Hydrides of the Transition Metals

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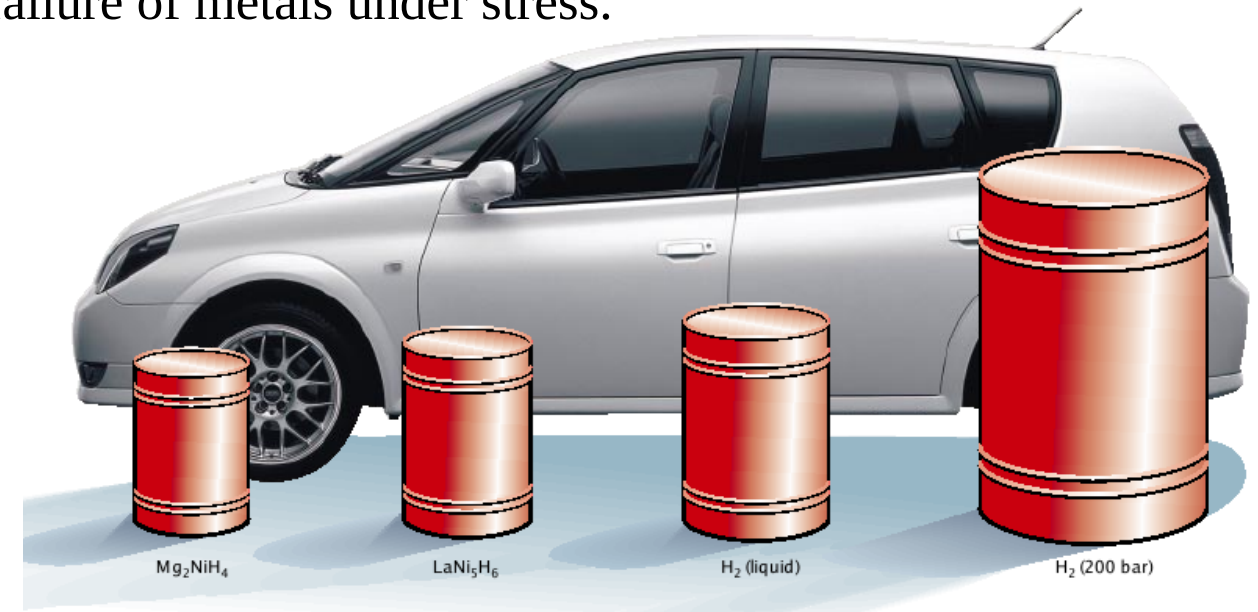
Overview

- Motivation
- Definitions
- Binary Transition Metal Hydrides
  - Structure
  - Properties
- Complex Ternary Metal Hydrides
  - Structure
  - Hydrogen Storage Properties

Motivation

- Metals can absorb large quantities of hydrogen at relatively low pressures and temperatures, making them attractive for on-board hydrogen storage.
- Vehicles will need compact, light, safe, and affordable containment.
- Reversible hydrogen exchange properties of intermetallic hydrides are utilized in rechargeable batteries.
- Structures are also of interest with respect to hydrogen embrittlement and the failure of metals under stress.



L. Schlapbach and A. Zuttel, *Nature* **414** (2001) 353-358.

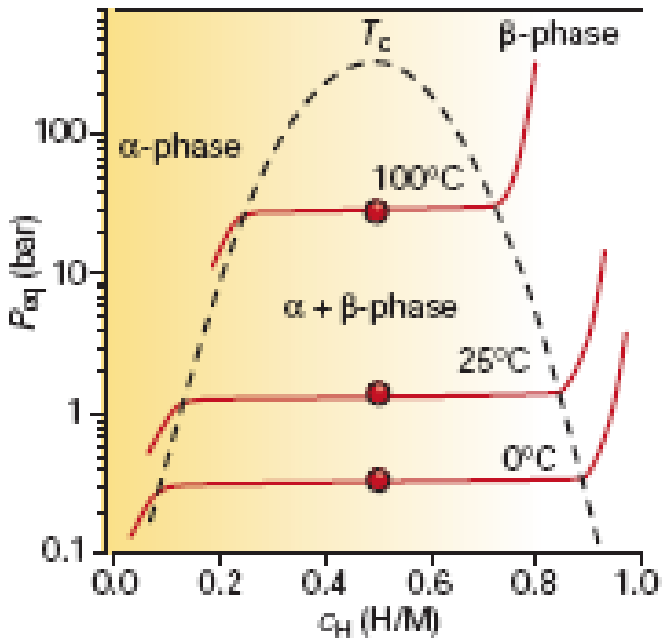
Definitions: What is a metal hydride?

