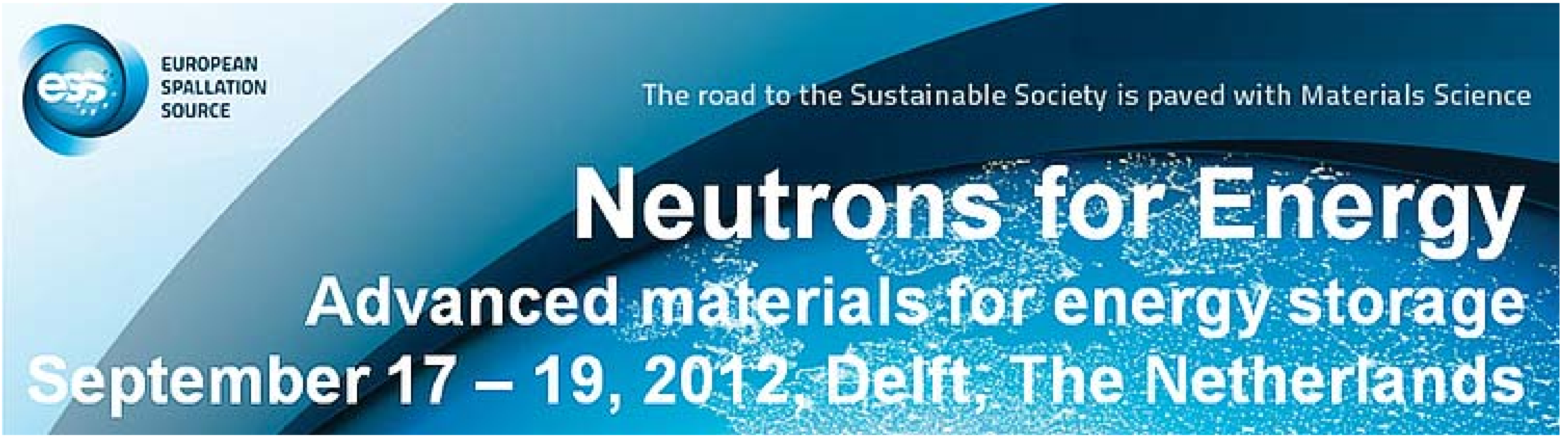


In situ studies of hydrogen desorption from metallic hydrides by neutron diffraction

M. Latroche,
V. Paul-Boncour, F. Cuevas

Institut de Chimie et des Matériaux de Paris Est
ICMPE - UMR 7182 - CNRS
Thiais, France

Outline

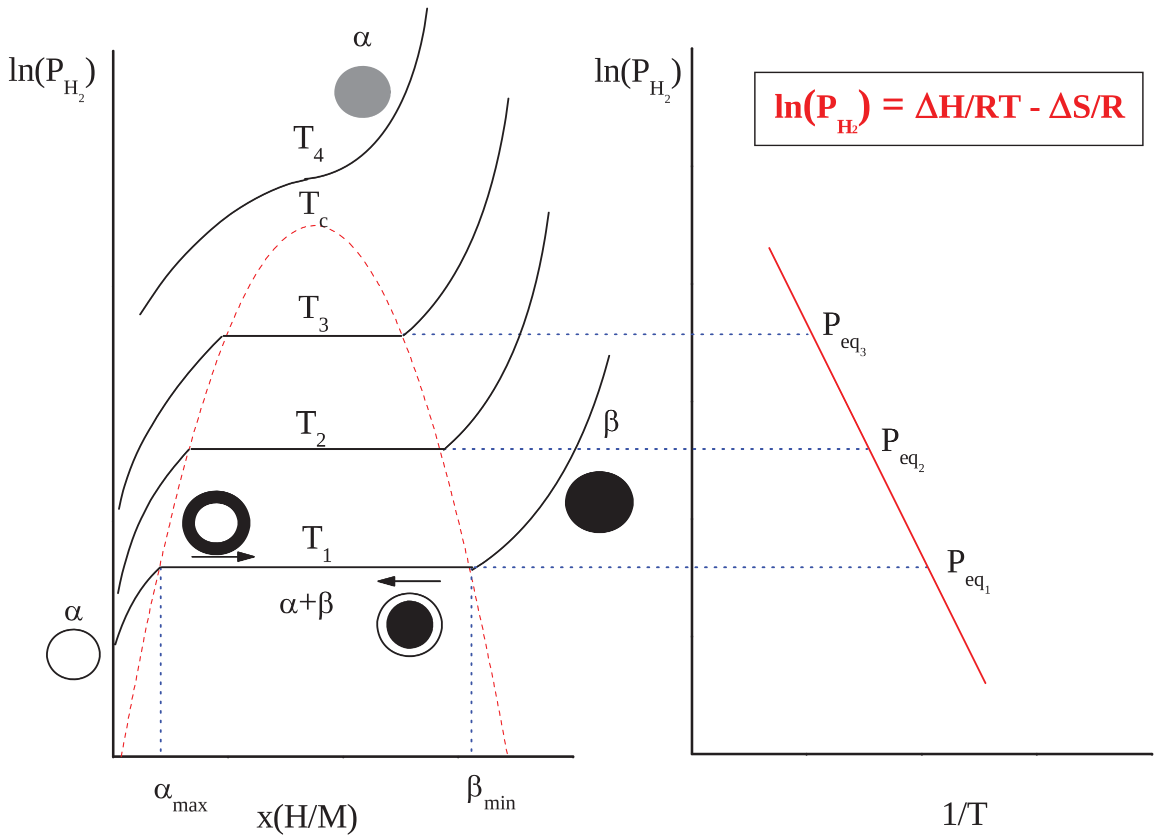
- ✓ Short introduction to metallic hydrides (MH)
- ✓ Neutron diffraction for MH investigation
  - o Steady state structural analysis
  - o Out of equilibrium study by coupled TDS/ND
- ✓ The peculiar cases of $TiNiH_x$ and YFe_2H_x
- ✓ Conclusions

Short introduction to metallic hydrides

Metallic hydride for solid gas storage

- Solid gas route (P_{eq} , $C(x)$, T)

$$M + {}^{x}/_{2} H_2 \leftrightarrow MH_x$$



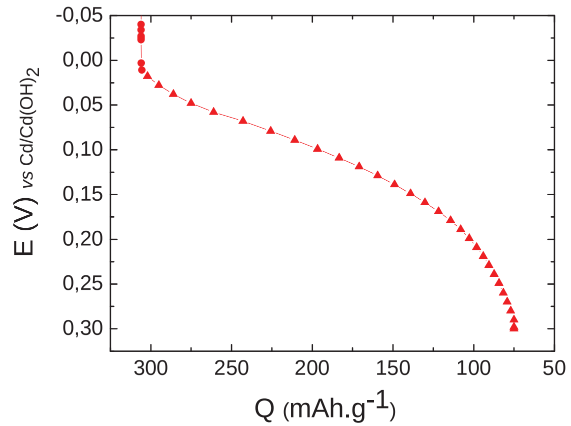
Short introduction to metallic hydrides

Metallic hydride for electrochemical storage

- Electrochemical route (E_{eq} ,Q(x), T)

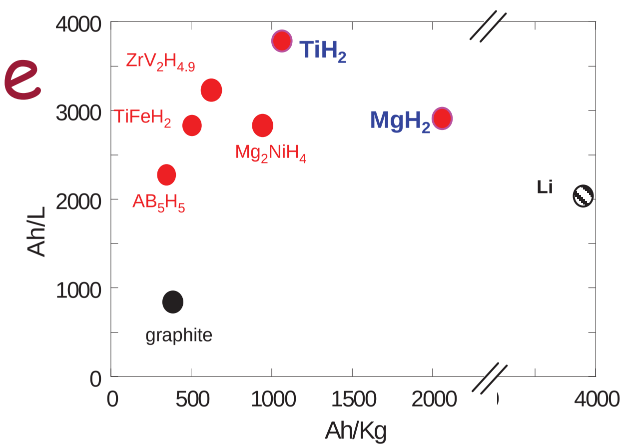
$$M + xH_2O + x\,e^- \leftrightarrow MH_x + xOH^-$$

$$E^{eq}_{MH_x} = -\frac{RT}{nF}\ln P_{H_2} - 0.926 \quad [\text{in V vs Hg/HgO}]$$



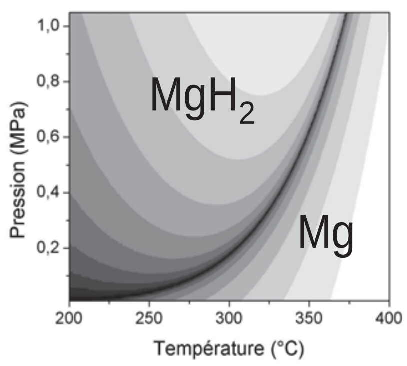
- Non aqueous electrochemical route

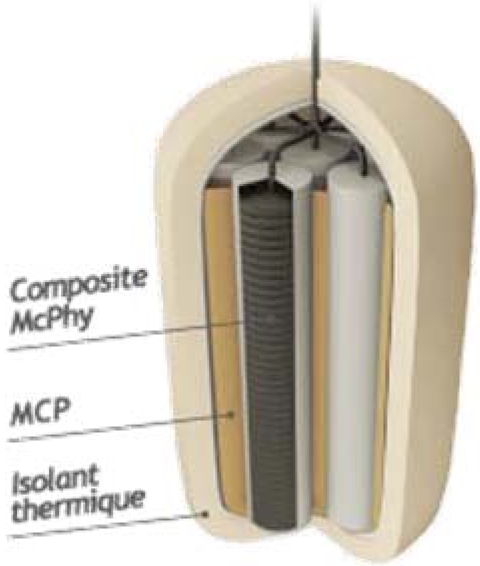
$$MH_x + x\,Li^+ + x\,e^- \leftrightarrow M + x\,LiH$$



Y. Oumellal, W. Zaïdi, J-P Bonnet,F. Cuevas, M. Latroche, J. Zhang, J-L Bobet, A. Rougier and L. Aymard. IJHE, 37 (2012) 7831-7835

Some successful applications of hydrides…





HEV Toyota Prius

NiMH traction batteries for Nice trams

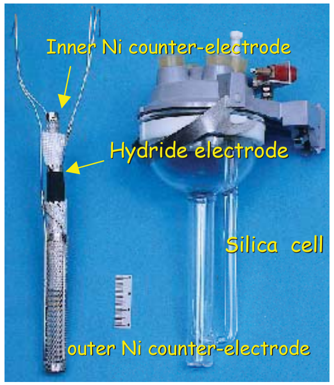
Other applications - emergency light units, telecommunications, cordless vacuum…

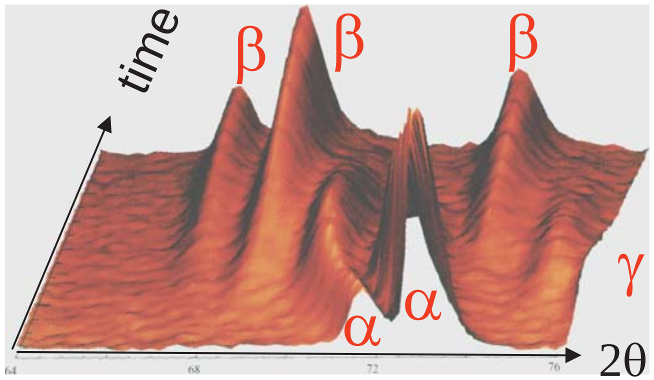
Neutron diffraction for MH investigation

✓ Crystal structure determination

- Quantification and location of H(D) content
- Evidence of phase transitions as a function of H(D) content

