The French Research network on Hydrogen energy

3éme reunion plénières de la Fédération Hydrogène (FRH2)

22-26/05/2023

Multiple phase transitions in $Y_{1-y}R_yFe_2$ hydrides and deuterides

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UPEC Université Paris-Est Créteil 50 ans 1970 • 2020

Outline

1. Interest of AB_2 Laves phase compounds
2. YFe_2 structure and influence of H absorption
3. Methods
4. Results
   - Structures of YFe_2D_x compounds
   - Phase transitions
     - Thermodesorption
     - Order-disorder transitions
     - Magnetic transitions
   - Magnetism and magnetic entropy In $Y_{1-x}R_xFe_2$ compounds
5. Conclusions

Wood museum, Taiwan

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1. Interest of *AB*$_2$ Laves phase compounds

- A large variety of *AB*$_2$ Laves phases: > 1000 compounds

- A great number of applications:

F. Stein, A. Leineweber, Laves phases: a review of their functional and structural applications and an improved fundamental understanding of stability and properties, J. Mater. Sci., 56 (2021) 5321-5427.

- *R*Fe_2: Giant magnetostriction for actuators, sonars …

- Hydrogen storage application :

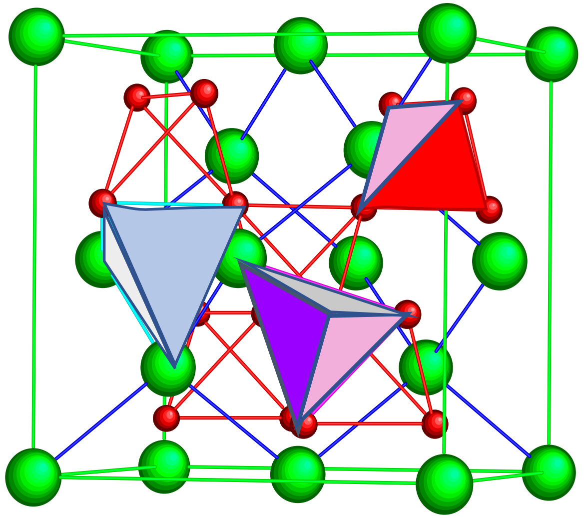
V.A. Yartys, M.V. Lototskyy, Laves type intermetallic compounds as hydrogen storage materials: A review, J. Alloys Compds, 916 (2022) 165219.

H. Kohlmann, Hydrogen order in hydrides of Laves phases, Z. Krist-Cryst Mater., 235 (2020) 319-332.

2. YFe_2 structure and H sites

Cubic C15 structure

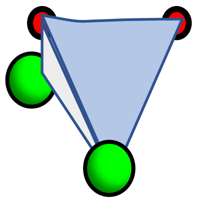
Fd-3*m* S.G. *a* = 7.36 Å



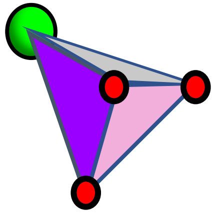
R_Y/R_{Fe} = 1.29 > 1.225

d_{Fe-Fe} = **2.60 Å > 2.49** Å (α-Fe)
d_{Fe-Y} = 3.05 Å
d_{Y-Y} = **3.186 Å < 3.56 Å** (Y)

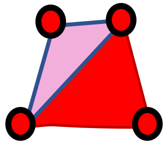
3 tetrahedral sites for H insertion



Y2Fe2 96*g* : 12 H/f.u.

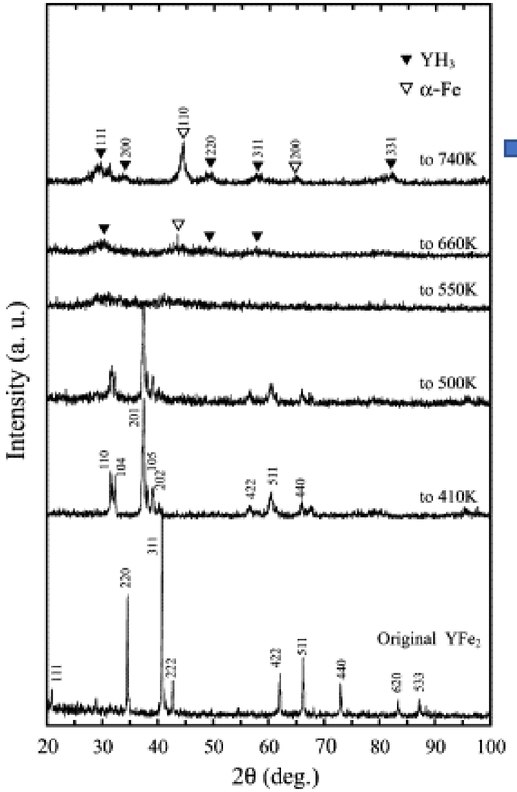


YFe3 32*e* : 4 H/f.u.



Fe4 8b : 1 H/f.u.

2. Hydride synthesis: Influence of *T* and *P*?

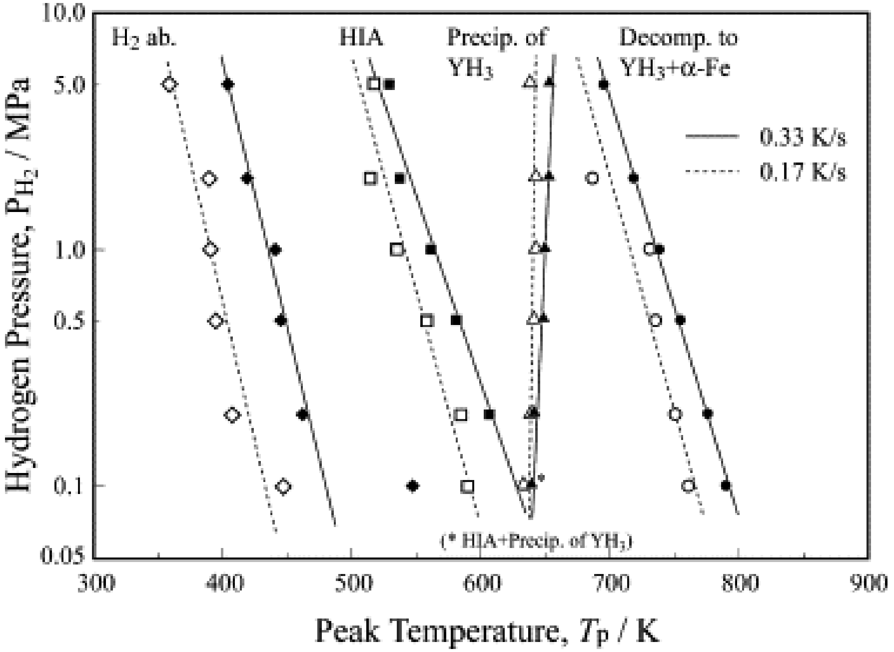


Decomposition in Fe and YH_3

Amorphisation (HIA)

Cristalline hydride

XRD patterns of YFe_2 heated a rate of 0.17 K/s and at the H_2 pressure of 1.0 MPa.



DSC: Peak temperature, T_p, of each reaction and the hydrogen pressure at two heating rates (10 and 20 K/min)

K. Aoki, H. W. Li, M. Dilixiati, and K. Ishikawa, Mater. Sci. Eng. A 449-451, 2 (2007).

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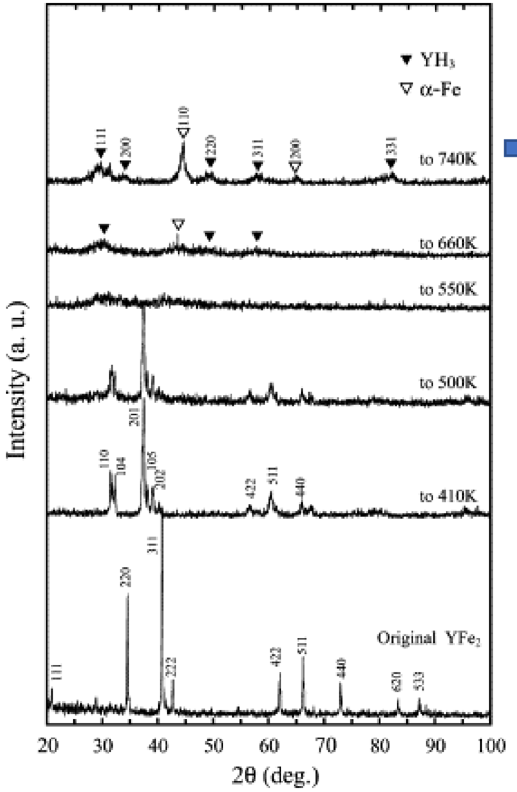

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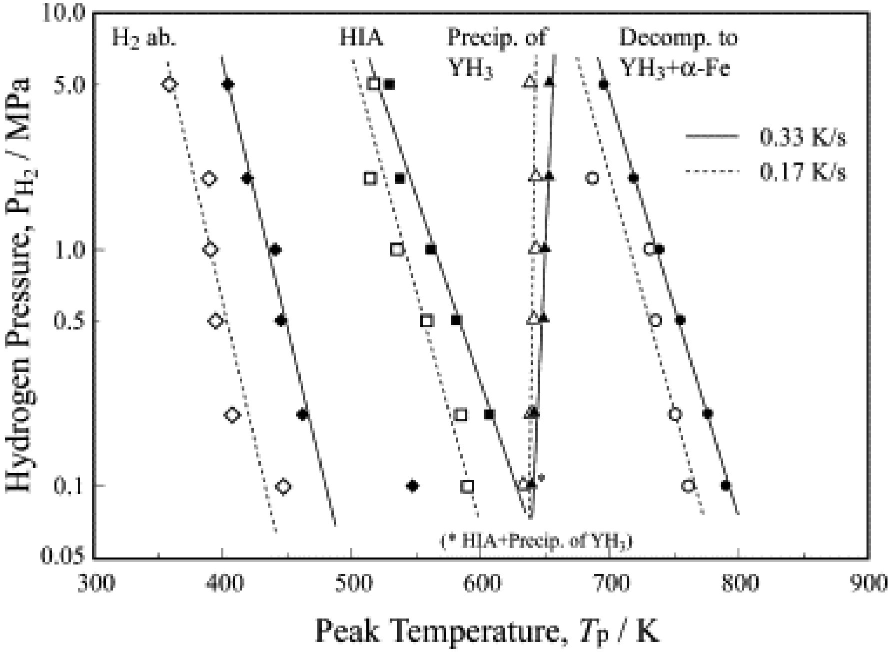

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2. Questions ?

How much hydrogen can be inserted in YFe_2?

In which sites?

What is the influence on H insertion in YFe_2 on:

- Thermodynamic
- Structural
- Magnetic

} Properties ?