Disassociated hydrogen atoms absorb or dissolve into the metal phase. The intermetalic phase, where H dissociates at random, is known as the **α-phase**.

- **The elements V, Nb, and Ta have α-solid solutions to $V_{0.05}$, $Nb_{0.1}$, and $Ta_{0.2}$ in their b.c.c. metal structures.**

Within the metallic phase, the hydrogen atoms can start to arrange themselves in a specific configuration with the metal atoms, forming the **metal hydride** phase, called the **β-phase**.

$LaNi_5$



L. Schlapbach and A. Zuttel, *Nature* **414** (2001) 353.

Binary Hydrides

f.c.c.

BiF_3

b.c.c.

NiAs

The known binary hydrides with definite structures.

Most form in MH_2 (fluorite) or MH_3 (tysonite) structures.

ScH_2	TiH TiH_2	VH VH_2	CrH CrH_2	MnH				$NiH_{0.6}$	
YH_2 YH_3	ZrH_2	NbH NbH_2						$PdH_{0.83}$	
LaH_2 LaH_3	HfH_2	$TaH_{0.9}$							

4f: MH_2 and MH_3

5f: MH_2 and/or MH_3

& Th_4H_{15}

A. F. Wells, *Structural Inorganic Chemistry, 5th ed.* Oxford Univ. Press, 1984.

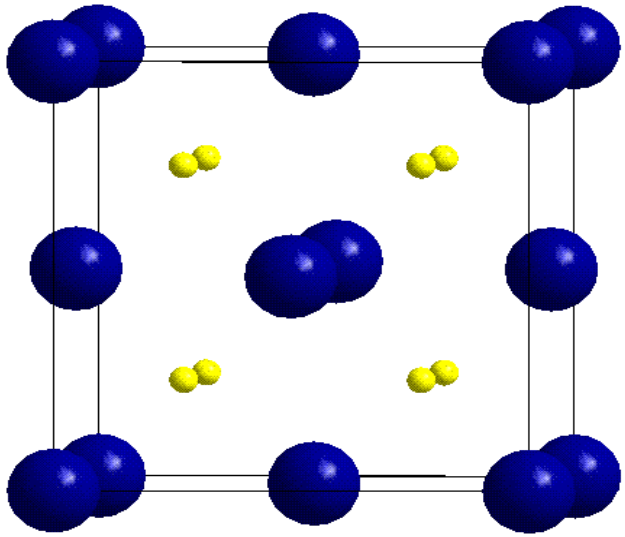
U. Muller, *Inorganic Structural Chemistry*, John Wiley & Sons, 1993.

MH_2: Fluorite type

TiH_2

- Fm-3m
- a = 4.4316 Å
- Ti 0 0 0
- H 0.25 0.25 0.25

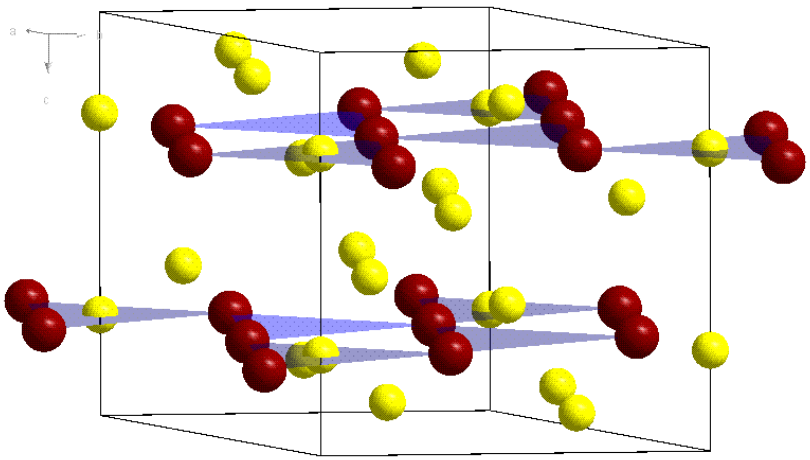
Structure of the dihydrides of Cr, the hcp elements Ti, Zr, and Hf, and 4f and 5f metals (except Eu and Yb)



Cubic above transition points.

