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Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology in Hydrogen-Based Energy Systems

13 - 18 June 2011

Neutron diffraction studies of metal hydrides
(Part 2)

J. Huot

Universite du Quebec a Trois-Rivieres
Canada
&
Institute for Energy Technology
Norway

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Neutron diffraction studies of metal hydrides (part 2)

J. Huot

Université du Québec à Trois-Rivières

UQTR
Université du Québec
à Trois-Rivières

Present address: *Institute for Energy Technology, Norway*

IFE Institute for Energy Technology

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Mg-based alloys

Nanocrystalline material

- Effect of ball milling on the hydrogen storage properties of magnesium hydride.
- High energy milling of MgD_2 produces a nanocrystalline structure made of a mixture of β-MgD_2 and the high temperature/high pressure phase γ-MgD_2.
- It seems that long milling time do not increases the ratio of γ-MgD_2/ β-MgD_2
- Neutron powder diffraction could give us some insight

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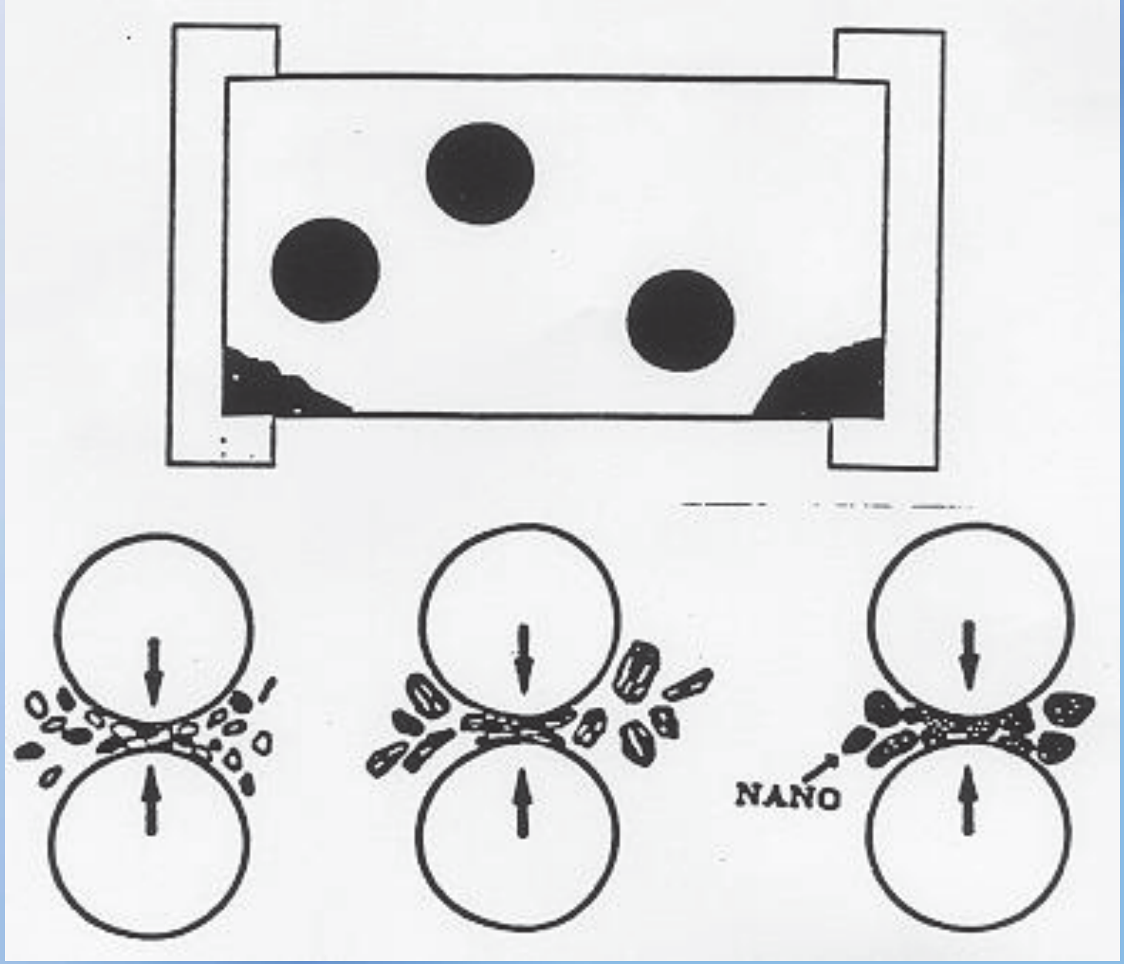
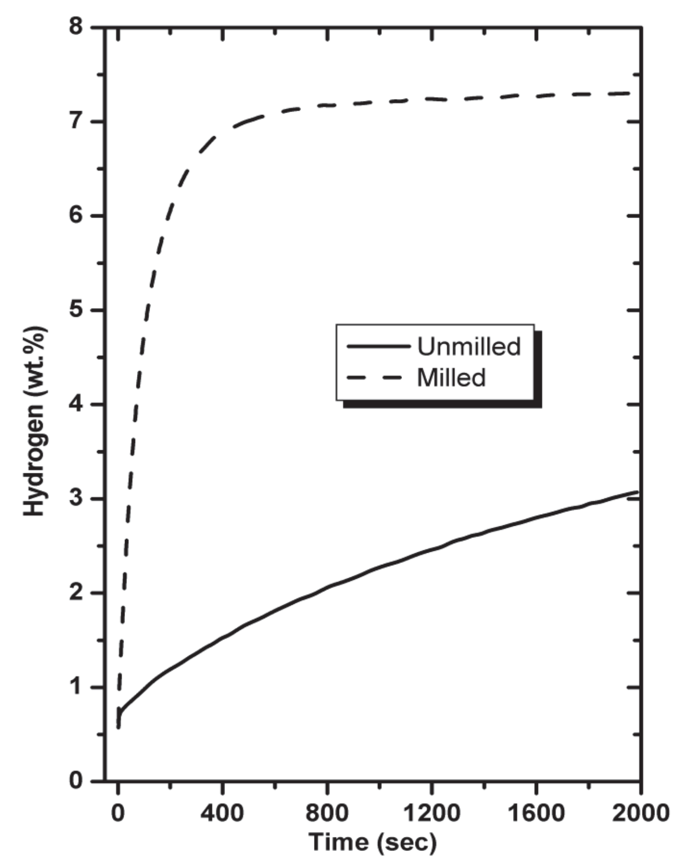
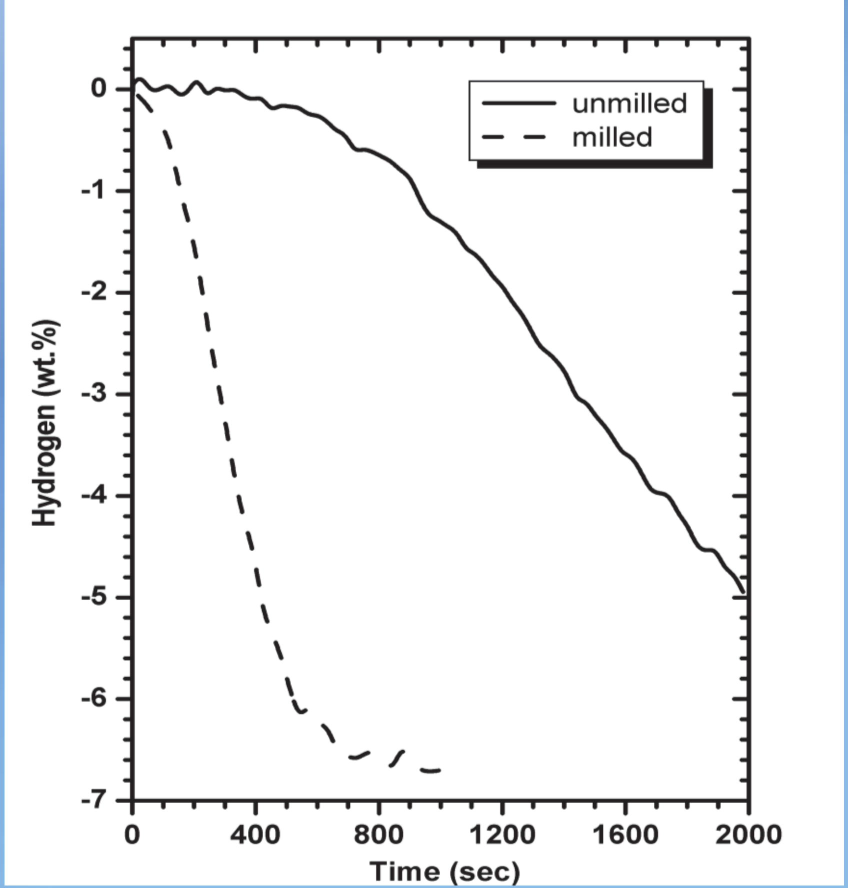
Ball milling technique



Hydrogen sorption properties

$T = 573K, P_{abs} = 1.0MPa, P_{des} = 0.015MPa$





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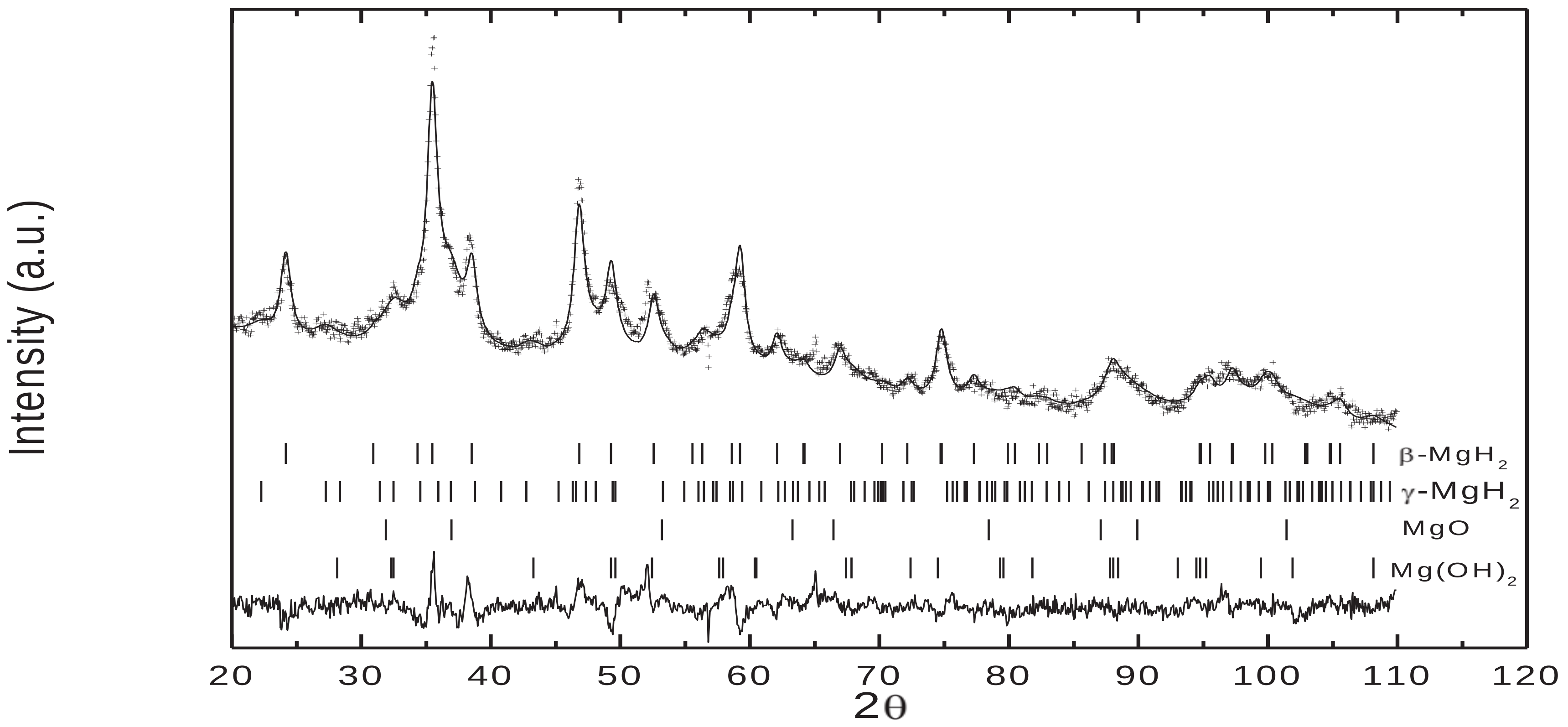
Neutron powder diffraction

- Chalk River
- C2 DUALSPEC high-resolution neutron powder diffractometer
- Room temperature
- wavelength of 1.3287 Å.
- Sample holder: cylindrical can made of vanadium
- Rietveld refinement: Fullprof

Pattern



Neutron powder diffraction of 20 hours milled nanocrystalline MgD_2. (crosses: experimental intensity, upper solid line: calculated intensity, lower line: residue).