3. Synthesis methods

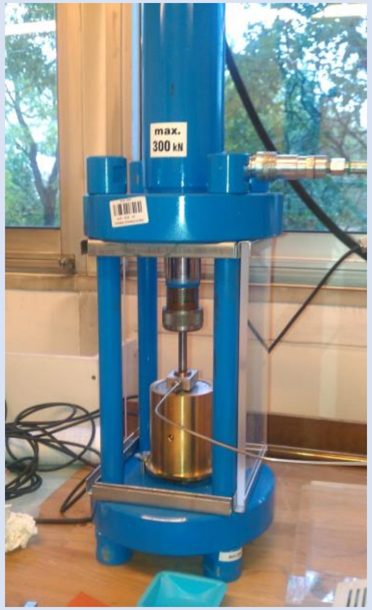
Alloy synthesis

Induction melting Y+Fe

+3 weeks annealing
at 1100 K
In silica tube under vacuum

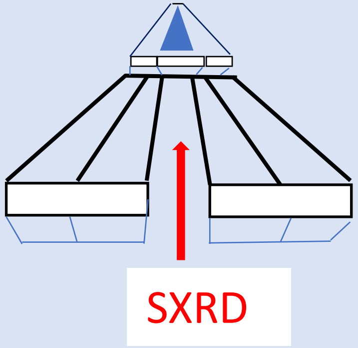
Hydride/deuteride synthesis

Home made
Sievert apparatus
P < 10 MPa, 410 K



High pressure
apparatus
P < 1 GPa, 373 K

S.M. Filipek, Poland



Diamond anvil

H_2 pressure
P < 100 GPa

P. Loubeyre, CEA-DAM

3. Characterization methods

Alloy composition

EPMA

Structure

XRD laboratory

Transition temperatures

DSC, Q100 TA instrument

Large scale facilities (structures)

Neutron center

LLB Orphée Laboratoire Léon Brillouin

Synchrotron center

SOLEIL SYNCHROTRON

Beam line

Cristal

Magnetic measurements

PPMS (QD),
9 T, 2-330 K

MANICS DSM8,
1.7 T, 300-900 K

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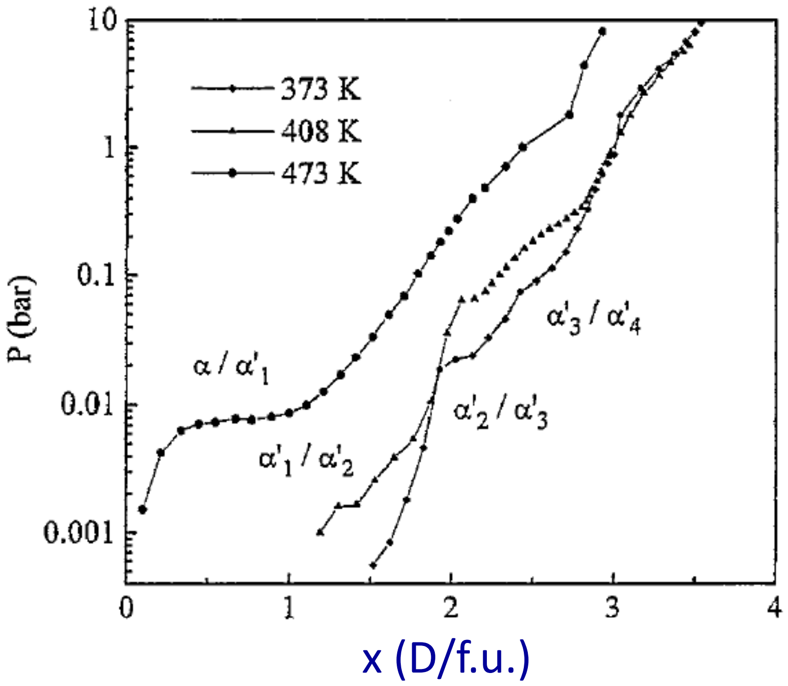
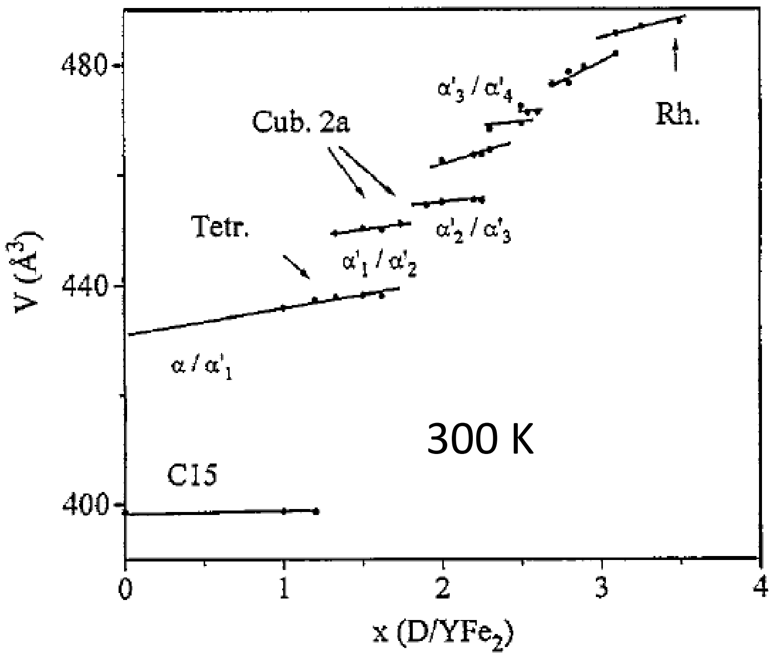
4. Results

Multiplateau isotherm



Several plateaus in PCT curves

Multi-phases

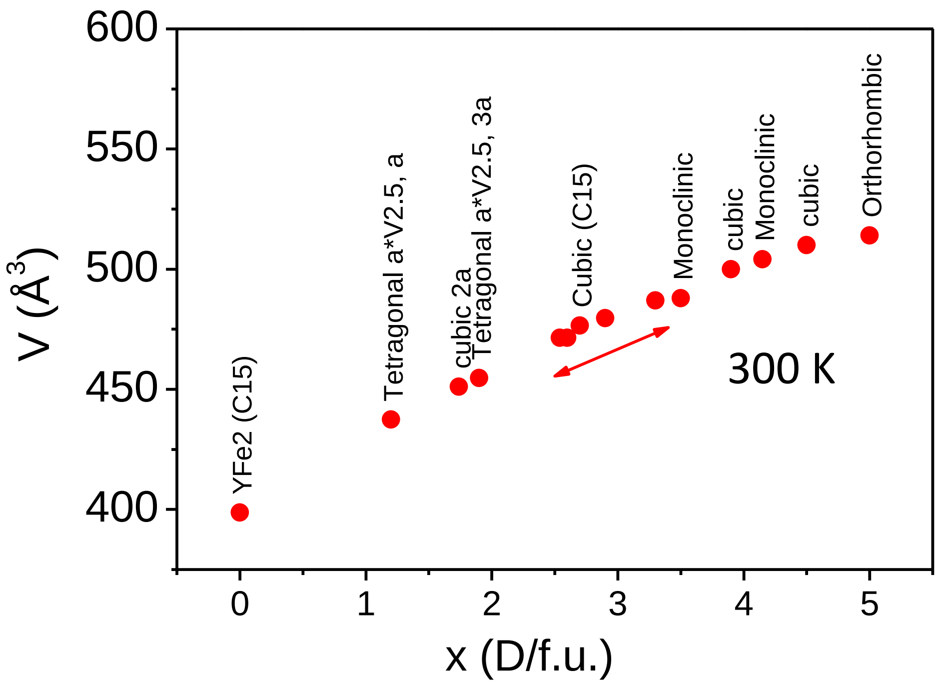


Several hydrides with different structures separated by two phase ranges

V. Paul-Boncour, M. Latroche et al, J. alloys Componds 255, 195-202 (1997).

4.1 Structural properties

SXRD + Neutrons : structure of single phase hydrides



- Cell volume increases versus D
- Lowering of crystal symmetry

Maximum H content?

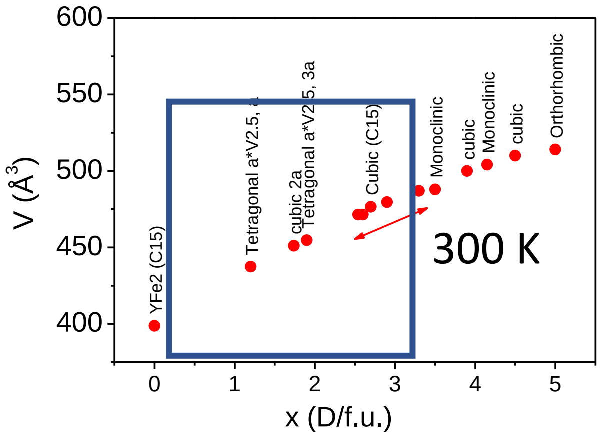
If all sites where filled 17 H/f.u.
But H-H > 2 Å and Fe4 site is empty

The capacity depends on the applied pressure:

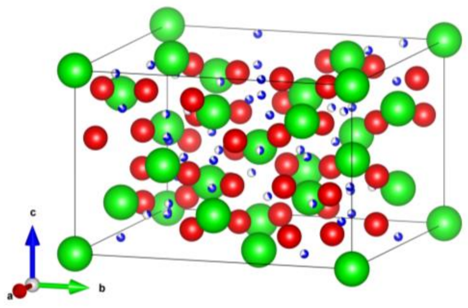
- Up to 1 MPa: **4.2 H/f.u.**
- under 0.8 GPa: **5 H/f.u.**
Remain stable when releasing pressure
- Under 35 GPa : **7-8 H/f.u.**