Tetragonal symmetry at lower temperatures.

MH_3: LaF_3, or Tysonite type



HoD_3

- P-3c1 (tetragonal)
- a = 6.30 Å
- c = 6.56 Å

Both 3 and 4-coordinate H

Metal is 11-coordinate

Structure of the trihydrides of 4f and 5f metals (except for La, Ce, Pr, Nd, and U)

- The surplus hydrogen in the $MH_{1.9}$ (fluorite) to MH_3 (tysonite) transition occupies the octahedral interstices of the fluorite structure.
- Trihalides of La, Ce, Pr, and Nd remain f.c.c. to MH_3.

Properties of Binary Hydrides

- Larger interatomic distances than parent metal
- Metallic or graphitic in appearance
- Metallic conductivity or semiconductivity
  - Resistivity increases with hydrogen absorption (metal to semiconductor)
    - $LaH_2 \rightarrow LaH_3$
    - $YH_2 \rightarrow YH_3$
    - $NdH_2 \rightarrow NdH_3$
- 4f hydrides are usually pyrophoric
- $PdH_{0.6}$, for example, holds 0.56% of its mass in hydrogen.
- Pressure and temperature range for reversible exchange are not attractive for mobile storage

Complex Ternary Hydrides

- A_xMH_z, where A is an alkali or alkaline-earth metal
- Structures characterized by the presence of complex anions of the form $[MH_z]^{2x-}$
- Geometries
  - Linear
  - Square Planar
  - Tetrahedral
  - Square Pyramidal
  - Octahedral

W. Bronger, Angew. *Chem. Int. Engl*. **30** (1991) 759 .

R. Bau, M. H. Drabnis, *Inorganica Chimica Acta* **259** (1997) 27-50.

Linear Geometry

Contain $[MH_2]^{n-}$ ions

Li_2PdH_2
Li_2PtH_2
Ca_2PdH_2
K_3PdH_3 (KHK_2PdH_2)

