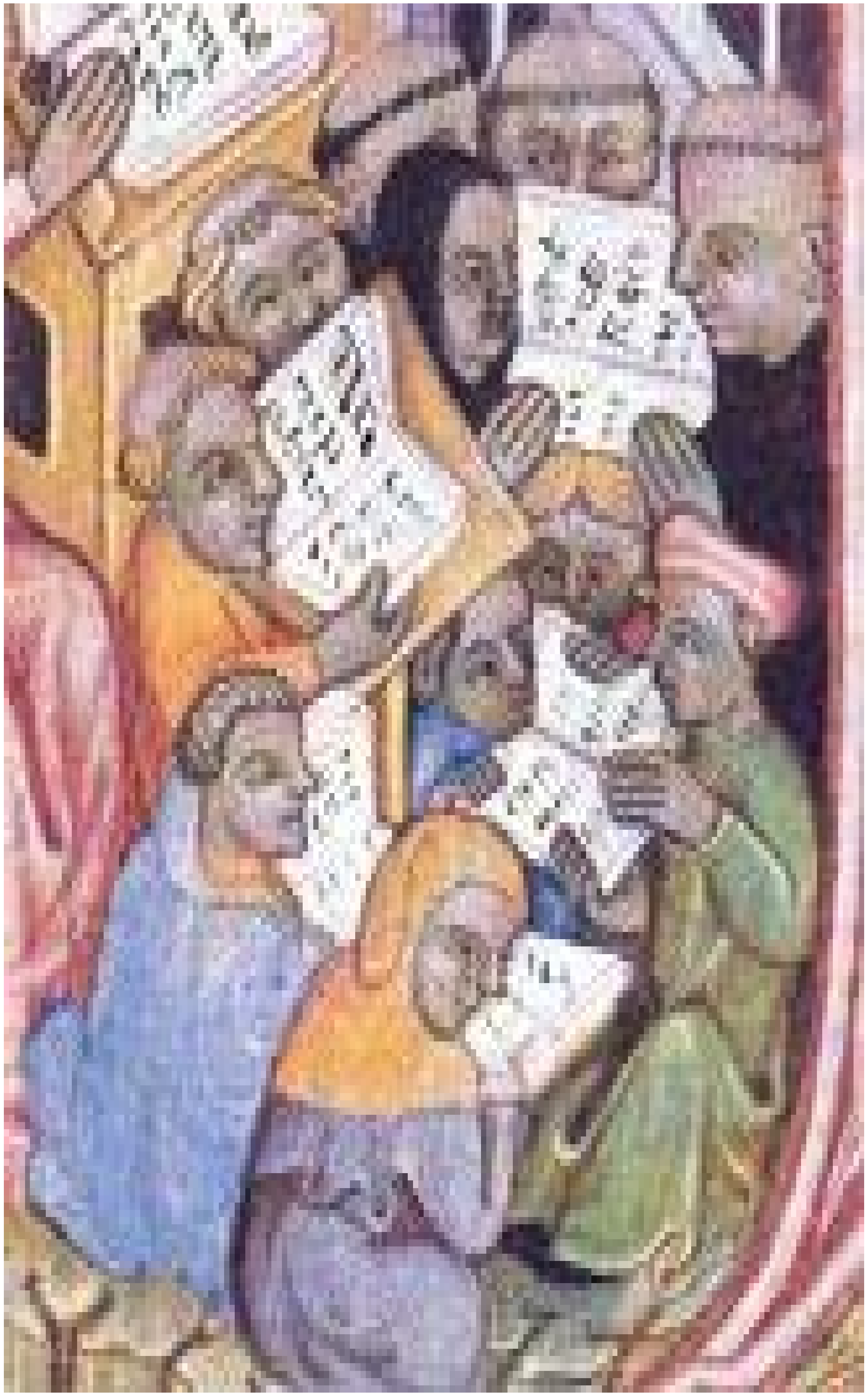


Hydrogen storage in metal hydrides – fundamental principles meet practical life

Ladislav Havela

Charles University, Prague
Czech Republic

Krakow 2021

C-based economy -> CO_2, Global Warming, dirt
H-based economy -> H_2O – clean, but several challenges

Interaction with hydrogen, H_2 storage

Volume comparison for storage

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

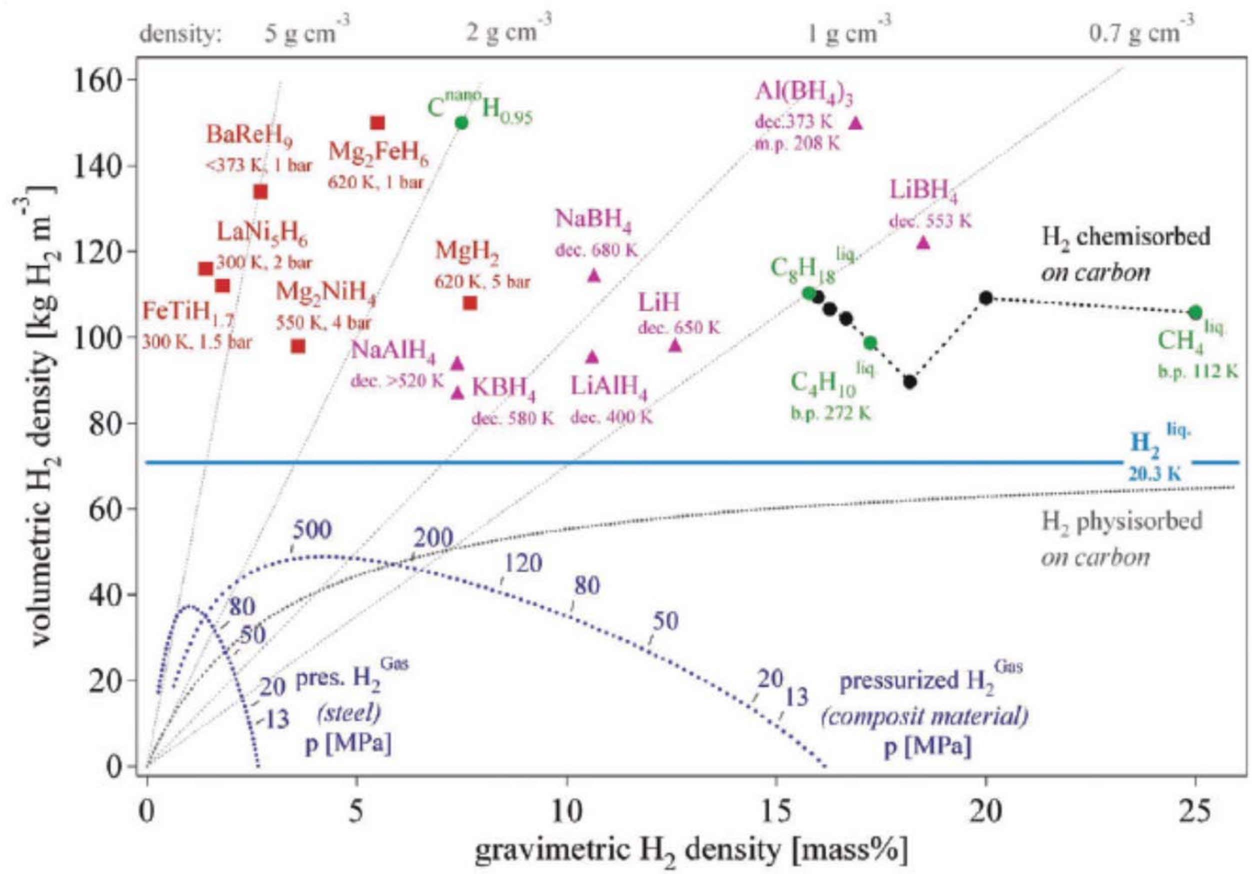
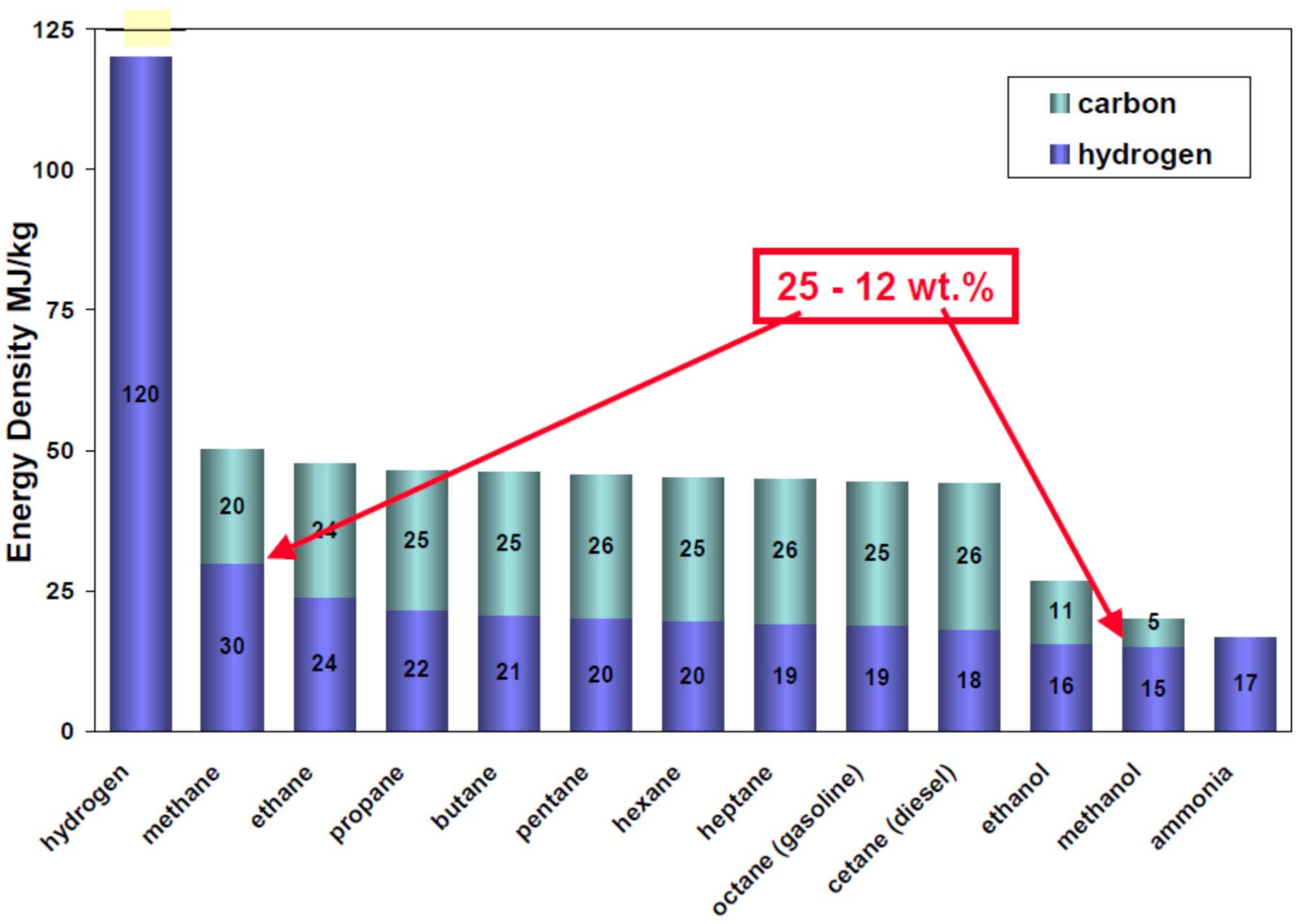


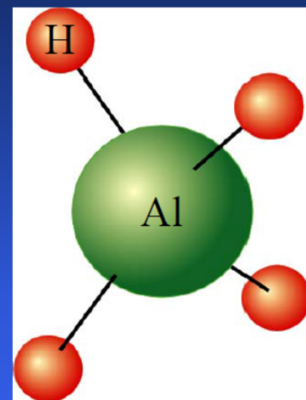
Fig. 7 Volumetric and gravimetric hydrogen density of some selected hydrides. Mg_2FeH_6 shows the highest known volumetric hydrogen density of 150 kg·m^{-3}, which is more than double that of liquid hydrogen. $BaReH_9$ has the largest H/M ratio of 4.5, i.e. 4.5 hydrogen atoms per metal atom. $LiBH_4$ exhibits the highest gravimetric hydrogen density of 18 mass%. Pressurized gas storage is shown for steel (tensile strength σ_v = 460 MPa, density 6500 kg·m^{-3}) and a hypothetical composite material (σ_v = 1500 MPa, density 3000 kg·m^{-3}).