Results β-MgD_2 phase

Parameter	**High temperature-high pressure**	**Ball-milled**	**Variation (%)**
a [Å]	4.5010(1)	4.521(1)	0.44
c [Å]	3.0100(1)	3.009(1)	-0.03
B_{iso}(Mg) [$Å^2$]	0.56(5)	1.2(1)	--
D (x/*a*)	0.3040(2)	0.2996(6)	-1.45
B_{iso}(D) [$Å^2$]	1.69(4)	2.54(9)	--

R_{Bragg} = 5.1%, R_F = 2.9%

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Results γ-MgD_2 phase

Parameter	High temperature-high pressure	Ball-milled	Variation (%)
a [Å]	4.5051(2)	4.50(1)	-0.1
b [Å]	5.4197(2)	5.46(1)	0.7
c [Å]	4.9168(2)	4.92(1)	0.1
Mg	0.3313(6)	0.320(5)	-3.4
B_{iso}(Mg) [Å^2]	0.18(6)	0.8(4)	--
D (x/*a*)	0.2727(5)	0.280(3)	2.7
D (y/*b*)	0.1089(4)	0.104(2)	-4.5
D (z/*c*)	0.0794(4)	0.073(5)	-8.0
B_{iso}(D) [Å^2]	1.30(6)	0.9(2)	--

$R_{Bragg} = 4.7\%$, $R_F = 2.5\%$

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Deuterium-magnesium distances (in Å) in MgD_2.

Phase	High temperature-high pressure	Ball-milled	Variation (%)
β-MgD_2	1.9351(9)	1.915(4)	-1.0
β-MgD_2	1.9549(6)	1.976(5)	1.1
γ-MgD_2	1.915(3)	1.92(2)	0.3
γ-MgD_2	1.943(3)	1.93(2)	-0.7
γ-MgD_2	2.004(3)	2.04(2)	1.8

Conclusion MgH_2

- **ball-milled β-MgD_2 and γ-MgD_2 structures are distorted compared to the same phases synthesised by high-pressure and high temperature.**
- **The Mg-D bond lengths are distorted in β-MgD_2.**
- **In γ-MgD_2 phase, only one bond length is distorted.**
- **This may be the explanation of the synthesis of γ-MgD_2 by energetic ball milling.**

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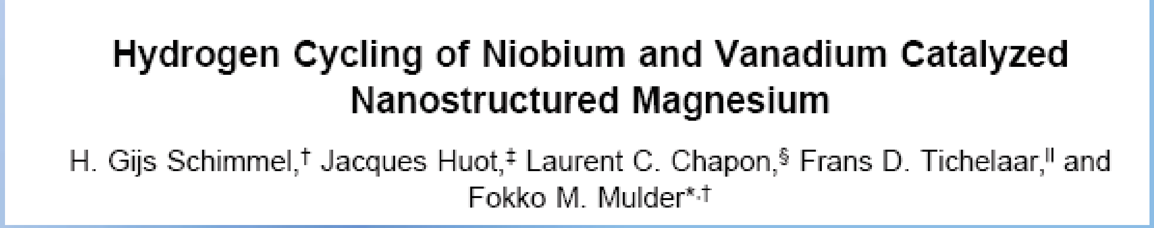
Catalytic mechanism of Nb in Mg

Nb and V (and their oxides) are known to improve hydrogen sorption kinetics on nanocrystalline MgH_2

Questions:

- What is the mechanism
- Which phases are importants
- What is the role of oxides



Hydrogen Cycling of Niobium and Vanadium Catalyzed Nanostructured Magnesium

H. Gijs Schimmel,[†] Jacques Huot,[‡] Laurent C. Chapon,[§] Frans D. Tichelaar,[∥] and Fokko M. Mulder[*,†]

J. AM. CHEM. SOC. 2005, *127*, 14348–14354

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Powder neutron diffraction

- ISIS
- GEM
- In-situ experiment
- T= 320°C, P up to 3 bar
- Loading and unloading of hydrogen by steps
- Diffraction pattern every 3 minutes
- Quartz sample container
- Rietveld refinement: GSAS

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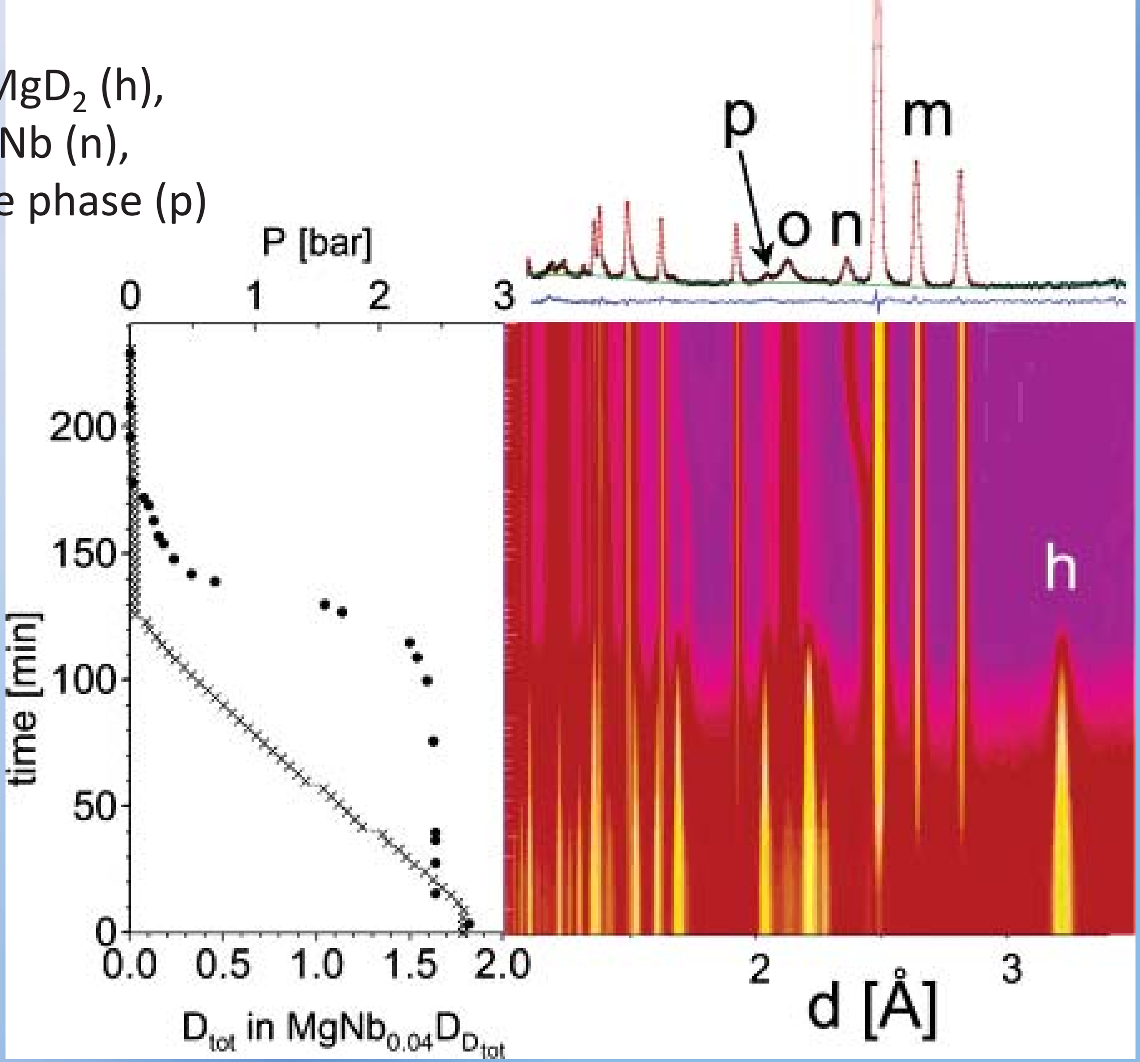
In-situ neutron diffraction $MgNb_{0.05}D$

Mg (m), MgD_2 (h),
MgO (o), Nb (n),
perovskite phase (p)



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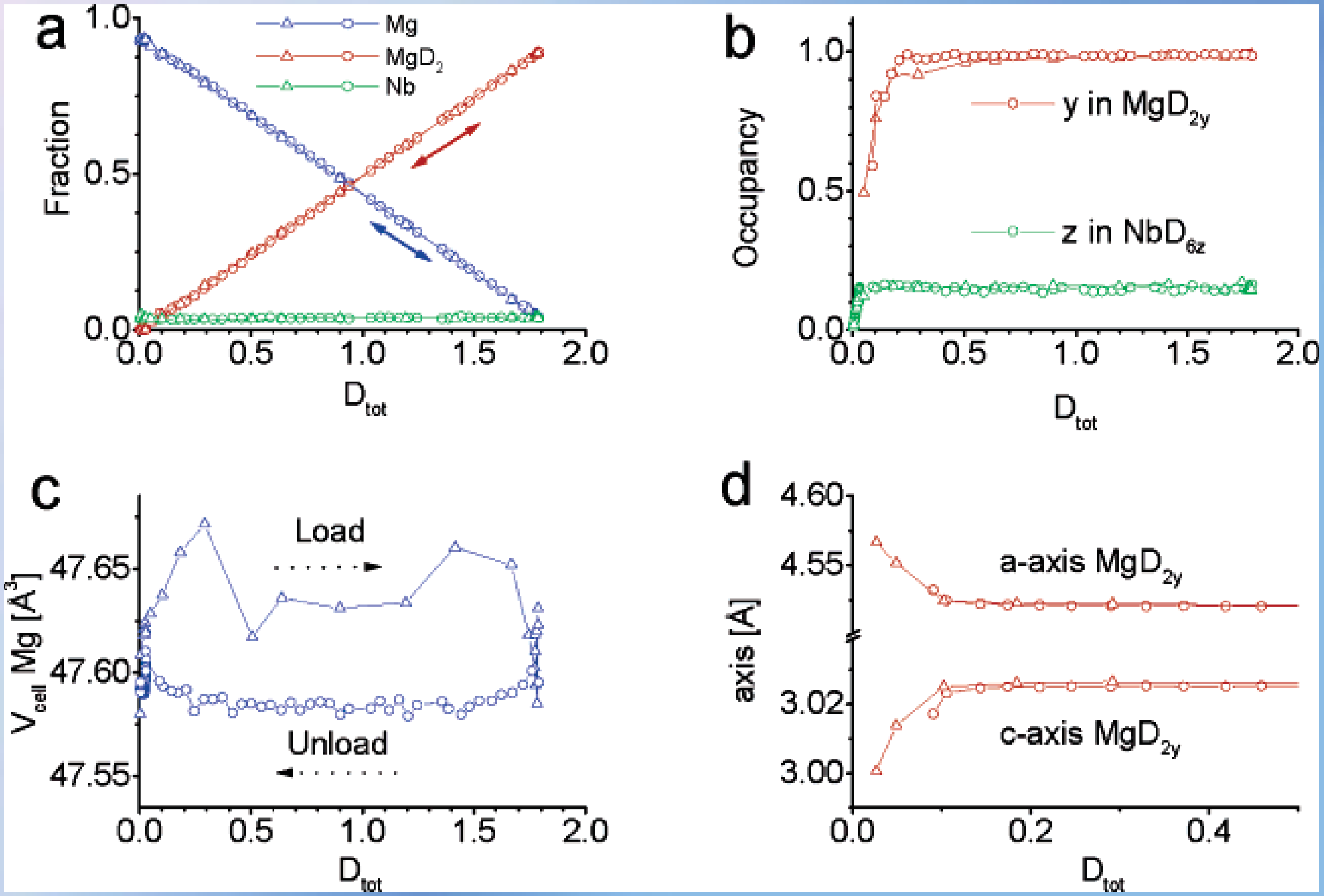
Loading (Δ) and unloading (O) of hydrogen as a function of hydrogen content D_{tot}



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Observations

- The site occupancy y of deuterium in MgD_{2y} can be as low as about $y = 0.5$, much lower than its stoichiometric value $y = 1$ in the bulk

- Individual Mg particles start with deuteriding (hydriding) with substoichiometric composition $MgD_{0.3}$.