V. Paul-Boncour, L. Guénée, et al, J. Solid State Chem. 142, 120-129 (1999).

4.1 Structural properties: distortion and surstructures (*x* < 3)



Only A2B2 sites
Alternance of Tetragonal and cubic structures

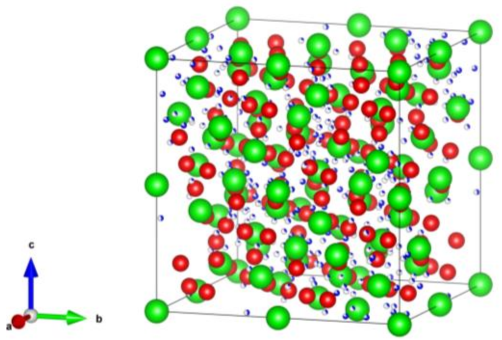


$YFe_2D_{1.3}$ tetragonal

D in 7 A2B2 sites

$a' = a*\sqrt{5}/2 = 11.985$ Å

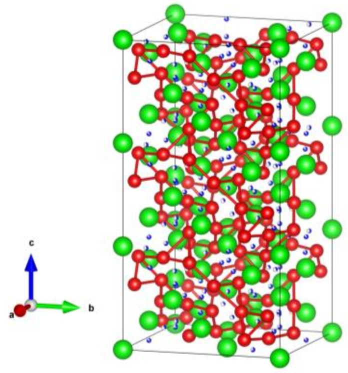
$c = a = 7.622$ Å



$YFe_2D_{1.75}$ cubic 2a

D in 9 A2B2 sites

$a' = 2a = 15.336$ Å

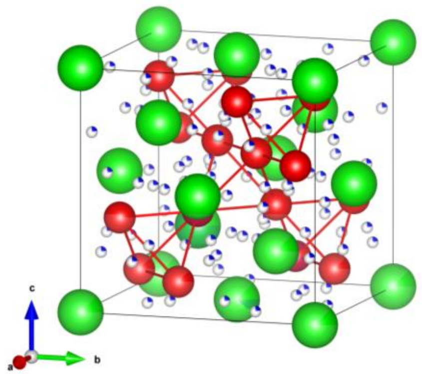


$YFe_2D_{1.9}$ tetragonal

D in 21 A2B2 sites

$a' = a*\sqrt{5}/2 = 12.15$ Å

$c' = 3a = 23.079$ Å



$YFe_2D_{2.6}$ cubic *a*

D in 1 A2B2 sites

$a' = 7.785$ Å

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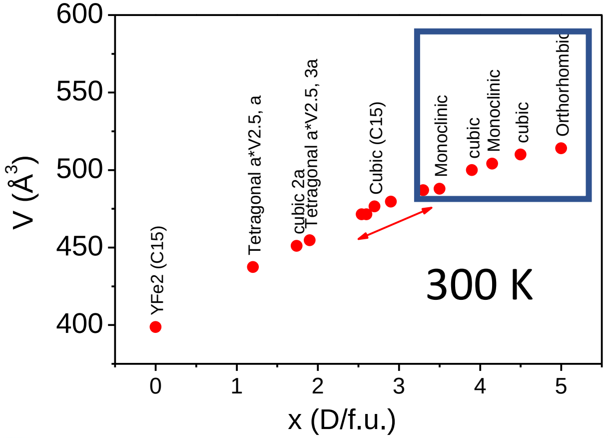
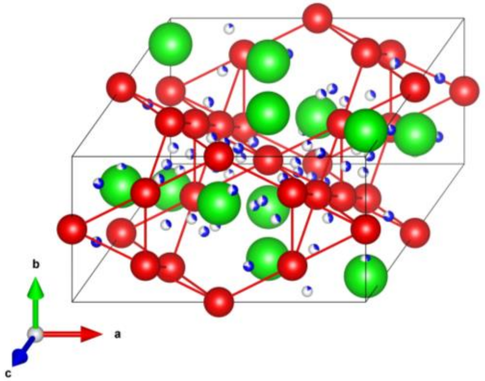
4.1 Structural properties: distortion and surstructures (*x* > 3)



Y2Fe2 + YFe3 sites
$d_{D-D} \geq 2$ Å

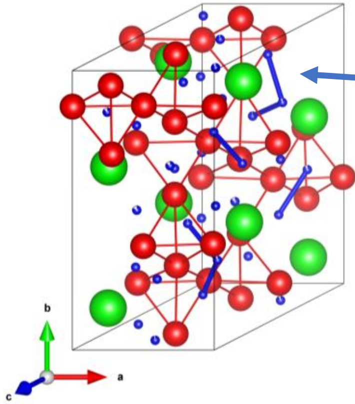
$2 < d_{D-D} < 2.1$ Å



$YFe_2D_{3.5}$ Monoclinic (*P1c1*)
D in 9 Y2Fe2 + 2 YFe3 sites

a = 15.754(2) Å, *b* = 5.633(1) Å
c = 9.476(1) Å, *β* = 144.55°

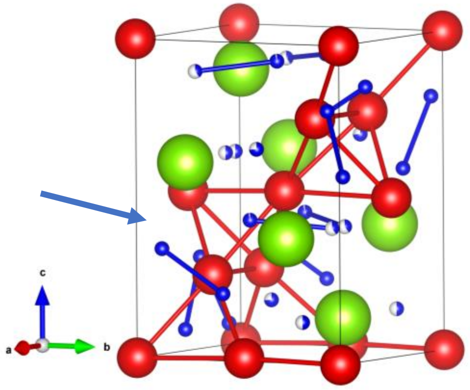
G. Wiesinger, V. Paul-Boncour, et al. J. Phys.: Condens. Matter 17, 898 **(2005).**



$YFe_2D_{4.2}$ Monoclinic (*P1c1*)
D in 15 Y2Fe2 + 3 YFe3 sites

a = 5.50663(4) Å, *b* = 11.4823(1) Å
c = 9.42919(6) Å, *β* = 122.3314(5)°

J. Ropka, et al., *J. Solid State Chem*. 182, 1907 (**2009**).



YFe_2D_5 Orthorhombic (*Pmn*2_1)
D in 6 Y2Fe2 + 2 YFe3 sites

a = 5.437 Å, b = 5.850 Å, c = 8.083 Å

V. Paul-Boncour, S. M. Filipek, et al. J. Phys.: Condens. Matter 15, 4349-4359 **(2003).**

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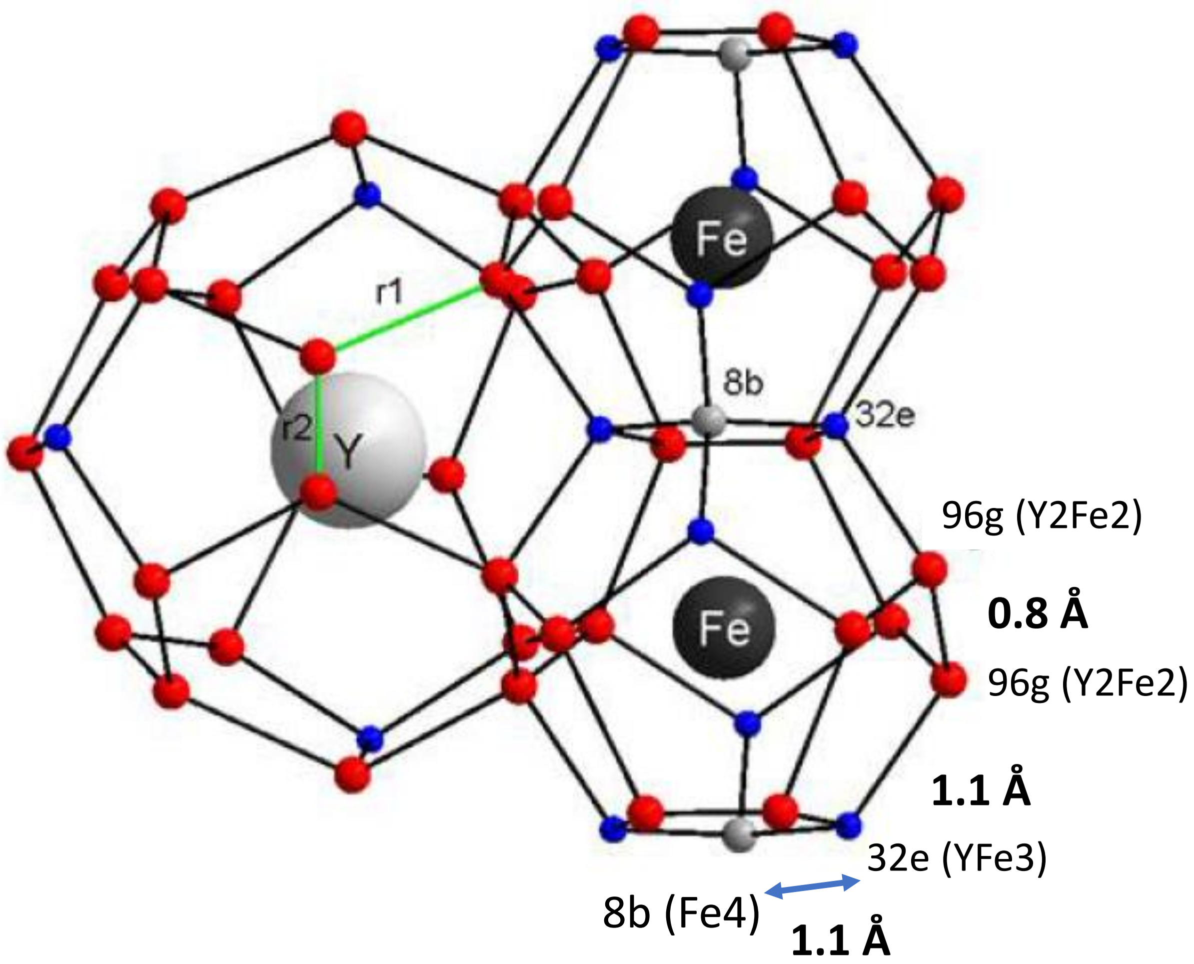
4. Filling of H sites