Specific energy of fuels



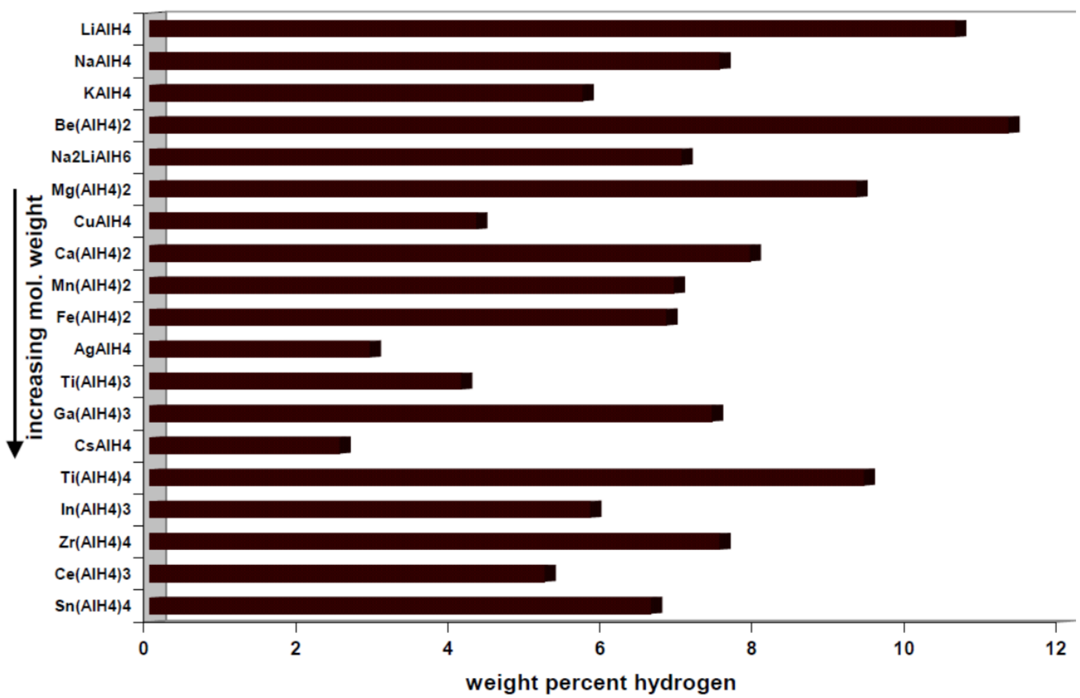
Renewed interest in complex hydrides

- Complex hydrides consist of a H=M complex with additional bonding element(s)
- Reversibility demonstrated in $NaAlH_4$
  - By Bogdanovic and Schwickardi (1996)
- Hydrogen complexes include
  - $(AlH_4)^-$ (alanates)
  - $(BH_4)^-$ H with Group VIII elements
- Advantages:
  - Can have lower formation energy
  - Can have high H/M.



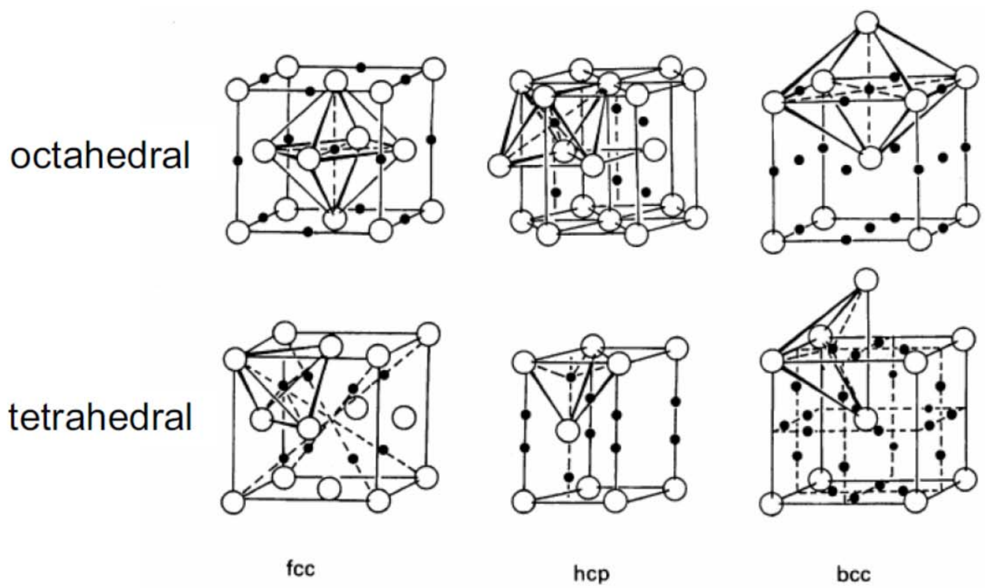
Issues with complex hydrides

- Reversibility
  - Role of catalyst or dopant.
- Thermodynamics
  - Pressure, temperature.
- Kinetics
  - Long-range transport of heavy species
- Capacity

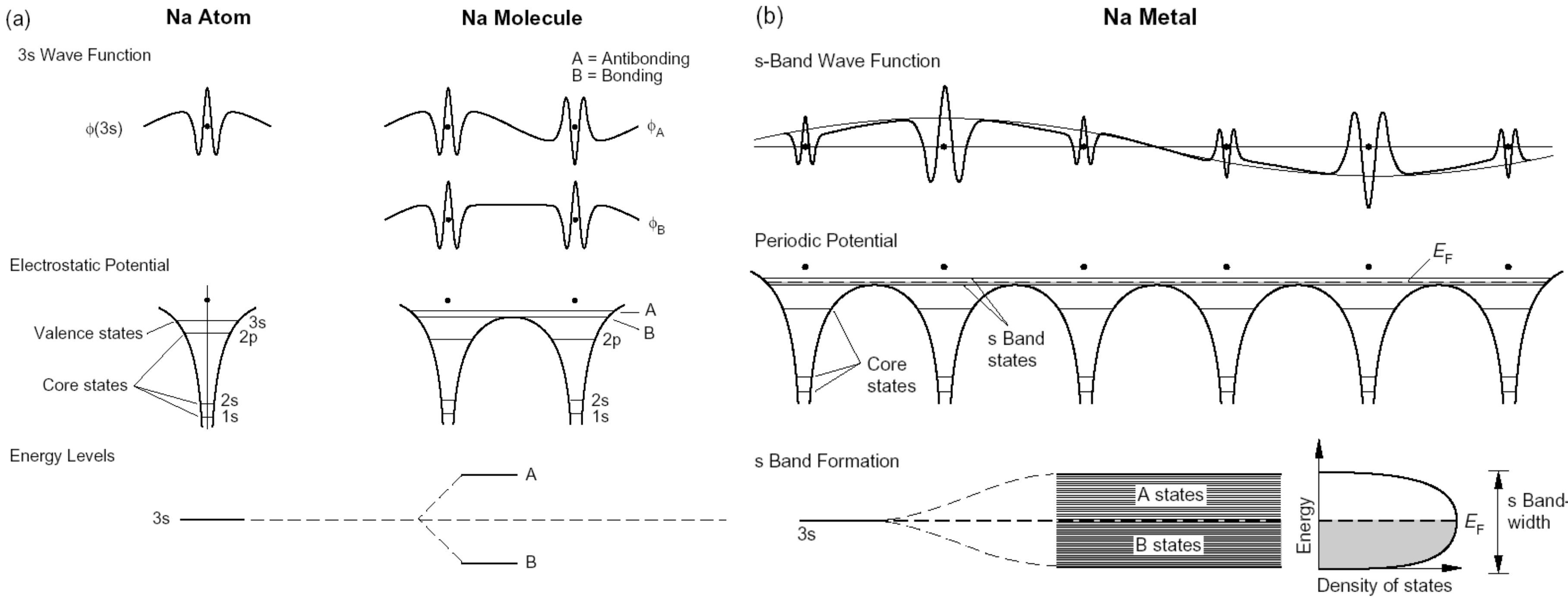


Metal hydrides – not all metals absorb H

Decisive is energy balance…
1. H bonding decreases energy
2. Volume expansion increase energy – work against elastic forces …several % to 60 % - powder
3. Disruption or weakening of existing bonds increases energy
4. Also dissociation of H_2 molecule plays a role



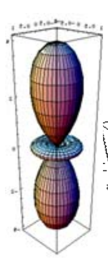
What are impacts on electrons?
2. Volume expansion
1. H bonding

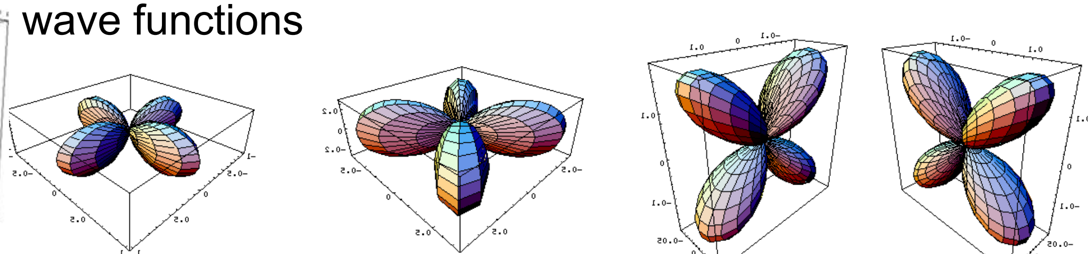


Periodic potential – Bloch wave functions, itinerant states

$$\Psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

But inner shells retain the localized, atomic wave functions





Two forms of description are mutually incompatible – how about the *5f* states?

The most interesting phenomena are at the crossover (verge of localization) – qualitatively new cooperative phenomena

Fermi gas – not too bad approximation

Free (non-intearcting) electrons + Fermi-Dirac statistics

A. J. Schofield 2

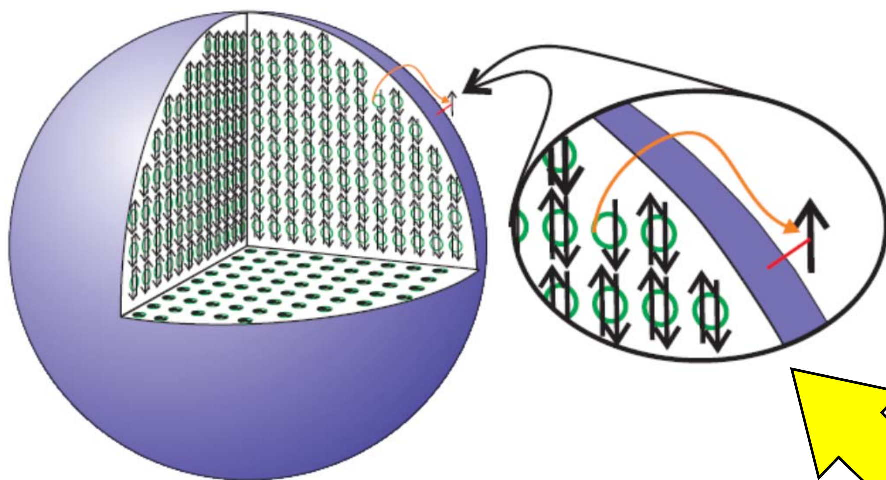


Figure 1: The ground state of the free Fermi gas in momentum space. All the states below the Fermi surface are filled with both a spin-up and a spin-down electron. A particle-hole excitation is made by promoting an electron from a state below the Fermi surface to an empty one above it.

