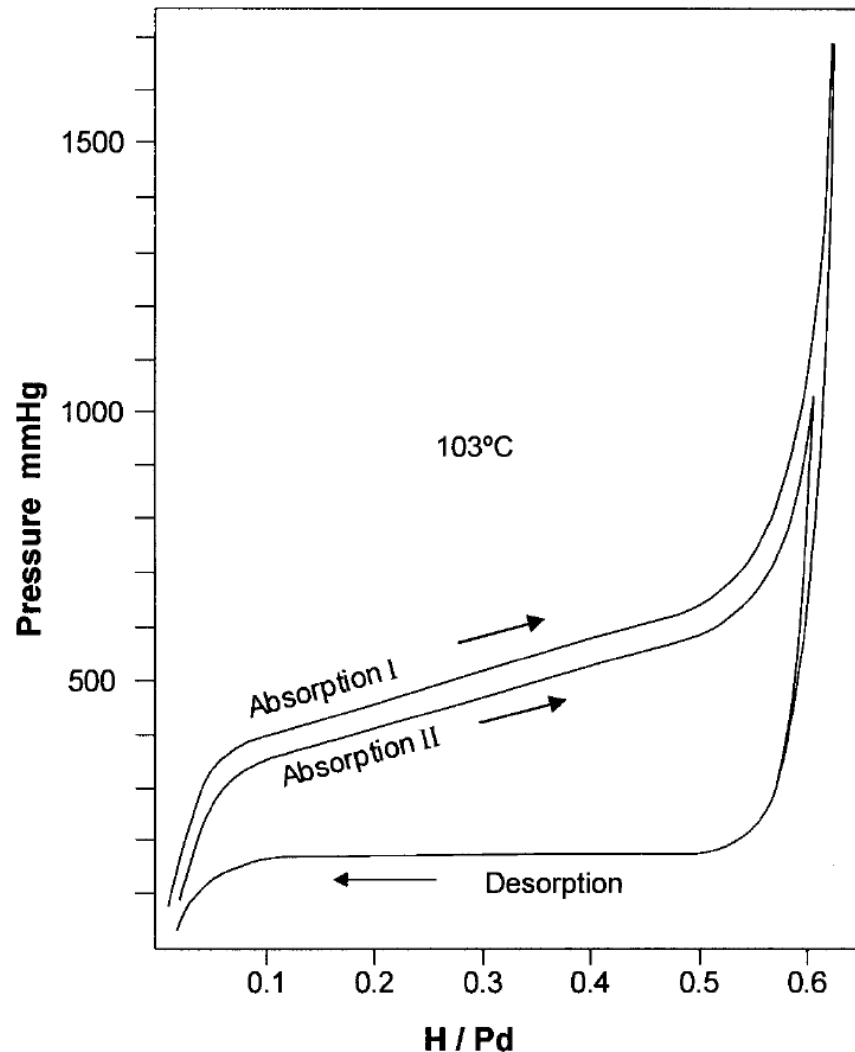


Fig. 57 Examples of alterations of p-n isotherms on recycling of hysteresis loops (after ref 119)

