

Structural and thermodynamic studies of some hydride forming RM_3 -type compounds (R=lanthanide, M=transition metal)

M. Latroche*, A. Percheron-Guégan

LCMTR, UPR209, ISCSA, CNRS, 2 Rue H. Dunant, 94320 Thiais Cedex, France

Received 28 August 2002; accepted 6 December 2002

Abstract

Intermetallic compounds RM_n (R=rare earth or transition metal, M=transition metal, $n=1, 2$ or 5) are able to store reversibly large amounts of hydrogen and are potential materials for energy storage either by solid–gas or electrochemical routes. Beside these compounds, relatively few works have been devoted to RM_3 compounds since the binary compounds exhibit rather low reversible capacities. New interests for this stoichiometry appear recently with ternary systems R–Mg–Ni (R=Lanthanide, Ca or Y) within the atomic composition 1:2:9. These compounds crystallise in an ordered variant of the $PuNi_3$ -type rhombohedral structure ($R\bar{3}m$ space group) and can be described as a stacking of RNi_5 (Häücke phase) and $MgNi_2$ (Laves phase) units. In this paper, we will review the different structural and thermodynamic properties of RM_3 -type compounds. Recent results on new ternary systems will be presented and discussed in relation with other systems.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; Intermetallics; Gas–solid reactions; Crystal structure and symmetry; X-Ray diffraction; Neutron diffraction

1. Introduction

According to the problems induced by the shortage of fossil energy and global warming, hydrogen is expected to be a promising energy vector for the near future. Its main interests are related to its important chemical energy per mass (142 MJ kg^{-1}) and its clean exhausts when used as a fuel. However, in order for hydrogen to become a viable solution to the environmental problems, storage processes must be improved in terms of specific capacity and security. Among the different ways to store hydrogen, absorption in solid is very attractive since it allows safe storage at pressure and temperature close to ambient conditions. However, weight capacities are still low for practical applications and many efforts are conducted worldwide to develop materials with improved performances regarding energy density.

A large number of metals and alloys are able to absorb large quantities of hydrogen. Among them, intermetallics RM_n (R=rare earth or transition metals, M=transition metal, $n=1, 2$ or 5) have been particularly studied in the past for both solid–gas and electrochemical energy stor-

age. On one hand, RM_5 -type compounds are now close to achievement despite some improvements still needed in terms of kinetics and cycle life. On the other hand, despite lighter molar mass and larger weight capacities, RM_2 - and RM -type alloys suffer from passivation, slow activation and corrosion in electrochemical medium. In between, relatively few works have been devoted to RM_3 compounds since these binary compounds exhibit rather low reversible capacities. However, new interests have been devoted to this compound family with the recent discovery of new pseudo-binary and ternary compounds involving lighter elements like Mg or Ca. In this paper, we will review the crystallographic and thermodynamic properties of this RM_3 family.

2. Binary systems

Binary compounds RM_3 with M=Fe, Co and Ni exists for most rare earths (except Pm and Eu) and Y. They crystallize either in the rhombohedral structure of $PuNi_3$ -type ($R\bar{3}m$ space group) [1] or in the hexagonal $CeNi_3$ -type structure ($P6_3/mmc$ space group) which differ only in the long range stacking arrangement. The $PuNi_3$ -type structure is trigonal but is commonly described in a hexagonal cell

*Corresponding author. Fax: +33-1-4978-1203.

E-mail address: michel.latroche@givt-cnrs.fr (M. Latroche).