$$E = \hbar^2 k^2 / 2m_e$$

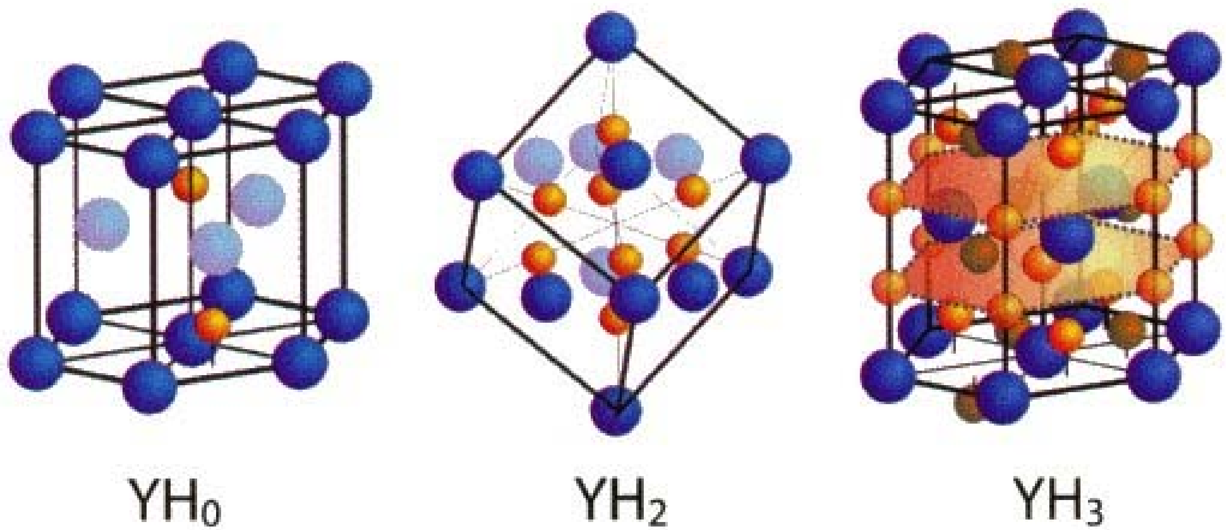
$$\mathbf{p} = \hbar \mathbf{k}$$

Free electrons in k-space

Only small amount of electrons (in the range $k_B T$ around the Fermi surface) affect properties as specific heat, susceptibility, resistivity…

switchable mirrors

Strongly electropositive **Y** has **1*4*d*** electron **+ 2*5*s*** electrons



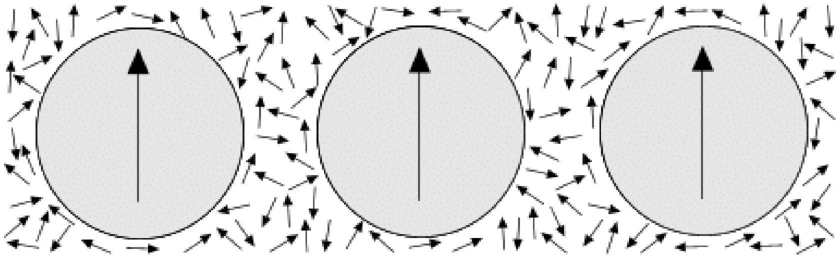
hcp	CaF_2	Hex.

$YH_{0-0.23}$ **$YH_{1.8-2.1}$** **$YH_{2.75-3.0}$**

Spin-spin exchange interaction between atoms mediated by
<u>RKKY</u> (Ruderman-Kittel-Kasuya-Yoshida) interaction
spin polarization of conduction electrons

$$\mathcal{H}_{ex} = -\sum_{n} \Gamma(\vec{r} - \vec{R}_n)\, \hat{s}(\vec{r}) \cdot \hat{S}_n$$

-4f metals, 4f intermetallics



Magnetic ordering temperatures of several ferromagnets

Material	T_C (K)
Co	1403
Fe	1043
Ni	631
Gd	293
$GdNi_2$	79
GdNi	64
$GdCl_3$	2.2
$SmCo_5$	993
$Nd_2Fe_{14}B$	585

***d*-metals: small magnetic moments but strong interaction – 3*d* band**

4*f*-metals: large moments from Hund rules, but 4*f* states deep inside atoms – how they interact?

GdH_2 – 21 K

GdH_3 – 3.3 K

But we are interested in....The Actinides

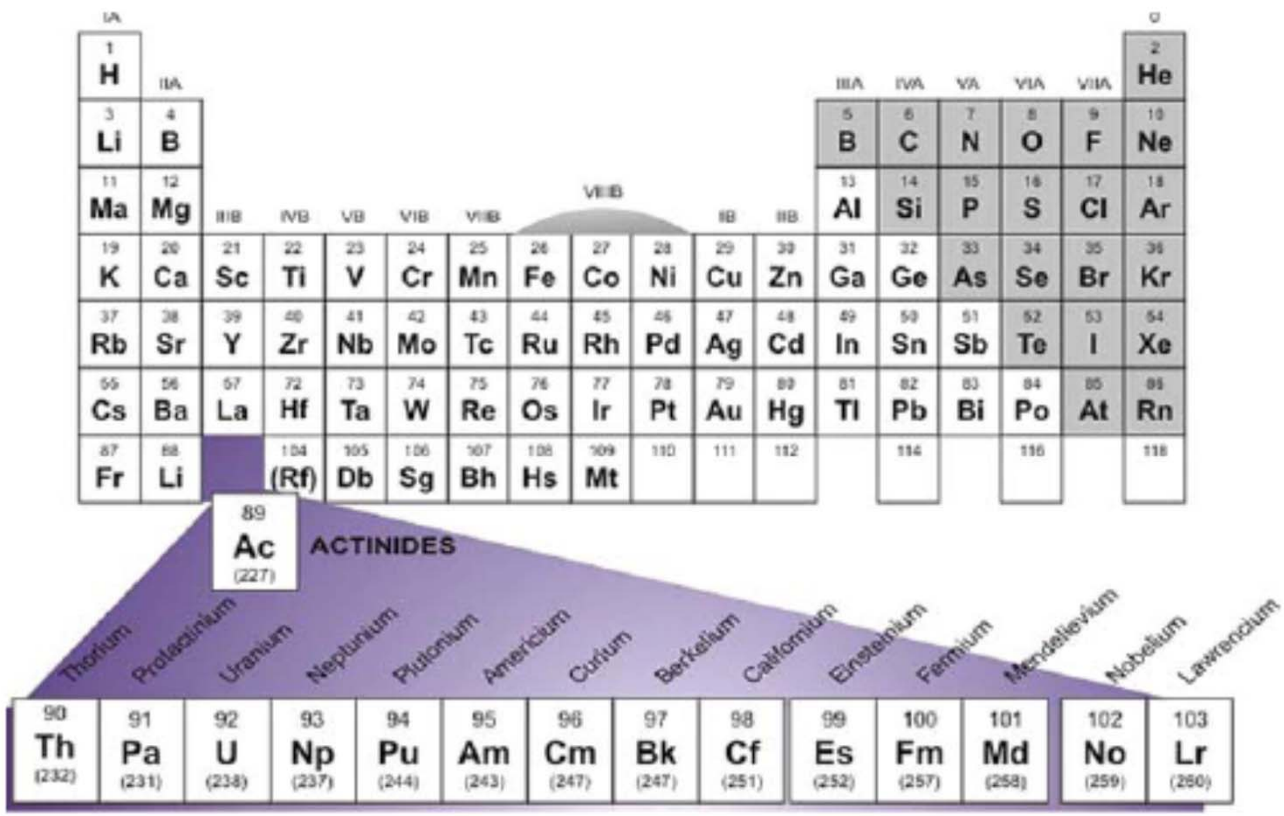


Figure 1. The periodic table of elements highlighting the actinide series, which encompasses thorium (Th) to Lawrencium (Lr).

Gradual filling of 5*f* states......6*d* states remain with low occupancy…also 7*s*

How the 5*f* states look like?

Actinides – 5*f* states

2 distinctly different parts of the series

Lanthanides

6*d*,7s

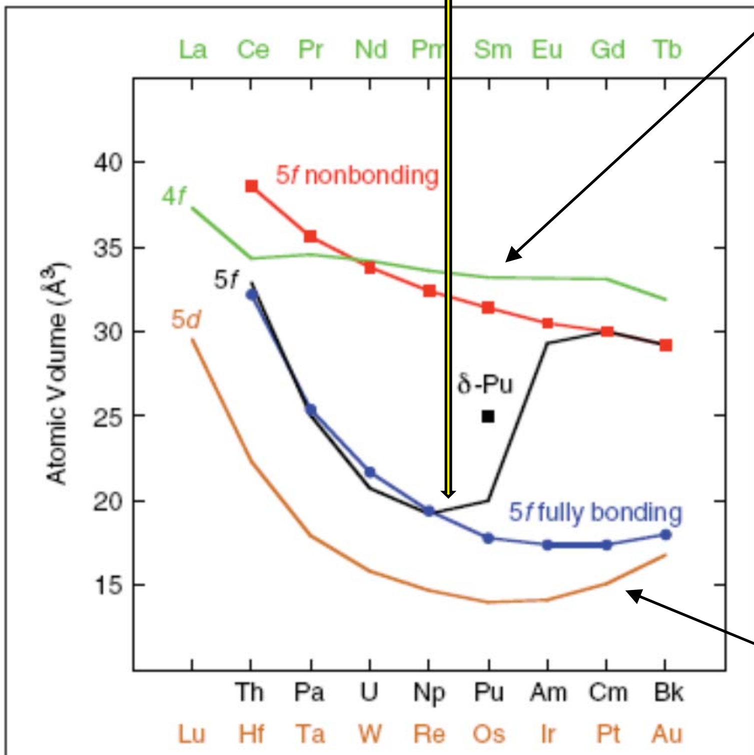
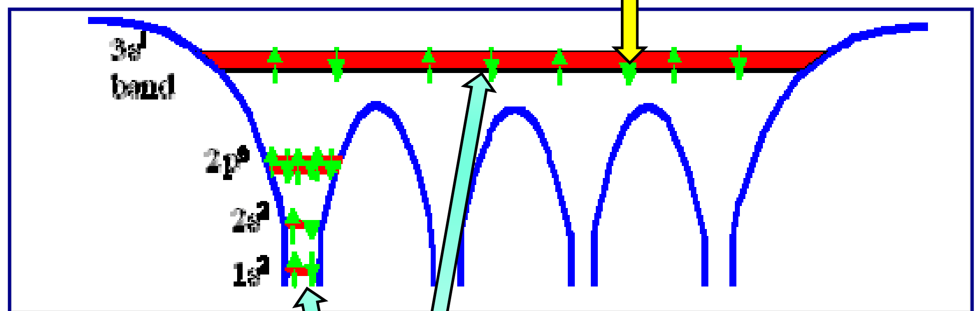


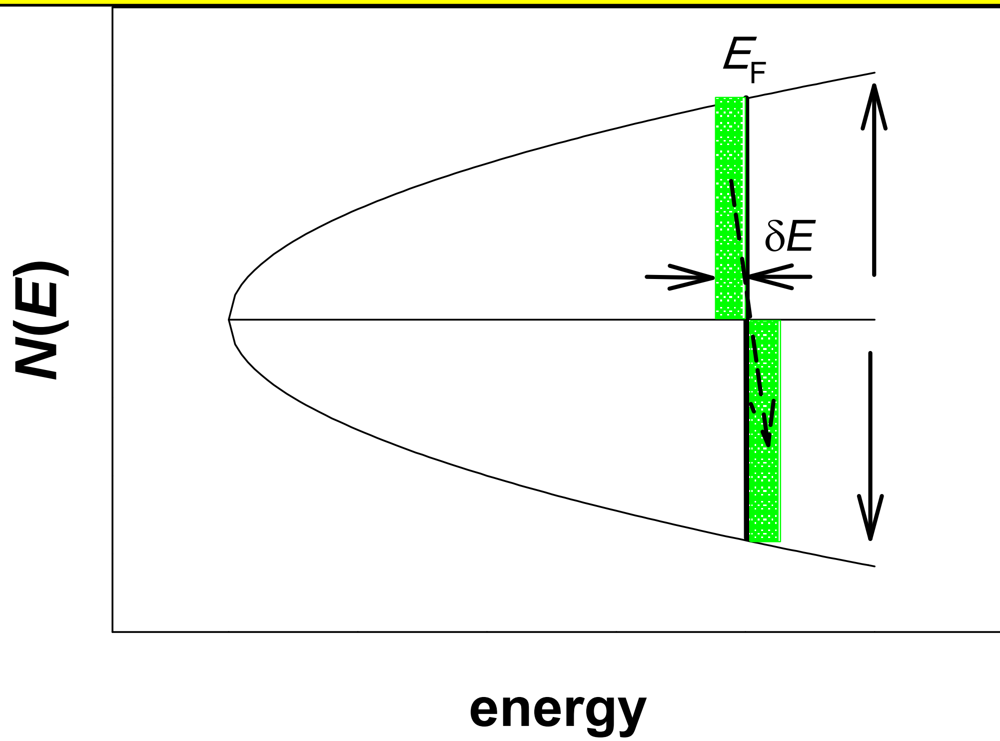
Figure 1. Measured atomic volumes of the actinide metals (5*f*) are shown with a black line, a brown line for the 5*d* transition metals, and a green line for the lanthanides (4*f*). The red "5*f* nonbonding" and blue "5*f* fully bonding" curves show results from model calculations, assuming the face-centered-cubic structure, where the 5*f* electrons are treated as part of the valence band and localized to nonbonding core states, respectively.