Example: In-situ ND of $LaNi_5$-type electrodes





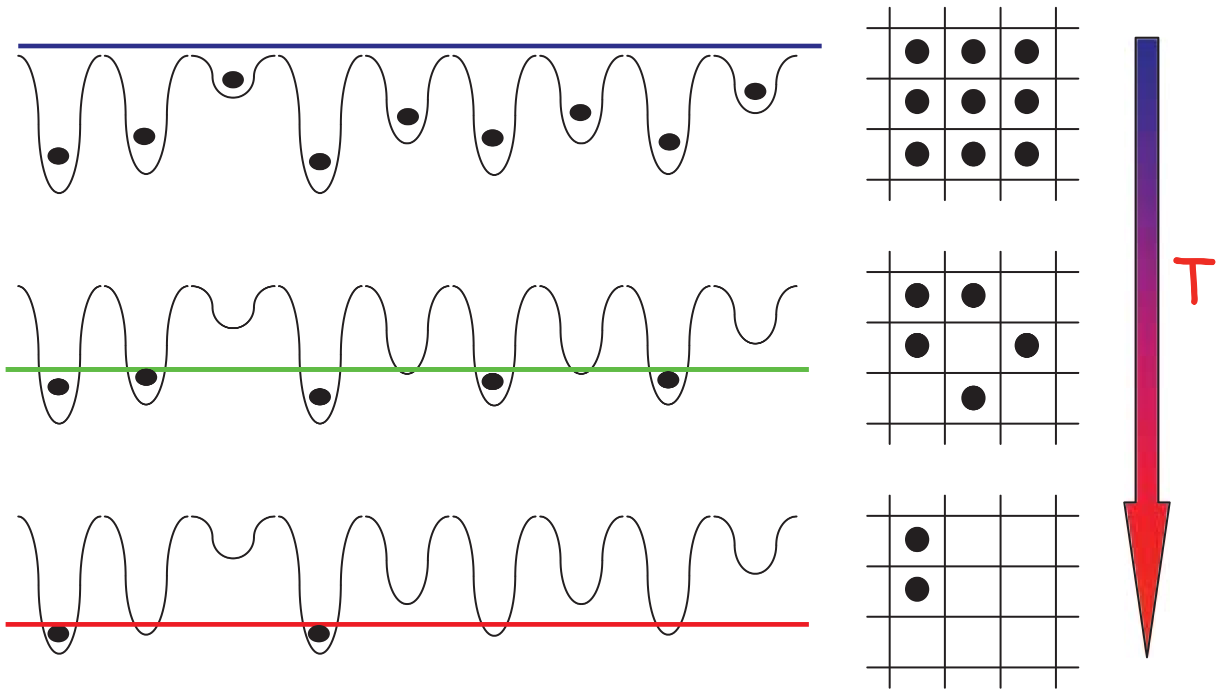
Latroche et al. JALCOM 293-295 (1999) 673

✓ Practical advantages of using ND as diffraction tool:

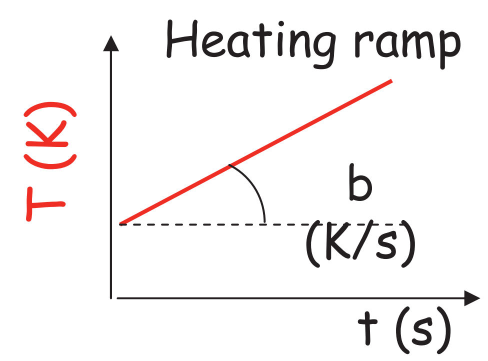
- Bulk analysis (high penetration depth of neutrons)
- Adaptable sample environment (furnace, cryostat, electrochemical cell…)
- Adapted time resolution for thermal desorption

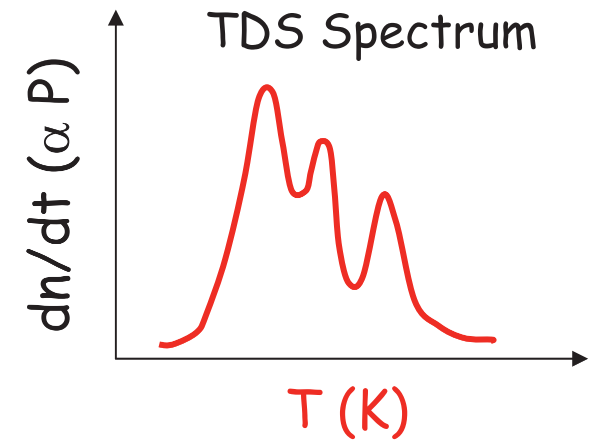
Thermal desorption spectroscopy (TDS)

Gas release measurement (H_2) while heating in a low pressure atmosphere



Potential energy diagrams

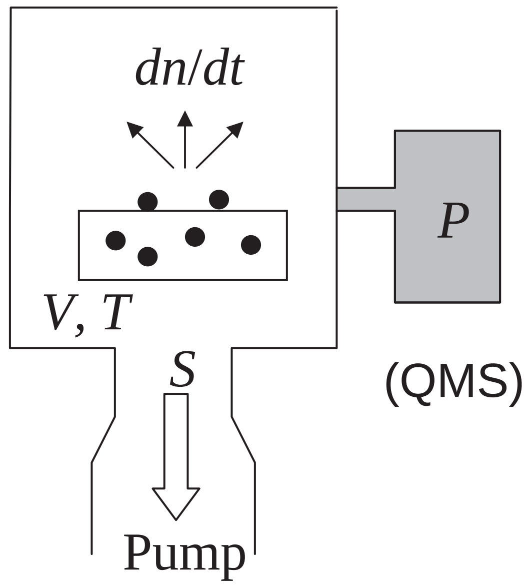




Thermal desorption spectroscopy (TDS)

- TDS: Experimental method

$$\frac{dn}{dt} = \underbrace{\frac{V}{KT}\frac{dP}{dt}}_{\text{Variation of P in the chamber}} + \underbrace{\frac{S}{KT}P}_{\text{Removal of gas by pumping}}$$



Thermal desorption spectroscopy (TDS)

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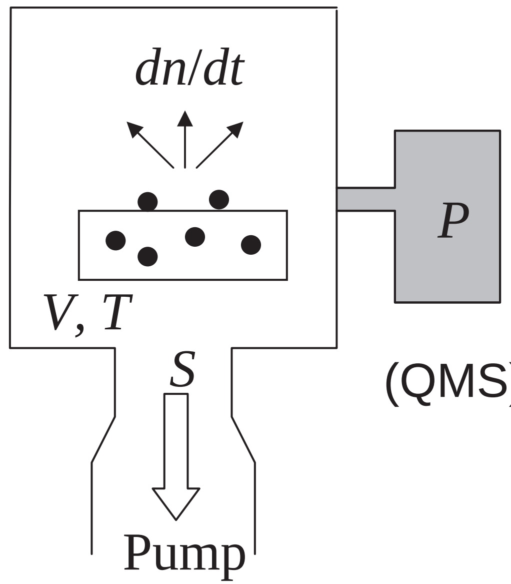
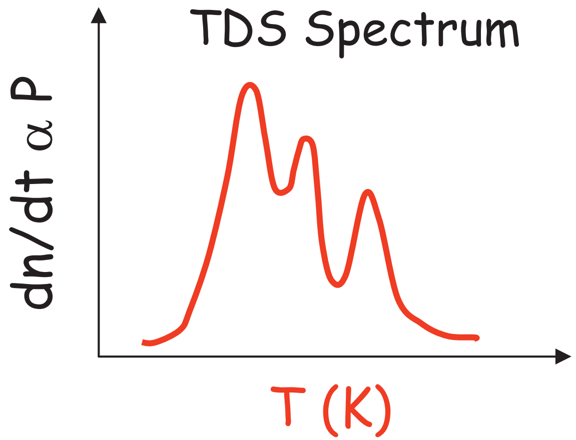


Small volume (V)
High pumping rate (S)

$$\frac{dn}{dt} \;\alpha\; P$$



TDS: what information can be obtained ?

✓ Temperature assessment of discrete desorption "states" (TDS peaks)

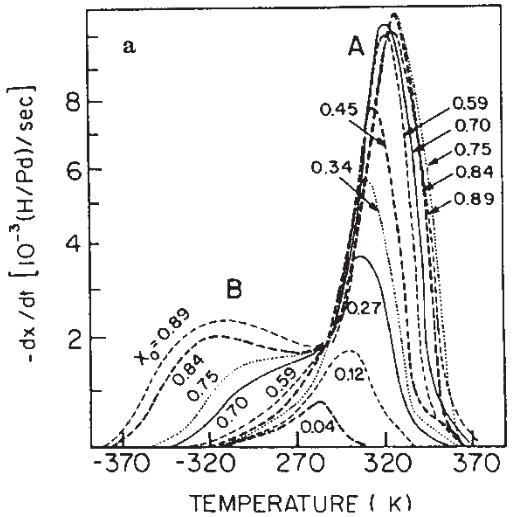
✓ Populations (integrated areas) and related activation energies (Kissinger plots)

✓ Determination of rate limiting steps (surface, trapping, diffusion, phase transformation) with a valid kinetic model : full spectra description.