- Increases of Mg cell volume is due to temperature effect.

- When NbD*x* releases its deuterium, the MgD_2 has vanished already completely. ⇒ NbD is doing the catalytic hydrogen splitting

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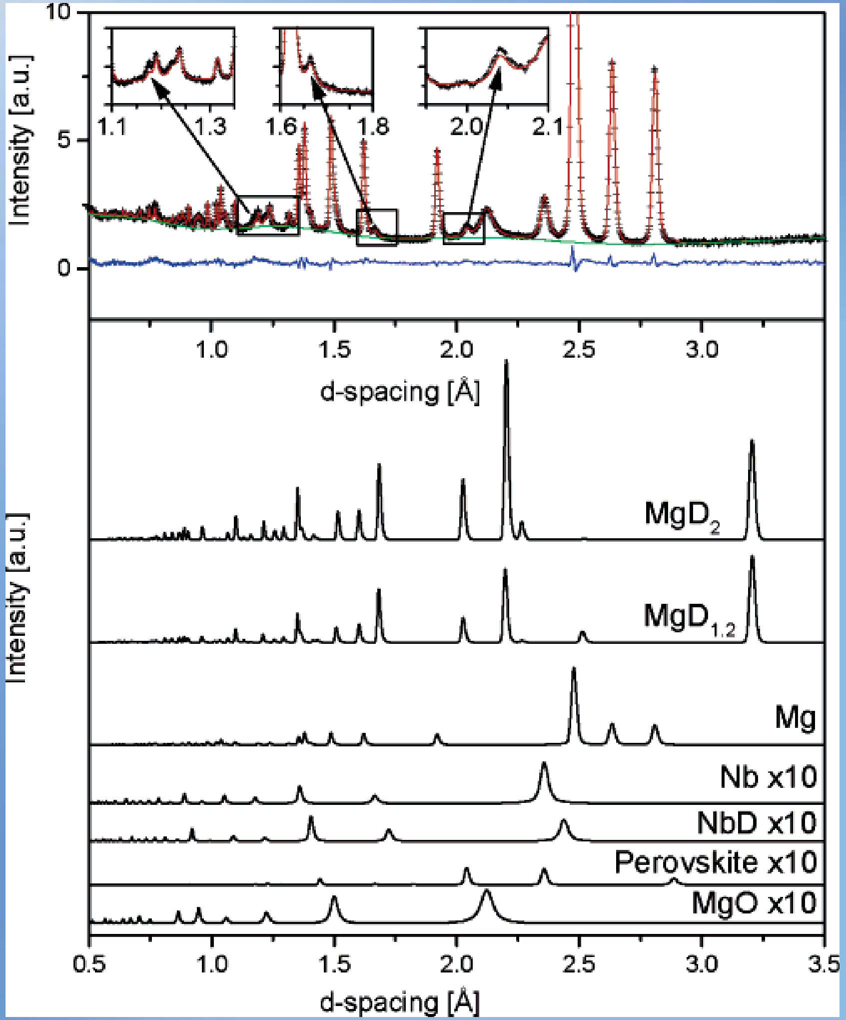
Rietveld refinement of the fully dehydrided sample.

The arrows indicate three unique peaks that belong to the perovskite phase



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Results

- Peaks could be indexed to a cubic perovskite phase with an estimated composition of $Nb-(Mg_{0.333}Nb_{0.667})O_3$
- This phase may also be catalytically active as well as proton transporting.
- During ball-milling process part of the Nb has been alloyed with the outer oxide layers of the Mg particles, leading to this perovskite phase
- Setting the molar amount of Mg to be100%, the sample contains 4% of Nb metal, 0.3% of $Nb(Mg_{0.333}Nb_{0.667})O_3$, and 7% of MgO

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Effect of nanostructure

From peaks broadness crystallite sizes of Mg and MgD_2 are almost the same (150 nm)

⇒The hydride phase cannot form a closed shell around a Mg nucleus

⇒ Contrary to polycrystalline case, the hydride phase could not block the hydrogen diffusion to the unreacted particles.

⇒ Faster kinetics.

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Effect of nanostructure

It appears that substoichiometric nanostructured MgH_x ($x << 2$) exists, which is impossible in bulk MgH_2.

Such a hydrogen deficient phase likely exhibits a much faster diffusion of hydrogen due to the large concentration of vacancies

Reason for this occurence

Nanostructured particles may not easily accommodate two phases with a (moving) boundary between them, because of the relatively large energy penalty of the induced strains. In such cases transition phases with intermediate composition could be found.

Also:

Area of the boundary (its energy), scales with the square of the particle size.

Energy difference between intermediate and stoichiometric phases scales with the cube of the particle size

$\Rightarrow$ there exists a certain particle size below which the intermediate composition phase appears energetically favorable

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Mg-Pd system

Magnesium:

- High hydrogen storage capacity (7.6 wt.%)
- Temperature of operation too high
- Slow kinetics
- First hydrogenation (activation) very slow

Palladium:

- Good catalyst
- Protection against air exposure (thin films)
- Expensive

Mg_6Pd

- Lowest peritectic
- Synthesized by melting (>1070K)
- Disproportionation reversible reactions

- ✓ **Y. Kume and A. Weiss, Journal of the Less-Common Metals 136, (1987) 51.**
- ✓ **T. Yamada, J. Yin, and K. Tanaka, Materials Transactions JIM 42 (11), (2001) 2415.**

Phase diagram

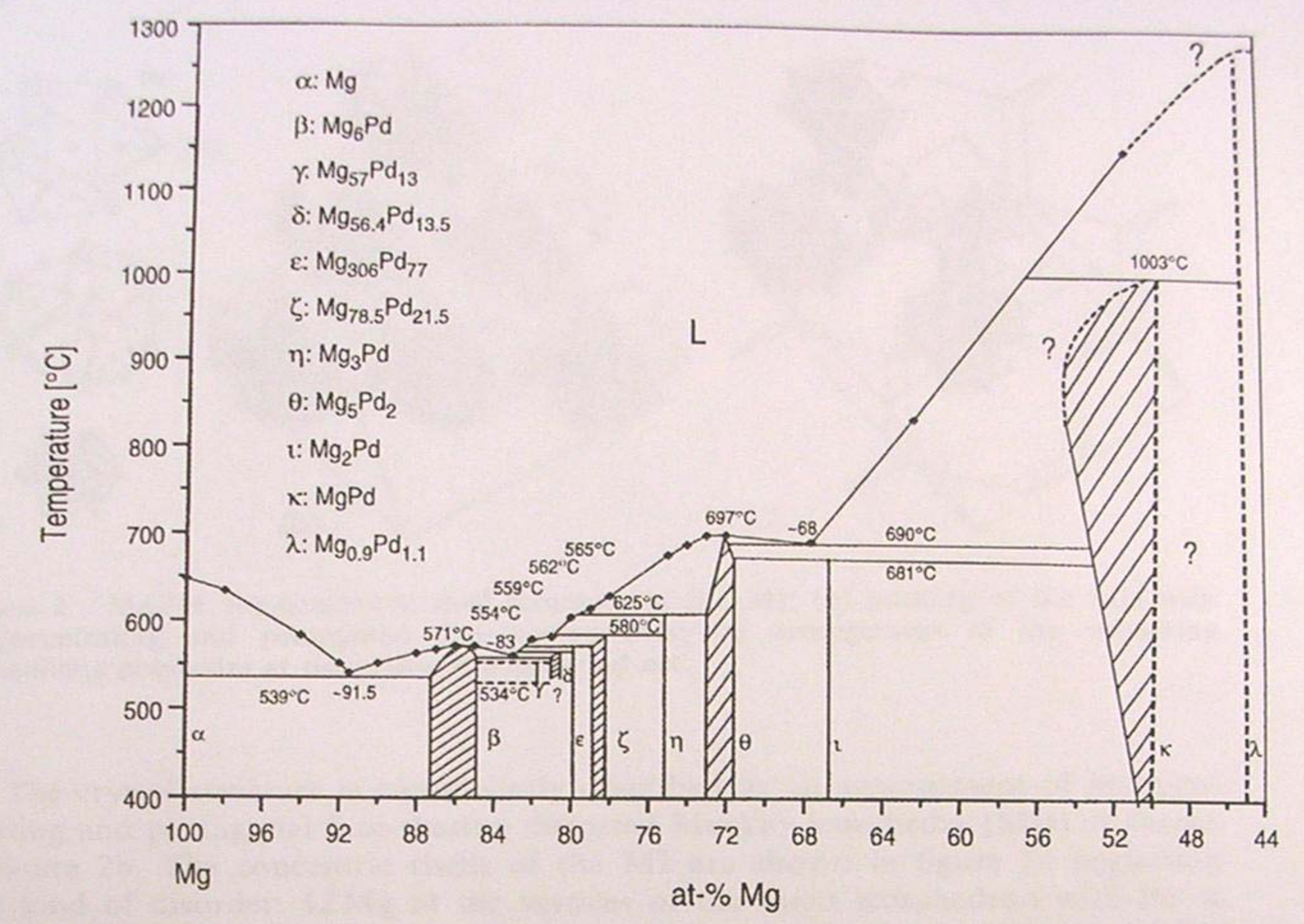


Figure 1. The Mg-rich part (44–100 at.% Mg) of the Mg–Pd phase diagram according to data from this study; only data points obtained from thermal analysis measurements are shown in the graph; the question marks and dashed lines indicate unresolved problems; phase labels are located in the Pd-rich two-phase fields.

J.P.A. Makongo et al., *Phil. Mag*. **86**(3-5), 427 (2006)

Mg_6Pd

Hydrogenation of Mg_6Pd is a three steps disproportionation reversible reactions.

$$2Mg_6Pd + 4.7H_2 \Leftrightarrow 2Mg_{3.65}Pd + 4.7MgH_2 \quad (1)$$

$$2Mg_{3.65}Pd + 4.7MgH_2 + 2.3H_2 \Leftrightarrow Mg_5Pd_2 + 7MgH_2 \quad (2)$$

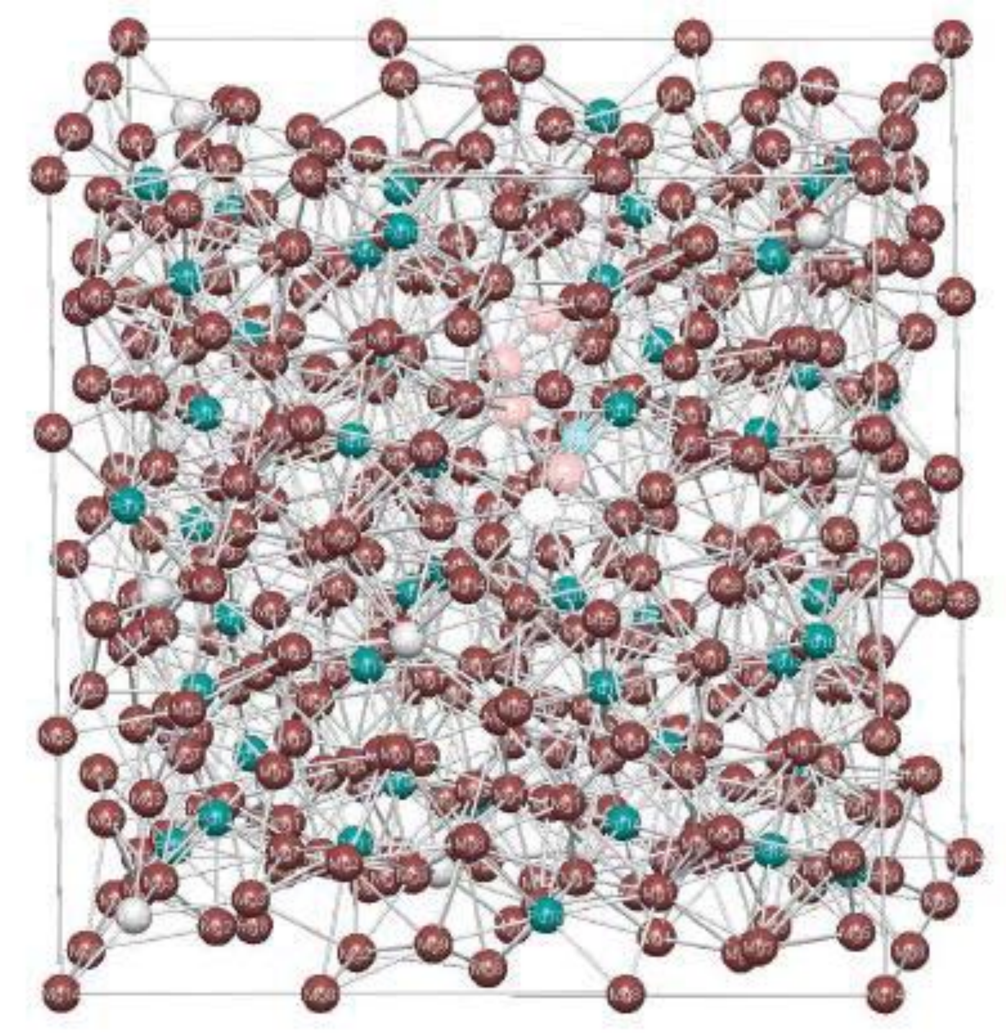
$$Mg_5Pd_2 + 7MgH_2 + 3H_2 \Leftrightarrow 2MgPd + 10MgH_2 \quad (3)$$