5*f*

Transition metals

Magnetic moments and their order can arise also in band case – exchange interactions cause unequal occupancy of states with different spin



Sub-bands with opposite spins

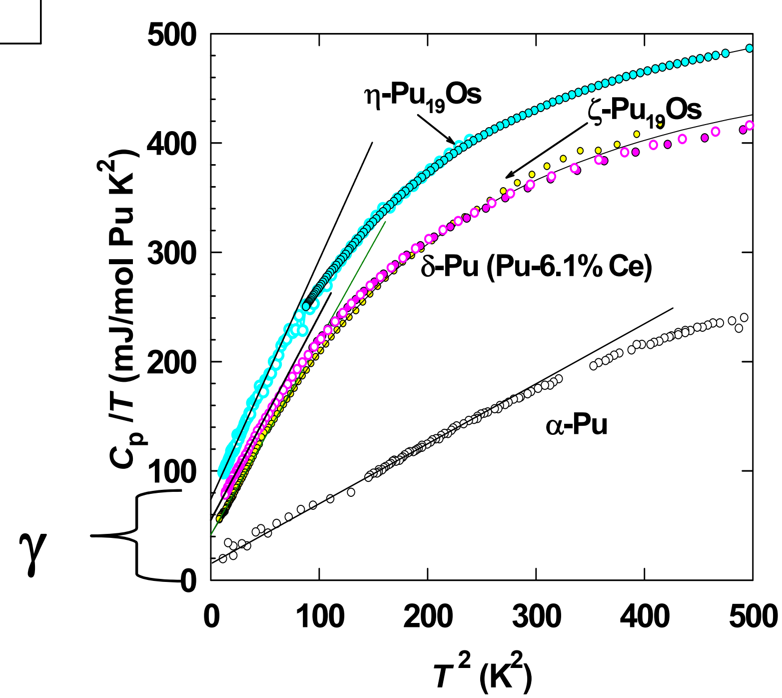
Exchange interactions – repulsion of electrons with the same spin is lower than for opposite spins

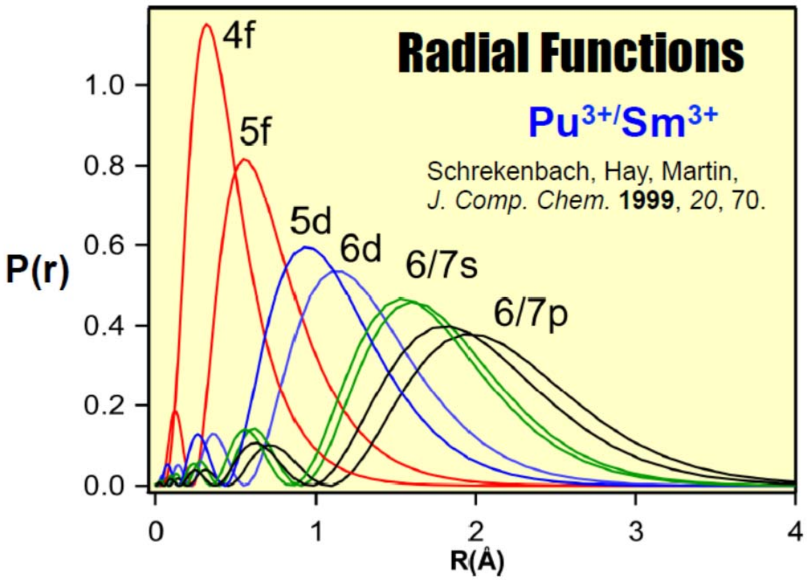
$U{*}N(E_F) > 1$ spontaneous splitting…….

Stoner criterion

$N(E_F)$ can be measured!!!

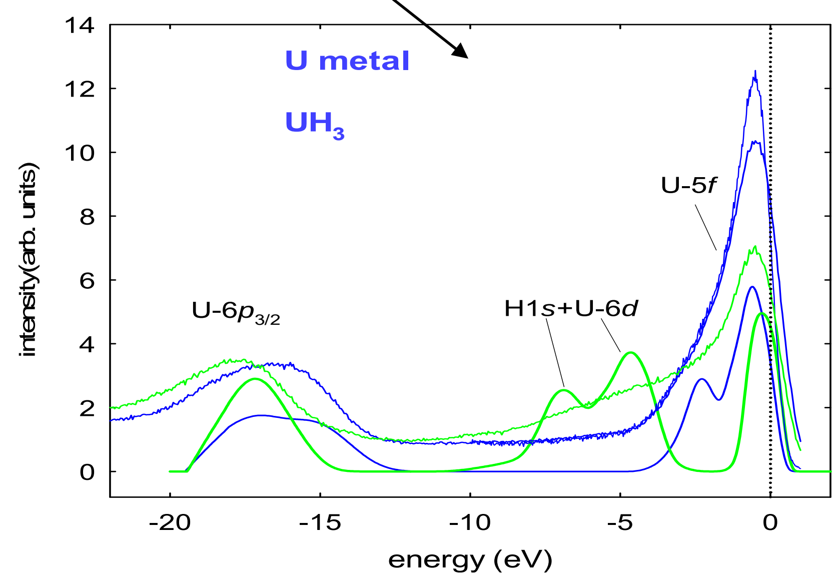
$C = \gamma T + \beta T^{3}$; $\gamma = 1/3 k_B \pi^2 N(E_F)$;
$\beta = (1944{*}10^3) n/\Theta_D^{\,3}$





Polar character of bonding –H likes to suck electrons from electropositive elements

Photoelectron spectroscopy



PHYSICAL REVIEW B **91**, 115116 (2015)

Electronic properties of α-UH$_3$ stabilized by Zr

I. Tkach,[1] M. Paukov,[1] D. Drozdenko,[1] M. Cieslar,[1] B. Vondráčková,[1] Z. Matěj,[1] D. Kriegner,[1] A.V. Andreev,[2] N.-T. H. Kim-Ngan,[3] I. Turek,[1] M. Diviš,[1] and L. Havela[1]
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(Received 23 December 2014; published 6 March 2015)

TABLE II. Site projected occupancies of individual states for α-UH$_3$ (at experimental lattice parameter) and bcc U with the same lattice parameter. Occupancies of particular states in interstitial areas are not included.

State	α-UH$_3$	bcc U
U-6*d*	0.63	1.22
U-7*s*	0.03	0.42
U-5*f*	2.71	2.62
H-1*s*	1.74	

PHYSICAL REVIEW B **91**, 115116 (2015)

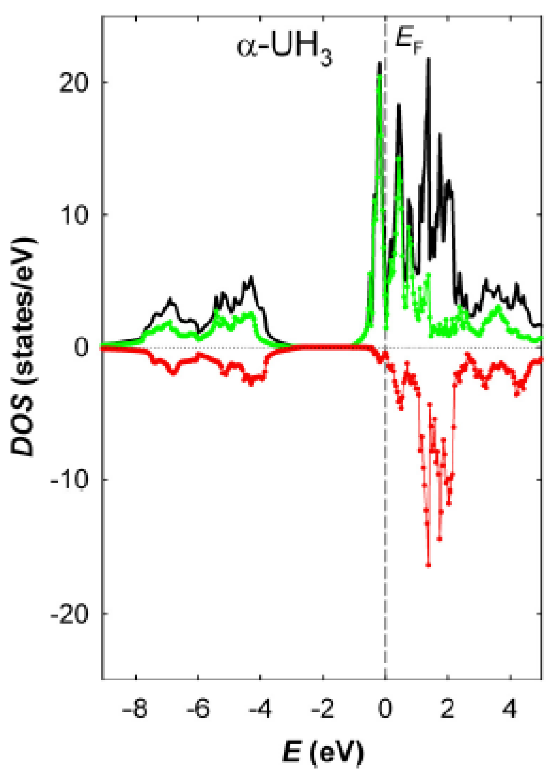


FIG. 10. (Color online) Total (black) and spin-resolved (
and red) density of states for α-UH$_3$ calculated using fully relat
FPLO method.

Charge transfer to H?
6*d*, 7*s* yes
5*f* no

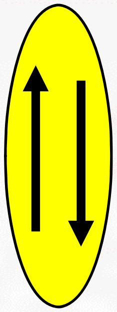
Robust ferromagnetism
Suppression of 5*f*-6*d* hybridization??

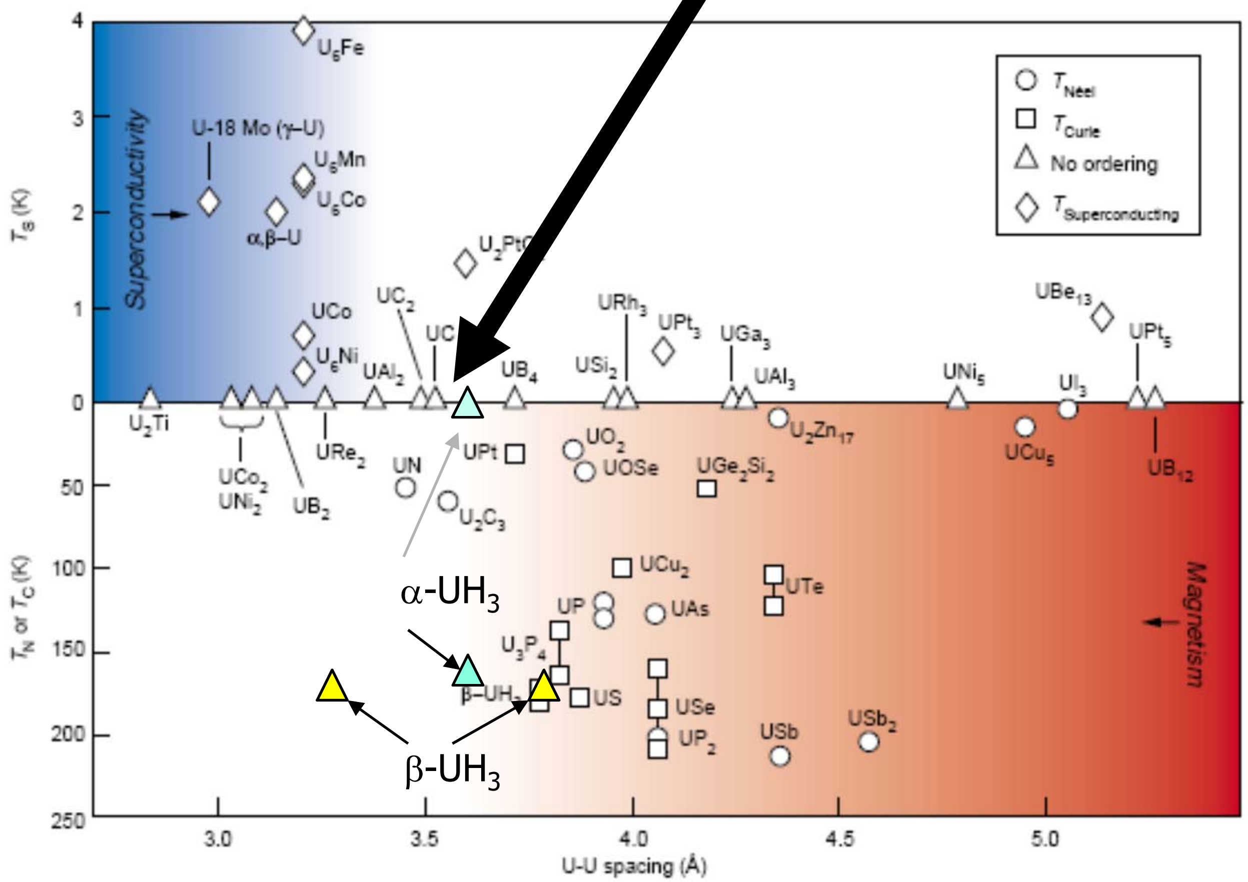
Increase of atomic radius between H and H$^-$

H : 0.032 nm
H$^-$: ≈ 0.1 nm

superconductivity

Hill limit





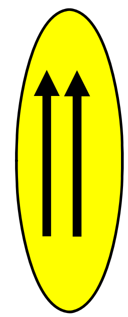


Figure 24. Hill Plot for Uranium Compounds

The Hill plot shows the superconducting or magnetic transition temperatures vs interatomic spacing separating the f electron atoms. We augmented the original Hill plot for uranium compounds to include more data—in particular, the transition temperatures of the

Magnetism – atoms cannot be too close together

f-electron spacings (blue quadrant), and the magnetic compounds at large f-electron spacings. The heavy-fermion superconducting compounds are exceptions. Although the spacing between the uranium atoms in those compounds is fairly large, the f electrons are still not fully localized and can condense into a superconducting state.