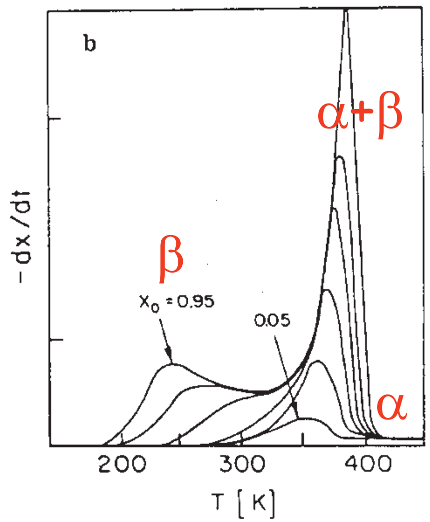
Example: TDS from PdH_x

Stern et al. J. Phys. F: Met. Phys. 14(1984)1625

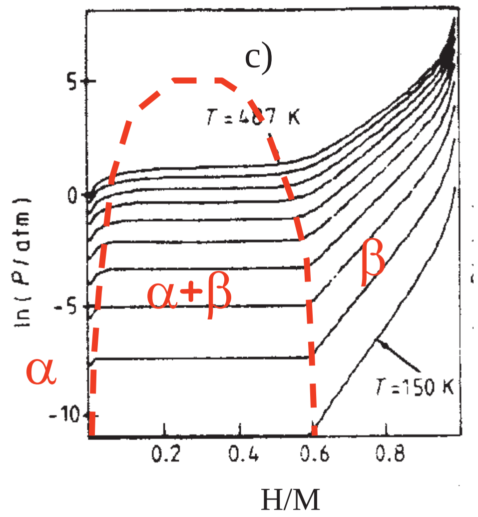
Measured



Simulated



PCT isotherms for simulation



TDS vs. ND

- <u>TDS</u>

Amount of desorbed H_2

Desorption mechanism

Surface recombination

H - Diffusion

Phase transformation

- <u>ND</u>

Amount and location of H in bulk

Crystal structure

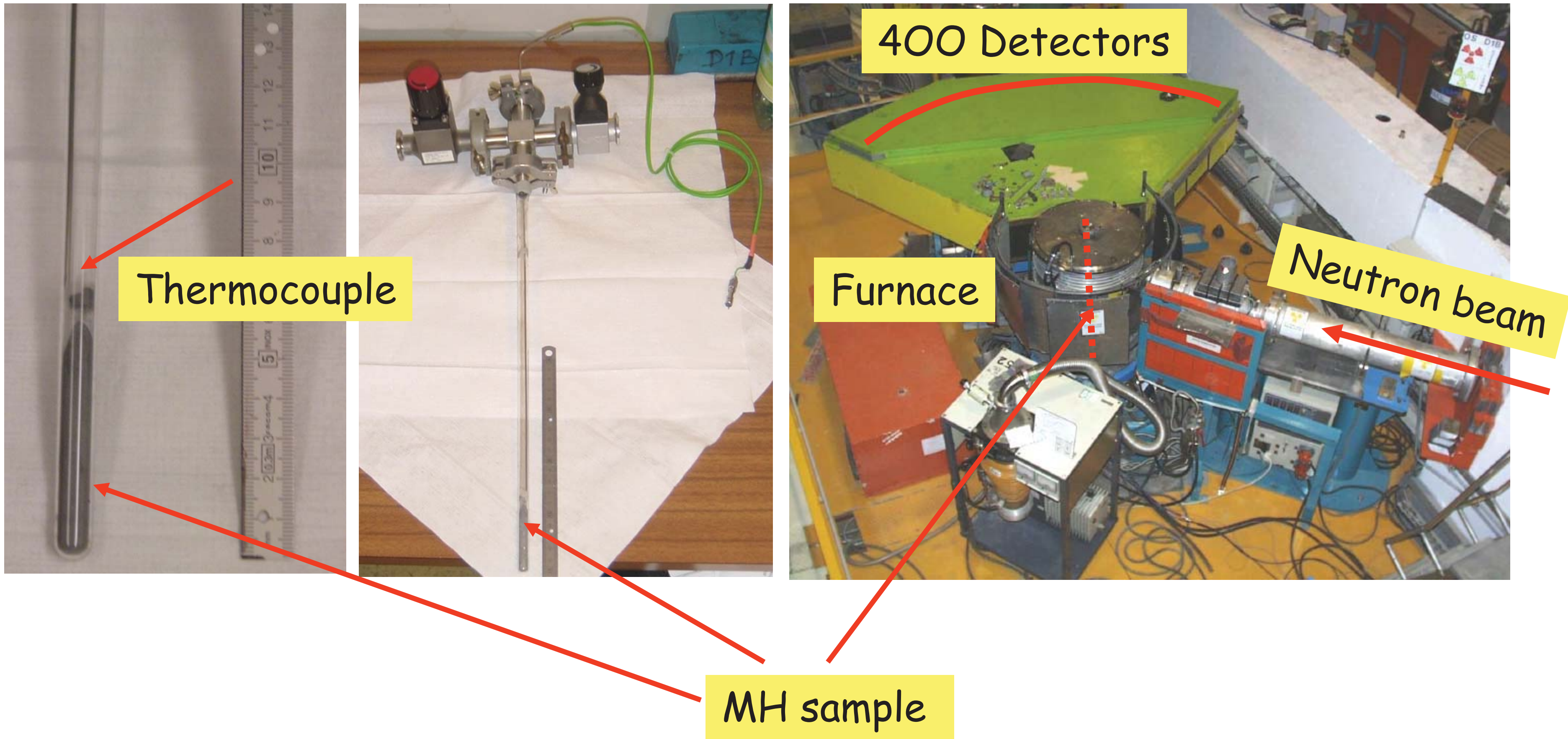
Phase transformation vs H-content

Order-disorder transitions

Amorphisation

Combined measurements TDS - ND

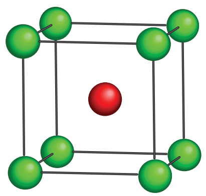
Silica container　　Vacuum and T connections　　Neutron beam line ILL - D1B



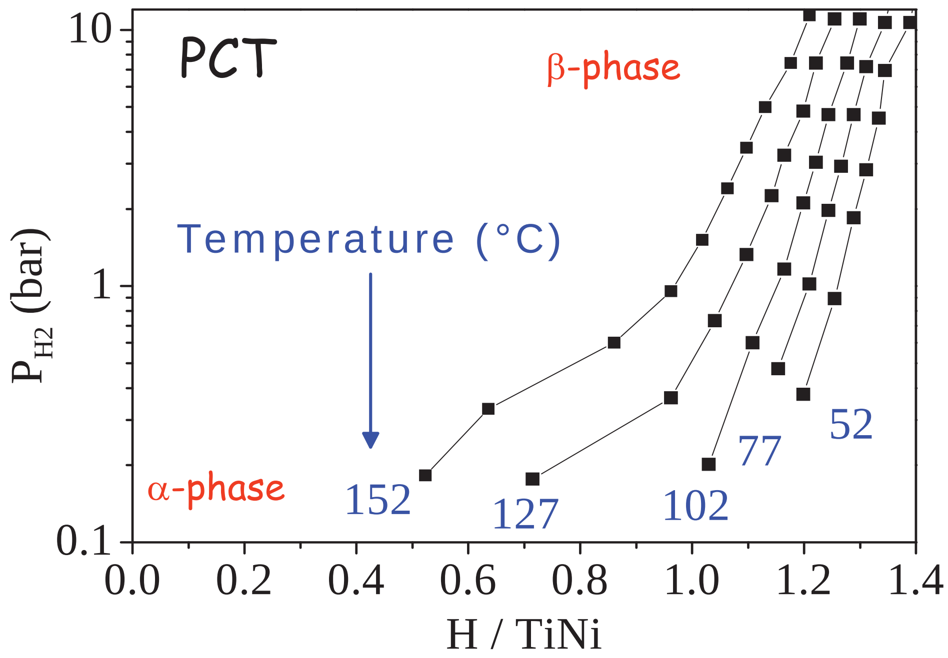
The case of TiNi-H_2

Sorption properties of the TiNi-H_2 system

Absorption by solid gas reaction: T = 150°C, P_{D2} = 4 MPa, t = 2 weeks
Measured concentration: $TiNiD_{1.35}$