Smallest distances between 2 96 g sites= 0.8 Å

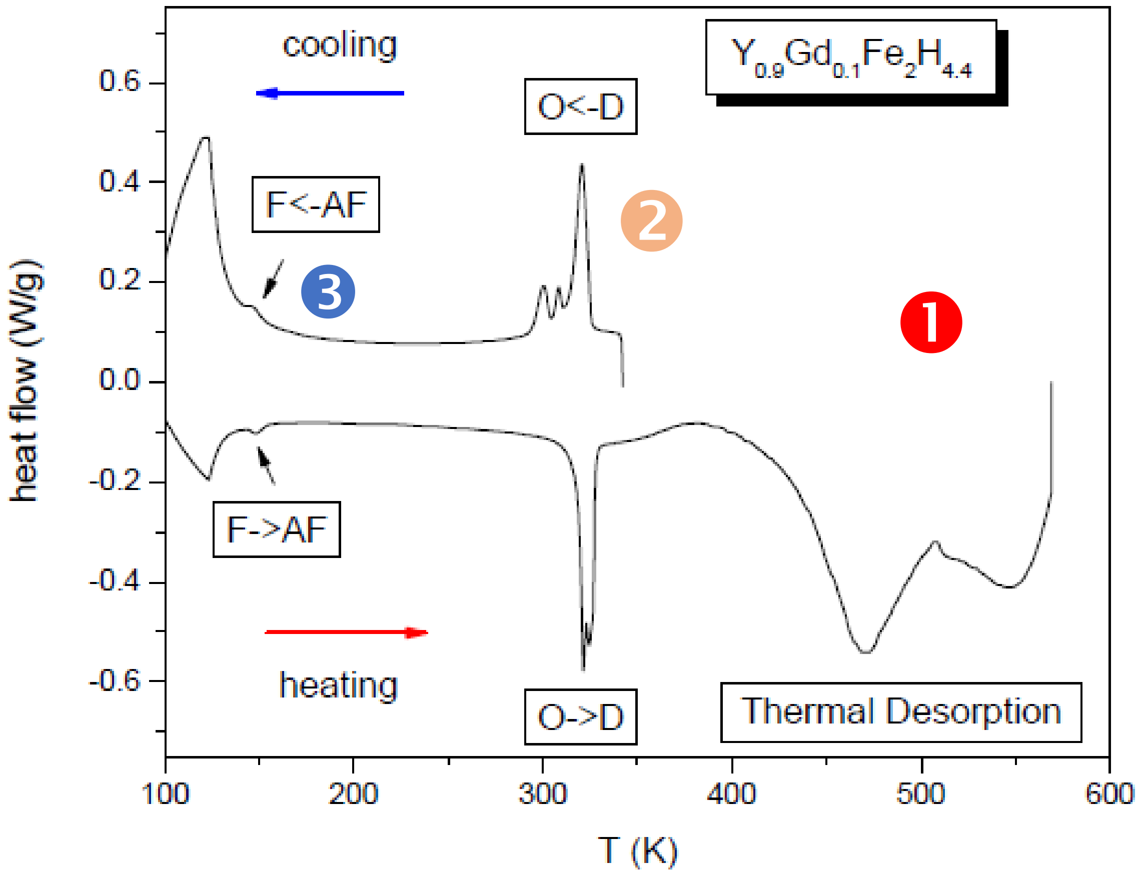
Switendick criterium:
Minimum H-H distances between H atoms > 2 Å
=> Several sites are not occupied

Size of the interstitial sites r > 0.4 Å

⇒ **Fe4 site is too small to accept H atoms**
⇒ **only Y2Fe2 and YFe3 sites are occupied**

4.2 Phase transitions

DSC



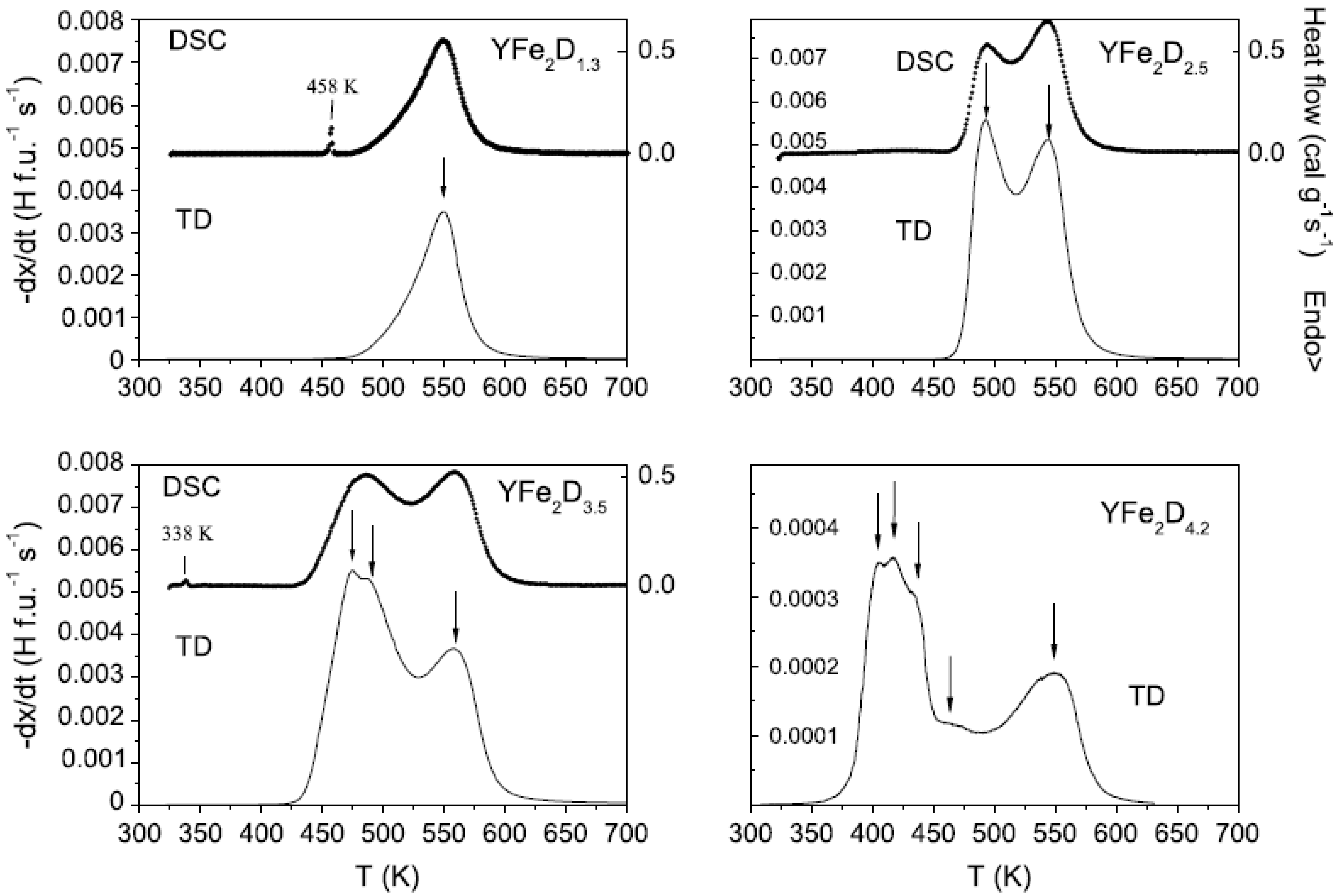
3 Different types of transition

❶ Thermal Desorption

➁ Order-Disorder transition

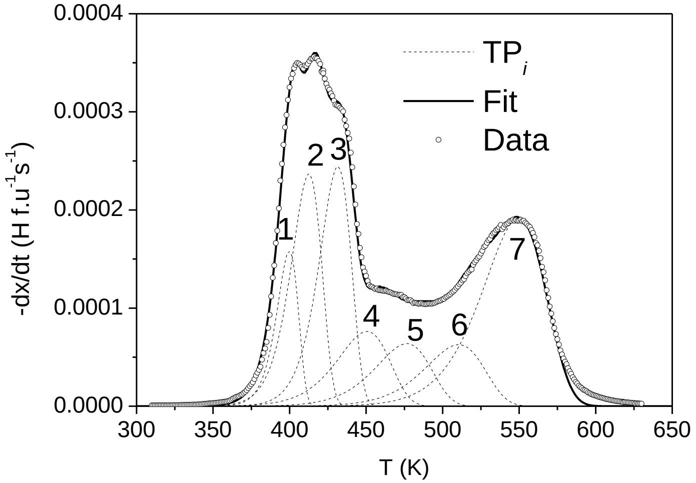
❸ Magnetic transitions

4.2.1 Thermal desorption

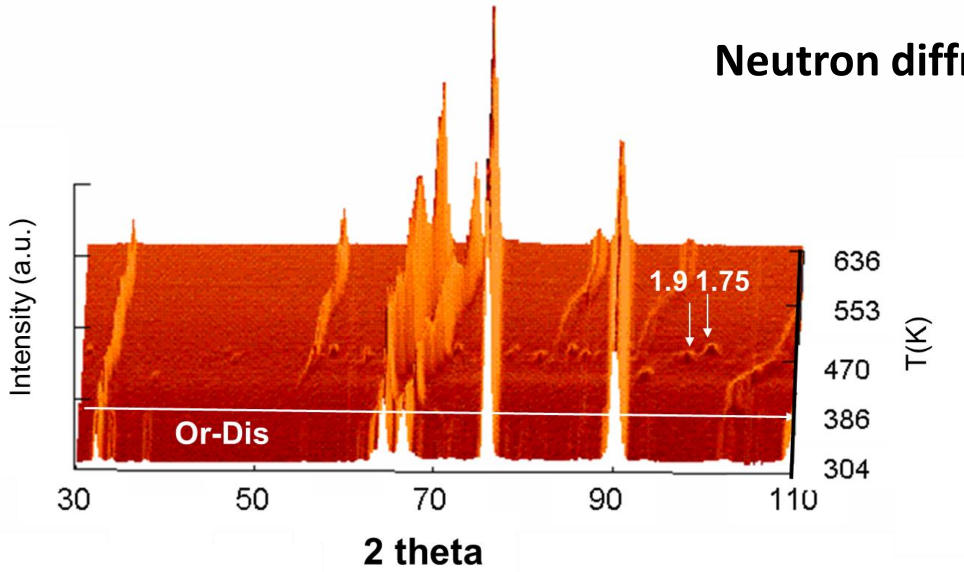


The number of peaks increases with D content: Each phase desorb at a different temperature

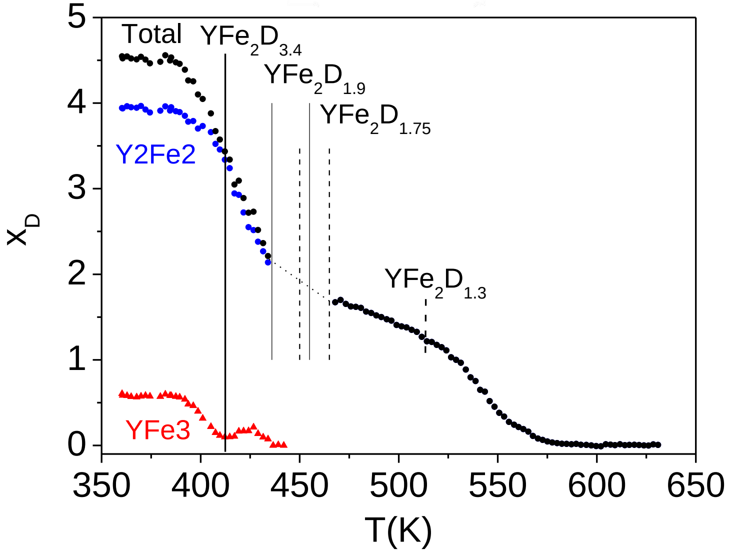
4.2.1 Thermal desorption $YFe_2D_{4.2}$



Neutron diffraction at D1B



Themal desoption (TPD):
Each peak corresponds to a phase desorption



The different phases
are observed upon desorption
Confirm:
Multipeak = multiphase