14 electron, d^{10} coordination

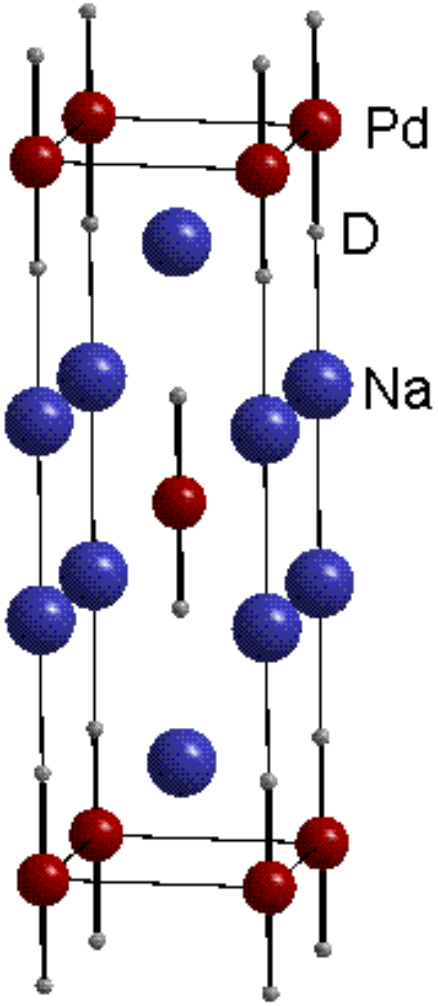
Tetragonal

I4/mmm

a = 3.599 Å

c = 11.327 Å

Na_2PdD_2

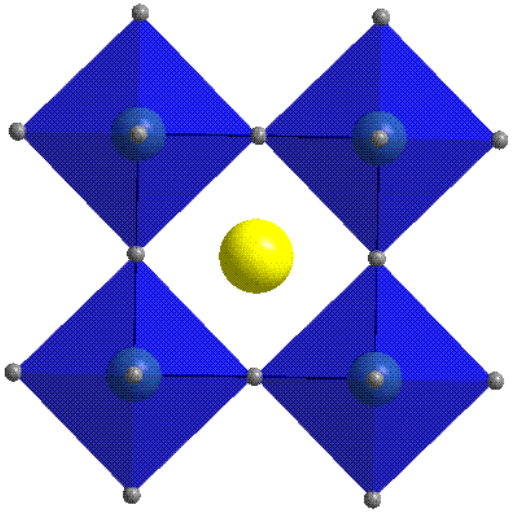


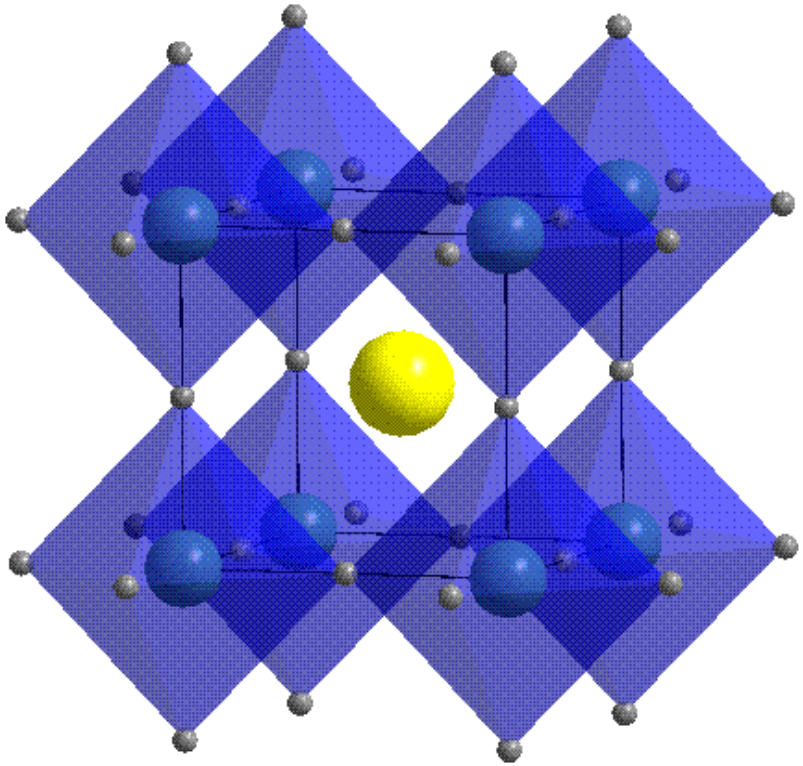
It's Perovskite-Like

- $CaPdH_2$
- Statistical distribution of $[PdH_2]^{2-}$ units, no preferred orientation

Pm-3m
a = 3. 690 Å

Ca	0	0	0
Pd	0.5	0.5	0.5
O	0.5	0	0

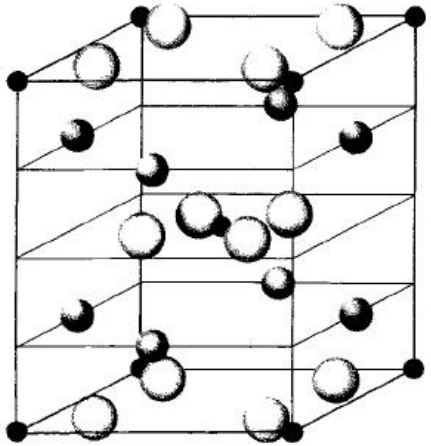




- H occupies the octahedral vertices to 2/3 on average

Square Planar Geometry

Contain $[MH_4]^{n-}$ ions



Li_3RhH_4

Na_2PdH_4

Zr_2CoH_5 (slightly distorted)