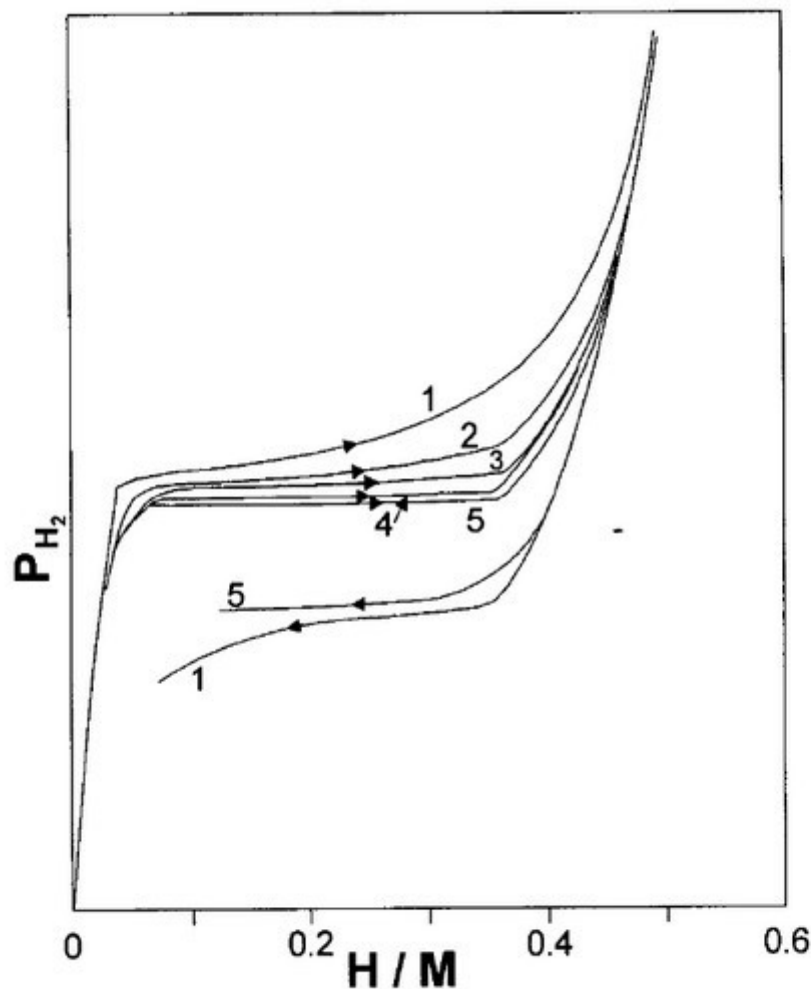
- Example for Pd
- Remaining hydrogen in metal lattice:
  - Loading is lower (hydrogen trapping)
  - Deloading is less fast
- Occlusion of hydrogen is happening

# Activation: Definition

Surface or structural modification of the bulk material to let the hydrogen enter.

- In metallic hydrides studies it can take the following forms:
  - An oxide layer that increases the micro-size topography features,
  - Mechanical cold-work in a lamination device,
  - A cycling of loading and deloading of hydrogen,
  - Co-deposition of metal hydride on the surface of a bulk,
  - Deposited film on the surface of bulk.

# Example of Pd activation process



Schematic representation of reduction with increasing cycling of overall magnitudes of hysteresis loops of p-n isotherms of Pd-rich alloys (after ref

# Activation: Consequences in CMNS

- The crystal surface and bulk are modified
  - This depend on the original state (annealed, rolled...)
  - For Ni, Pd (fcc) dislocations are produced through the miscibility gap
- The metal load easily and in a reproducible manner
- Diffusivity is increased
- Deloading too...

# Hydrogen as a Lubricant!

- When inserted in the metal, hydrogen is not a proton, but a neutral atom.
  - Hence electron screening also act within the lattice of the metal
  - Super loading rates can occur (e.g  $\text{Pd}_\alpha = 4.1 \times 10^{-7} \text{ cm}^2/\text{s}$ ;  $\text{Ni}_\alpha = 7.12 \times 10^{-10} \text{ cm}^2/\text{s}$ )
- The discrepancies between lattice parameter will increase the defects density
  - Hydrogen will generate vacancies defects after its passage,
  - But it will make a strain field ahead within the crystal structures
- In full: hydrogen, when inserted in the metal lattice that has proper crystalline structure to allow diffusion will generate large density of defects promote better loading

# Method: Experimental vs. Practical

- Experiments are necessary to understand nature's behavior
- They are NOT design to prove a technological solution
- Production of results will enhance our comprehension of nature
- THEN we can design a material and conditions that will have a practical application
- The other way around is very ineffective, as shown that 32 years of research in cold fusion have yield no practical application in the commercial world
- Hence I beg your understanding that current experiment schedule is not meant to produce a advancement in practical solution, but in theoretical understanding.

# Essential Steps

- Reduction of the oxides
  - => Increased specific surface of the sample
  - => Allow better adsorption
- Absorption and desorption cycling
  - => Improve the loading in general
  - => Increase electron screening potential
- Diffusion of  $H^0$  in the metal
  - => Increase electron effective mass



Thank you!  
Any questions?