T. Leblond, V. Paul-Boncour, F. Cuevas, O. Isnard, and J. F. Fernandez, Int. J. Hydr. Energ. **34, 2278-2287 (2009).**

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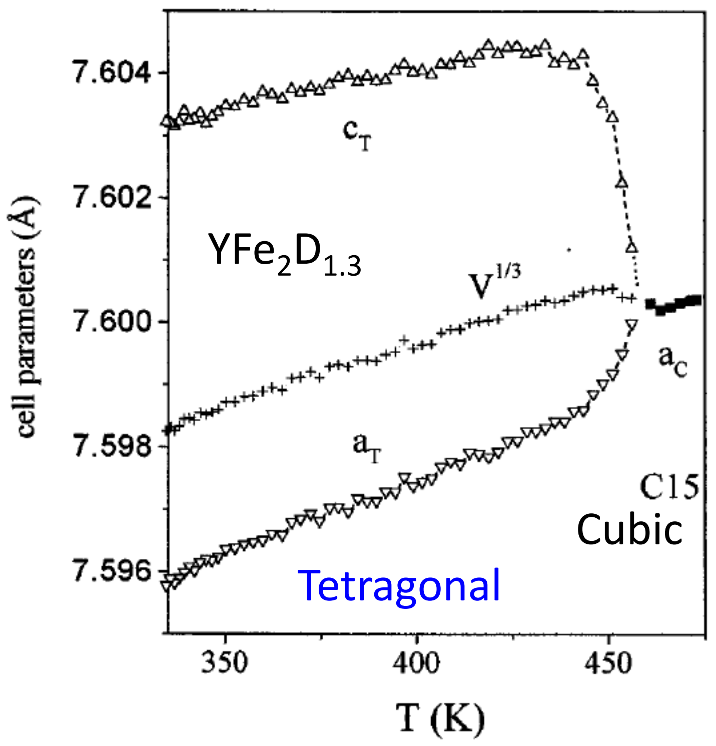
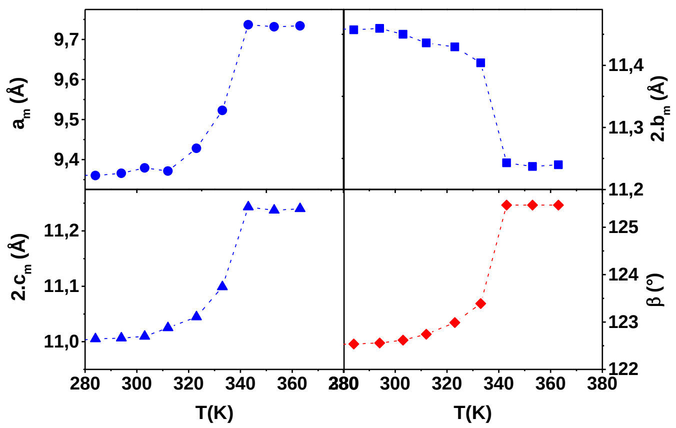
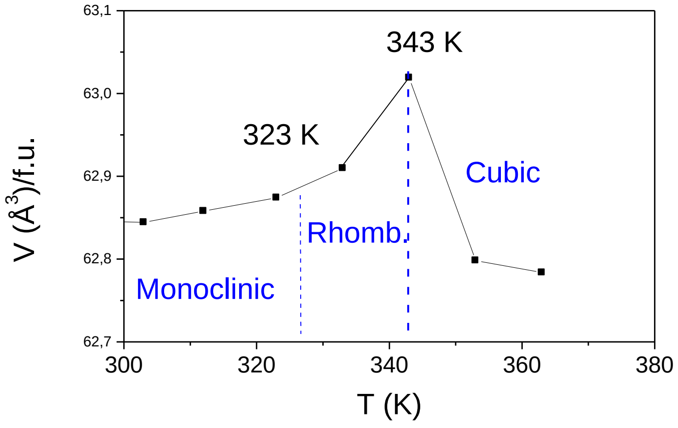
4.2.2 Order-disorder transitions



$YFe_2D_{1.3}$: At 450 K Reversible tetragonal–cubic transition

V. Paul-Boncour, L. Guénée, et al, J. Solid State Chem. **142,** 120-129 (1999).





$YFe_2D_{4.2}$: 2 steps

Transition from monoclinic to cubic via a rhombohedral structure

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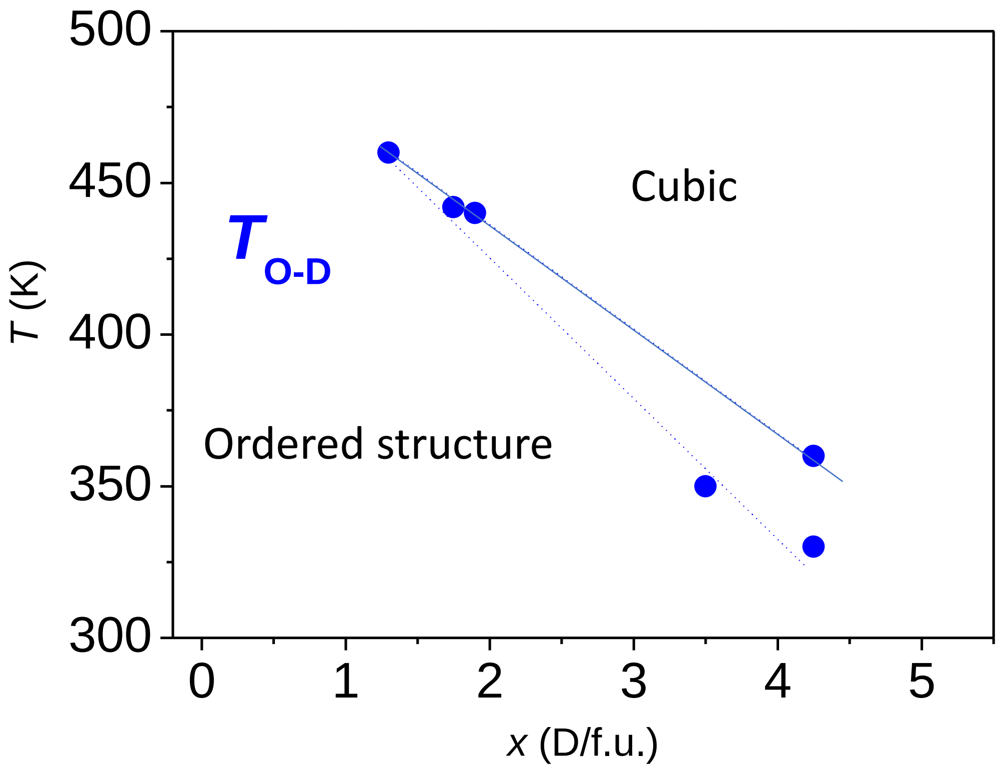
4.2.2 order-disorder transitions



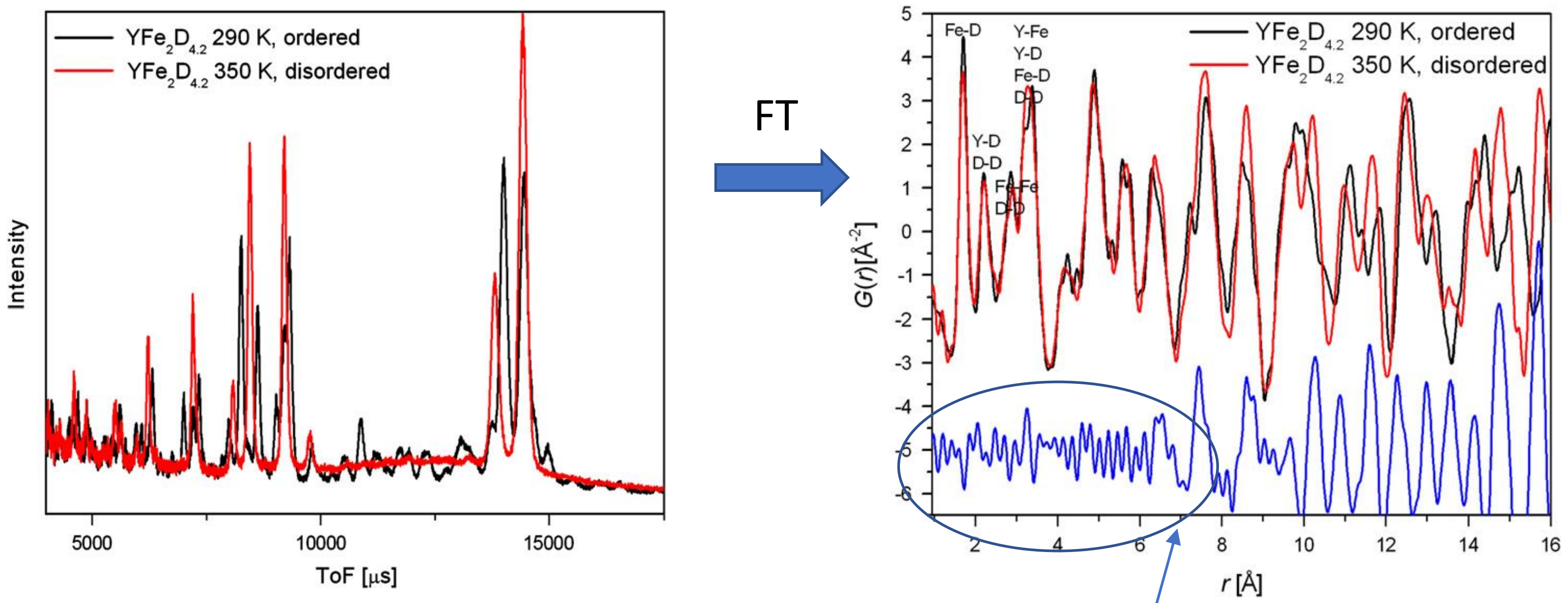
Transitions from
ordered to cubic disordered phases

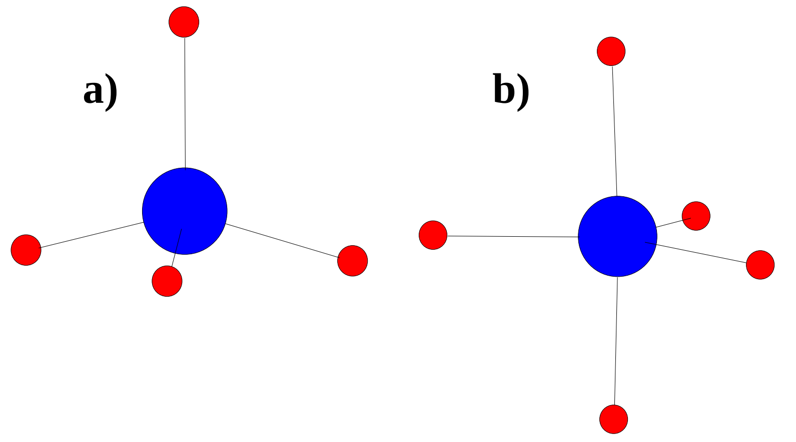
- T_{O-D} decreases versus D content
- x = 4.2 : the transition occurs in 2 steps
- x= 5 : remains orthorhombic: No O-D transition