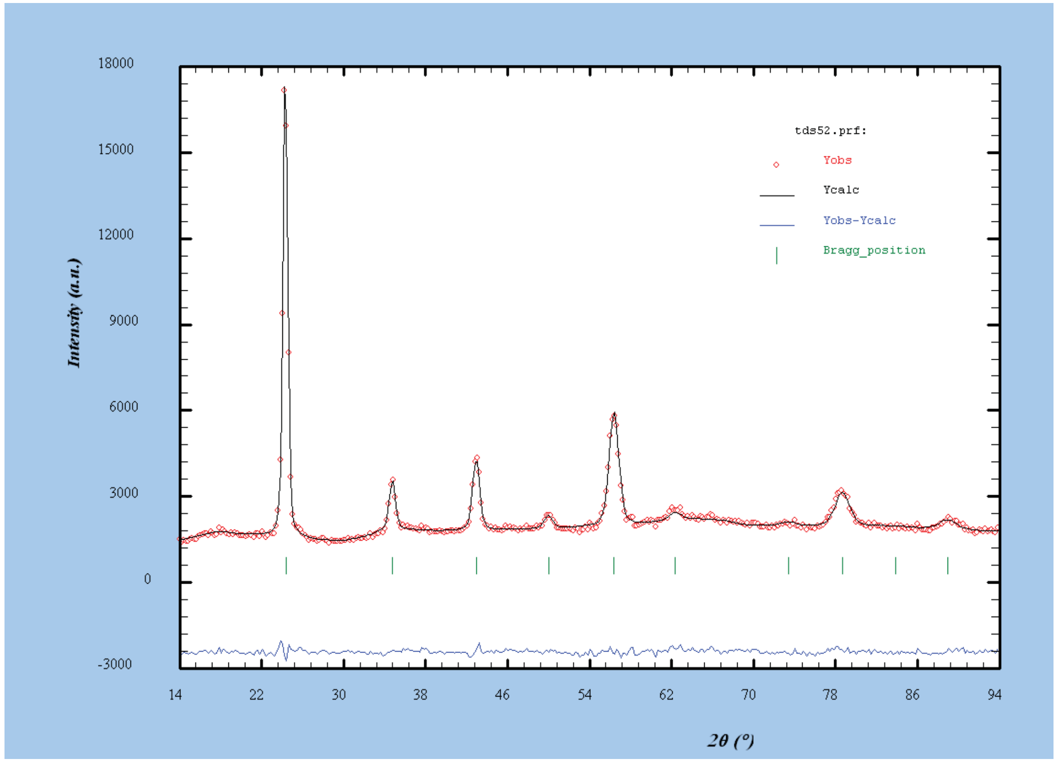


Pm $\overline{3}$*m*
Vol/TiNi = 27 Å^3

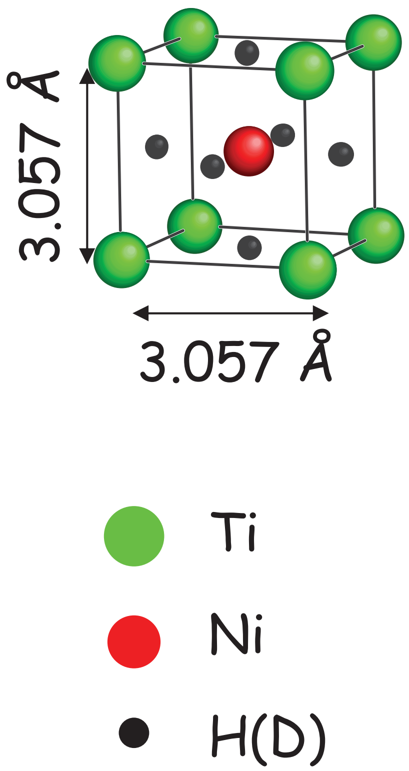


Burch and Mason, J. Chem. Soc. Faraday Trans. I 75 (1979) 561

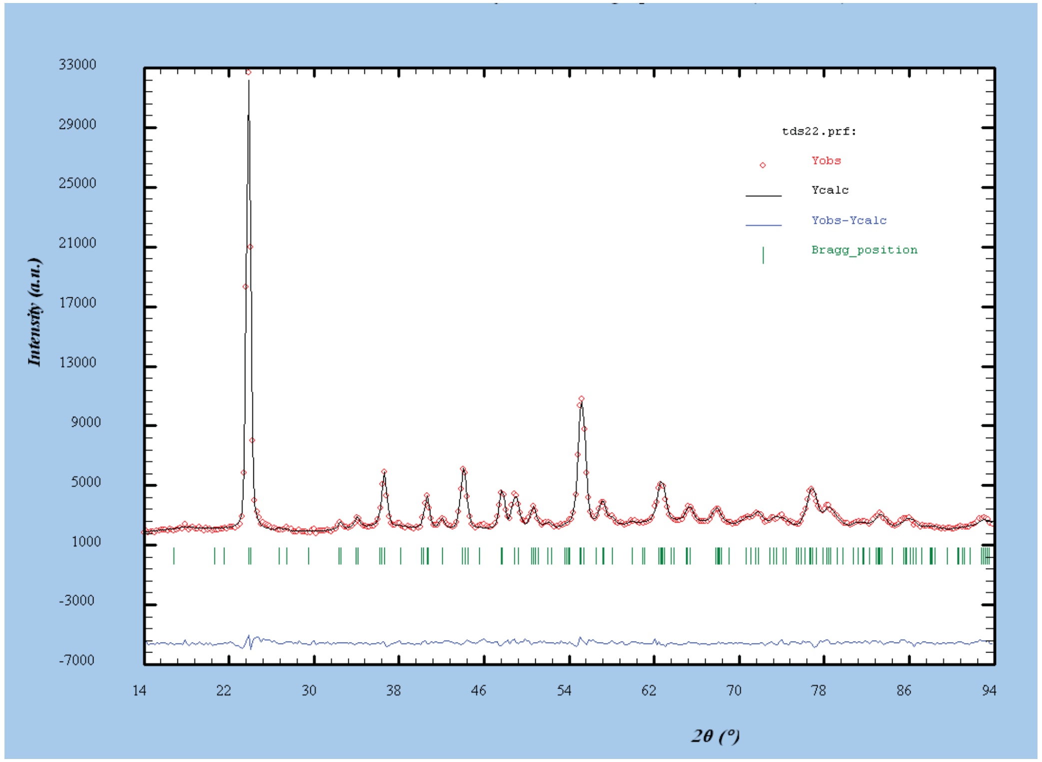
Structural properties of the α phase

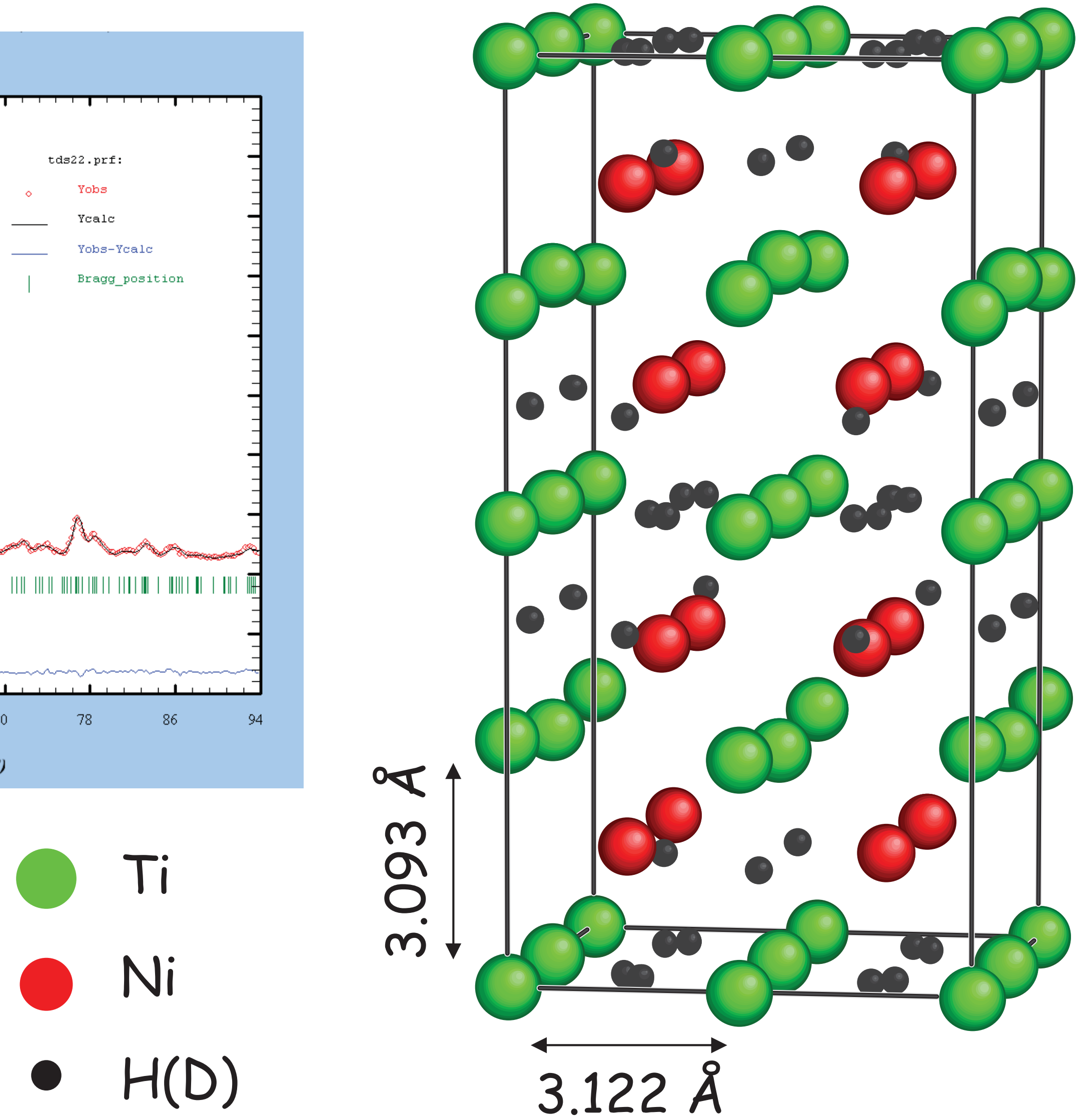


$Pm\,\bar{3}m$
D/TiNi = 0.29
Vol/TiNi = 28.7 Å^3



Structural properties of the β phase

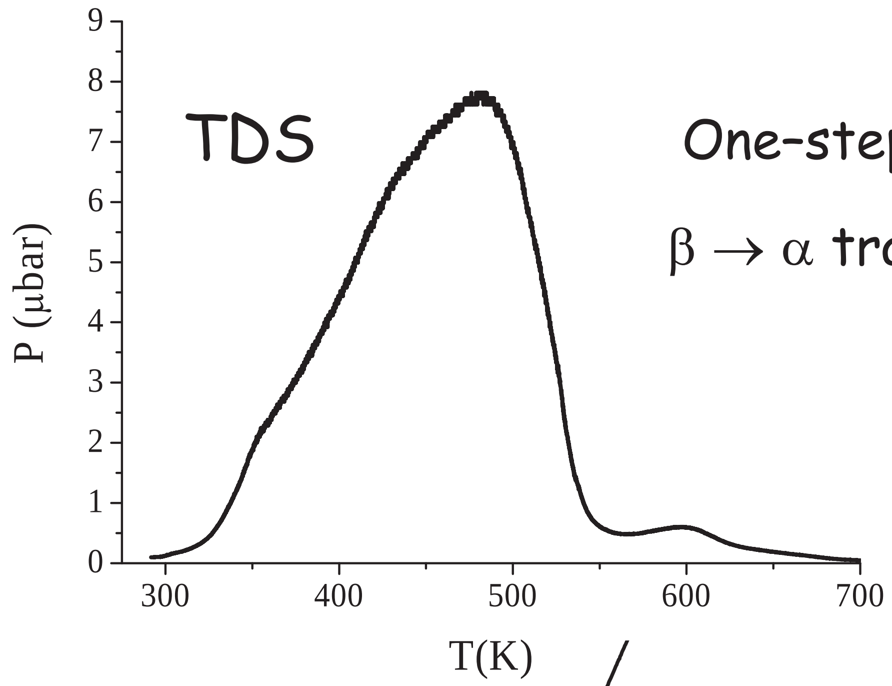




I4/mmm
D/TiNi = 1.14

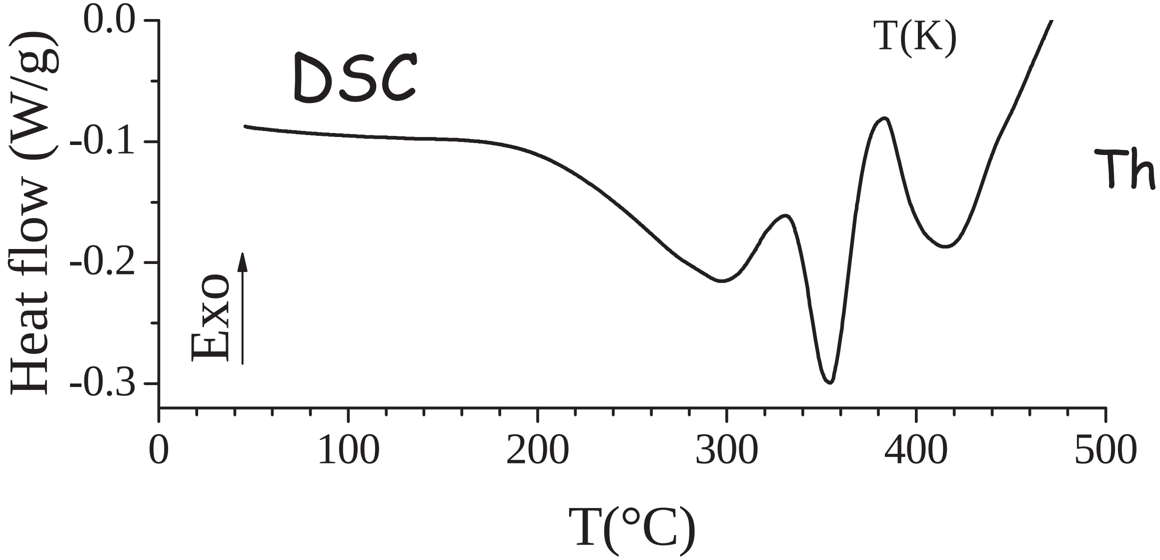
Soubeyroux et al., JALCOM 196 (1993) 127

Hydrogen desorption from $TiNiH_{1.4}$



One-step desorption

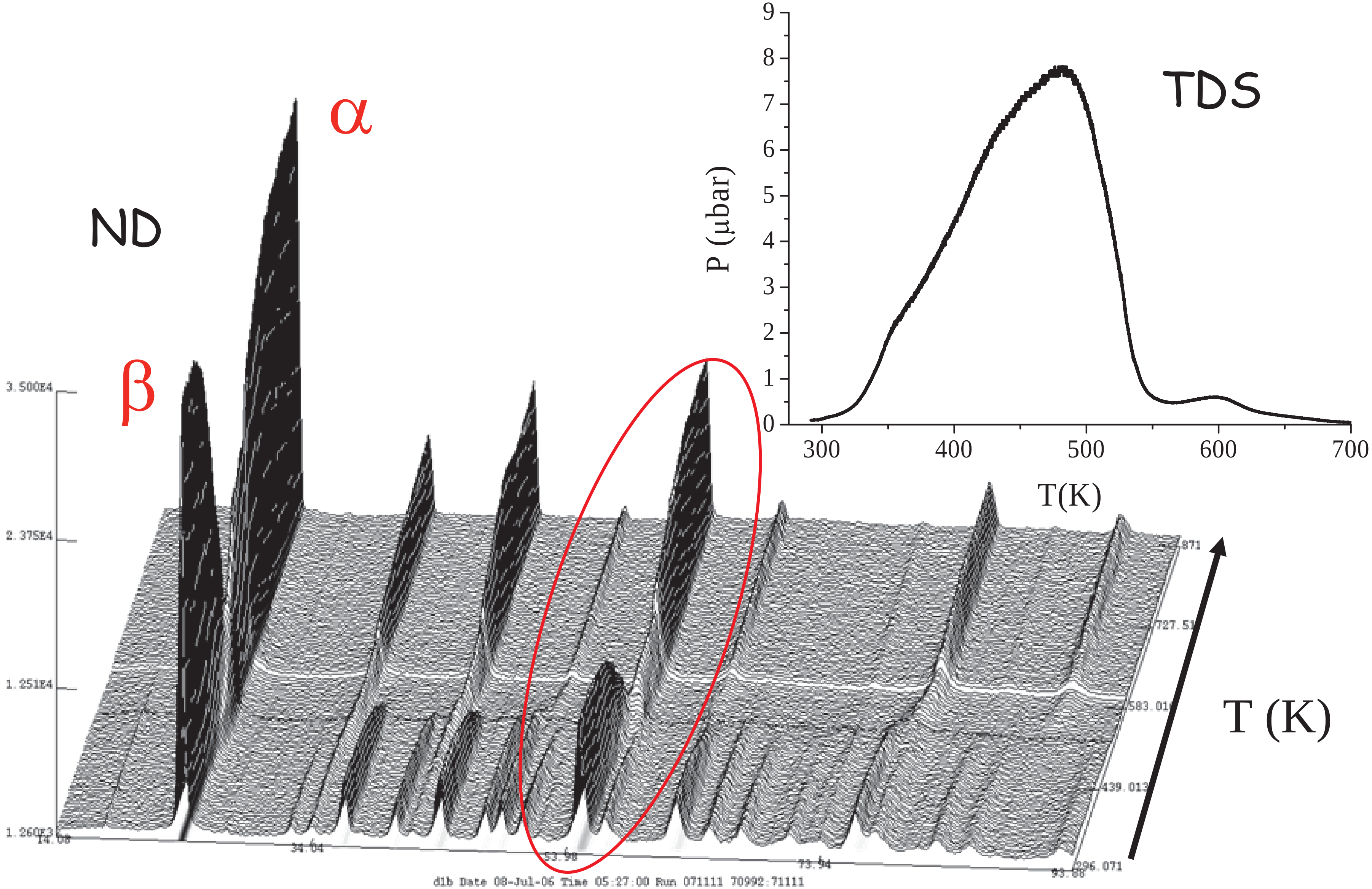
$\beta \rightarrow \alpha$ transformation