H_2 attacks U breaking it into fine pyrophoric powder (detrimental for devices)

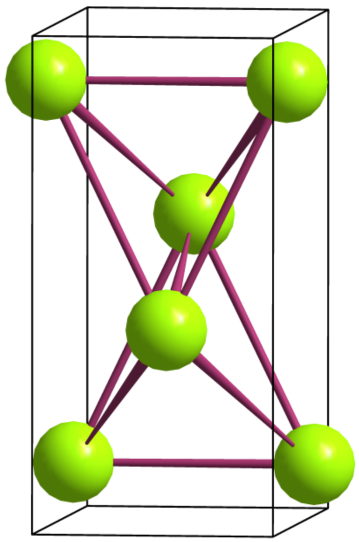
Can be H_2 used to tune Properties of U?
Yes!!!

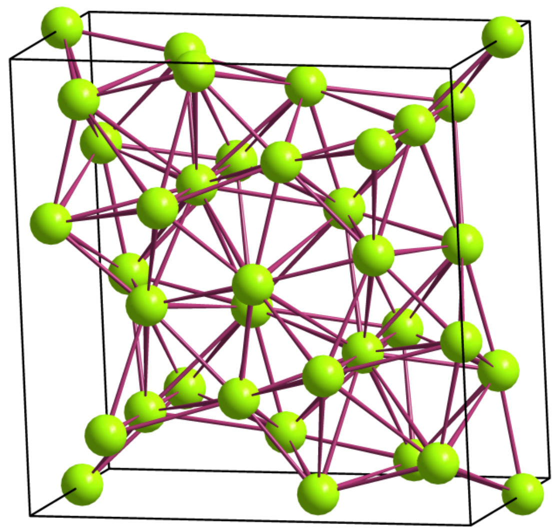
Can be U used to store H_2?
Yes...works very well
For Tritium

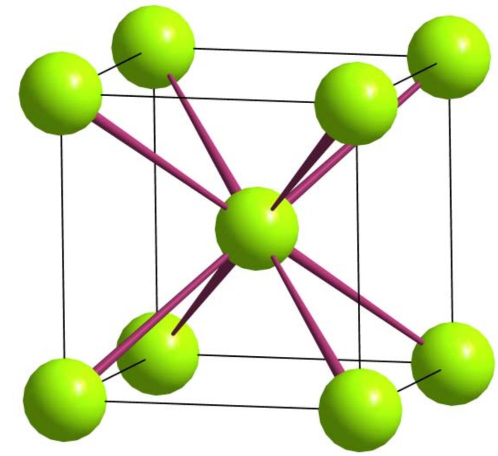
U forms UH_3. Pressure of H_2 at 700 K – 1000 mbar at 300 K – 10^{-4} mbar

Uranium – 3 allotropic phases

Can be stabilized by > 18 at.% Mo
how about less Mo
and ultrafast cooling?







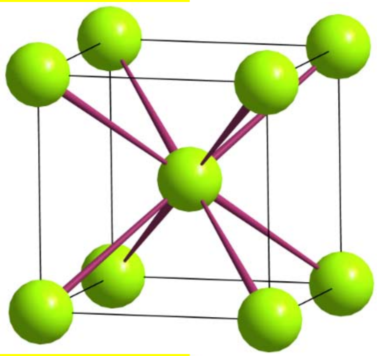
	α	β	γ
structure	orthorhombic	tetragonal	cubic (*bcc*)
density	19.07 g/cm^3	18.17 g/cm^3	17.94 g/cm^3
shortest U-U distance	2.837 Å	2.889 Å	3.067 Å
temperature	below 942 K	942-1049 K	1049-1408 K

γ-U stable with respect to irradiation, corrosion, hydrogen.. Low enriched U nuclear fuel

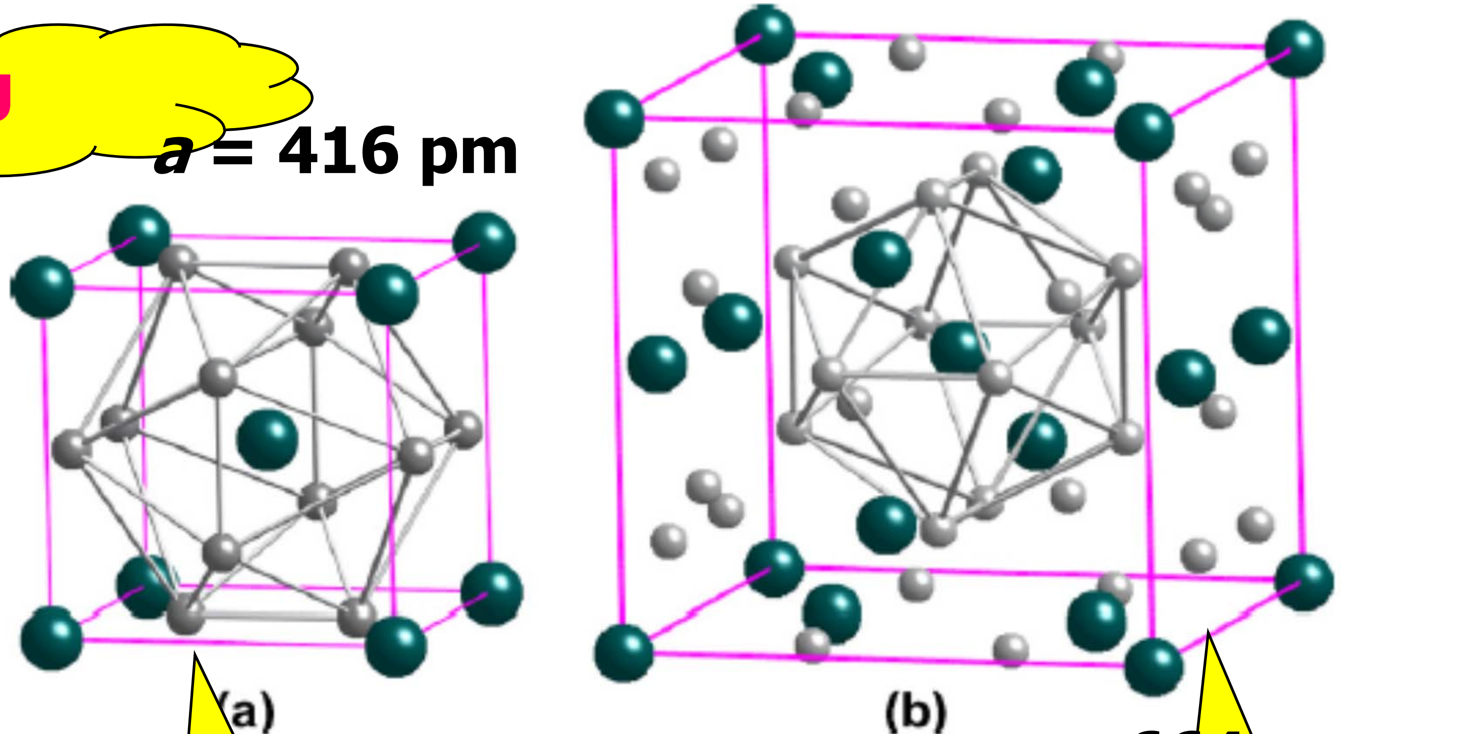
But - what are low-*T* electronic properties ??

γ-U

a **= 416 pm**



a **= 352 pm**



a **= 664 pm**

α-UH_3

$d_{U\text{-}U}$ = 360 pm

β-UH_3

$d_{U\text{-}U}$ = 330 pm

Ferro- or para ? Either T_C = 165 -170 or 0

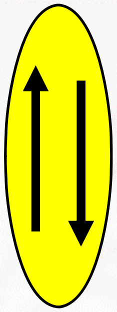
Lawson et al. 1991

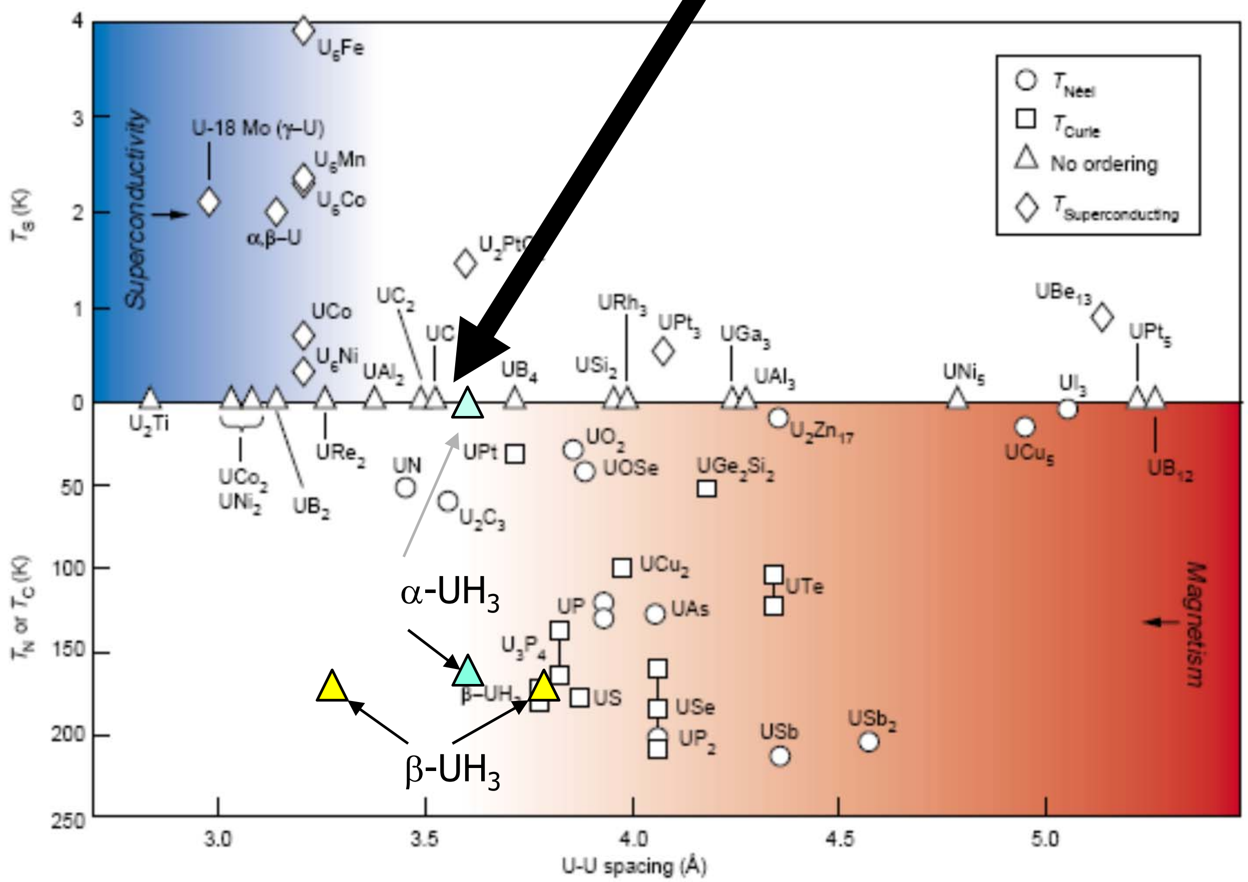
Ferro- T_C = 165 -170 K, μ = 0.9 μ_B

Trzebiatowski et al. 1952

superconductivity

Hill limit





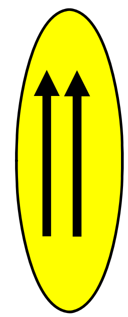
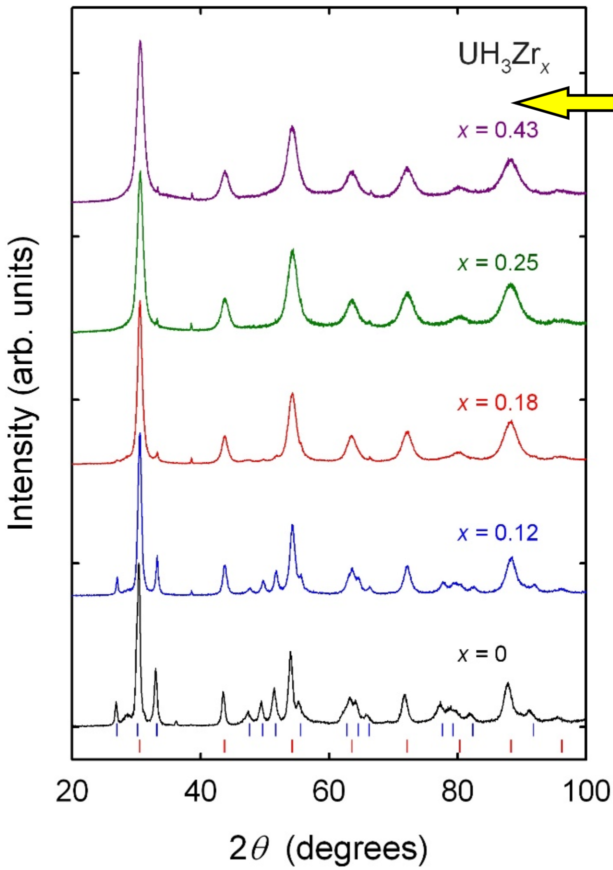


Figure 24. Hill Plot for Uranium Compounds

The Hill plot shows the superconducting or magnetic transition temperatures vs interatomic spacing separating the f electron atoms.