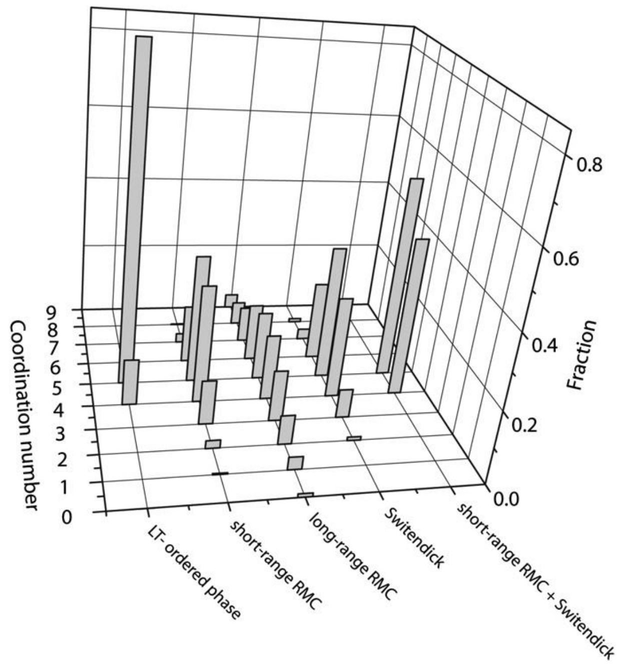
V. Paul-Boncour, L. Guénée, et al, J. Solid State Chem. **142,** 120-129 (1999).

4.2.2 Order-disorder transitions

Partial distribution function = PDF (Local order)







- ➢ The local order is preserved up to 6 Å

And diverge for larger distances (Difference)

- ➢ **$d_{D\text{-}D}$ ≥ 2 Å (switendick)**
- ➢ **FeD_4 and FeD_5 polyedrea (RMC)**: not pure random distribution

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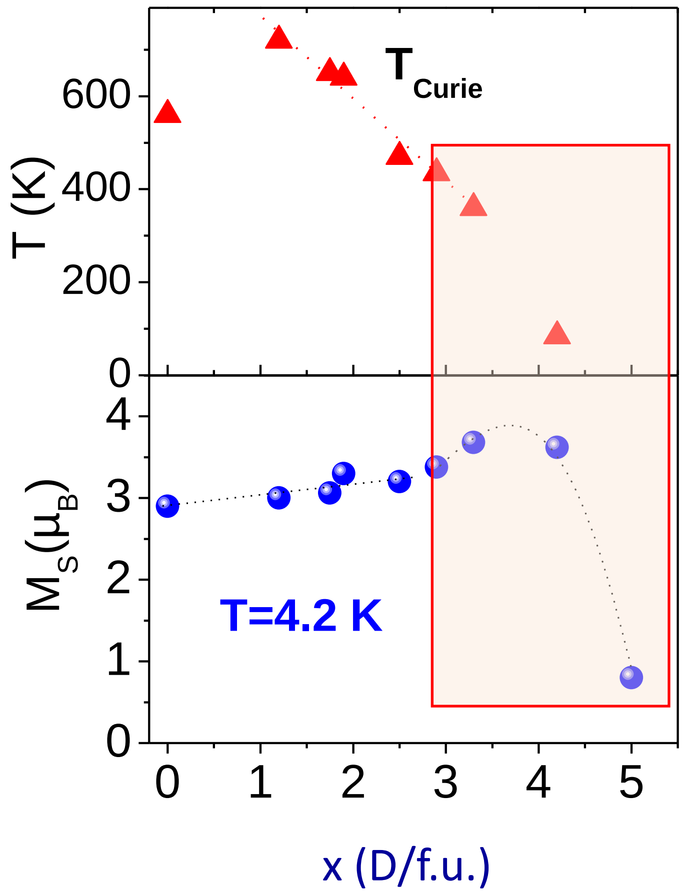
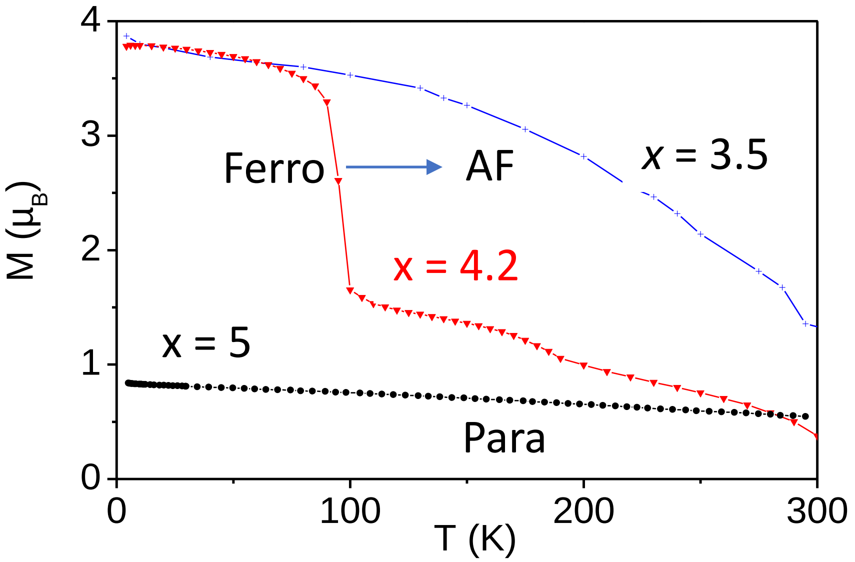
J. Ropka, R. Cerný, and V. Paul-Boncour,
J. Solid State Chem. **184, 2516-2524 (2011).**

4.2.3 Magnetic transitions in YFe_2D_x compounds

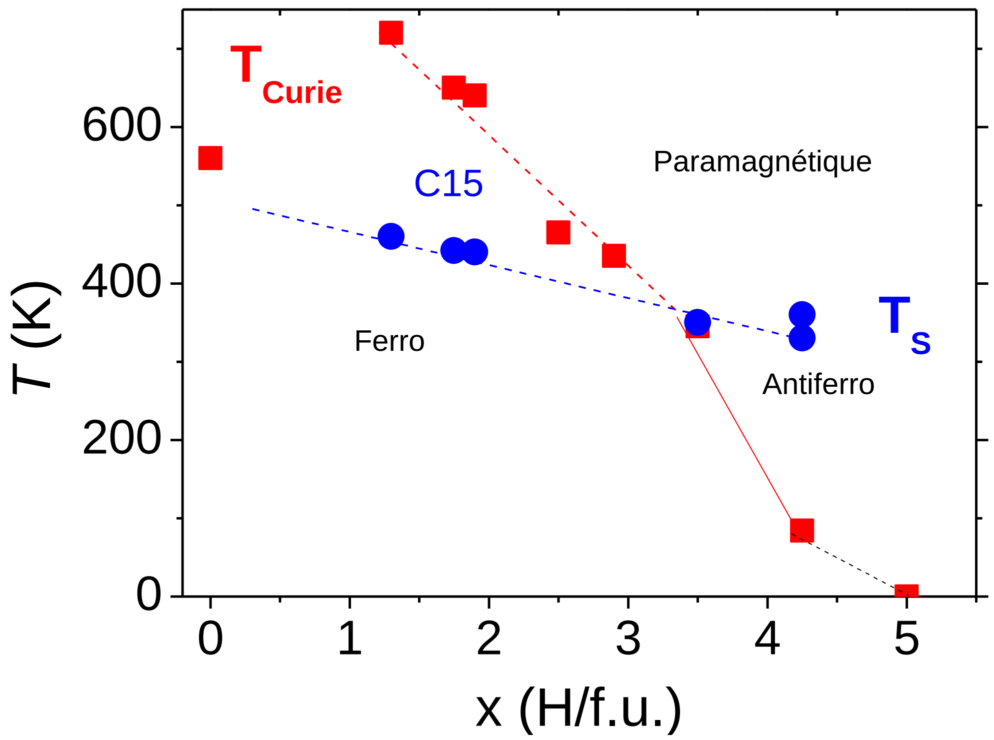




Large changes of magnetic behaviour above *x*= 3.5 D/f.u.:
x < 3.5: Ferromagnetic
x = 4.2: Ferro-Antiferromagnetic
x = 5: Paramagnetic

- Competition between cell volume increase and Fe-H bonding

4.2.3 Magnetic transitions in YFe_2D_x compounds

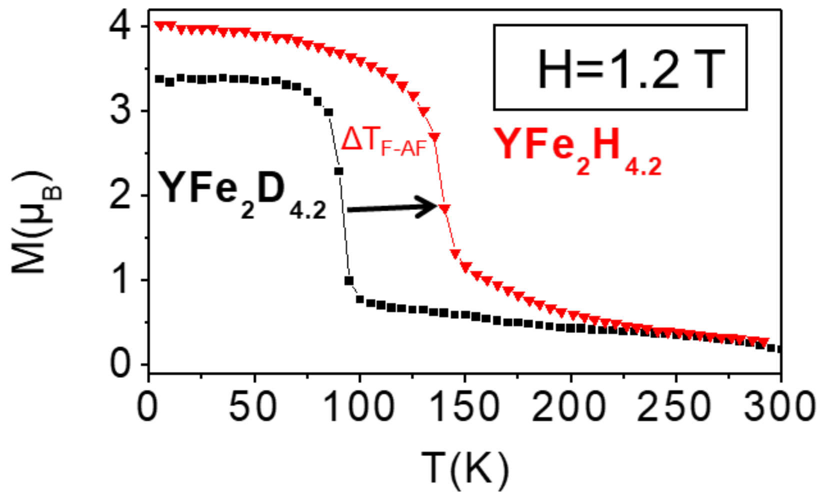


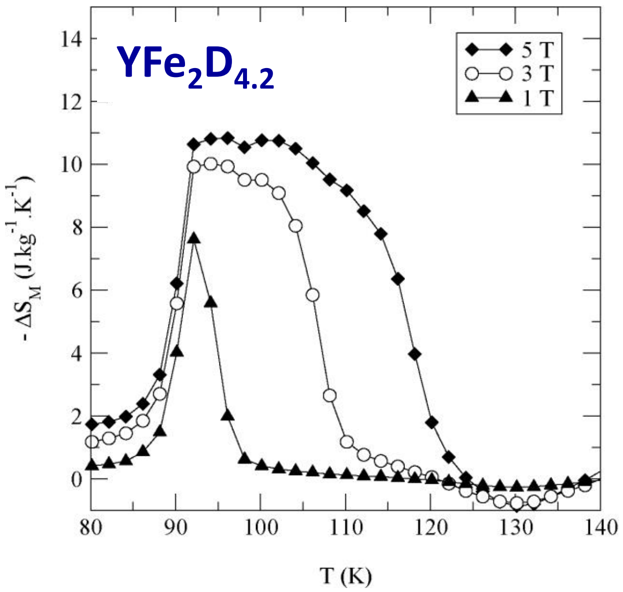
Magnetic and O-D transitions are not correlated