J. Dufour and J. Huot, JALCOM, 446-447, 147 (2007).
J. Dufour and J. Huot, JALCOM, 439, L5 (2007).

Crystal structures

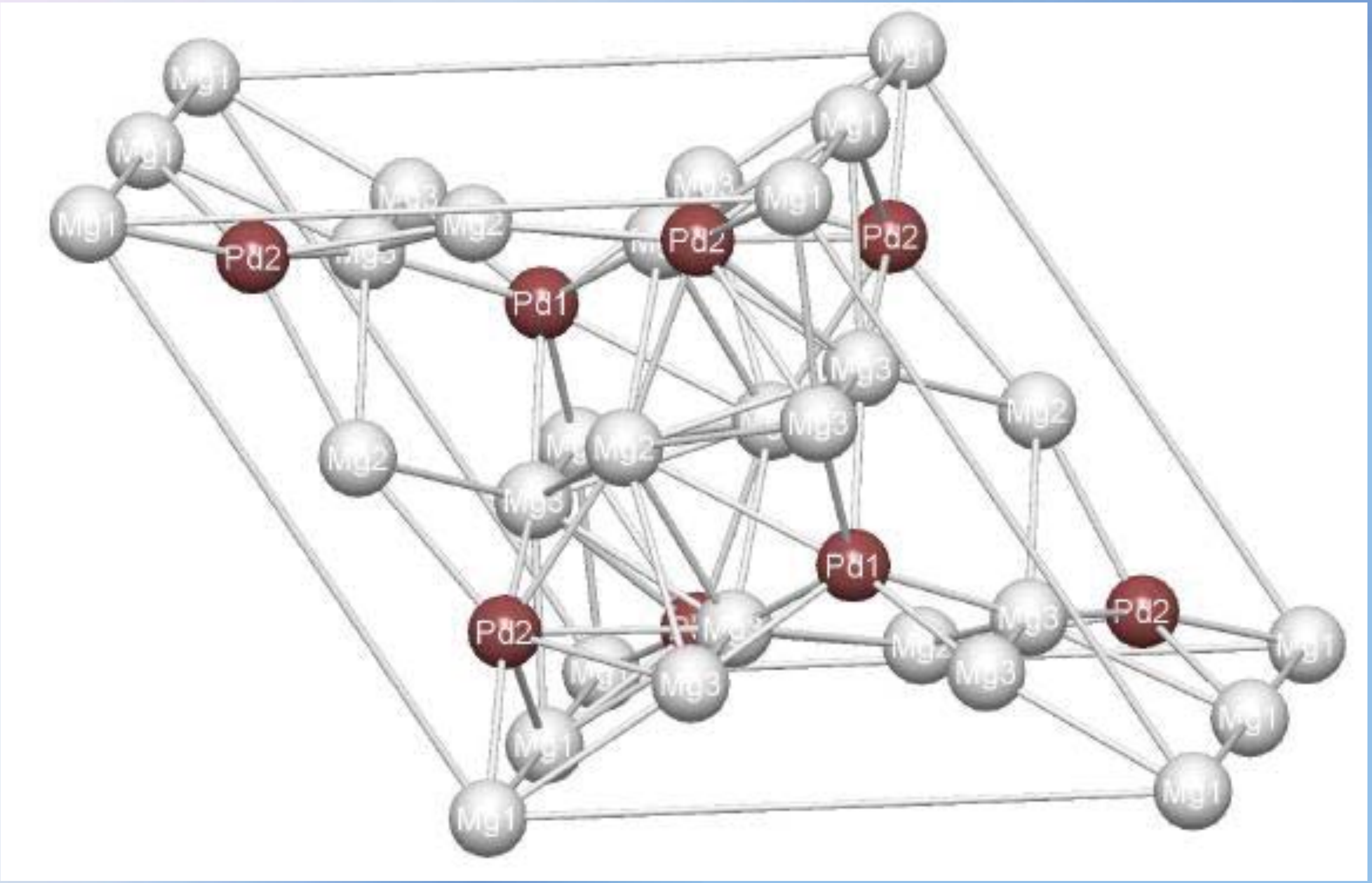
Phase	**Space Group**	**Lattice parameters**
Mg_6Pd	**F-43m**	**a = 20.108**
$Mg_{3.65}Pd$ **($Mg_{78.5}Pd_{21.5}$)**	**?**	**?**
Mg_5Pd_2	**$P6_3/mmc$**	**a = 8.6598** **c = 8.1688**
MgPd	**Pm-3m**	**a = 3.12**