Magnetism – atoms cannot be too close together

f-electron spacings (blue quadrant), and the magnetic compounds at large f-electron spacings. The heavy-fermion superconducting compounds are exceptions. Although the spacing between the uranium atoms in those compounds is fairly large, the f electrons are still not fully localized and can condense into a superconducting state.



α-UH_3

D = 10-20 nm

Magnetic Properties of α-Uranium Hydride

by

A. ŚLIWA and W. TRZEBIATOWSKI

Presented by W. TRZEBIATOWSKI on March 10, 1962

BULLETIN DE L'ACADÉMIE POLONAISE DES SCIENCES
Série des sciences chimiques
Volume X, No. 5, 1962

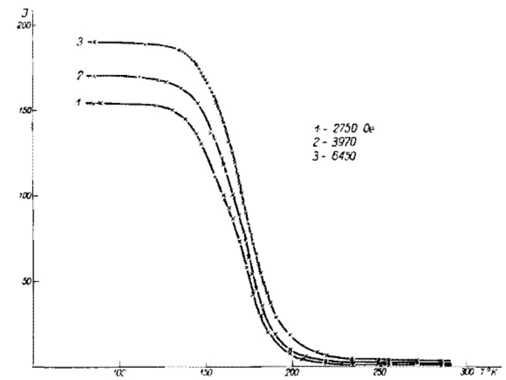
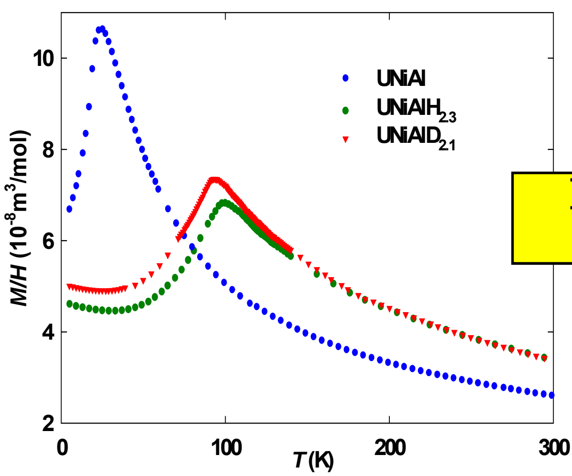


Fig. 1. Magnetization of α-UH_3 containing 25% β-UH_3

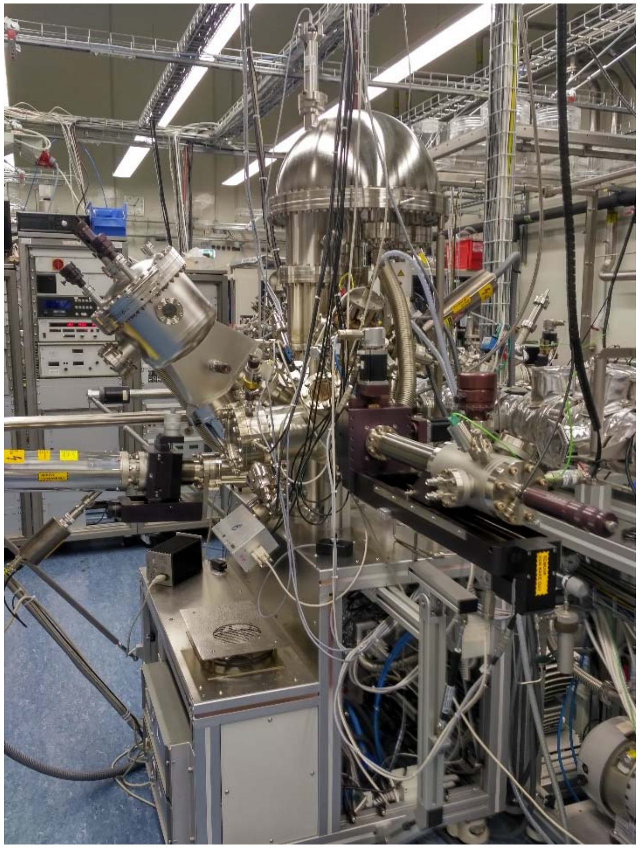


Increase of ordering T in antiferromagnet

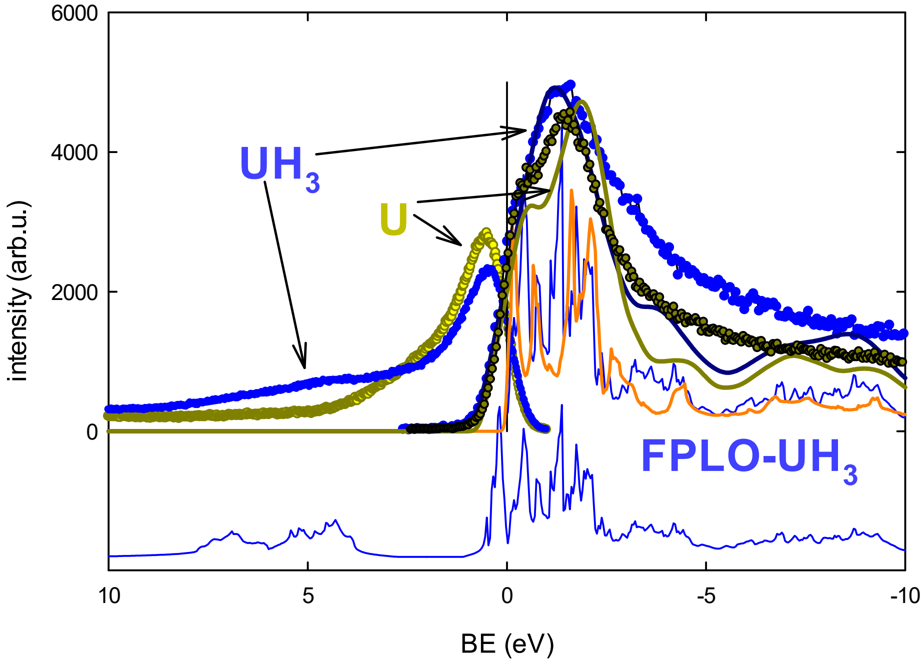
UH_3 – ferromagnet with T_C = 165 K

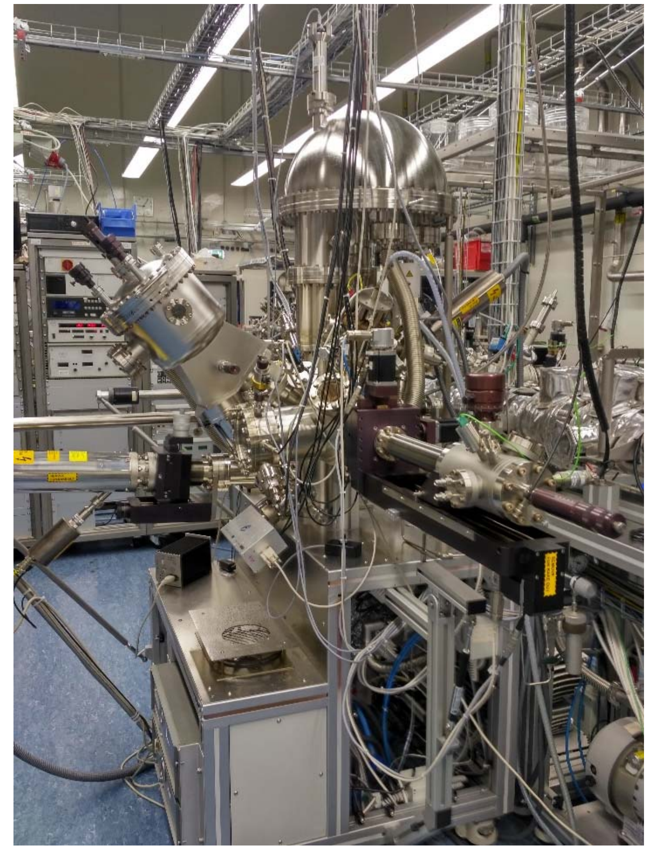
Synthesis of films by sputter deposition

- U and Mo targets with voltage independently controlled
- Thoriated W heated filament for stabilizing plasma
- Ar gas (10^{-3} mbar) , variable concentration of H_2
- Si wafer or fused silica substrates
- Purity monitored by O-1*s* (XPS) and O-2*p* (UPS) lines



Combined with BIS



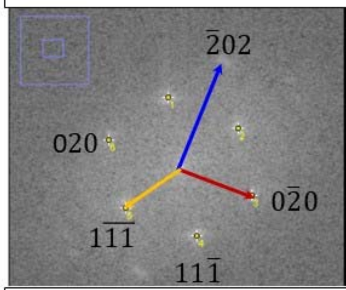


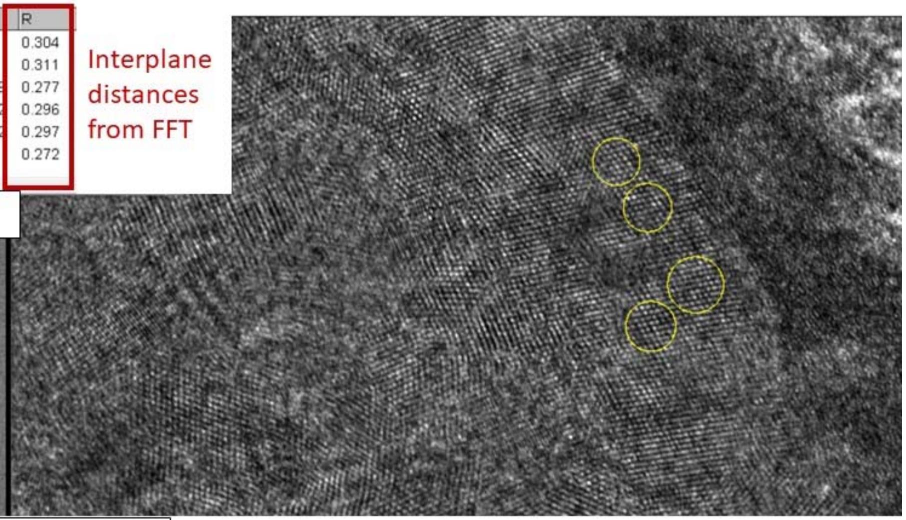
BIS shows the s-o splitting for U metal. It is smeared in UH_3 due to spin-up and spin-down splitting. More spectral weight at higher energies…6*d* states.