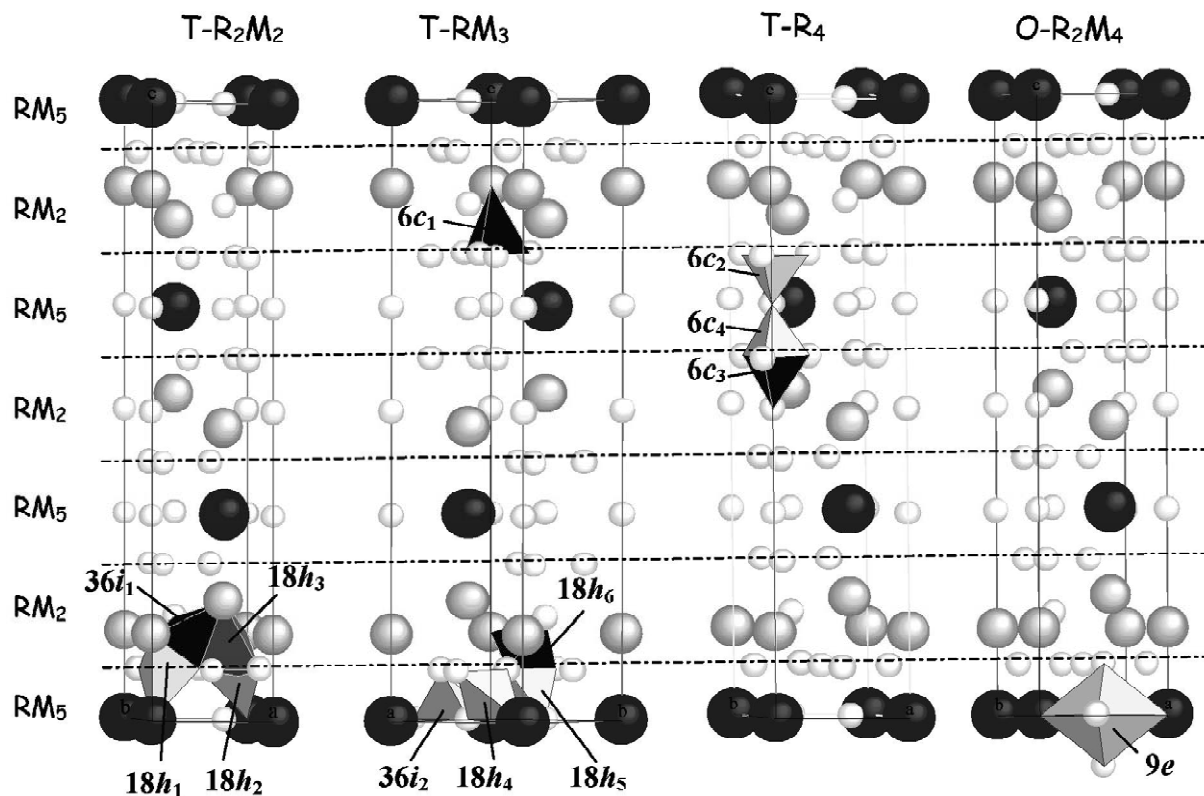


Fig. 1. PuNi_3 -type rhombohedral crystal structure (space group $R\bar{3}m$) in hexagonal description showing the stacking of RM_5 and RM_2 units along the c -axis. R atoms lying on sites $3a$ and $6c$ are colored in black and light-grey, respectively. Nickels are shown as small white spheres. The four types of hydrogen sites are shown as tetrahedrons (R_2M_2 , RM_3 and R_4) and octahedron (R_2M_4) within the metallic structure and are labeled according to Table 1.

as shown in Fig. 1. It consists of a stacking of different blocks along the c -axis. From this point of view, the structure can be seen as an intergrowth between RM_5 and RM_2 units following the scheme: $\text{RM}_5 + 2\text{RM}_2 = 3\text{RM}_3$ [2]. It is worth noting that in the hexagonal description of the PuNi_3 structure, there are two sites available for the rare earth: $3a$ and $6c$. All atoms in site $3a$ belong to the RM_5 blocks whereas atoms in position $6c$ are located in the RM_2 units (Fig. 1). For the whole series of rare earths, the cell volume evolution is generally well described by the so-called lanthanide contraction according to the atomic radius decrease of the $4f$ elements [3].

From theoretical investigations, some authors [4,5] proposed maximum hydrogen storage capacities between 5.6 and 6 H atoms per formula units (i.e. about 1.5 H/metal). As a matter of fact, when exposed to hydrogen, RM_3 binary compounds exhibit various behaviours depending on the elements. Oesterreicher et al. [6] reported that the compound LaNi_3 reacts spontaneously with hydrogen to form an amorphous hydride LaNi_3H_5 . Other compounds shows various hydrogen absorption ranging from 1.8 H/f.u. (0.52%) for the dihydride of HoNi_3 [7] up to 4 H/mol (1.5 wt.%) for YNi_3 [8]. Higher hydrogen capacities (close to 6 H/f.u.) have been reported by Lushkinov et al. [9]. These high pressure measurements

under 2000 atm agree with the predicted maximum capacities (1 atm = 101325 Pa).

Phase diagrams for the different systems $\text{RM}_3\text{-H}_2$ ($M = \text{Ni, Co and Fe}$) have been investigated regarding hydrogen absorption properties by several authors. For the RNi_3 system, both YNi_3 and CeNi_3 were investigated by Van Essen and Buschow [10]. A capacity of 3 H/f.u. was reported for CeNi_3 at 50°C with an equilibrium pressure of 0.09 atm, whereas the hydride $\text{YNi}_3\text{H}_{1.2}$ has a plateau pressure of 0.25 atm at the same temperature. For ErNi_3 , a pressure close to 1 atm was measured by Verbetsky et al. [11] at -40°C . Hydrogen phase diagrams were also investigated by Burnasheva et al. [12] for various rare earths ($R = \text{La, Pr, Nd and Sm}$). Capacities ranging from 5.2 to 4.7 H/f.u. were obtained under 50 bar of hydrogen pressure at 293 K. Some authors mention the appearance of two plateaus in these systems (like for ErNi_3 [13,11]) that were attributed to the existence of a dihydride and a tetrahydride phase.