K_2PtH_4

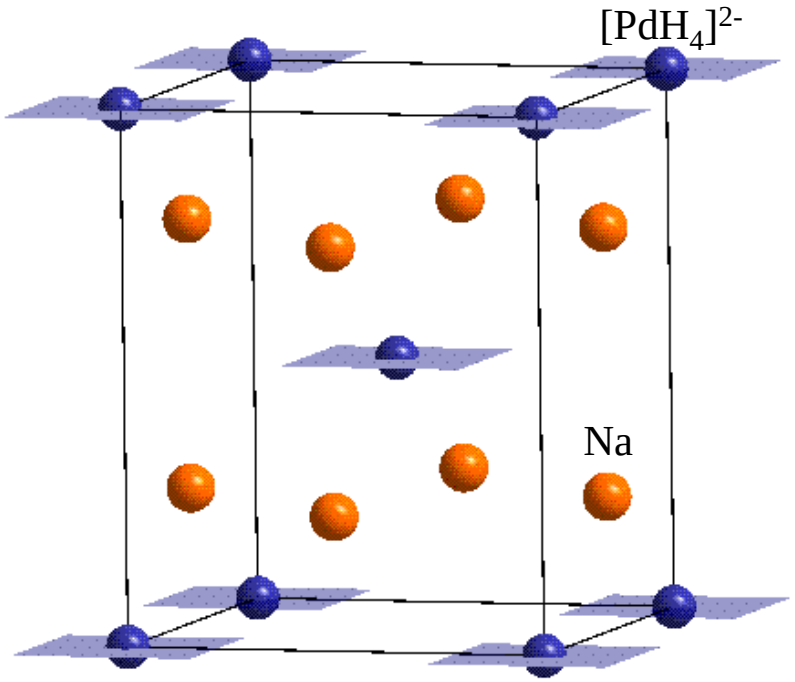
16 electron, d^8 coordination

Tetragonal

I4/mmm

a = 5.338 Å

c = 6.614 Å



Higher Coordination

Tetrahedral
Contain $[MH_4]^{n-}$ ions

Mg_2NiH_4

K_3MnH_5 (KHK_2MnH_4)

18 electron, d^{10} coordination
(Ni, Mn)

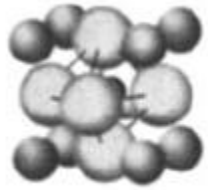
Square-Pyramidal
Contain $[MH_5]^{4-}$ ions

Mg_2CoH_5

Sr_2RhD_5*
Sr_2IrH_5*
Mg_3RuH_6*

18 electron, d^8 coordination
(Co, Rh, Ir, Ru)

*Disorder over octahedral sites



Octahedral
Contain $[MH_6]^{4-}$ ions

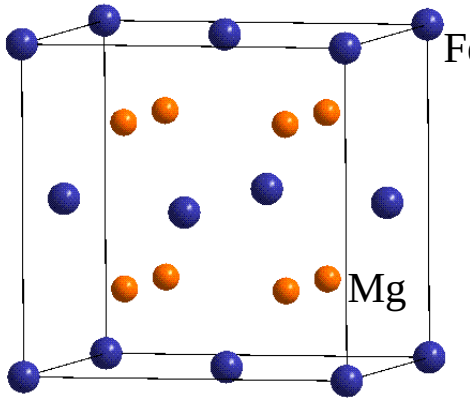
Mg_2FeH_6

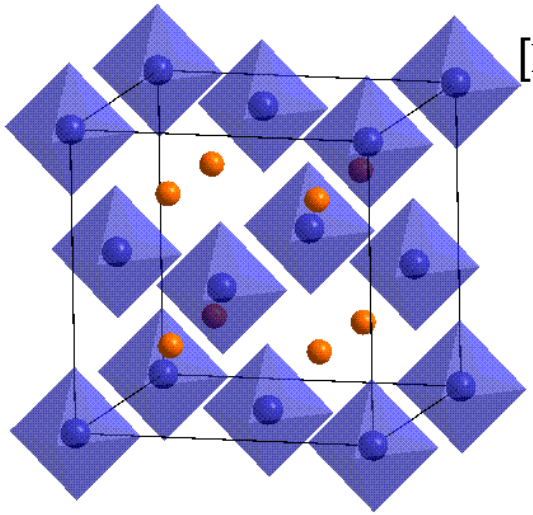
Sr_2RuH_6
Ca_2OsD_6
Na_3IrH_6

18 electron, d^6 coordination
(Fe, Re, Ru, Os, Rh, Ir, Pt)