Crystal structure Mg_6Pd



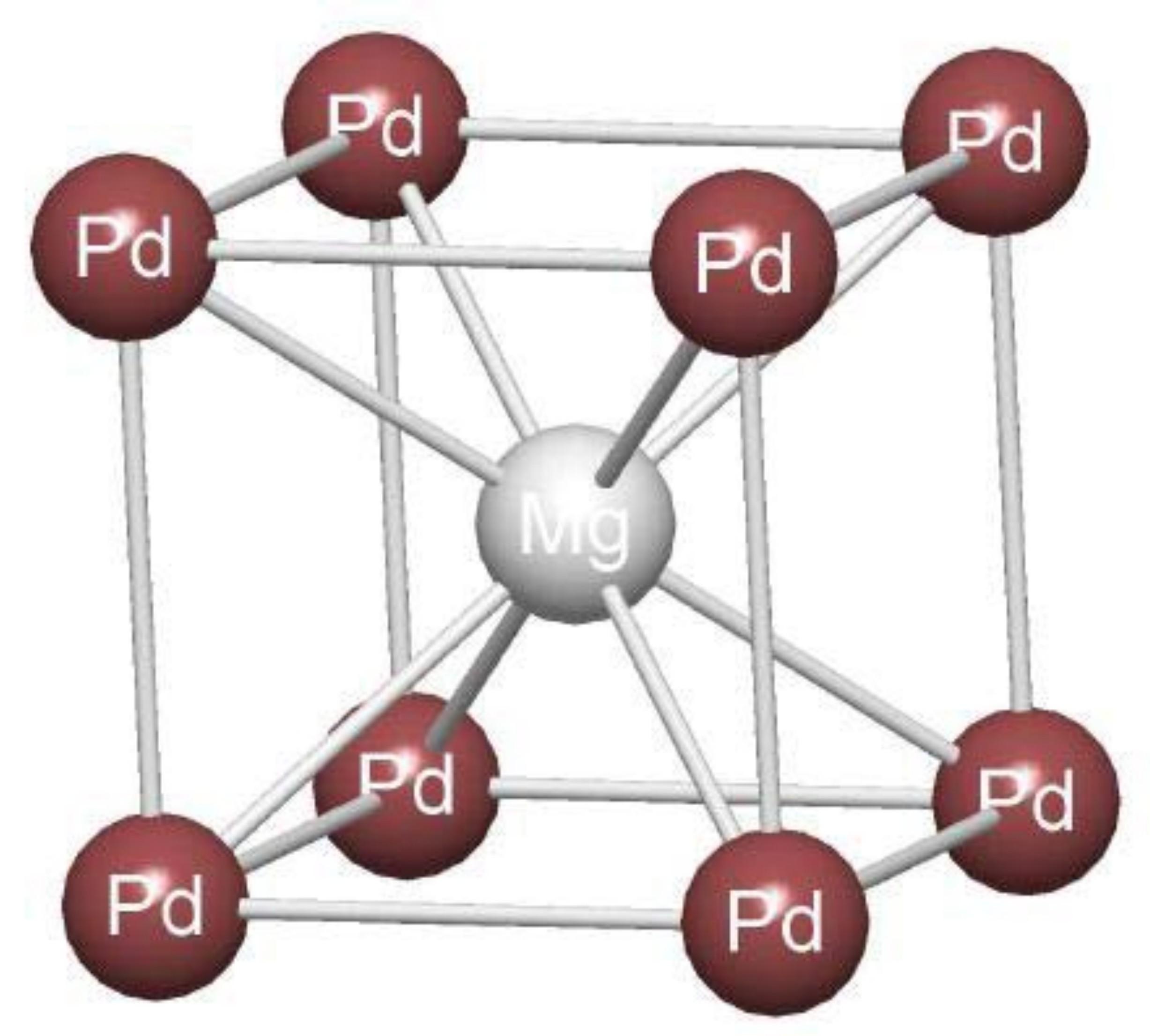
cF396

Crystal structure Mg_5Pd_2



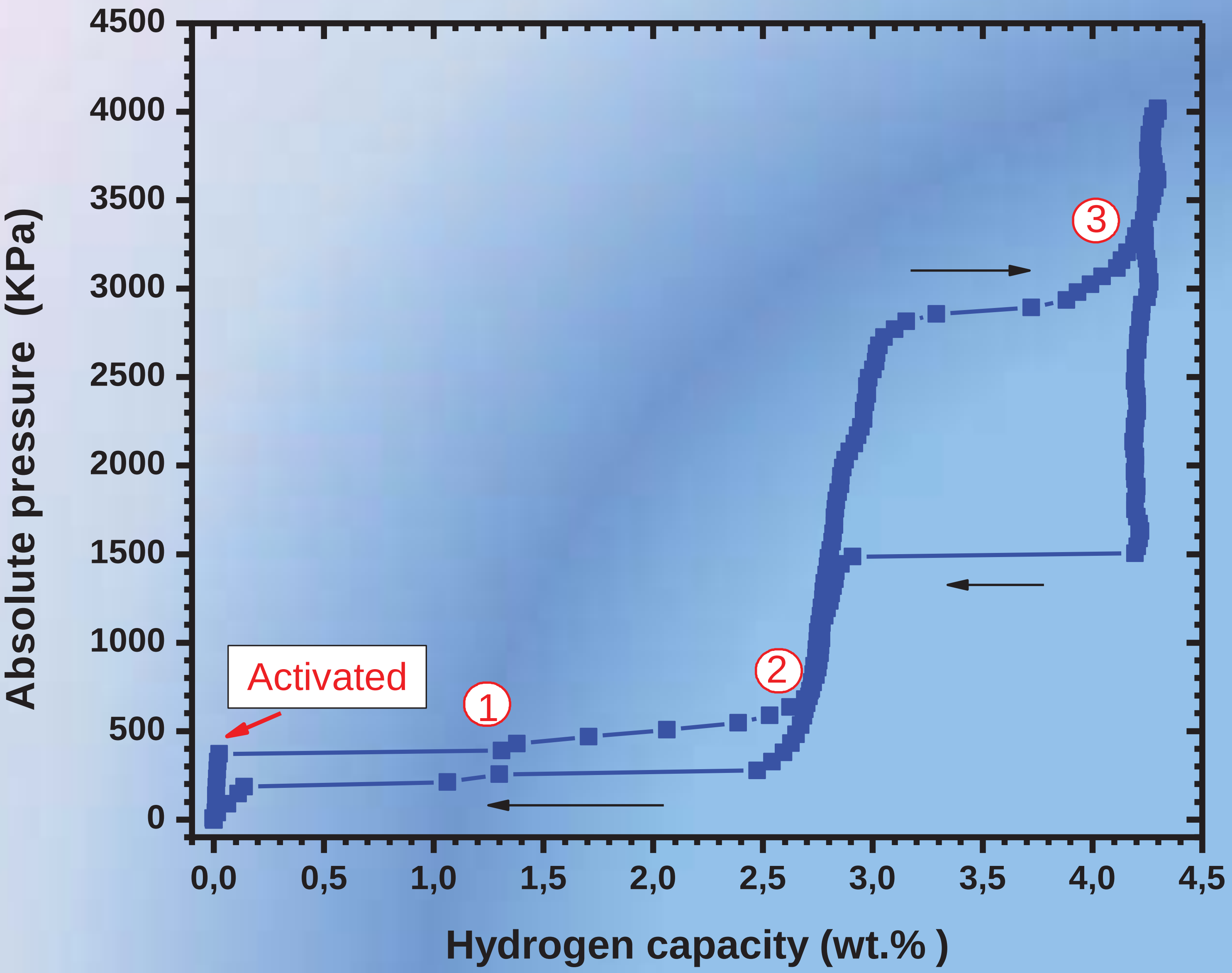
hP28

Crystal structure MgPd

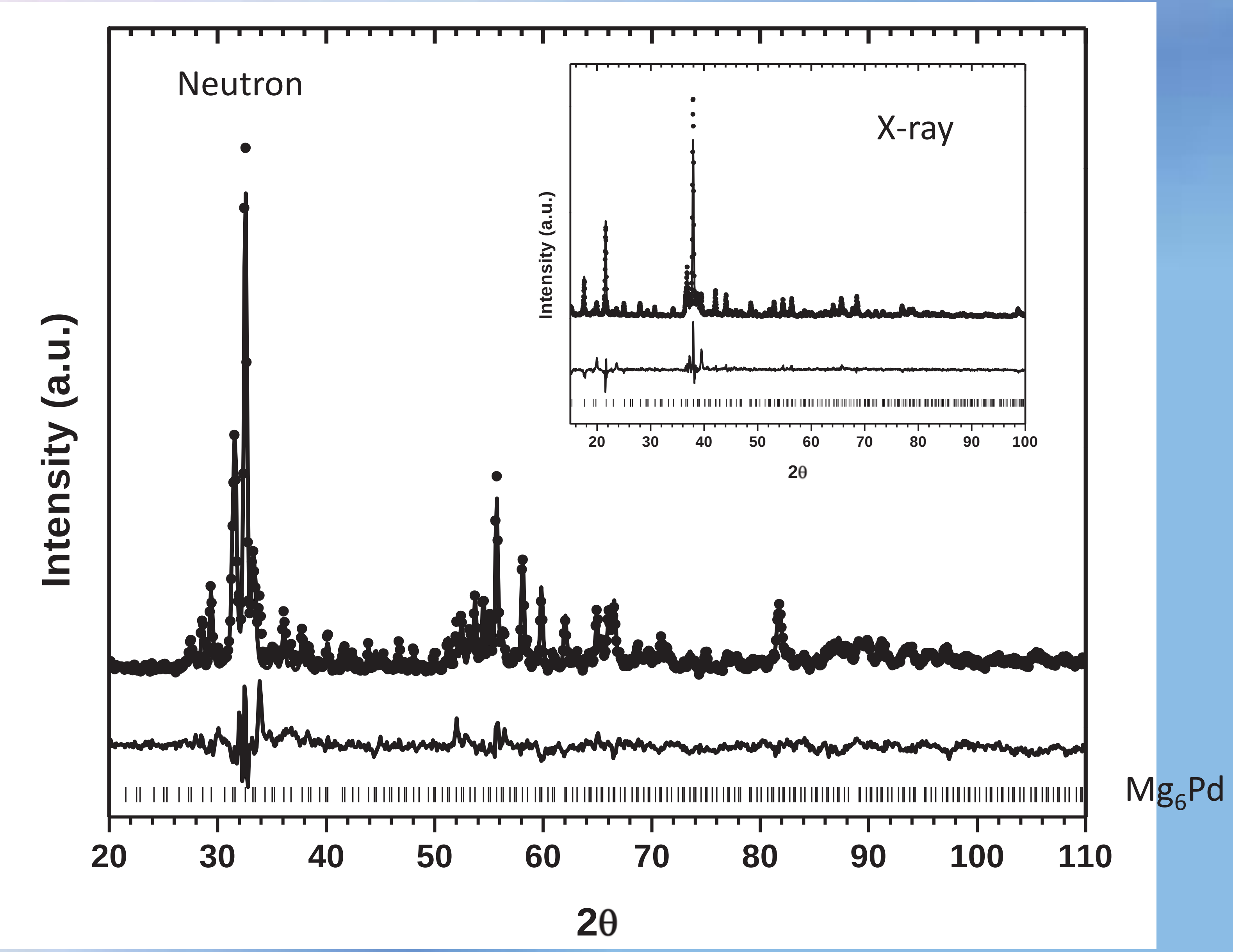


cP2

PCT 623 K


Absolute pressure (KPa)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Hydrogen capacity (wt.%)
0,0
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
Activated
①
②
③

Fully dehydrogenated



Mg_6Pd

Atom	Wyckoff position	Coordinates	U_{iso} (10^{-2} Å^2)
Pd	16*e*	(x, x, x) x = 0.1676(3)	0.06 (fixed)
Pd	16*e*	(x, x, x) x = 0.4063(2)	0.02 (fixed)
Pd	16*e*	(x, x, x) x = 0.9007(3)	1.1(2)
Pd	16*e* (occ = 0.324)	(x, x, x) x = 0.6690(8)	3.2 (fixed)
Mg	16*e* (occ = 0.676)	(x, x, x) x = 0.6690(8)	0.6(7)
Mg	4*d*	(3/4, 3/4, 3/4)	6(2)
Mg	16*e*	(x, x, x) x = 0. 1932(4)	0.4 (fixed)
Mg	24*f*	(x, 0, 0) x = 0.376(1)	2.4(5)
Mg	24*f*	(x, 0, 0) x = 0.104(1)	2.4(8)
Mg	24*g*	(x, 1/4, 1/4) x = 0.053(1)	0.4(4)
Mg	48*h*	(x, x, z) x = 0.1493(7) z = 0.033(1)	2.9(4)
Mg	48*h*	(x, x, z) x = 0.0932(5) z = 0.2702(7)	0.9(3)
Mg	48*h*	(x, 2x, z) x = 0.1478(7) z = 0.528(1)	1.0(5)
Mg	48*h*	(x, x, z) x = 0.0550(4) z = 0.7647(8)	1.2(4)
Mg	48*h*	(x, x, z) x = 0.2018(6) z = 0.9111(9)	2.9(5)

U_{iso} parameters for magnesium atoms could be divided in two groups:

148 Mg atoms with $U_{iso} > 2 \times 10^{-2}$ Å^2
194.82 Mg atoms with $U_{iso} < 2 \times 10^{-2}$ Å^2

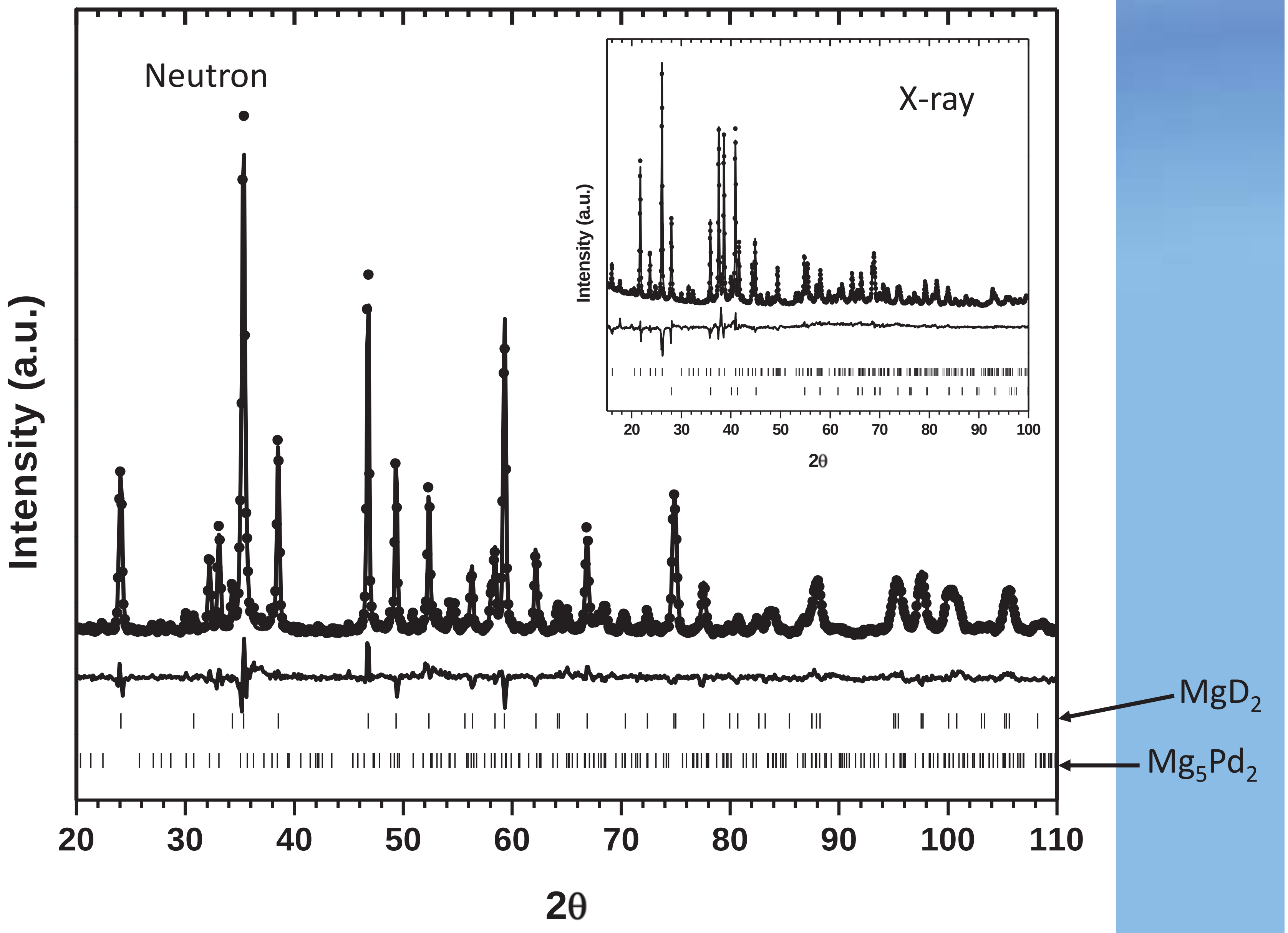
Number of Pd atoms in the unit cell: 53.18

Ratio 194.82/53.18 = 3.66

Ratio of magnesium and palladium atoms of the alloy $Mg_{78.5}Pd_{21.5}$ is 3.65!