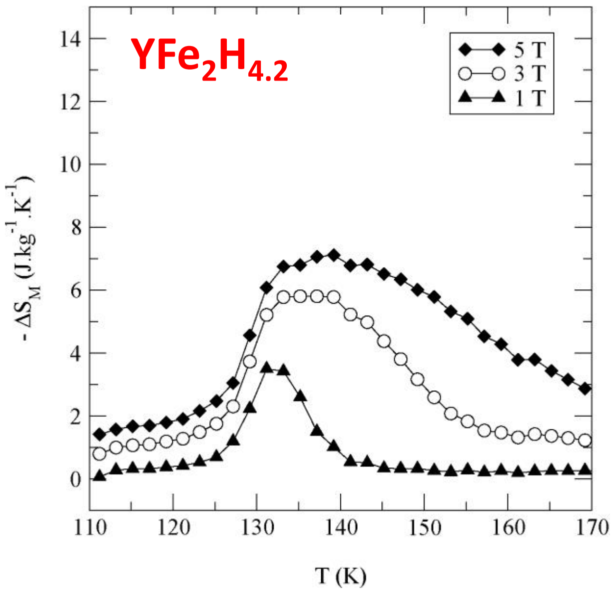
Larger decrease for TMag versus x

They cross at *x*=3.5

4.2.3 Isotope and magnetocaloric effect in $YFe_2(H,D)_{4.2}$







Giant isotope effect:
First order ferro-Antiferro transition:
T_{F-AF} increases from 84 to 131 K
ΔT = 47 K or 50 % increase of T_{F-AF}

Magnetocaloric effect:
Large effect comparable to Gd

ΔS (0-5 T) = -11 and -7 J/K.kg

Magnetic refrigeration:

=> Increases T_{F-AF} near room temperature

V. Paul-Boncour and T. Mazet, J. Appl. Phys. ***105,*** *013914 (2009)*

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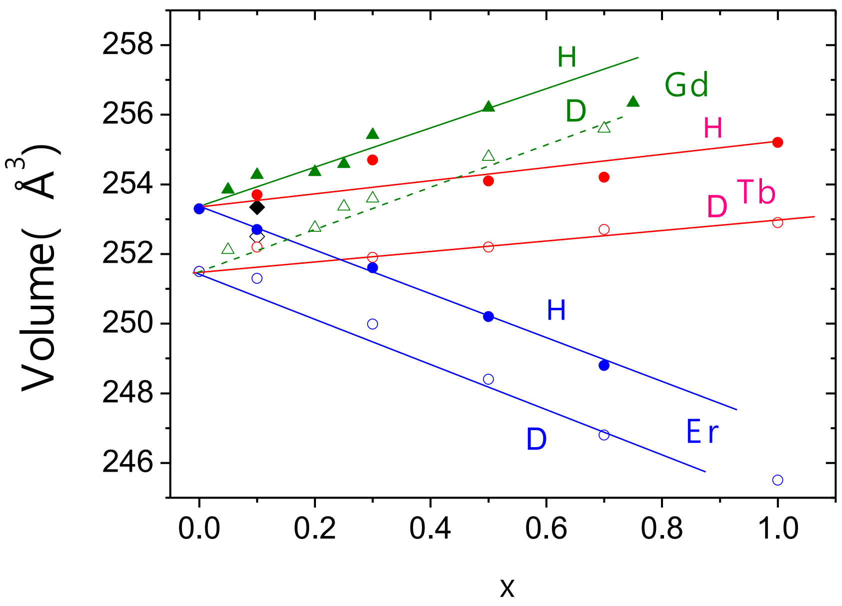
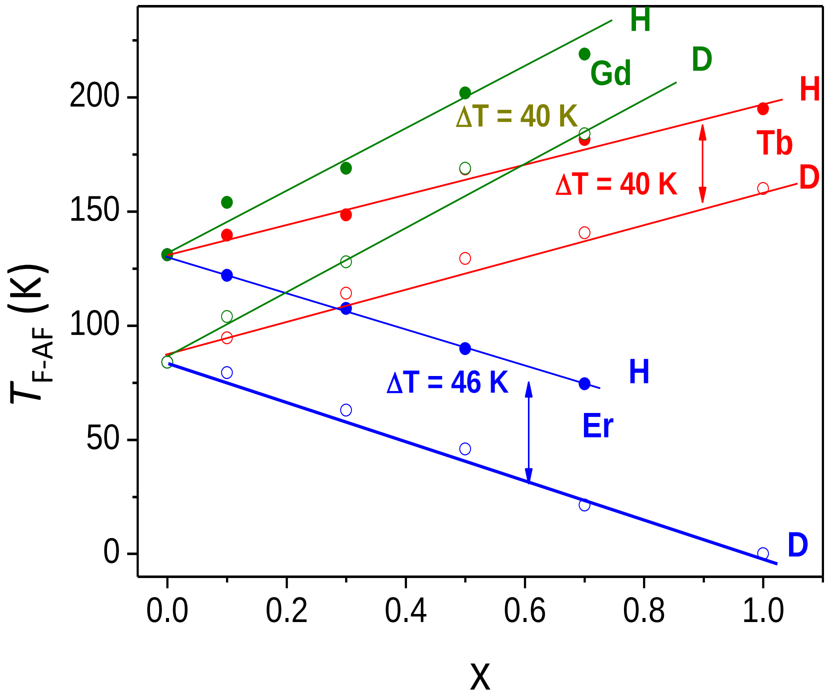
4.2.3 Influence of *R* for Y substitution in $Y_{1-x}R_xFe_2D_x$ compounds

$Y_{1-x}R_xFe_2(H,D)_{4.2}$





To increase $T_{F\text{-}AF}$: change the volume by *R for Y* substitution

***T* hydride > *T* deuteride (ΔT = 40 to 46 K)**

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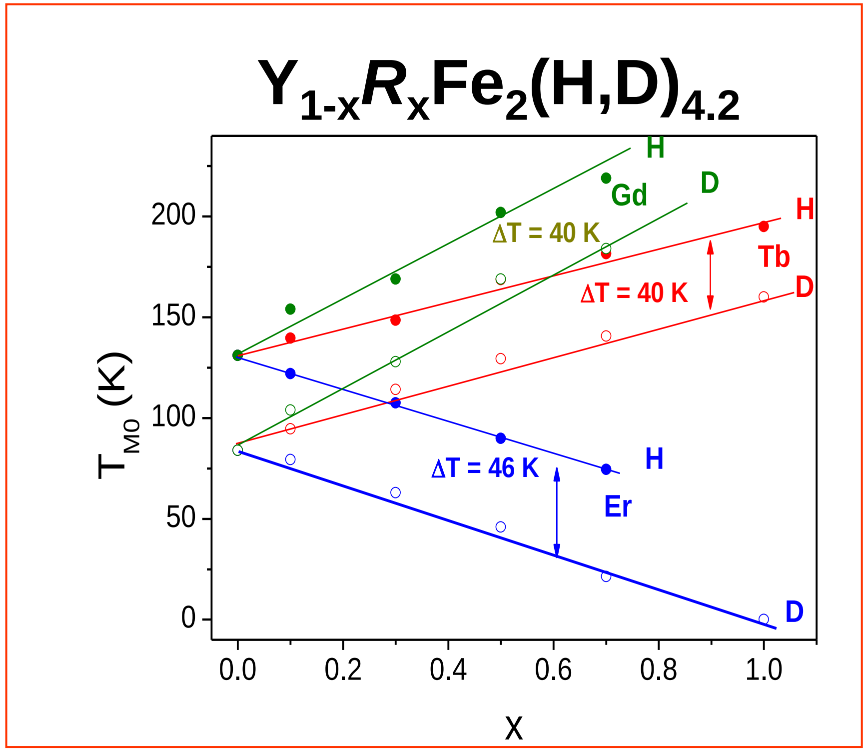
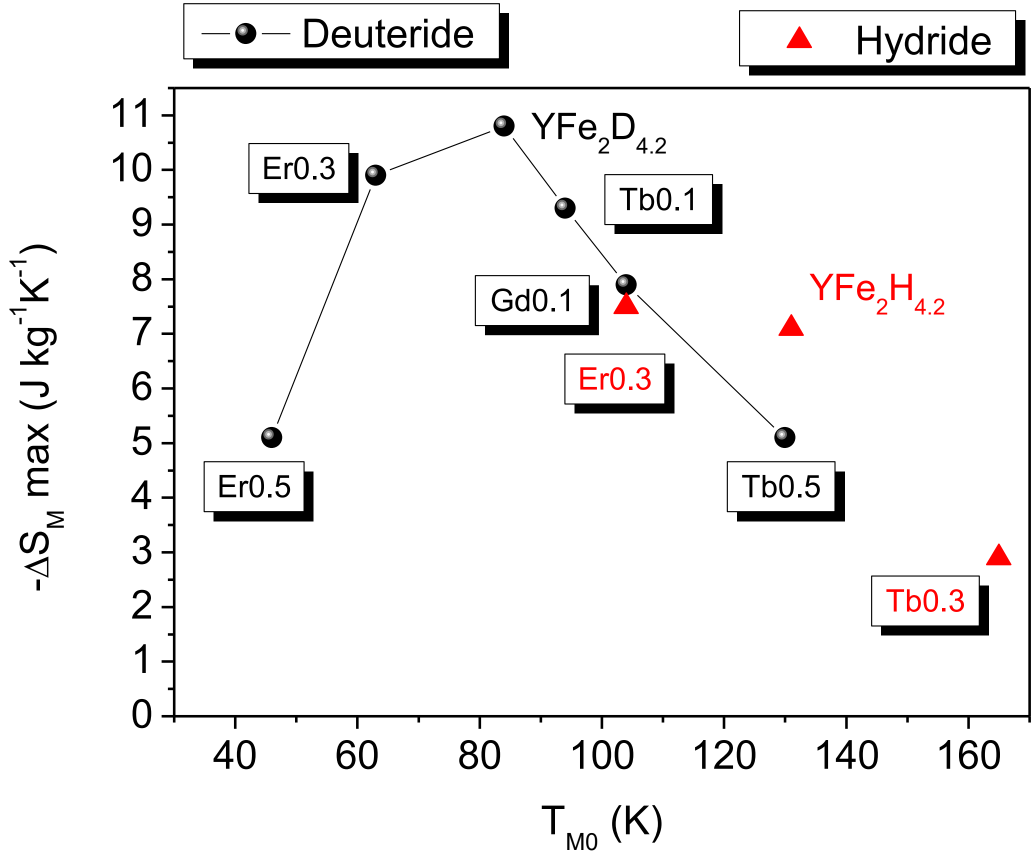
4.2.3 Influence of *R* for Y substitution in $Y_{1-x}R_xFe_2D_x$ compounds