The structures of these ternary hydrides can be related in a very simple way…

K_2PtCl_6 Parent Structure





Octahedral Complexes: Mg_2FeD_6

- Fe and Mg form in the fluorite structure
- D (or H) decorate Fe in an octahedral coordination

This is also the structure of many high temperature forms of the tetrahedral and square pyramidal coordination compounds.

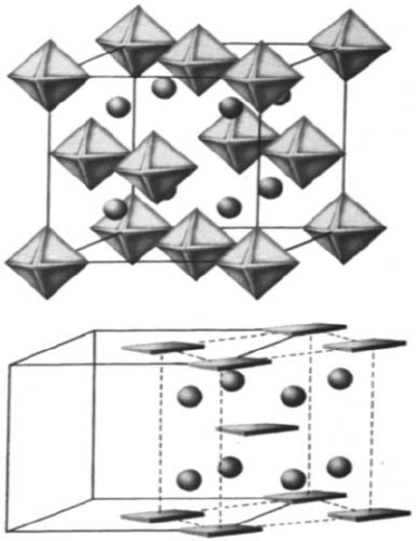
- Ni equivalent: 2/3 (4/6) occupation of the octahedra
- Co equivalent: 5/6 occupation

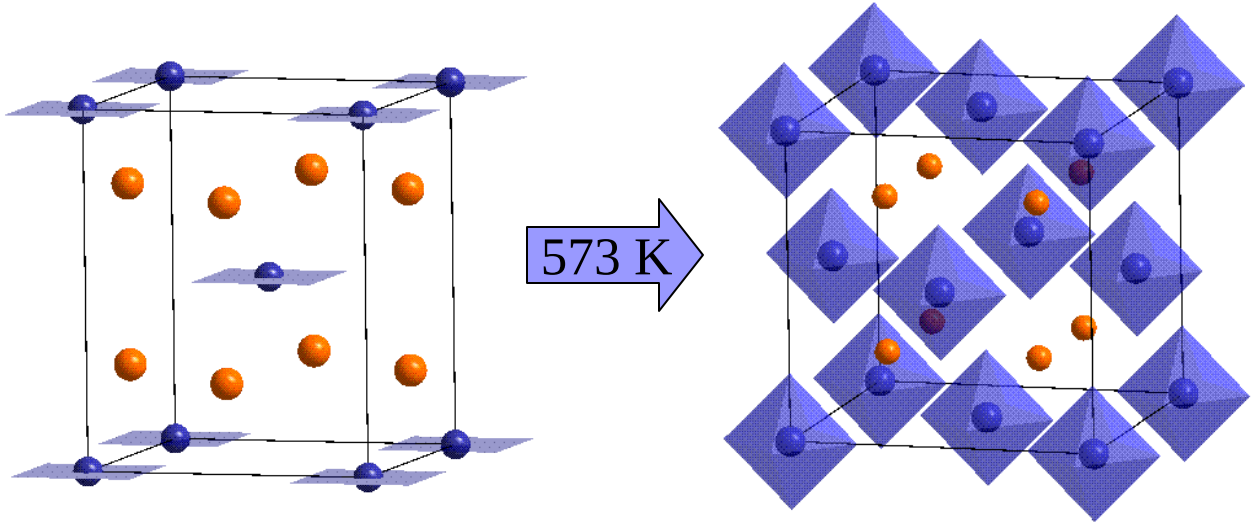
Phase Transitions

Tetragonal (low temperature) phase goes to cubic (high temperature) phase

In this case the cubic phase has 2/3 occupancy of the hydrogen octahedral positions