The existence of two plateaus in the pressure composition isotherms was also established for the $\text{RCO}_3\text{-H}_2$ system. As an example, YCo_3 shows a first hydride YCo_3H (β phase) at about 0.005 atm [10], followed by the formation of a second hydride phase YCo_3H_4 (γ phase) [14] at about 0.45 atm. Similar behavior is also observed

for GdCo_3 for which the first plateau extends to the composition $\text{GdCo}_3\text{H}_{2.2}$ and the second to the composition $\text{GdCo}_3\text{H}_{4.6}$ [15]. In the same way, Bechman et al. [16] reported on the coexistence of α - β and β - γ domains in the isotherm curves for $R=\text{Gd, Tb, Dy, Ho}$ and Er . As a general rule, formation of the β hydride results in an expansion of the c parameter without appreciable change in the a parameter whereas formation of the γ hydride induces expansion of the a parameter. The RFe_3 family of compounds absorb typically 3 H/f.u. at room temperature. The isotherms curves of the RFe_3 compounds exhibit usually one single phase transition [16]. The hydrogen absorption does not involve a change of the crystallographic structure of these compounds but merely causes the expansion of the lattice involving an increase of both a and c parameters [17].

The influence of Ni replacement by Co and further by Fe on the hydriding and thermodynamic properties of RM_3 binary compounds is not easy to draw since they exhibit rather different hydrogen contents, in some cases the coexistence of two hydride phases and various data measured at different temperatures. However, for the $\text{YM}_3\text{-H}_2$ system, Van Essen and Buschow [10] reported that the stability of the hydrides increases from Ni to Fe. It is commonly admitted in the RM_5 systems that a linear inverse relation exists between the logarithm of the plateau pressure of the hydrides and the cell volume of the intermetallics [18]. Such a relation can be proposed for the YM_3 system according to the cell volume increase observed for YNi_3 , YCo_3 and YFe_3 whereas their equilibrium pressure decreases. This argument is also supported by the works published by Bechman et al. [16] on the RFe_3 and RCo_3 systems for which the equilibrium pressures measured at 150 °C for $R=\text{Gd, Tb, Dy, Ho}$ and Er shows a significant increase whereas the cell volumes shrink according to the well known effect of the lanthanide contraction. As a conclusion it can be said that the stability increases from Ni to Fe and decreases with the atomic number R.

Few hydrides have been investigated from a structural point of view. Andresen attempted to investigate LaNi_3D_2 [19] but failed to report a reliable structure due to decomposition already reported by Oestereicher. Amorphisation of this latter compound was also reported by Chen et al. [20]. However, Burnasheva et al. [12] succeeded in the preparation of crystalline RNi_3 hydrides for $R=\text{La, Pr, Nd}$ and Sm using a so called soft synthesis method consisting to provide very pure hydrogen in small increments to the alloy at room temperature under moderate pressure (0.8 to 1.5 bar). For all samples, X-ray diffraction analysis shows a reduction of the a parameter (−2.2%) and a strong increase of c (up to 32%) keeping the PuNi_3 -type structure. For other elements ($R=\text{Ho, Er, Y}$), the PuNi_3 -type structure is preserved upon hydrogenation and neither decomposition nor structural changes are reported. Determination of the different available sites

for hydrogen within the PuNi_3 structure has been made by Burnasheva et al. [7] and Yartys' et al. [21]. There are 13 possible sites divided into 12 tetrahedrons (T) and only one octahedron (O). Depending on the nature of the surrounding metal atoms, the sites can be described using the four following different environments: three T-M_4 , five T-RM_3 , four $\text{T-R}_2\text{M}_2$ and one $\text{O-R}_2\text{M}_4$. The different Wyckoff positions are reported in Table 1. Five sites are located in the RM_2 units and six ones lie within the RM_5 blocks. The peculiar case of sites $18h_1$ and $18h_2$ must be described separately since these sites are located at the boundary between the two kinds of blocks. To determine whether or not such a site belongs to one unit or the other one can compare the z position of the proton to the z position of the nickel atom occupying site $18h$ of the metallic sublattice that determines the limit between the two blocks. If the protons are lower than the nickel then they belong to the RM_5 units. Finally, it should be also mentioned that sites $18h_1$ and $18h_2$ are very similar to site $6m$ described for the LaNi_5 -type hydrides.