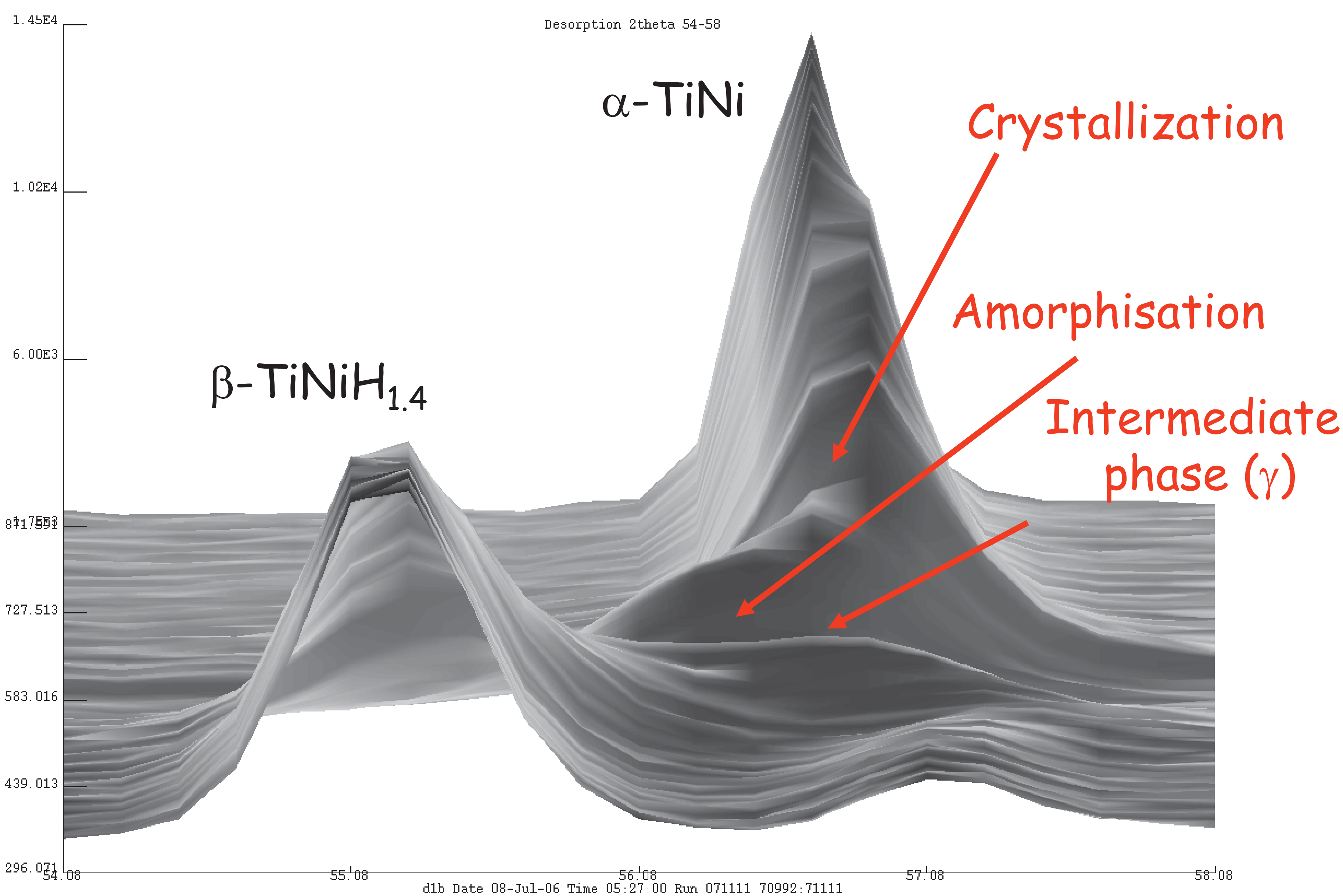


Three-step desorption

?

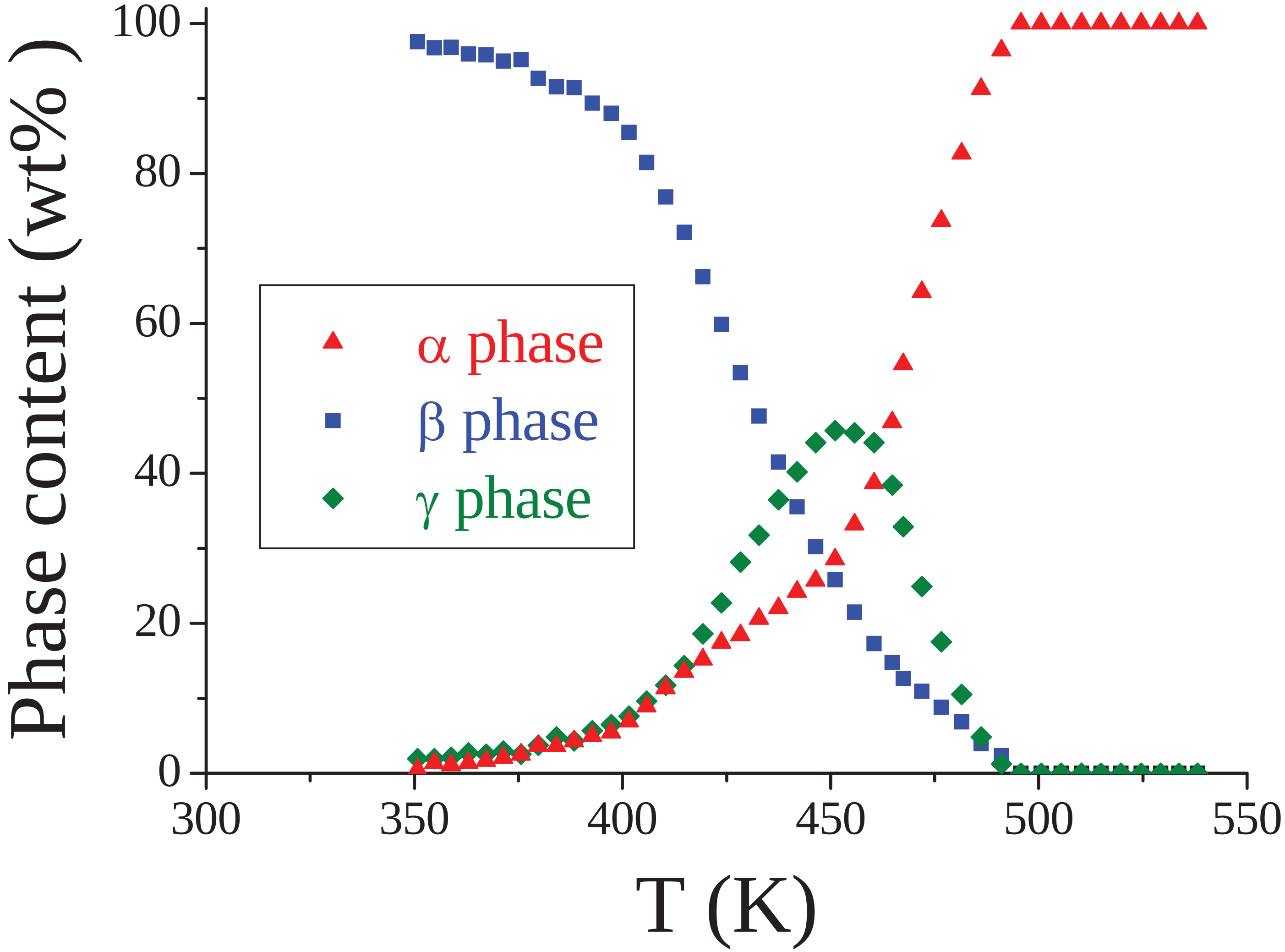
Coupled TDS-ND experiment

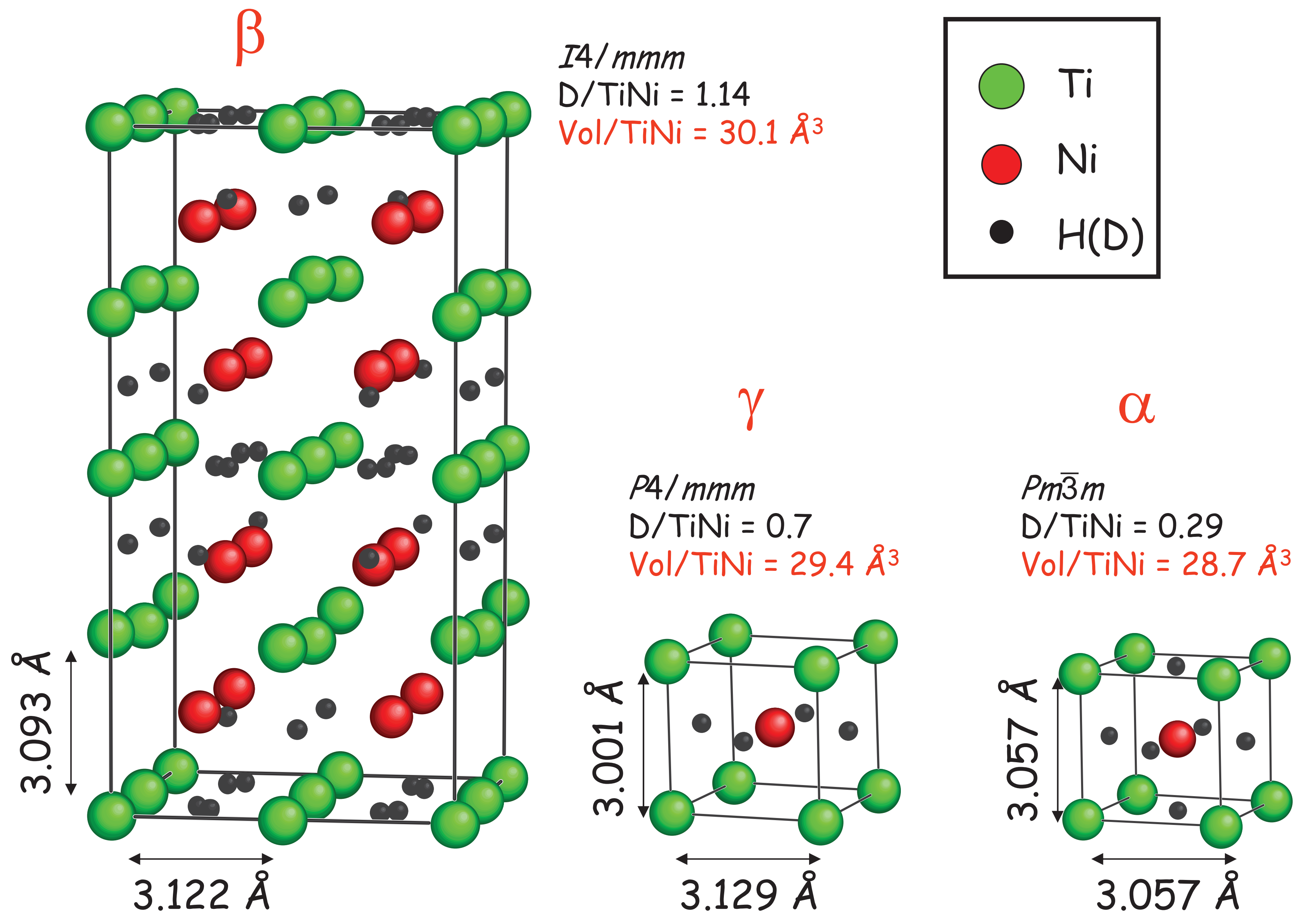




Desorption 2theta 54-58
1.45E4
1.02E4
6.00E3
727.513
583.016
439.013
296.071
54.08
55.08
56.08
57.08
58.08
d1b Date 08-Jul-06 Time 05:27:00 Run 071111 70992:71111
α-TiNi
β-TiNiH1.4
Crystallization
Amorphisation
Intermediate phase (γ)