	Area	Mean	Min	Max	X	Y	R
1	0.000	190	190	190	9.671	8.663	0.304
2	0.000	170	170	170	10.953	9.222	0.311
3	0.000	149	149	149	11.198	10.449	0.277
4	0.000	197	197	197	10.191	11.172	0.296
5	0.000	170	170	170	8.886	10.682	0.297
6	0.000	146	146	146	8.589	9.428	0.272

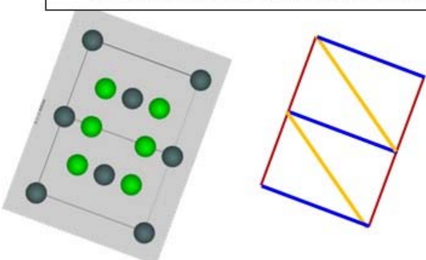
Interplane distances from FFT

FFT, diffraction planes



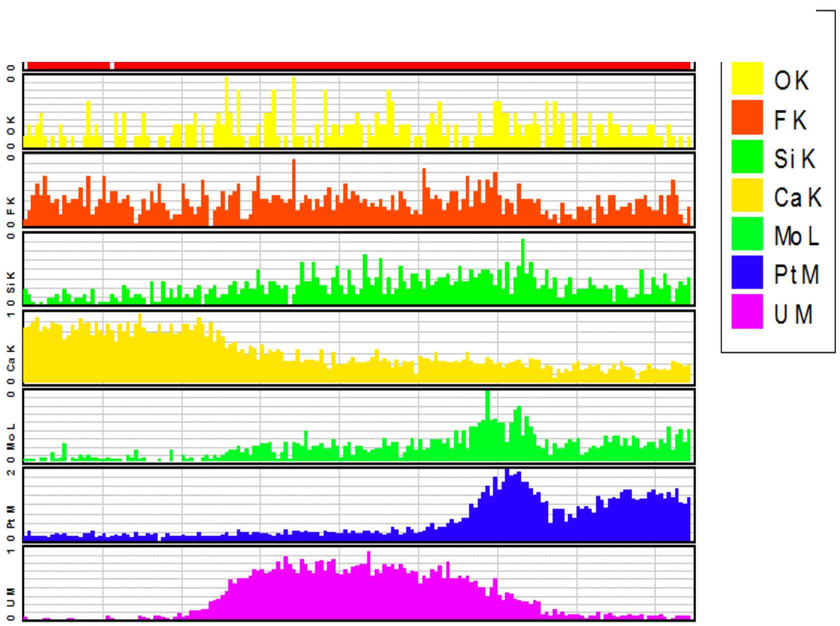


Orientation of cristal in real espace



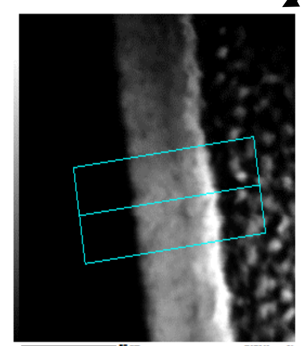
Axis [011] of UH_2 $d_{111}=0.302/d_{200}=0.2745$

100 diffracting planes
110 diffacting planes
111 diffacting planes



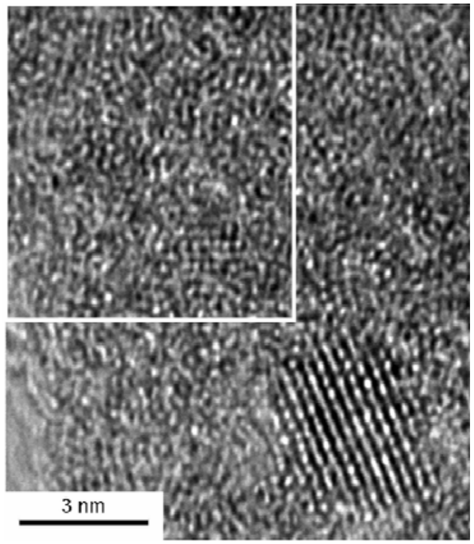
UH_2 film

Pt

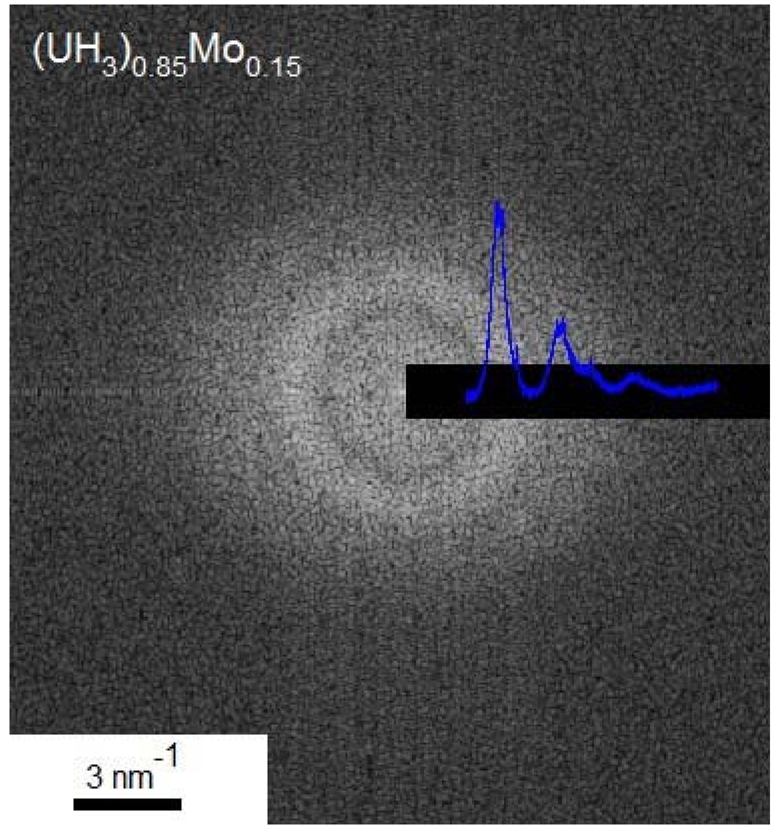


CaF_2

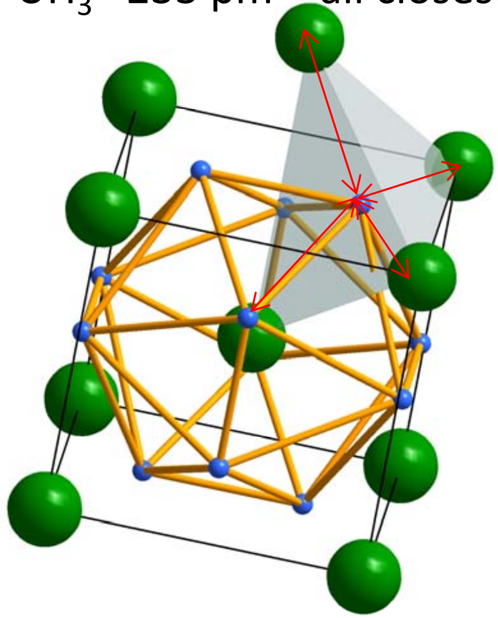
HRTEM



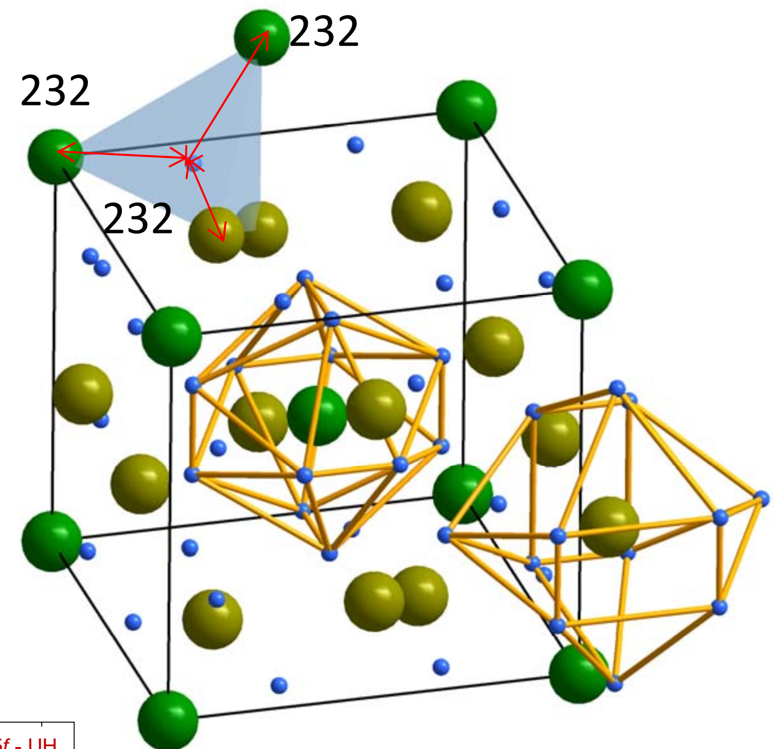
Ultrananocrystallinity with high anisotropy means a non-collinear ferromagnetism with random distribution of easy magnetization directions