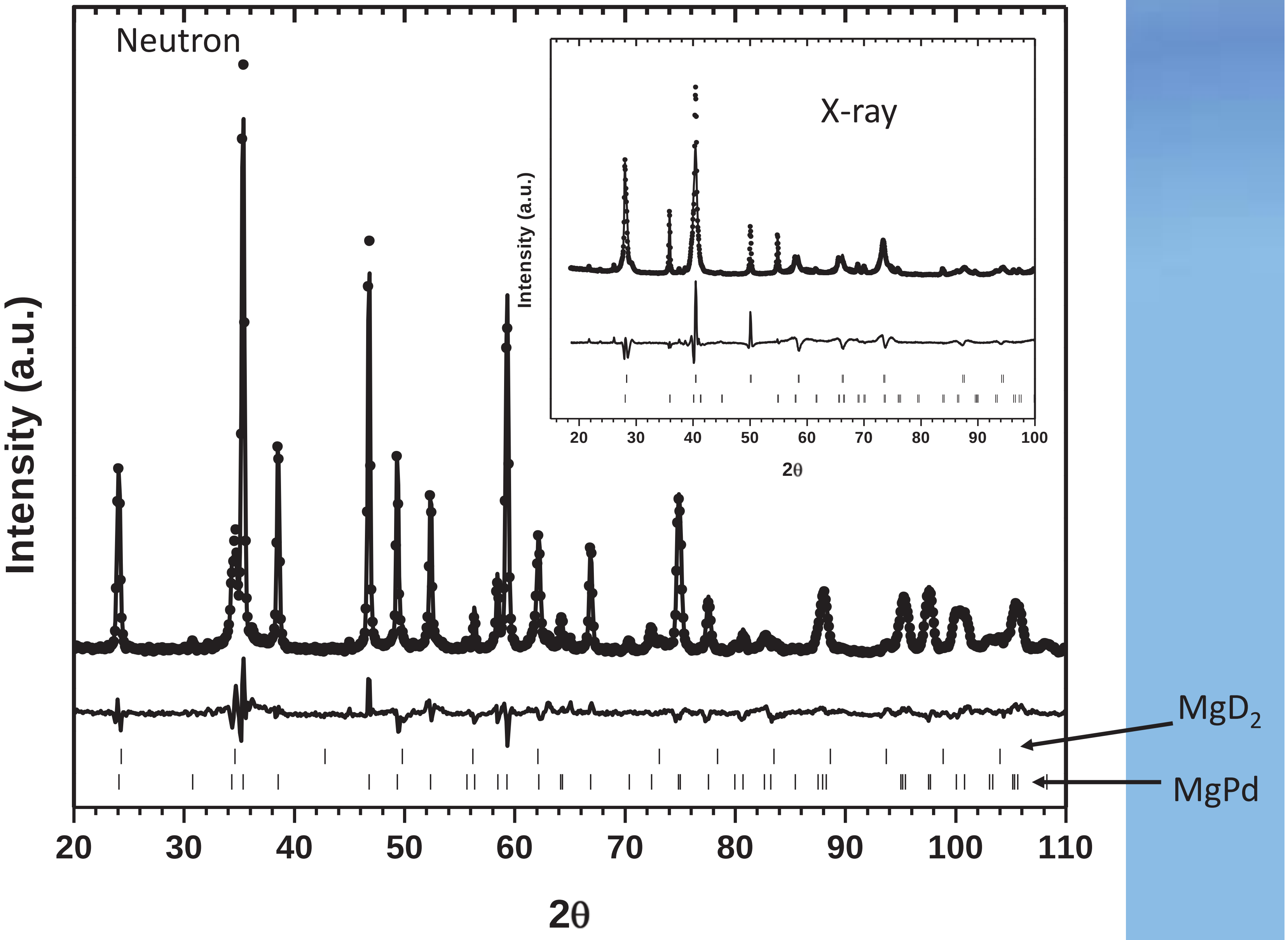
Is it just coincidence?

Reaction 2 products.



Atom	Wyckoff position	Coordinates	U_{iso} (10^{-2} Å^2)
Mg_5Pd_2: Space group: $P6_3/mmc$ (194); *a* = 8.6735(5) Å; *c* = 8.1745(7) Å ; V =532.57(6) Å^3			
Pd	2*d*	(1/3, 2/3, 1/4)	1.3(3)
Pd	6*h*	(x, 2x, 1/4) x = 0.1223(3)	0.7(1)
Mg	2*a*	(0, 0, 0)	0.3(3)
Mg	6*h*	(x, 2x, 1/4) x = 0.4585(6)	0.9(2)
Mg	12*k*	(x, 2x, z) x = 0.1932(4) z = 0.9400(7)	2.2(2)
MgD_2: Space group: $P4_2/mnm$ (136); *a* = 4.5029(1) Å; *c* = 3.0126(1) Å ; V =61.084(5) Å^3			
Mg	2*a*	(0, 0, 0)	1.31(4)
D	4*f*	(x, x, 0) x = 0.3040(2)	2.17(3)
R-factors: PND: R_{wp}=5.69%; R_p=4.33%; XRD: R_{wp}=11.78%; R_p=8.73%; Combined: R_{wp}=6.04%; R_p=4.50%; χ^2 = 2.905			

Reaction 3 products



Third plateau

Atom	**Wyckoff position**	**Coordinates**	**U_{iso} (10^{-2} Å^2)**
MgPd: **Space group: $Pm\text{-}\bar{3}mc$ (221); *a* = 3.1570(3) Å; V =31.46(1) Å^3**			
Mg	**1*a***	**(0, 0, 0)**	**2.4(3)**
Pd	**1*b***	**(1/2, 1/2, 1/2)**	**1.7(2)**
MgD_2: **Space group: $P4_2/mnm$ (136); *a* = 4.5036(1) Å; *c* = 3.0127(1) Å ; V =61.106(6) Å^3**			
Mg	**2*a***	**(0, 0, 0)**	**1.21(4)**
D	**4*f***	**(x, x, 0)** **x = 0.3043(2)**	**2.19(3)**
R-factors: **PND: R_{wp}=5.86%; R_p=4.47%; XRD: R_{wp}=21.29%; R_p=16.55%;** **Combined: R_{wp}=6.72%; R_p=4.78%; χ^2 = 5.695**			

Phase abundances in wt.% as determined from Rietveld refinements and calculated from reactions 2 and 3.

Reaction	Phases	Neutron	X-ray	Calc
2	Mg_5Pd_2	65.8(4)	60.0(4)	63
	MgD_2	34.2(2)	40.0(9)	37
3	MgPd	48(1)	48.3(6)	48
	MgD_2	52.2(2)	52(1)	52

Crystallite sizes and strains as determined from Rietveld refinements of neutron patterns.

Reaction	Alloy	Crystallite size (nm)	Strain (%)
Activated	Mg_6Pd	61(3)	---
2	Mg_5Pd_2	79(6)	0.4(1)
3	MgPd	46(10)	1.92(2)

Crystallite sizes and strains of MgD_2 as determined from Rietveld refinements of neutron diffraction patterns.

Reaction	Crystallite size (nm)	Strain (%)
2	99(3)	0.31(3)
3	119(5)	0.38(2)

Conclusion

Confirmation of end products for reactions (2) and (3).

For each reaction, magnesium atoms with high values of thermal parameters seem to be the ones that form magnesium hydride upon hydrogenation.

High hysteresis in the pressure–composition–temperature curve may be related to the important level of strain in the magnesium hydride phase.

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Effect of iron on the hydriding properties of the Mg_6Pd hydrogen storage system

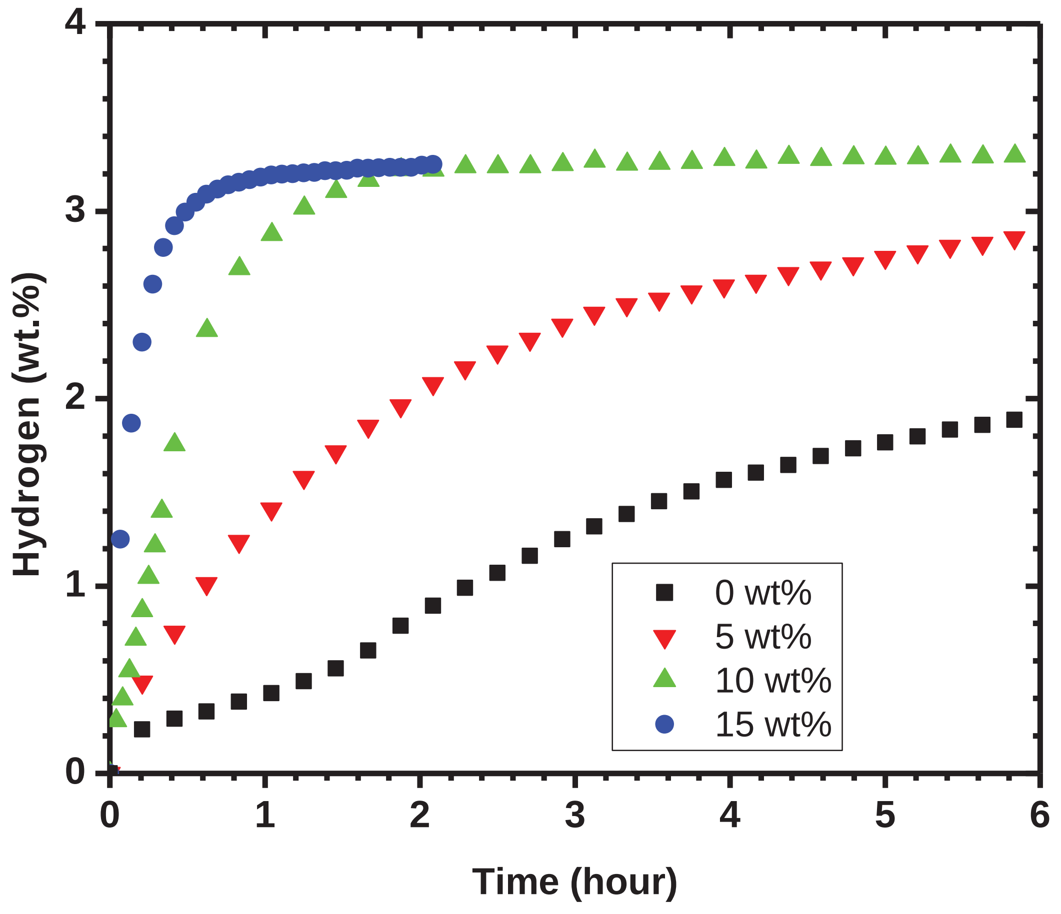
J.-G. Roquefere[a], *J. Lang*[a], *A. Yonkeu*[b,1], *J. Dufour*[a], *J. Huot*[a,*]

[a]Institut de Recherche sur l'Hydrogène, Université du Québec à Trois-Rivières, 3351 Boul. des Forges, Trois-Rivières, Québec, Canada G9A 5H7
[b]Canadian Neutron Beam Centre, National Research Council of Canada, Building 459, Station 18, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0

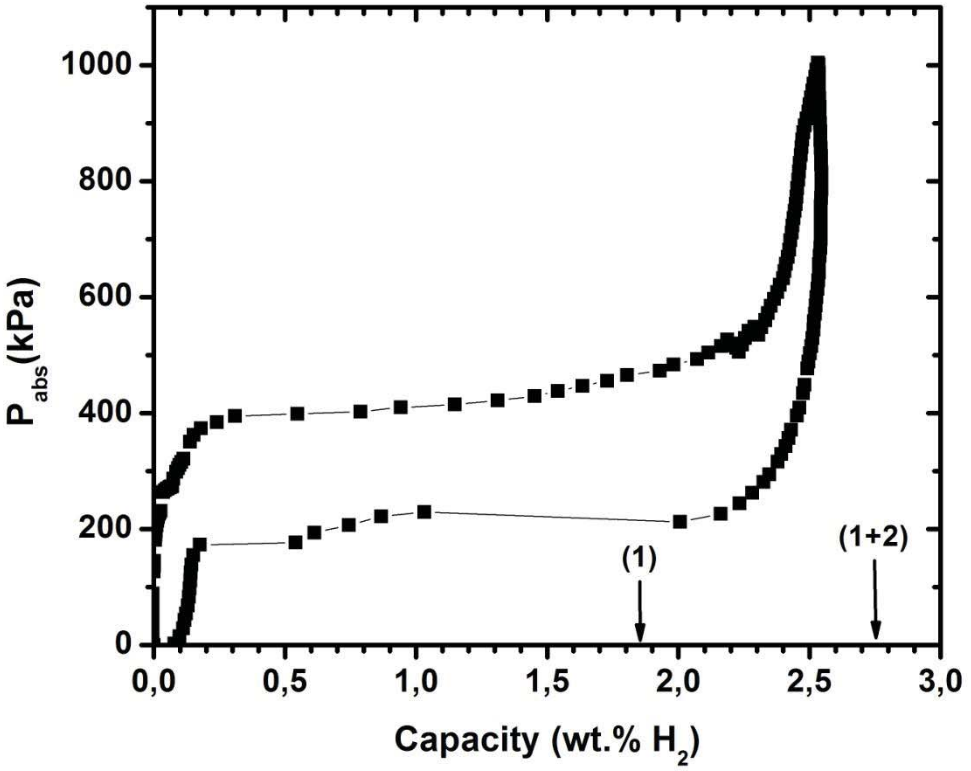
Alloys prepared by ball milling ⇒ possible contamination by iron

Could iron be a catalyst for Mg_6Pd ?