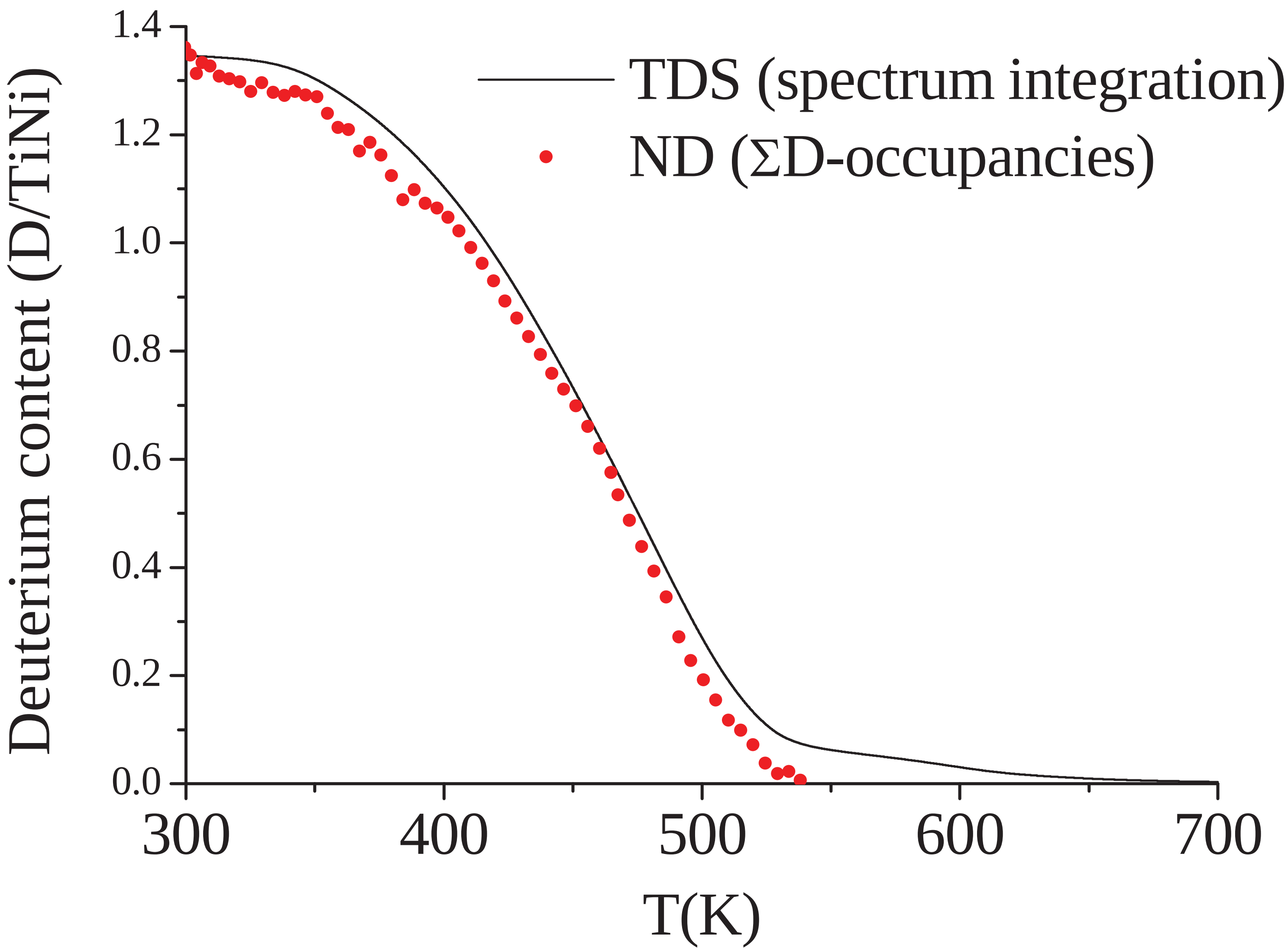
Results of Rietveld refinement



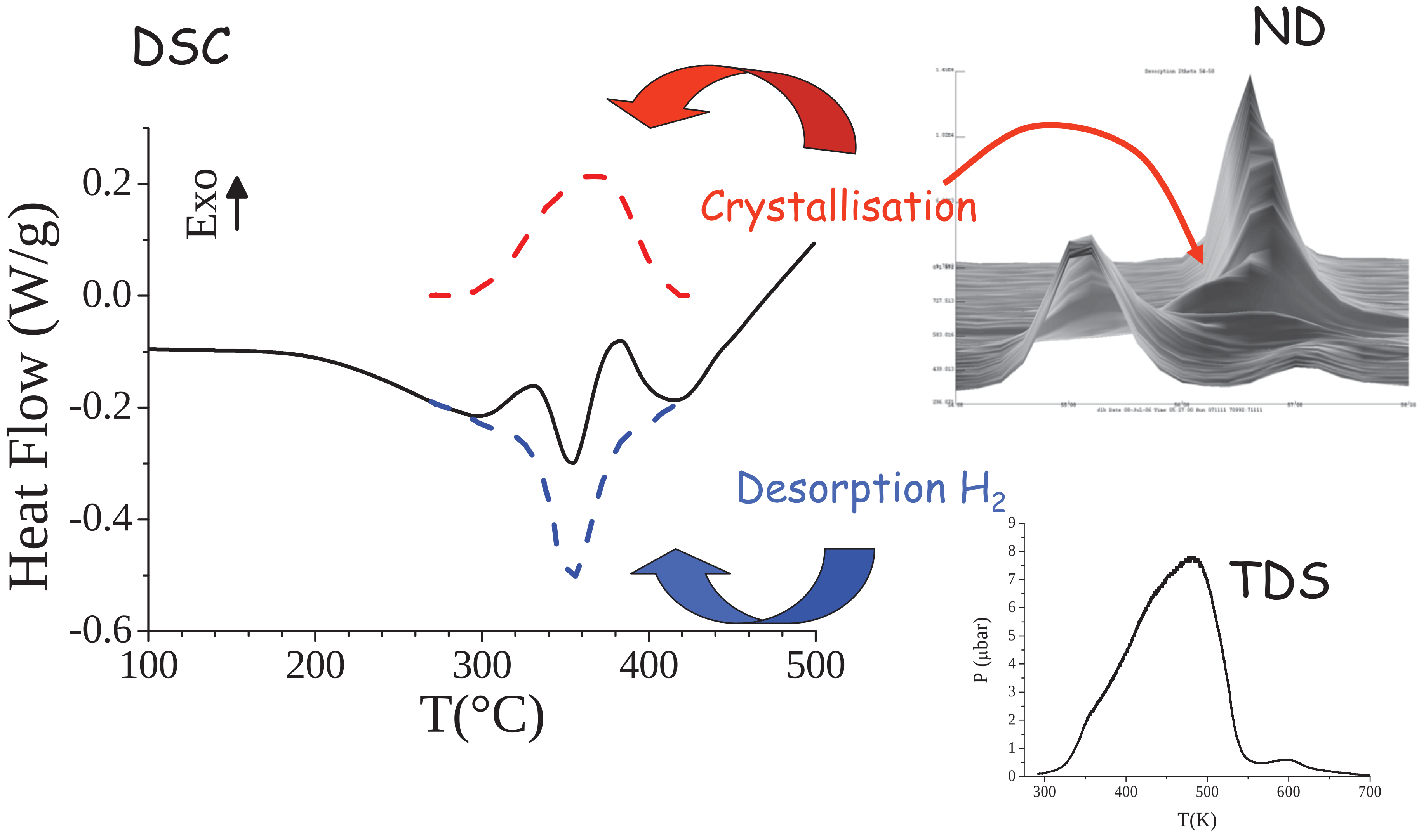


β
$I4/mmm$
D/TiNi = 1.14
Vol/TiNi = 30.1 Å³
3.093 Å
3.122 Å
γ
$P4/mmm$
D/TiNi = 0.7
Vol/TiNi = 29.4 Å³
3.001 Å
3.129 Å
α
$Pm\bar{3}m$
D/TiNi = 0.29
Vol/TiNi = 28.7 Å³
3.057 Å
3.057 Å
Ti
Ni
H(D)

Comparison of ND and TDS H-contents



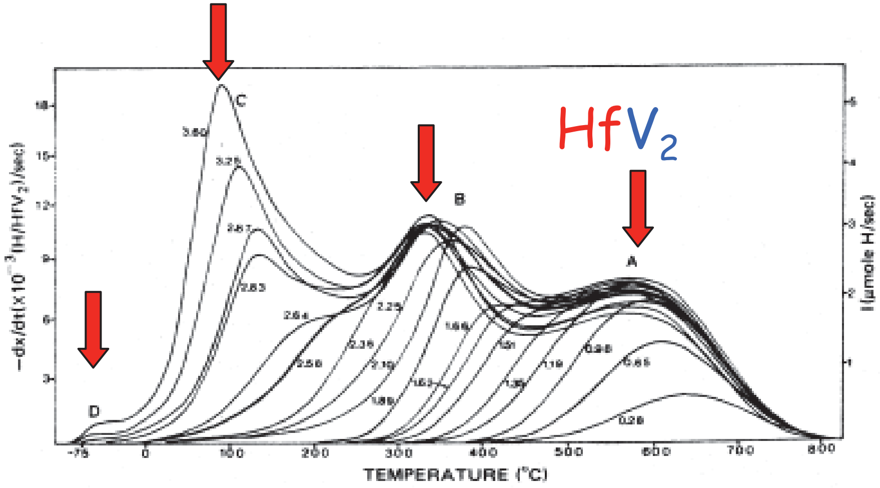
Comparison of ND, TDS and DSC



The case of YFe_2-H_2

Motivation

Multi-peak TDS spectra of Laves *C15* hydrides attributed to H-desorption from energetically different interstitial sites



Stern et al. JALCOM 88 (1982) 431

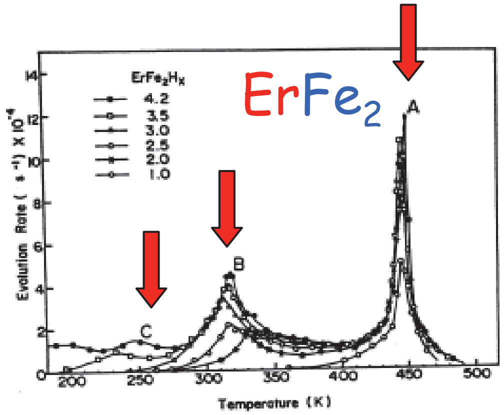
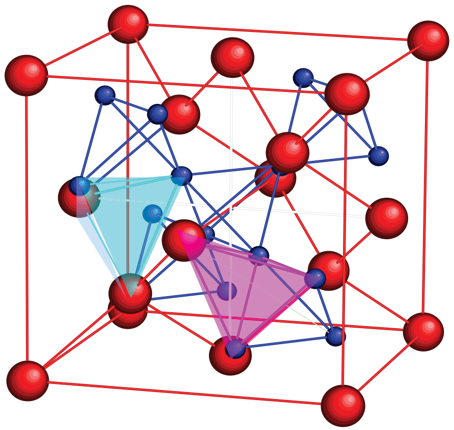


Fig. 1. The desorption spectra of $ErFe_2$-H system for various initial hydrogen concentrations for the ranges $1.0 \le x \le 4.2$.

Park et al. Scr. Metall. 23 (1989) 1525

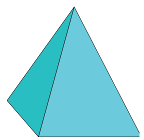


AB_2D_x

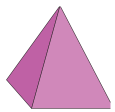
A

B

ND: Only 2 types of site occupied !