From the neutron diffraction analysis of $\text{HoNi}_3\text{D}_{1.8}$, Burnasheva et al. found only two occupied sites: 71% of the deuterium lies in the interstice $\text{T-R}_2\text{M}_2$ $18h_1$ (that can be considered within the RM_5 unit according to the above statement) and the remaining atoms are located in the site T-RM_3 $6c_1$ (RM_2 unit). For CeNi_3 , a different behaviour is observed. Upon hydrogenation, the hydride phase CeNi_3H_3 is formed [10] accompanied by a huge uniaxial expansion of the cell ($\delta a/a = -0.80\%$, $\delta c/c = 30.76\%$). Interstitial sites in the CeNi_3 -type structure have been described by Takeshita et al. [4]. Recently, Yartys' and co-workers [22,23] investigated the crystal structure of the deuteride $\text{CeNi}_3\text{D}_{2.7}$ and found an orthorhombic symmetry lowering into the $Pm\bar{c}n$ space group. Contrary to what is observed in $\text{HoNi}_3\text{D}_{1.8}$, deuterium was only located within the RM_2 units.

Table 1
Available crystallographic sites for hydrogen in the PuNi_3 -type structure (space group $R\bar{3}m$)

Structure block	Wyckoff position	Site symmetry
RM_2 units	$6c_1$	T-RM_3
	$6c_3$	T-M_4
	$18h_3$	$\text{T-R}_2\text{M}_2$
	$18h_6$	T-RM_3
	$36i_1$	$\text{T-R}_2\text{M}_2$
RM_5 units	$6c_2$	T-M_4
	$6c_4$	T-M_4
	$9e_1$	$\text{O-R}_2\text{M}_4$
	$18h_4$	T-RM_3
	$18h_5$	T-RM_3
	$36i_2$	T-RM_3
RM_5/RM_2 units	$18h_1$	$\text{T-R}_2\text{M}_2$
	$18h_2$	$\text{T-R}_2\text{M}_2$