T_{max} =230 K

Substitution decrease ΔS_M

Evolution of ΔS_M max (ΔH=5T)

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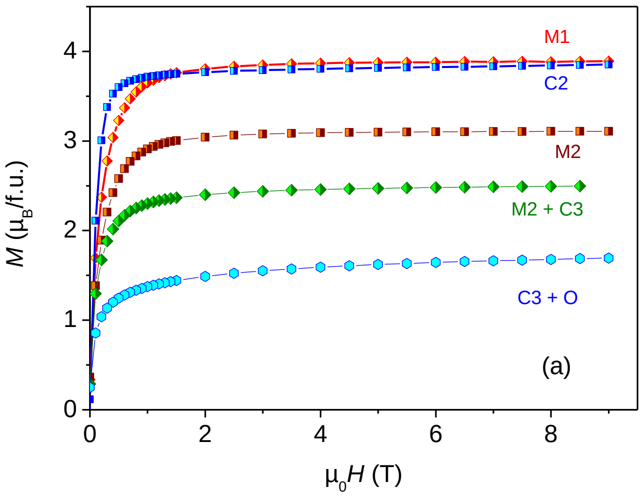
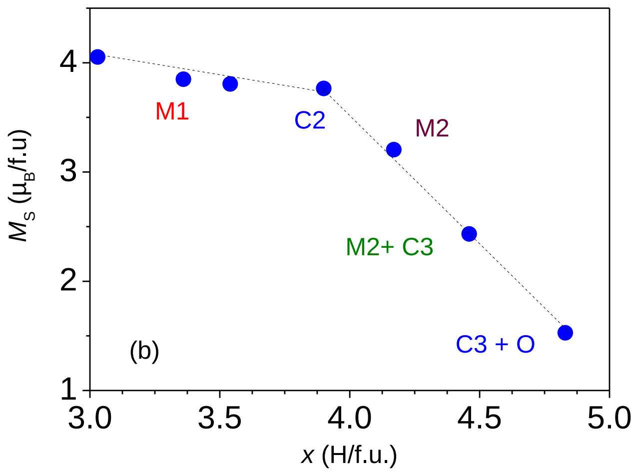
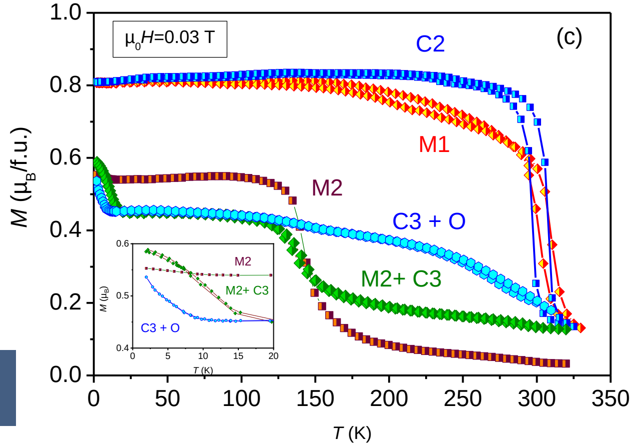
4.2.3 Magnetic properties of $Y_{0.9}Gd_{0.1}Fe_2H_x$

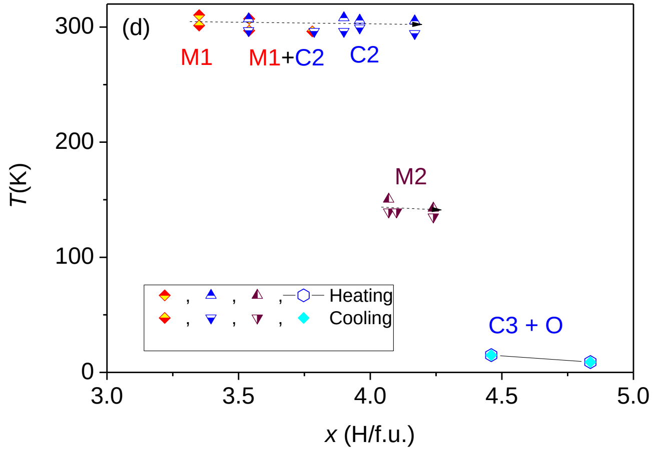




Saturation magnetization at 5 K versus H content

M_S decreases versus H content:
Change of dM/dx slope above 4 H/f.u.





Magnetic ordering temperatures versus H content

T_c decreases by step versus H content:
M1 and C2: T_C = 300 K
M2: T_{F-AF} =150 K

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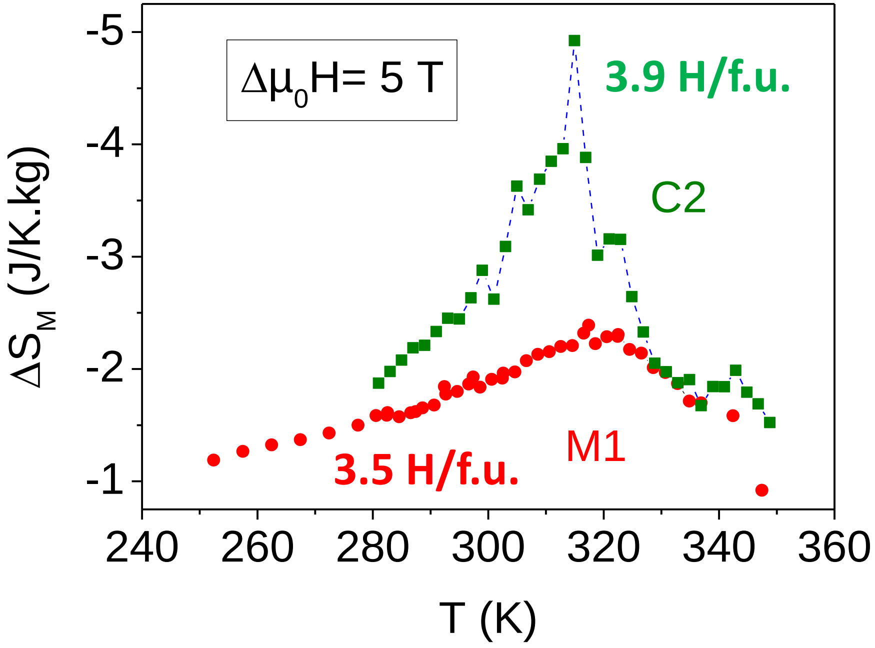
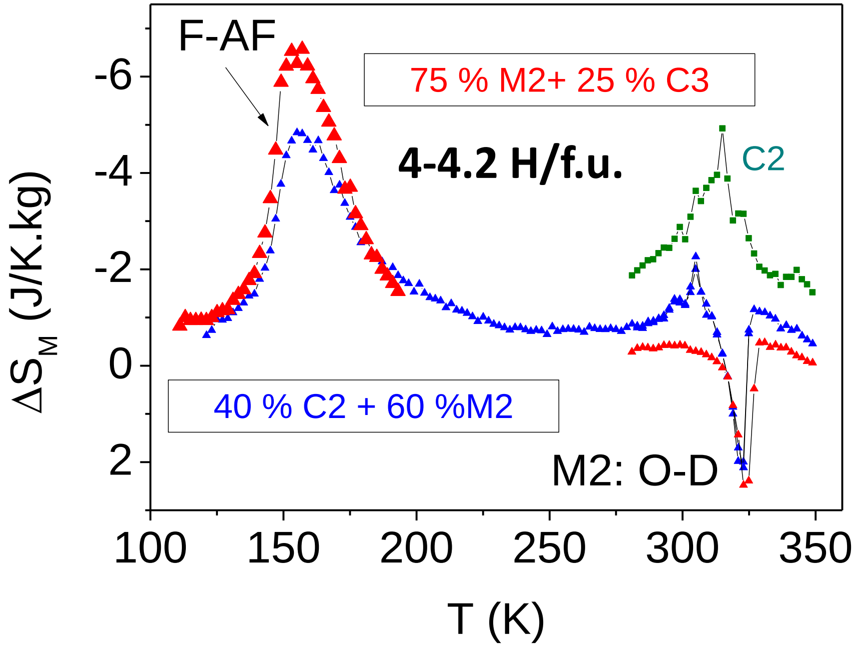
4.2.3 Magnetic entropy variations in $Y_{0.9}Gd_{0.1}Fe_2(H,D)_x$





ΔS_M peaks due to magnetocaloric effect associated to magnetic transitions:

At 310K: ΔS_M (M1) < ΔS_M (C2) 2nd order/ 1st order
At 150 K: ΔS_M (M2) due to F-AF transition
At 325 K : Inverse MCE effect at 325 K due to the structural O-D transition

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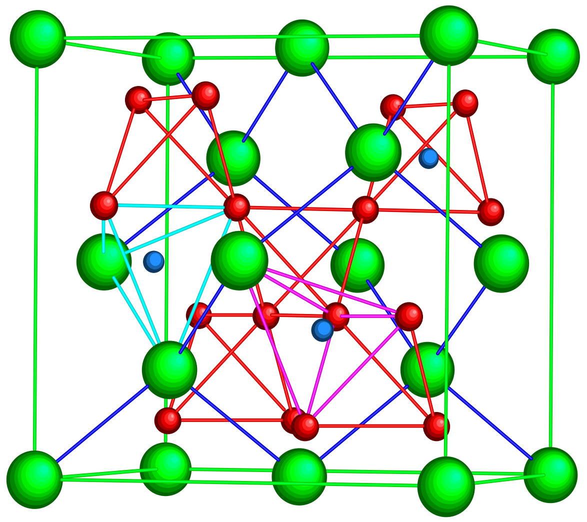
5. Conclusions



$$YFe_2 + H_2 =$$

5. Conclusions: YFe_2H_x : a true Swiss knife!

Multi-states (cristalline, amorphous, nano)

Multi-plateaux isotherm

Multi-phases (> 10)

Multi-structures (> 7)

Multi-transitions

Multi-peak desorption

Multi-Magnetic entropy variation

Multi magnetic structures