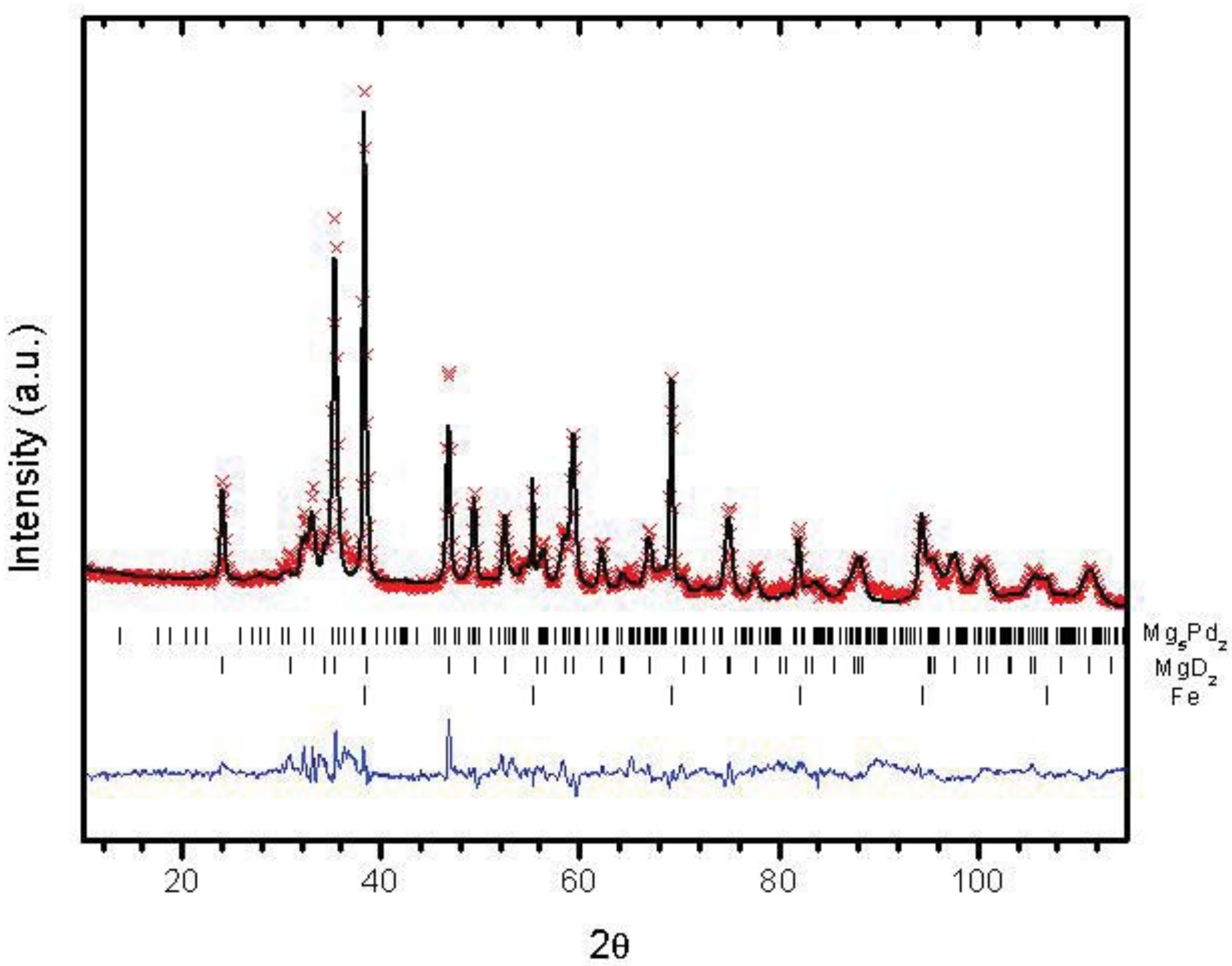
First hydrogenation (activation) kinetics of Mg_6Pd + x wt.% Fe (x = 0, 5, 10, 15) at 573K under 2 MPa of hydrogen.



Pressure-Composition-Isotherm of Mg_6Pd + Fe at 573 K. Arrow marked (1) indicates the theoretical capacity of reaction (1). Arrow marked (2) indicates the theoretical capacity of reactions (1) and (2).



PND pattern and Rietveld refinement on the products of reaction (2).



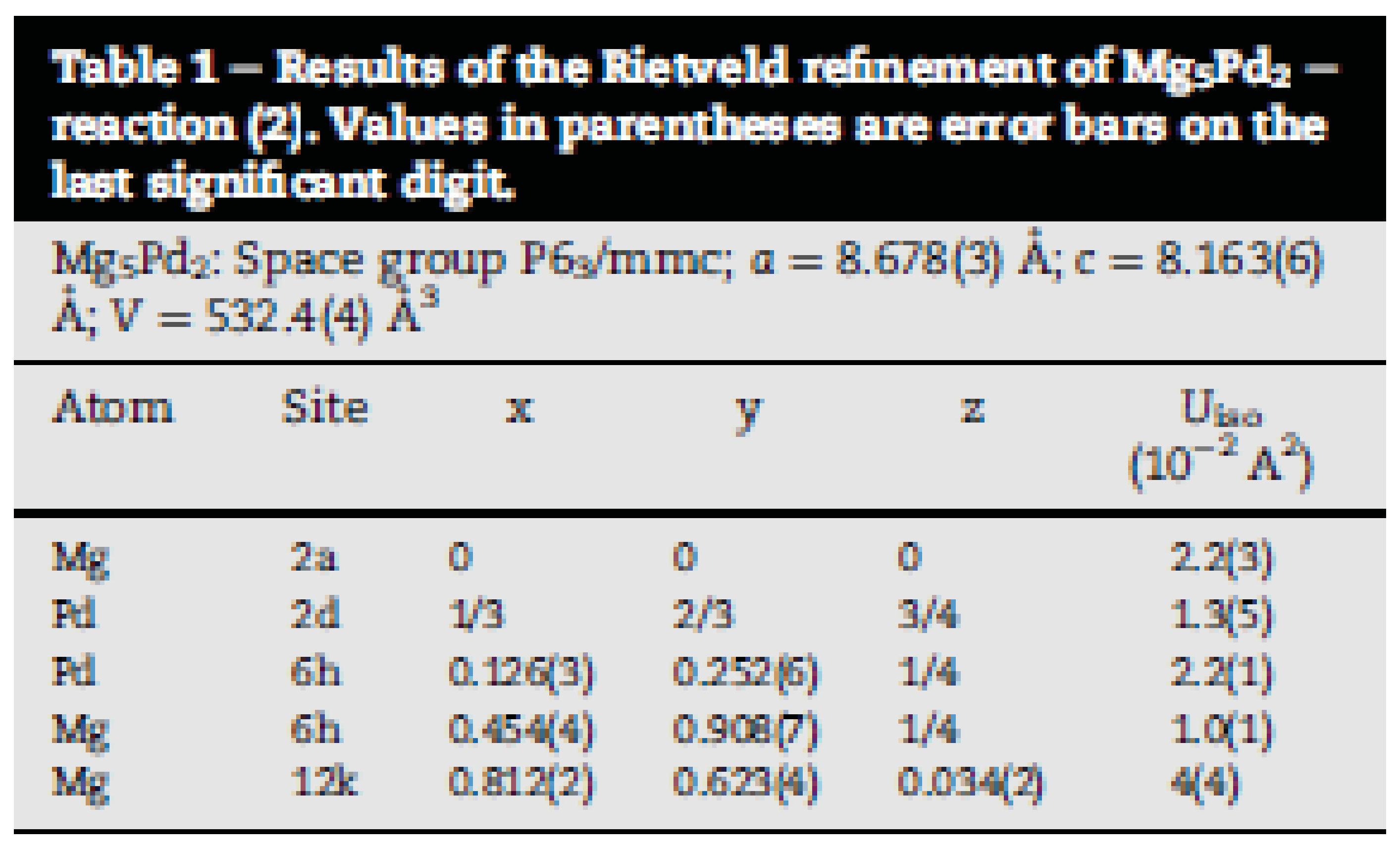
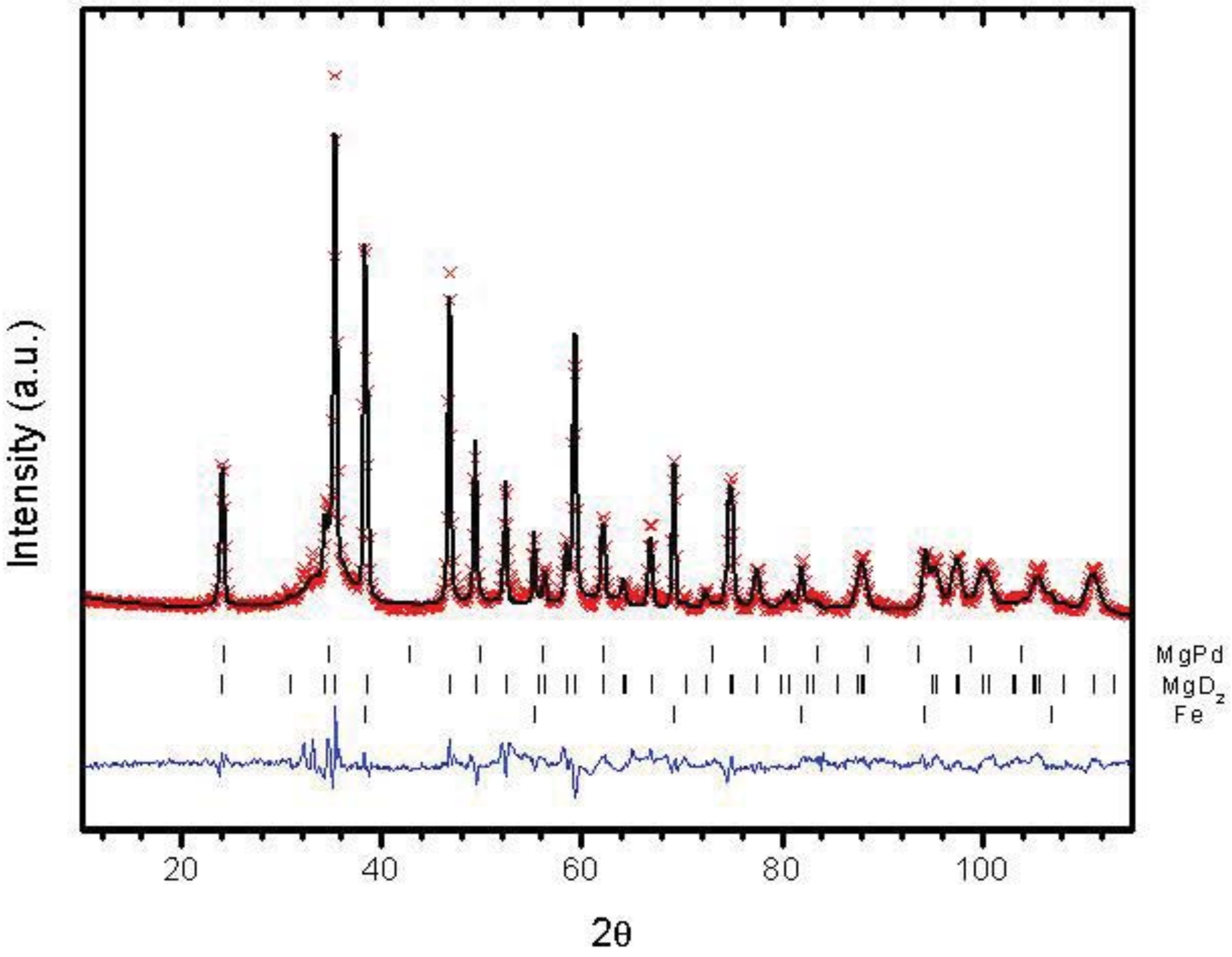


Table 1 – Results of the Rietveld refinement of Mg_5Pd_2 – reaction (2). Values in parentheses are error bars on the last significant digit.