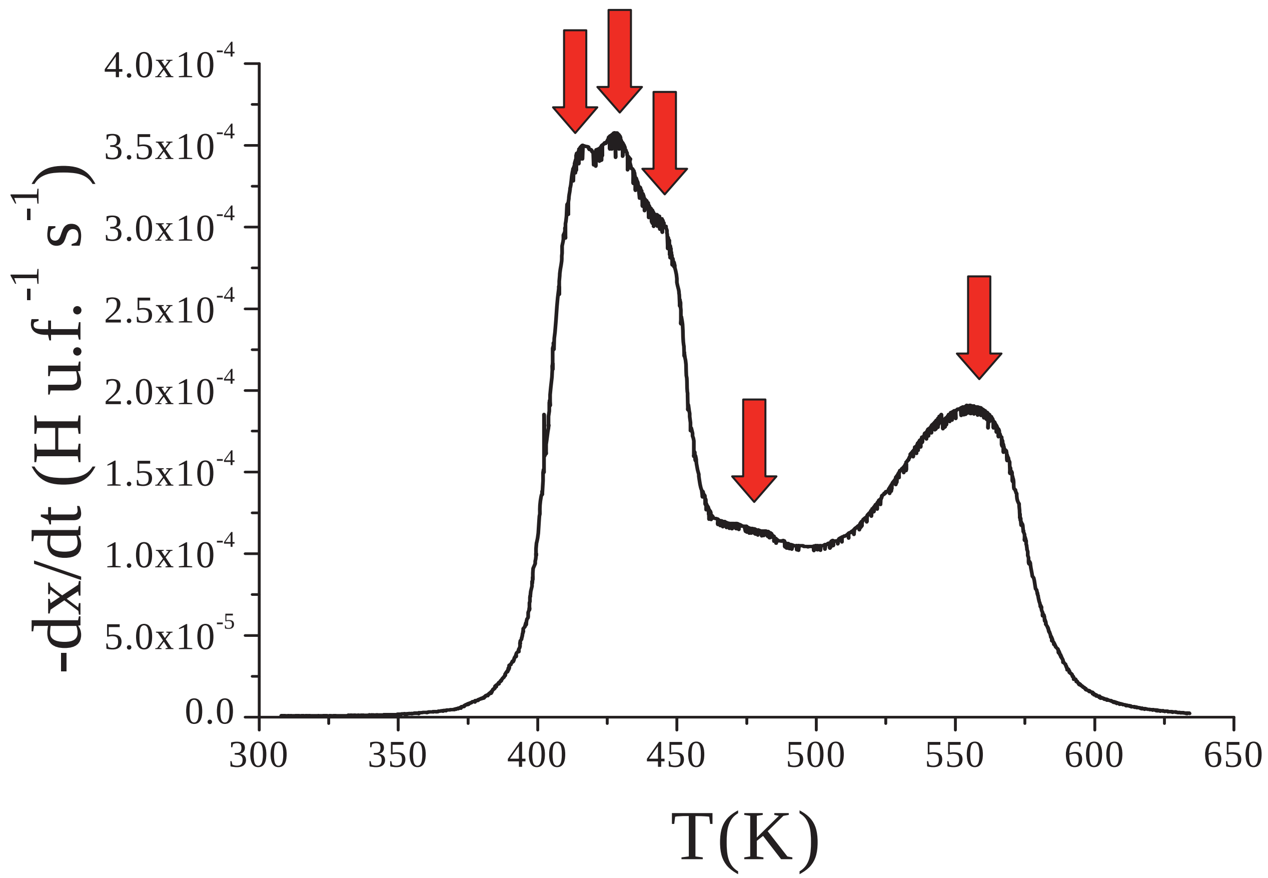


A_2B_2 $x \le 3$

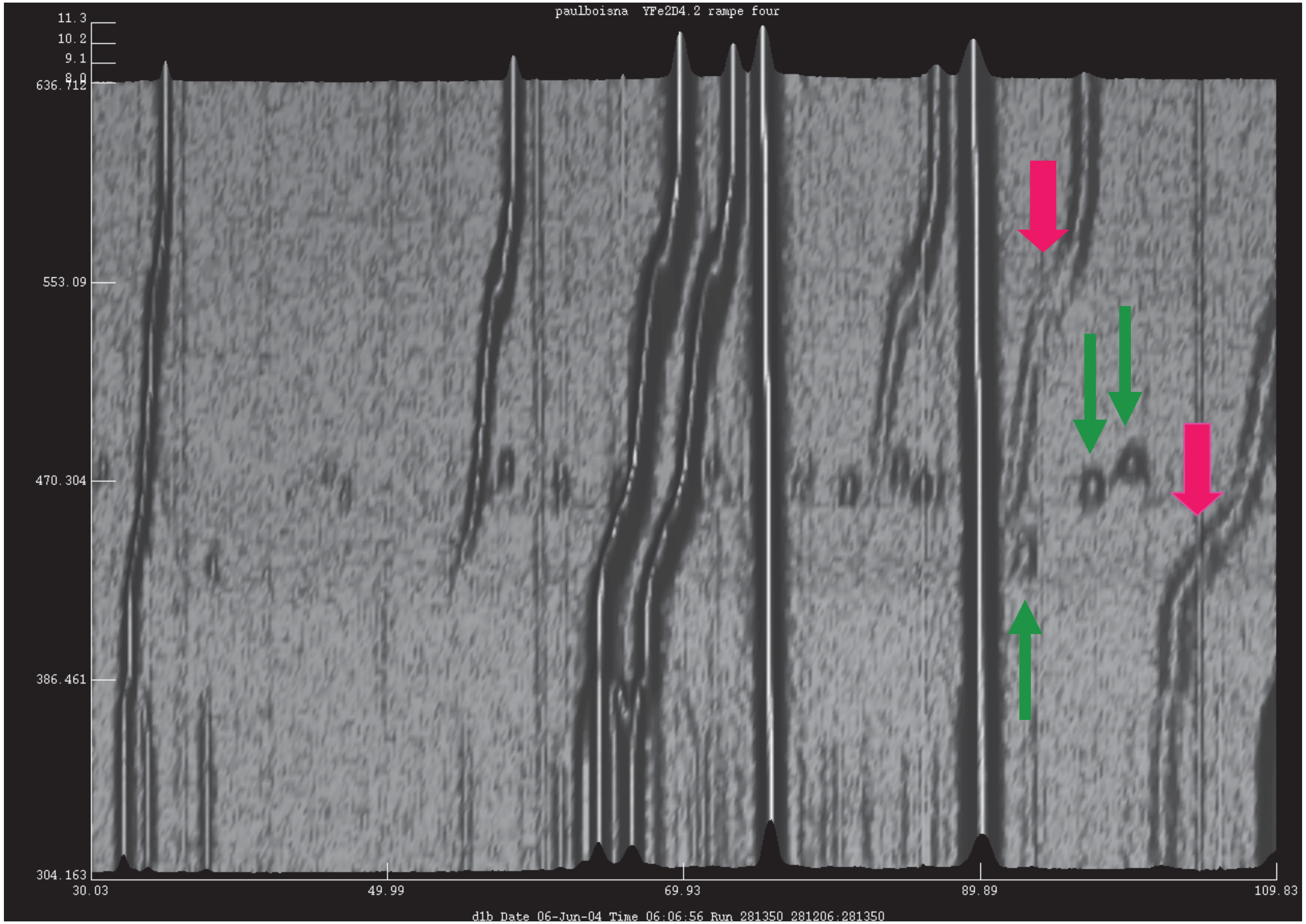


AB_3 $x > 3$

Coupled TDS-ND experiment for $YFe_2D_{4.2}$



Coupled TDS-ND experiment for $YFe_2D_{4.2}$



Phase transformations

Order-disorder transitions

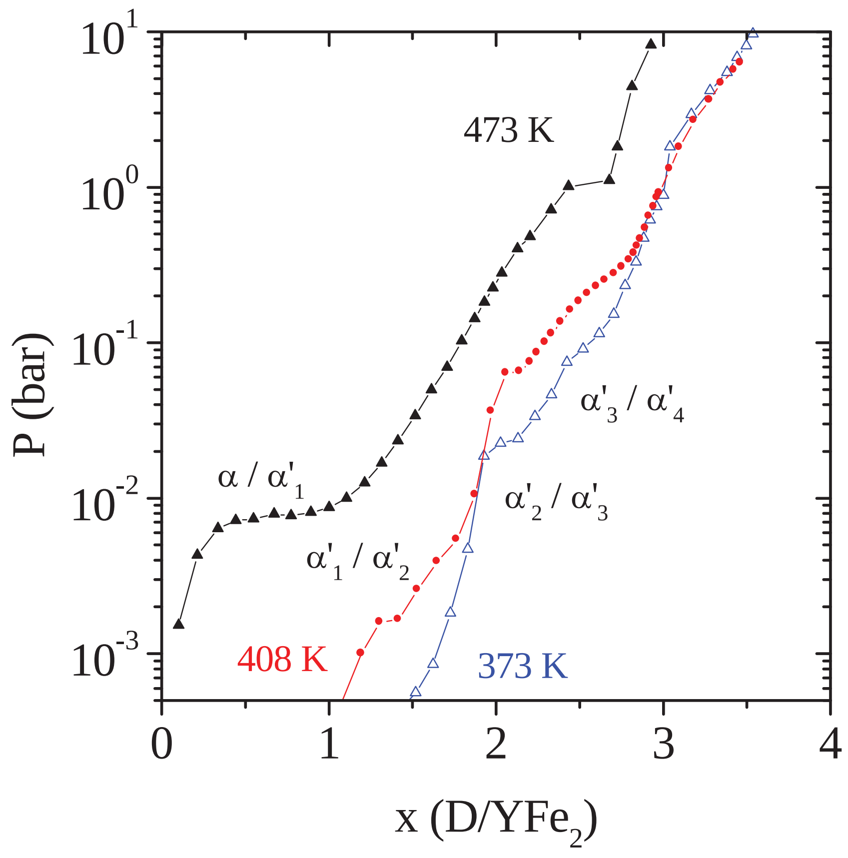
C15

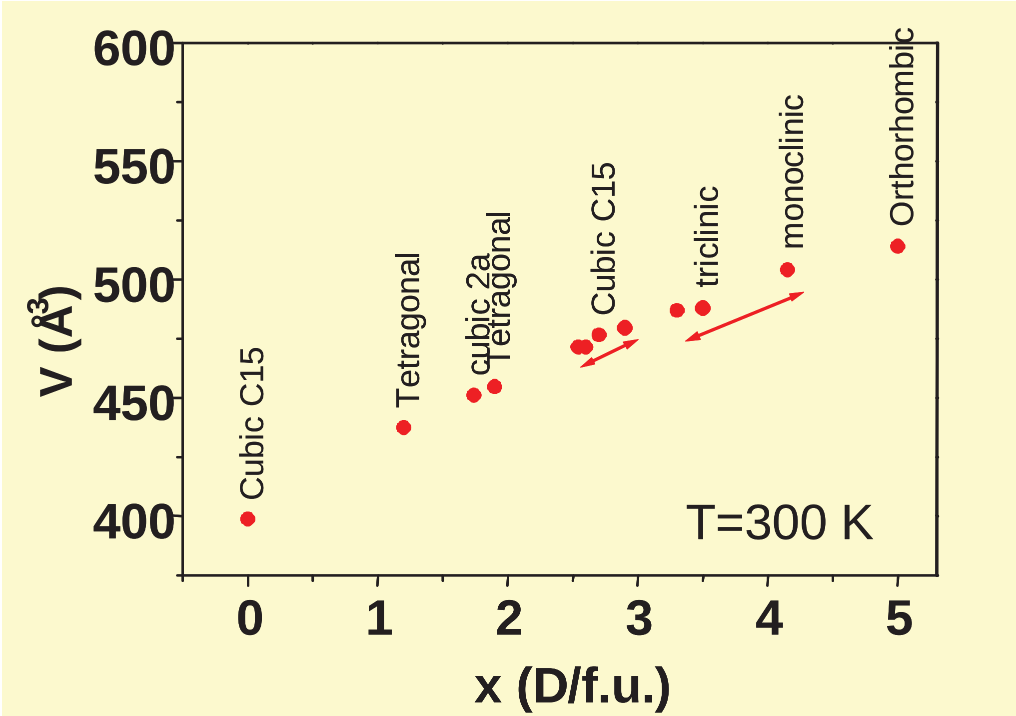
380K

monoclinic

Thermodynamic & crystal structure for YFe_2-D_2

- Multi-plateau isotherms





V. Paul-Boncour, JSSC 142 (1999) 120

Simulation of the TDS spectrum

Successive phase transformation: Johnson-Mehl-Avrami (JMA) equation

$$F_i = 1 - \exp\left\{-(k_i t)^{\eta_i}\right\} \;,\; k_i = k_o \exp\left(-\frac{E_i}{RT}\right) \;,\; K_o \sim hT/K \sim 10^{-13}\ s^{-1}$$