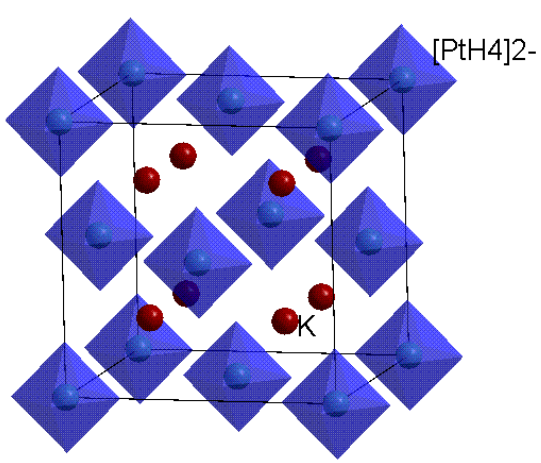
Na_2PtD_4





Dynamic Hydrogen Ligand

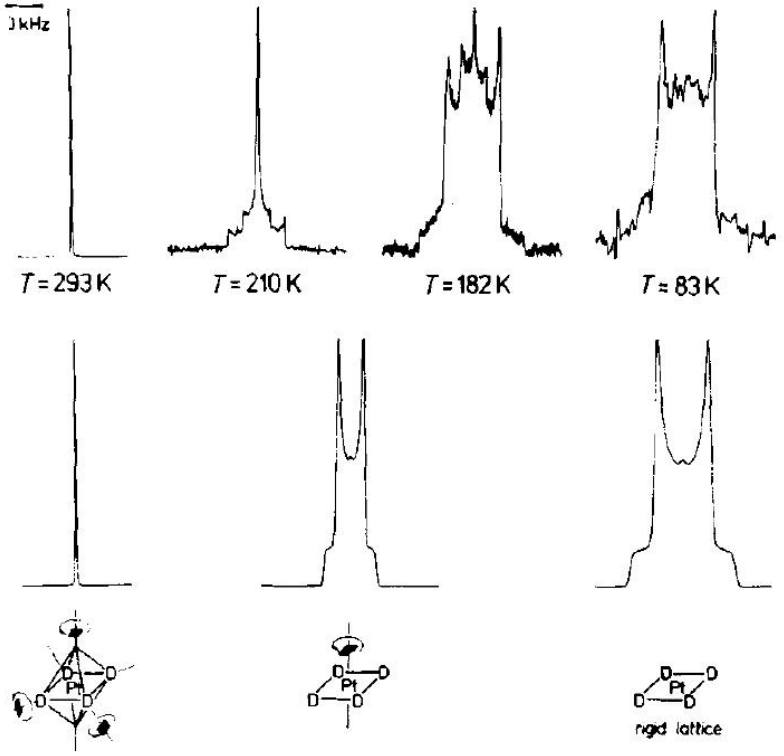
K_2PtD_4: The four hydrogens ligands attached to the Pt atom with d^8 configuration give planar coordination (Phase transition at 195K).