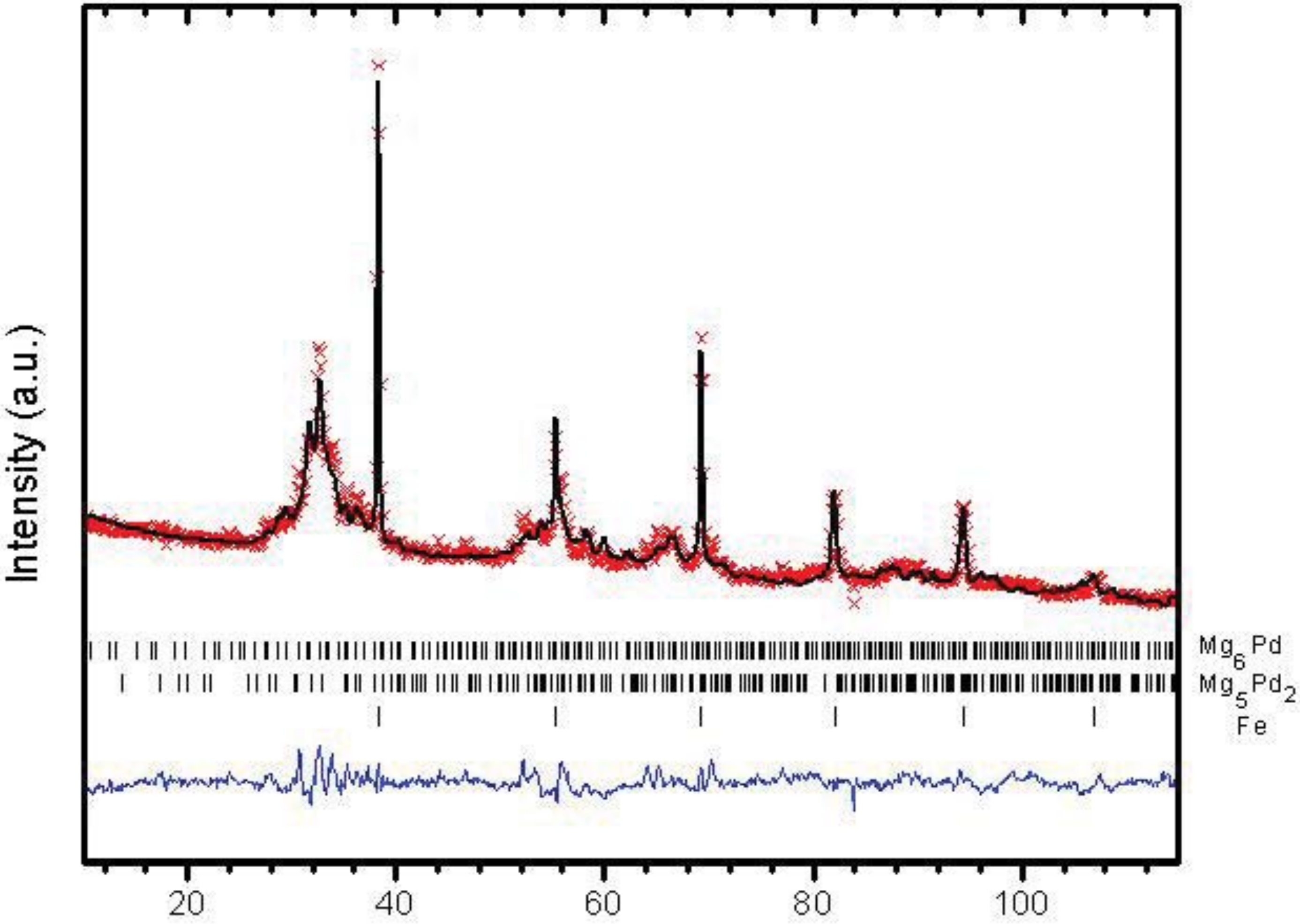
Mg_5Pd_2: Space group $P6_3/mmc$; $a = 8.678(3)$ Å; $c = 8.163(6)$ Å; $V = 532.4(4)$ Å^3

Atom	Site	x	y	z	U_{iso} (10^{-2} Å^2)
Mg	2a	0	0	0	2.2(3)
Pd	2d	1/3	2/3	3/4	1.3(5)
Pd	6h	0.126(3)	0.252(6)	1/4	2.2(1)
Mg	6h	0.454(4)	0.908(7)	1/4	1.0(1)
Mg	12k	0.812(2)	0.623(4)	0.034(2)	4(4)

PND pattern and Rietveld refinement on the products of reaction (3).



PND pattern and Rietveld refinement on the products of the system fully desorbed.



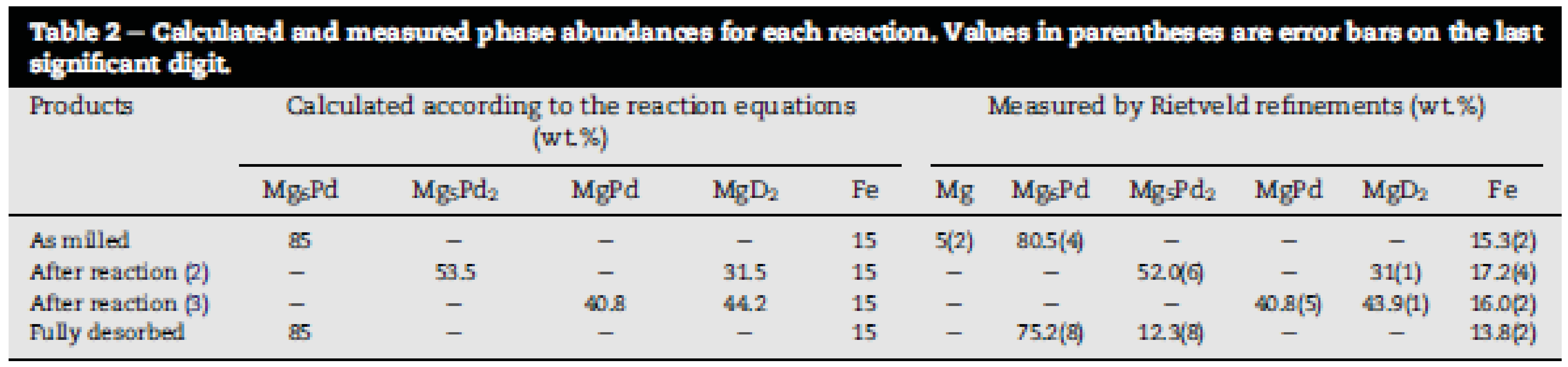


Table 2 – Calculated and measured phase abundances for each reaction. Values in parentheses are error bars on the last significant digit.

Products	Calculated according to the reaction equations (wt.%)					Measured by Rietveld refinements (wt.%)					
	Mg_6Pd	Mg_5Pd_2	MgPd	MgD_2	Fe	Mg	Mg_6Pd	Mg_5Pd_2	MgPd	MgD_2	Fe
As milled	85	–	–	–	15	5(2)	80.5(4)	–	–	–	15.3(2)
After reaction (2)	–	53.5	–	31.5	15	–	–	52.0(6)	–	31(1)	17.2(4)
After reaction (3)	–	–	40.8	44.2	15	–	–	–	40.8(5)	43.9(1)	16.0(2)
Fully desorbed	85	–	–	–	15	–	75.2(8)	12.3(8)	–	–	13.8(2)

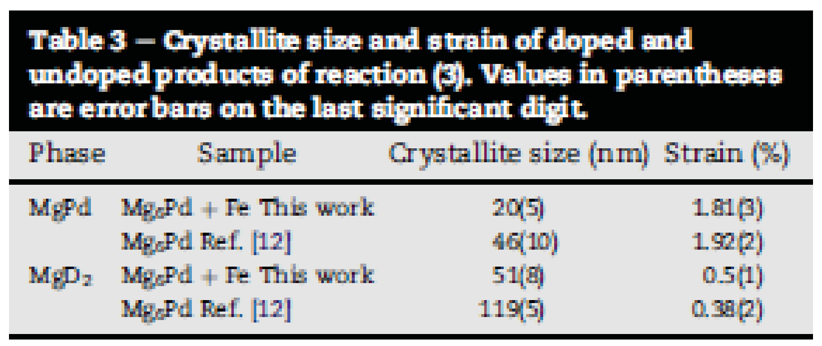


Table 3 – Crystallite size and strain of doped and undoped products of reaction (3). Values in parentheses are error bars on the last significant digit.

Phase	Sample	Crystallite size (nm)	Strain (%)
MgPd	Mg_6Pd + Fe This work	20(5)	1.81(3)
	Mg_6Pd Ref. [12]	46(10)	1.92(2)
MgD_2	Mg_6Pd + Fe This work	51(8)	0.5(1)
	Mg_6Pd Ref. [12]	119(5)	0.38(2)

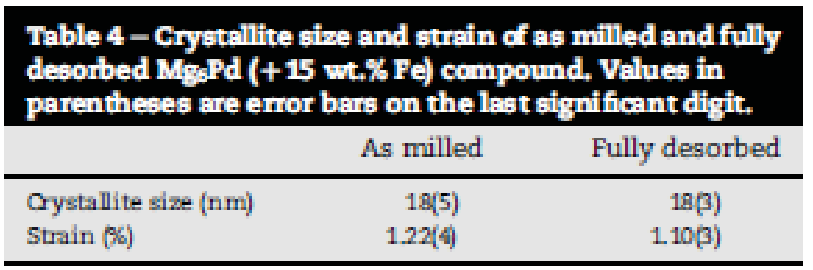
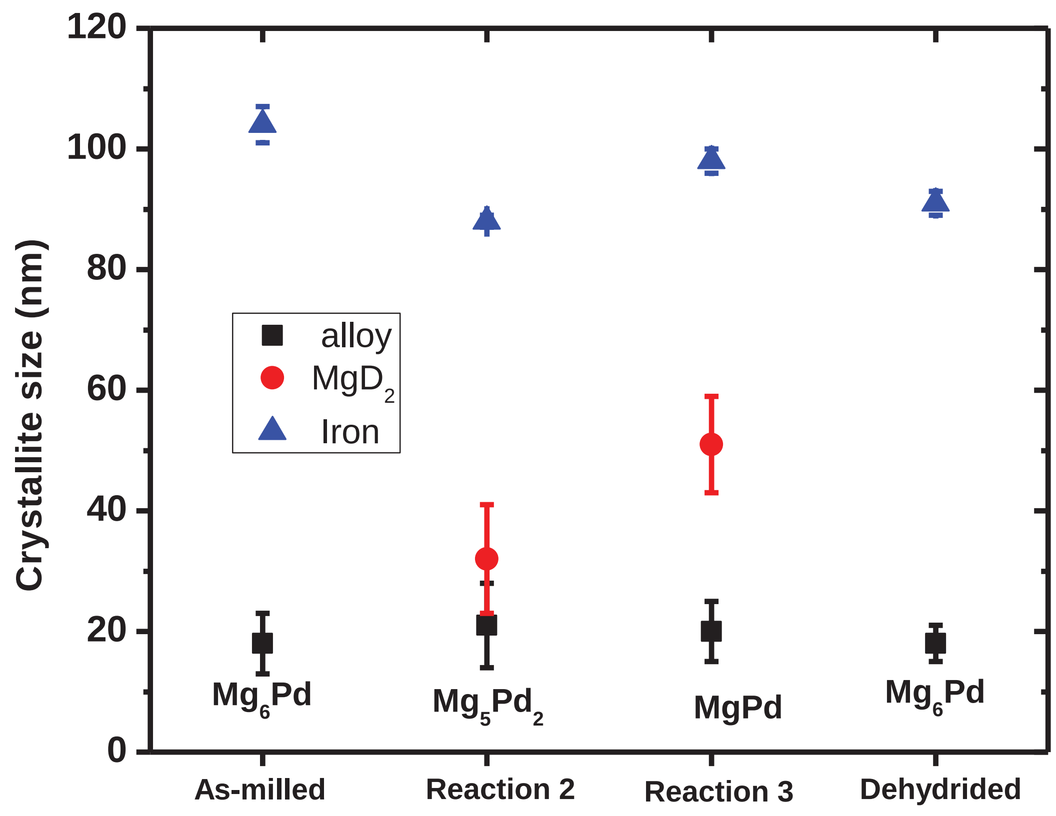


Table 4 – Crystallite size and strain of as milled and fully desorbed Mg_6Pd (+15 wt.% Fe) compound. Values in parentheses are error bars on the last significant digit.

	As milled	Fully desorbed
Crystallite size (nm)	18(5)	18(3)
Strain (%)	1.22(4)	1.10(3)

Crystallite size of each phase as a function of the hydriding reaction.



Conclusion

- Addition of iron drastically modifies both hydriding properties and structural properties of the Mg6Pd system.

- Presence of iron seems to reduce the crystallite size of alloys and hydride phases

Neutron diffraction

Neutron diffraction played a crucial role in the understanding of metal hydrides and will remain a privileged tool for the development of new metal hydrides for practical applications.

Université du Québec à Trois-Rivières