α-UH_3 233 pm – all closest U atoms

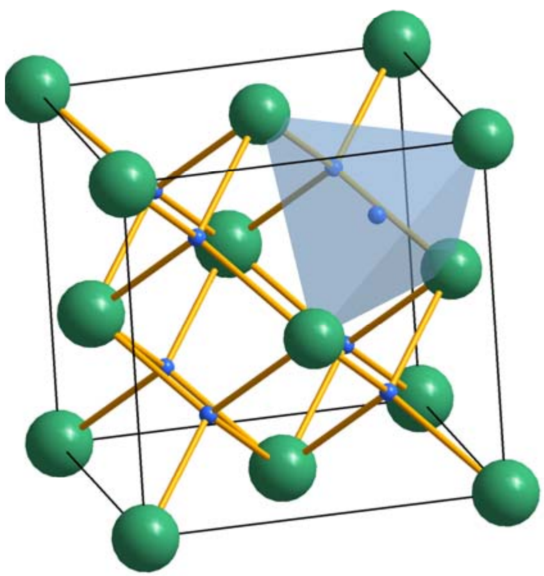


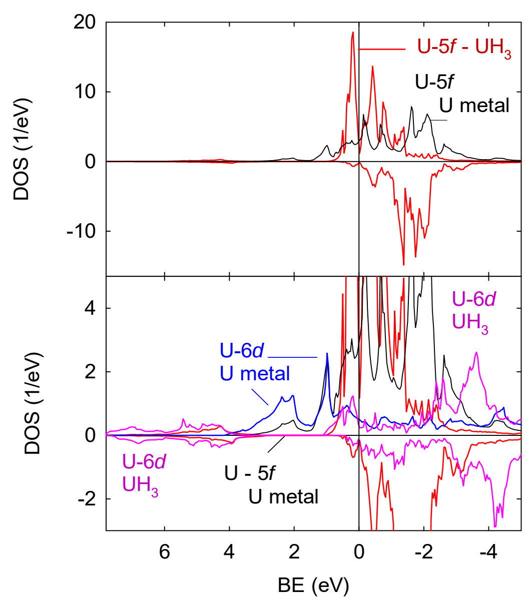
β-UH_3



Identical tetrahedra ..as molecules.. which determine T_C

UH_2 232 pm – all closest U atoms





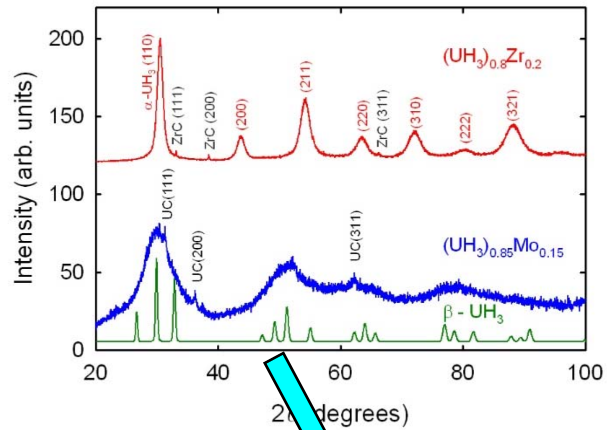
r_U =156 pm
r_H = 37 pm

r_H = 76 pm in UH_3 or UH_2

On the way to H^-

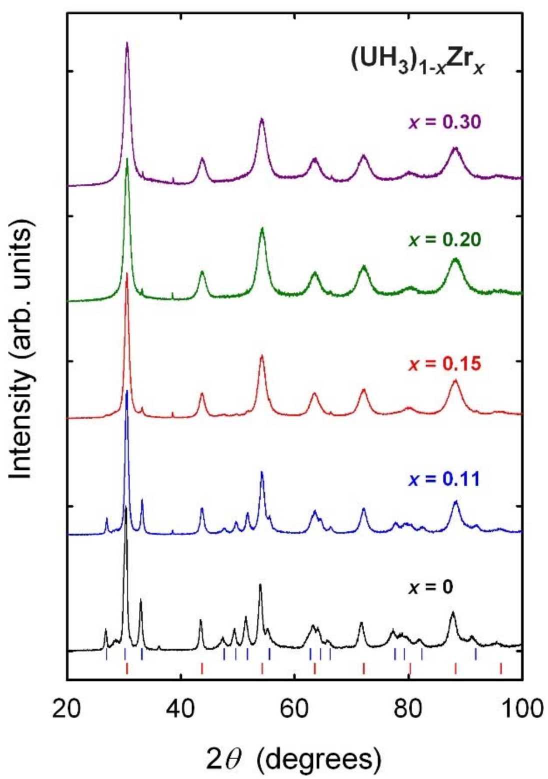
Polar bonding in metallic state

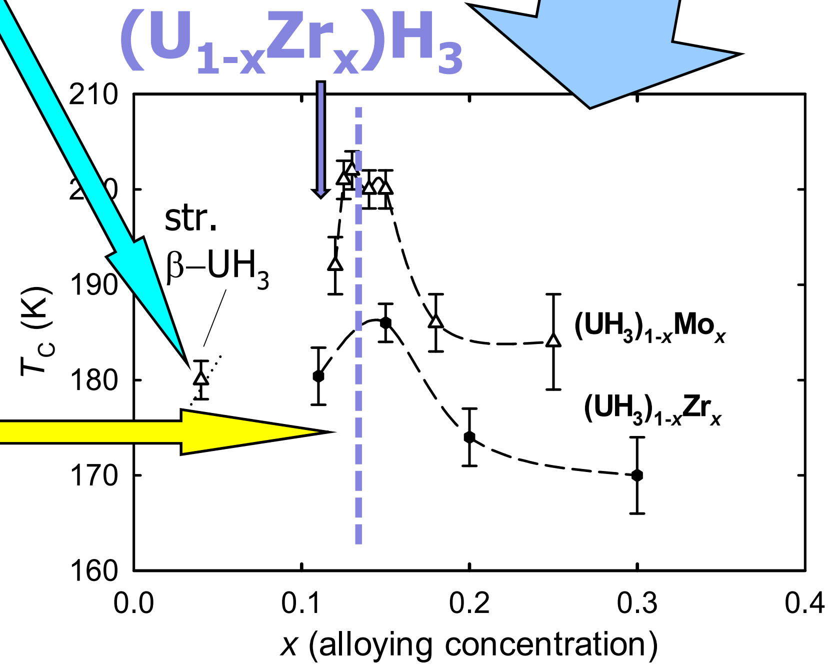
Doping by Mo or Zr



β-UH_3

D = 2-3 nm





α-UH_3

D = 10-20 nm

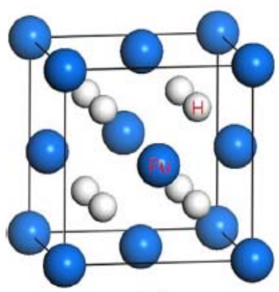
5*f* band ferromagnets?

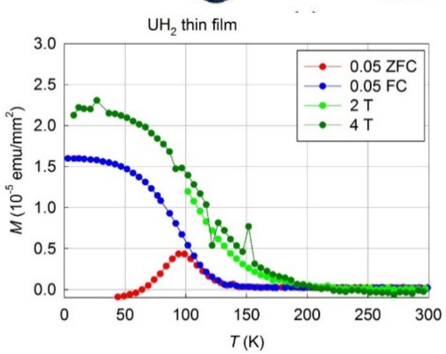
$U + H_2$

UH_8 and other hyper-hydrides

U

UH_2

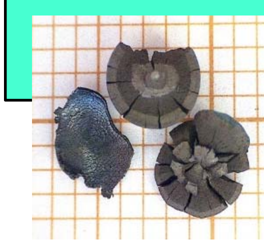




β-UH_3

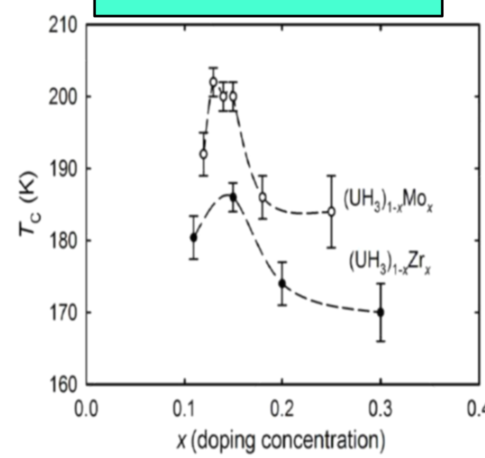
crystalline
T_C = 165 K

Nano-
crystalline
T_C = 165 K
(+Mo)
T_C = 200 K



α-UH_3
T_C = 165 K

(+Zr)
T_C = 185 K



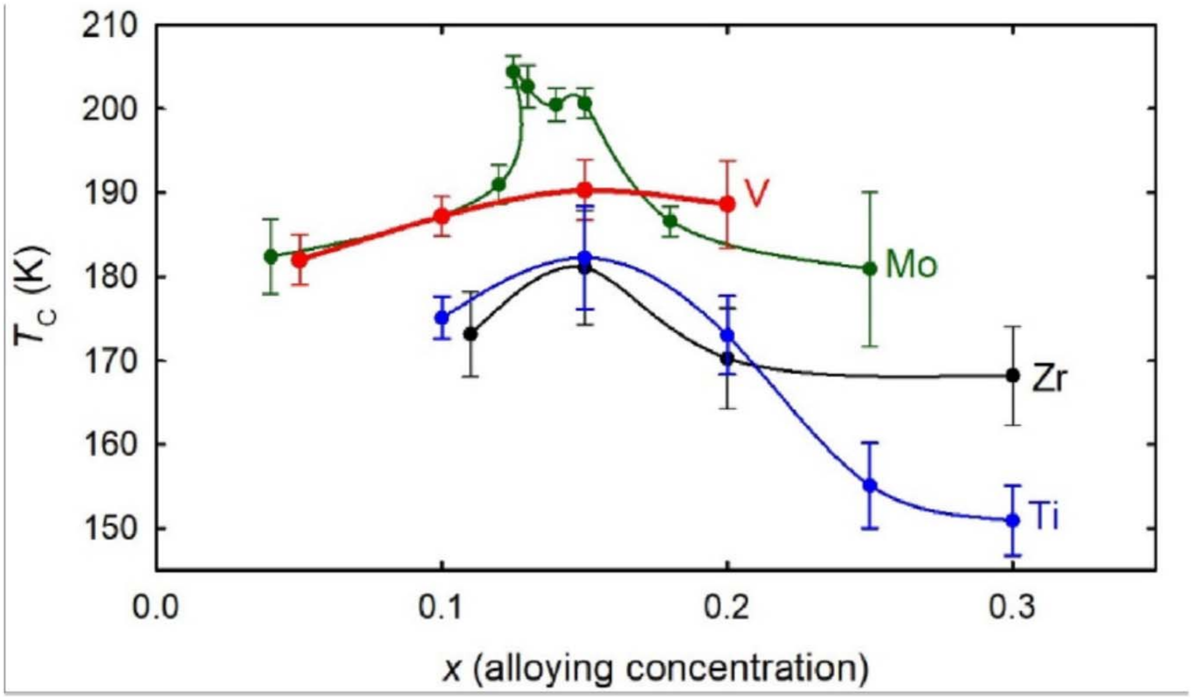


Fig. 6. Concentration dependence of the Curie temperature in the series $(UH_3)_{1-x}$(V-Mo-Zr–Ti)$_x$.

Maximum T_C values found universally for the T concentrations 12-15 at.% suggest that 1/8 (i.e. 0.125) of the U atoms can be safely replaced still maintaining H atoms stable inside the tetrahedra. **H-U ratio increases. U electropositive.**

U-H interaction plays a dominant role!

Conclusions:

In U-H there is evidence for a charge transfer towards H, similar to e.g. pnictides.

In U-H, partial depletion of 6*d* and 7*s* states (5*f* band remains at E_F) may lead to strong magnetism, normally negatively affected by the 5*f* – 6*d* hybridization. Strong magnetism and partial localization despite short U-U spacings

Robust ferromagnetism opens an avenue for thin-film devices (Giant magnetoresistance, large exchange bias)

Old publications can be seen from a new perspective….combined physics-chemistry view brings benefits

Main collaborators: Poland (prof. Kim et al.)

Prague – Germany

Volodymyr Buturlim – bulk properties

Ilja Turek, Martin Divis, Jindra Kolorenč, Dominik Legut - calculations

Daria Drozdenko, Zdenek Matej, Milan Dopita, Mirek Cieslar, Mayerling Martinez – XRD, TEM, EBSD, EXAFS, PDF

Sasha Koloskova, Frank Huber, Thomas Gouder, A. Seibert – XPS, UPS, BIS

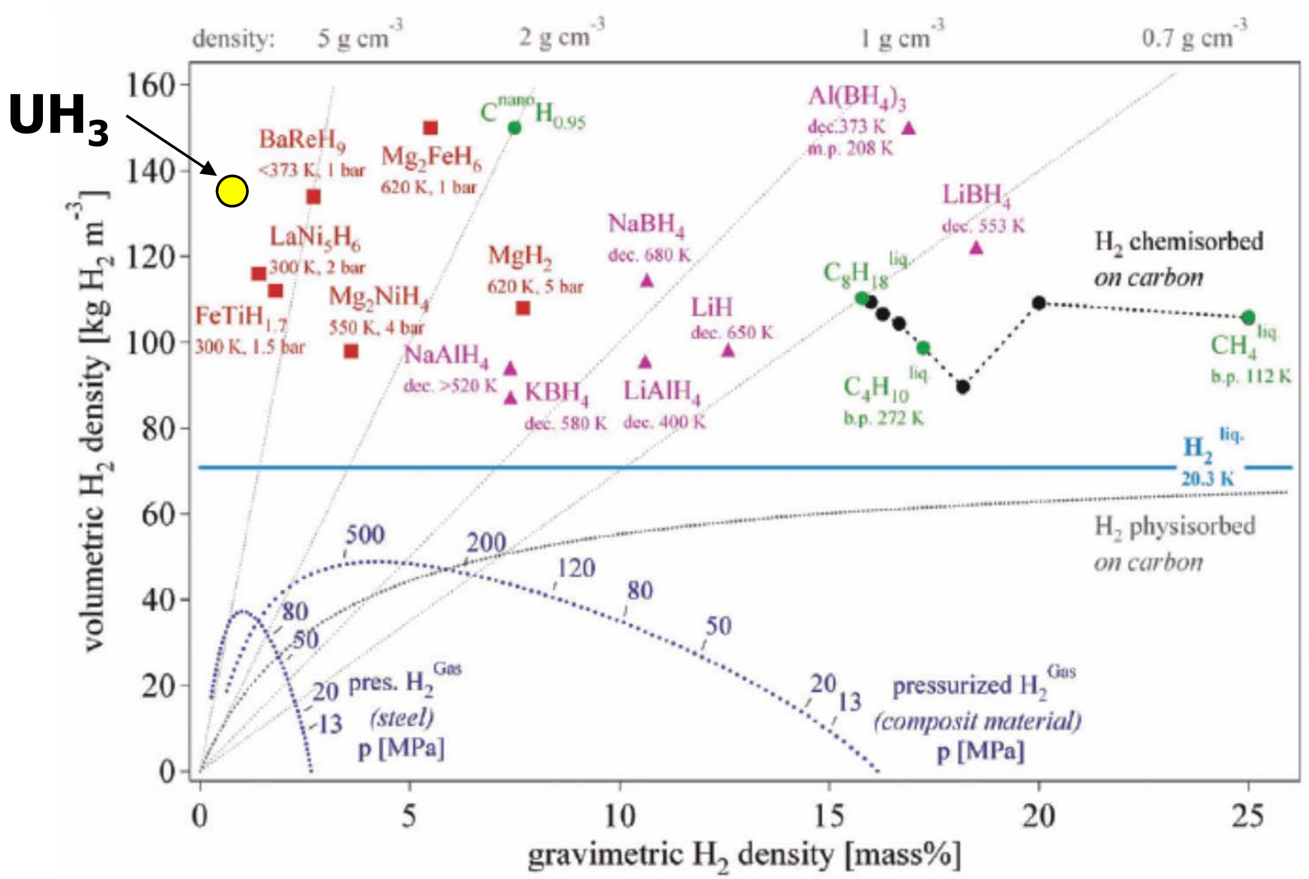


Fig. 7 Volumetric and gravimetric hydrogen density of some selected hydrides. Mg_2FeH_6 shows the highest known volumetric hydrogen density of 150 kg·m^{-3}, which is more than double that of liquid hydrogen. $BaReH_9$ has the largest H/M ratio of 4.5, i.e. 4.5 hydrogen atoms per metal atom. $LiBH_4$ exhibits the highest gravimetric hydrogen density of 18 mass%. Pressurized gas storage is shown for steel (tensile strength σ_v = 460 MPa, density 6500 kg·m^{-3}) and a hypothetical composite material (σ_v = 1500 MPa, density 3000 kg·m^{-3}).