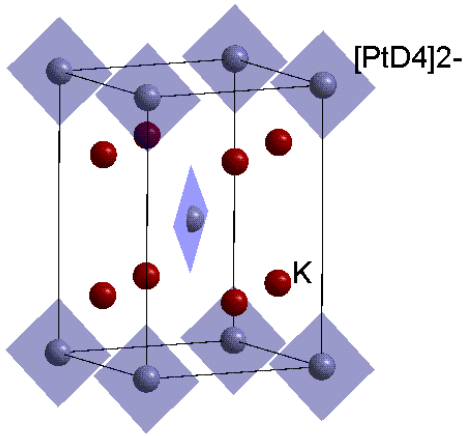


Cubic

Fm-3m

a = 8.025 Å





Tetragonal

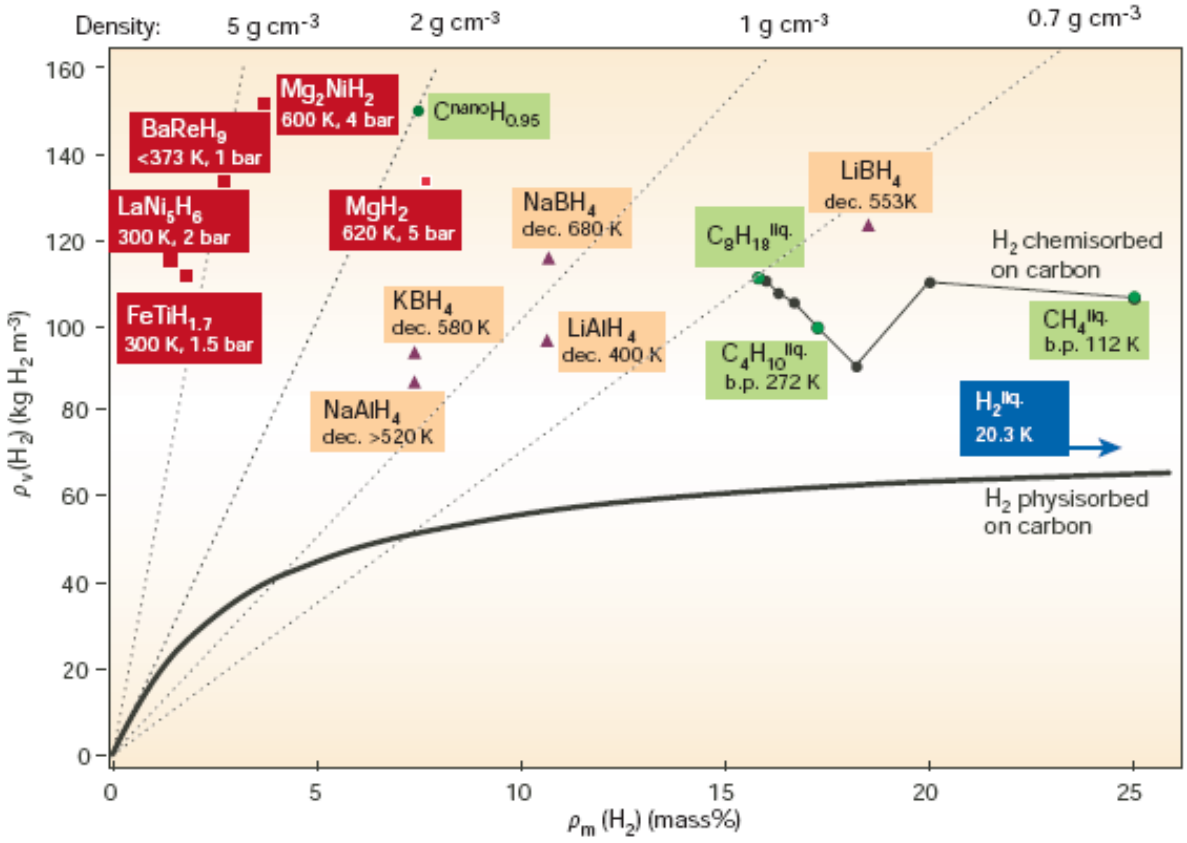
P42/mnm

a = 5.582 Å

c = 8.089 Å

W. Bronger, *Angew. Chem. Int. Ed. Engl.* **30** (1991) 759.

Storage Properties



- Need 4-5 mass % to be feasible (DOE targets 6.5%)
- $LaNi_5H_6$, for example is too expensive
- $MgNaH_4$ requires too high of a temperature
- Many are too heavy…

The search continues…

Summary

- Transition metal oxides are an important class of materials for reversible hydrogen storage
- Binary transition metal hydrides form predominantly in the flourite or tysonite structures, with stoichiometry MH_2 and MH_3, respectively
- Ternary Metal Hydrides contain an alkali or alkaline earth metal and a transition metal, or an alloyed phase of metals. Structures can be depicted with coordination ions in familiar crystal structures.
- Many metal hydrides are not well characterized or understood.

Other interesting work…

- V. Paul-Boncour, L. Guenee, M. Latroche, A. Percheron-guegan, B. Ouladdiaf, F. Bouree-Vigneron, *J. Sol. St. Chem.* **142** (1999) 120-129.

- M. Latroche, J.-M. Joubert, A. Percheron-Guegan, and F. Bouree-Vigneron, *J. Sol. St. Chem.* **177** (2004) 1219-1229.