$$F_i \approx 1 - \exp\left\{-(k_i \frac{RT^2}{\beta E_i})^{\eta_i}\right\}$$

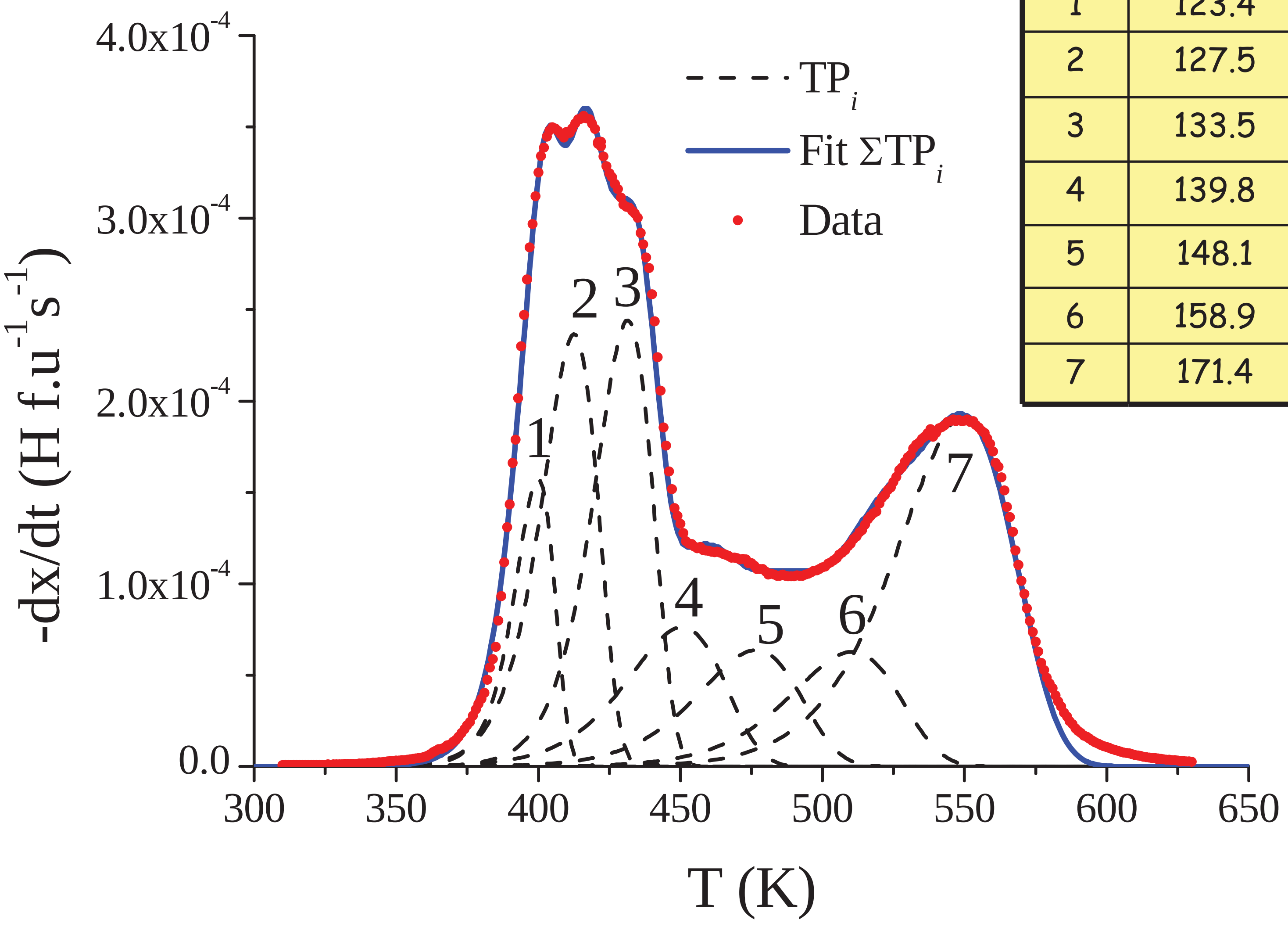
J. Farjas, P. Roura, "Modification of the Kolmogorov-Johnson-Mehl-Avrami rate equation for non-isothermal experiments and its analytical solution", Acta Mater., 54 (2006) 5573-5579

$$\frac{dF_i}{dt} = \eta_i k_i (1 - F_i)\left[-\ln(1 - F_i)\right]^{(\eta_i - 1)/\eta_i}$$

$\Rightarrow$ Fit of TDS spectrum to i-phase transformations

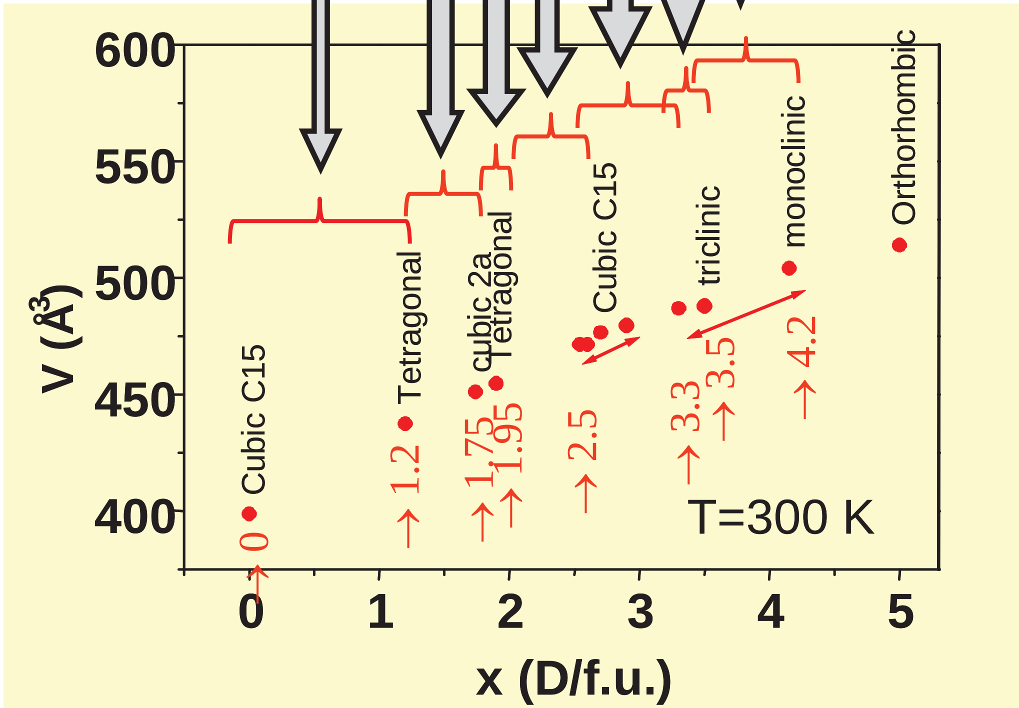
$$\boxed{-\frac{dx}{dt} = \sum_{i=1}^{n} \Delta x_i \frac{dF_i}{dt}}$$

Fit of the TDS spectrum

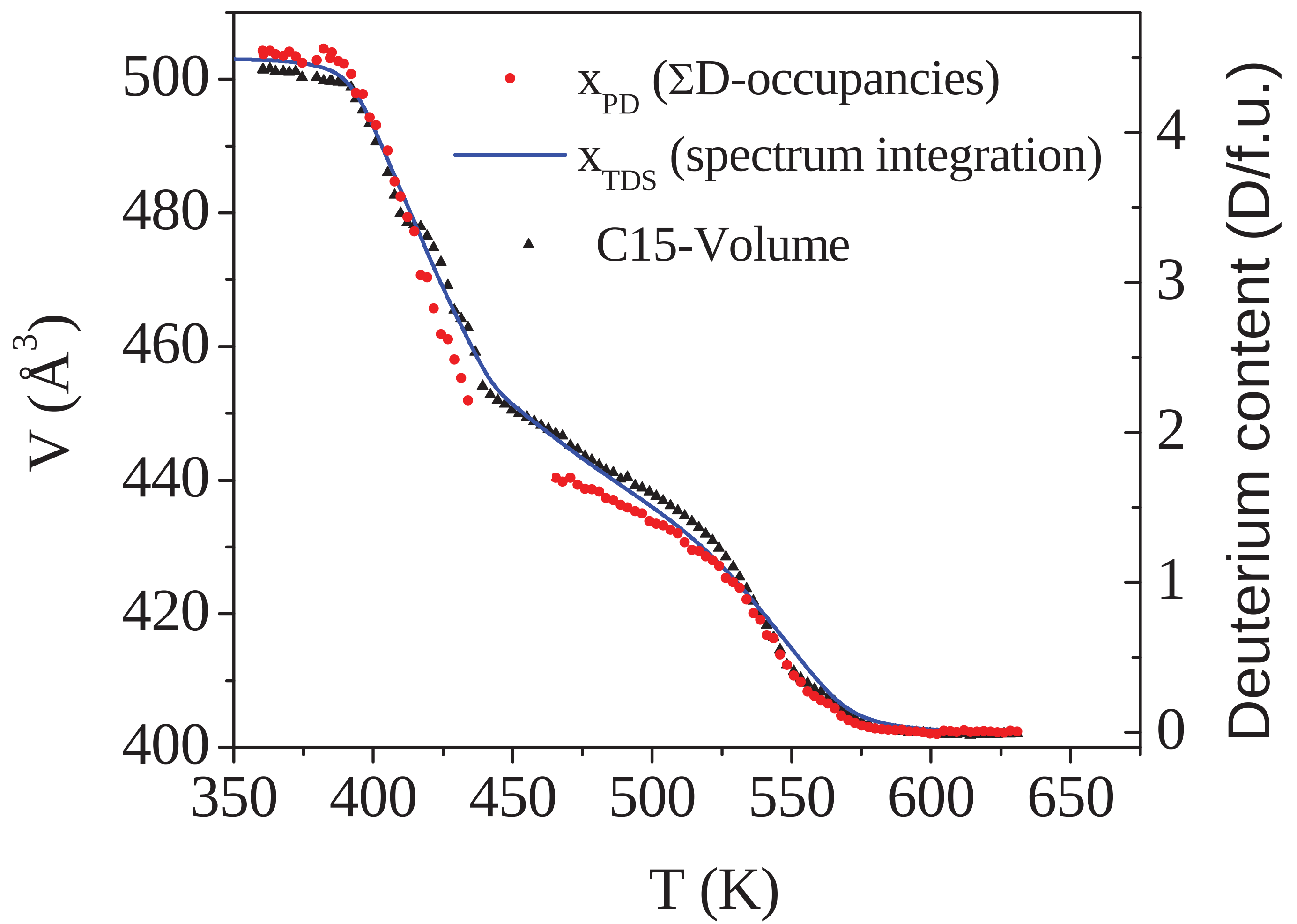


Peak	Ea (kJ/mol)	n	Δx (D/f.u.)
1	123.4	1.5	0.34
2	127.5	1.1	0.73
3	133.5	1.1	0.78
4	139.8	0.7	0.40
5	148.1	0.7	0.35
6	158.9	0.7	0.37
7	171.4	0.7	1.22

Peak	Δx (D/f.u.)	Assigned Phase Transformation
1	0.34	$YFe_2D_{4.2} \rightarrow YFe_2D_{3.85}$
2	0.73	$YFe_2D_{3.85} \rightarrow YFe_2D_{3.15}$
3	0.78	$YFe_2D_{3.15} \rightarrow YFe_2D_{2.35}$
4	0.40	$YFe_2D_{2.35} \rightarrow YFe_2D_{1.95}$
5	0.35	$YFe_2D_{1.95} \rightarrow YFe_2D_{1.60}$
6	0.37	$YFe_2D_{1.60} \rightarrow YFe_2D_{1.20}$
7	1.22	$YFe_2D_{1.20} \rightarrow YFe_2$



Comparison of ND and TDS H-contents



T. Leblond et al., IJHE, 34(2009) 2278

Conclusions (I)

✓ Thermal desorption from $TiNiD_{1.4}$ hydride occurs through an intermediated hydride phase of medium H-content: γ-$TiNiD_{0.7}$.

✓ $\gamma \rightarrow \alpha$ phase transformation generates compound amorphisation.

✓ DSC measurements are explained by the combined effects of endothermic hydrogen desorption and exothermic alloy crystallization.

Conclusions (II)

✓ Multi-peak TDS spectrum for YFe_2 hydride is well-described by consecutive phase transformations.

✓ Multiple C15 Laves phases have been evidenced by ND and XRD diffraction measurements .

✓ Same description may account for multi-peak TDS spectra observed for many C15 Laves phases.

Conclusions (III)

✓ TDS set-up can be easily implemented in ND beam-line

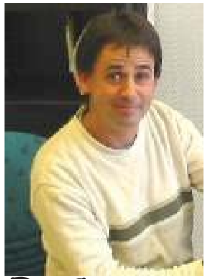
✓ Coupling of TDS - ND techniques is a very powerful tool to characterize hydrogen desorption from solids, particularly when phase transformations take place

Acknowledgments

ICMPE
Institut de Chimie et des Matériaux Paris-Est

V. Paul-Boncour

T. Leblond



F. Cuevas

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