Table 2
Thermodynamic and crystallographic data for various RM_3 compounds

Composition	H/mol	H/metal	Wt.%	P_{eq} (atm)	T (°C)	Structure type	Space group	a (Å)	c (Å)	V (Å ³)	$\delta a/a$	$\delta c/c$	$\delta V/V$	H/RM ₂	H/RM ₅	Ref.
Binary compounds																
YNi ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.978	24.449	524.66	–	–	–	–	–	[47]
YNi ₃	1.2	0.3	0.45	0.25	50.0		$\bar{R}3m$	4.996	24.350	526.35	0.46	–0.29	0.64	–	–	[10]
YNi ₃	4.0	1.0	1.51	?	?		$\bar{R}3m$	5.283	26.820	648.26	6.13	9.70	23.56	–	–	[48]
CeNi ₃	–	–	–	–	–	CeNi ₃	$P6_3/mmc$	4.960	16.550	352.61	–	–	–	–	–	[10]
	2.7	0.67	0.85	–	–	CeNi ₃ D ₃	$Pm\bar{c}n$	$a=4.890$ $b=8.559$	21.590	451.81	–1.50	30.68	28.12	4.14	0.00	[22,23]
	3.0	0.75	0.95	0.09	50.0		$P6_3/mmc$	4.920	21.640	453.65	–0.81	30.76	28.65	–	–	[10]
	5.1	1.27	1.61	No plateau	–		$P6_5/mmc$	4.900	22.340	464.52	–1.01	35.48	32.75	–	–	[9]
HoNi ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.951	24.210	514.35	–	–	–	–	–	[3]
	1.8	0.45	0.53	–	–		$\bar{R}3m$	4.990	26.120	563.25	0.75	7.89	9.51	0.78	3.83	[7]
ErNi ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.940	24.250	512.50	–	–	–	–	–	[9]
	3.7	0.88	1.0	1.3	25.0		$\bar{R}3m$	5.180	26.270	610.45	4.86	8.33	19.11	–	–	[9,49]
	4.9	1.22	1.43	1.2	–40.0		$\bar{R}3m$	5.210	26.450	621.77	5.47	9.07	21.32	–	–	[9,11]
YCo ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	5.018	24.384	531.65	–	–	–	–	–	[24]
Beta phase	1.0	0.25	0.38	–	–		$\bar{R}3m$	5.021	25.890	565.16	0.06	6.18	6.30	1.50	0.00	[24]
Beta phase	1.0	0.25	0.38	0.005	50.0		$\bar{R}3m$	5.013	25.860	562.80	0.16	6.55	6.89	–	–	[10]
Beta phase	1.9	0.47	0.72	–	–		$\bar{R}3m$	5.014	26.754	582.54	0.07	9.72	9.57	2.85	0.00	[24]
Gamma phase	3.8	0.95	1.43	0.45	75.0		$\bar{R}3m$	5.241	26.401	628.03	4.44	8.27	18.11	2.10	7.38	[25,50]
CeCo ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.950	24.800	526.25	–	–	–	–	–	[9]
	4.0	1.0	1.26	0.2	50.0		$\bar{R}3m$	4.960	32.690	696.48	0.20	31.81	32.35	–	–	[9,10]
	6.1	1.52	1.92	1730	–		$\bar{R}3m$	5.030	32.980	722.63	1.62	32.98	37.32	–	–	[9]
ErCo ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.978	24.250	520.42	–	–	–	–	–	[51]
	4.1	1.02	1.19	–	–		$\bar{R}3m$	5.217	26.123	615.74	4.80	7.72	18.32	4.20	6	[25]
YFe ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	5.137	24.610	562.42	–	–	–	–	–	[10]
	4.8	1.2	1.87	<10–5	50.0		$\bar{R}3m$	5.375	26.460	662.03	4.63	7.52	17.71	–	–	[10]
GdFe ₃	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	5.160	24.720	570.00	–	–	–	–	–	[9]
	4.0	1.0	1.23	–	–		$\bar{R}3m$	5.380	26.880	673.79	4.26	8.74	18.21	–	–	[9,49]
	5.0	1.25	1.54	–	–		$\bar{R}3m$	5.500	26.660	698.42	6.59	7.85	22.53	–	–	[9]
Pseudo-binary compounds																
CeNi ₂ Co	–	–	–	–	–	CeNi ₃	$P6_3/mmc$	4.950	16.460	349.28	–	–	–	–	–	[9]
	3.5	0.87	1.11	–	–		$P6_3/mmc$	4.890	21.780	451.03	–1.21	32.32	29.13	–	–	[9]
	5.6	1.40	1.77	1810	25.0		$P6_5/mmc$	4.970	22.270	476.39	0.40	35.30	36.39	–	–	[9]
CeY ₂ Ni ₉	–	–	–	–	–	PuNi ₃	$\bar{R}3m$	4.971	24.538	525.14	–	–	–	–	–	[40]
	7.7	0.85	0.91	0.12	25.0		$\bar{R}3m$	4.871	31.297	643.09	–2.01	27.54	22.46	3.9	0.00	[42]
Ternary compounds																
Y _{0.5} Ca _{0.5} MgCaNi ₉	–	–	–	–	–	LaMg ₂ Ni ₉	$\bar{R}3m$	4.928	23.889	502.36	–	–	–	–	–	[37]
	11.5	0.96	1.75	2	–10.0		$\bar{R}3m$	5.171	25.270	585.24	4.94	5.78	16.50	–	–	[37]
CaMg ₂ Ni ₉	–	–	–	–	–	LaMg ₂ Ni ₉	$\bar{R}3m$	4.905	23.787	495.57	–	–	–	–	–	[36]
	8.1–9.2	0.71	1.38	0.2	0.0		$\bar{R}3m$	5.198	25.579	598.51	5.98	7.53	20.77	–	–	[36]
La _{0.65} Ca _{0.35} Mg _{1.32} Ca _{0.68} Ni ₉	–	–	–	–	–	LaMg ₂ Ni ₉	$\bar{R}3m$	4.952	23.907	507.77	–	–	–	–	–	[38]
	13.0	1.08	1.88	2	10.0		$\bar{R}3m$	5.243	25.646	610.51	5.87	7.27	20.23	–	–	[38]
LaY ₂ Ni ₉	–	–	–	–	–	LaMg ₂ Ni ₉	$\bar{R}3m$	5.036	24.502	538.04	–	–	–	–	–	[40]
	12.8	1.07	1.51	0.1	25.0		$\bar{R}3m$	5.395	26.886	677.74	7.14	9.73	25.96	2.7	6.2	[42]

Equilibrium pressure P_{eq} at temperature T has been given only when available from the literature. Cell parameters are given for the starting intermetallic compounds and for the hydrides at the given composition in H/mol with cell volume expansion. Hydrogen contents in both RM₂ and RM₅ units are given in H/formula unit.

The crystal structures of RCO_3 hydrides have been investigated by neutron diffraction for $\text{R}=\text{Er}$ and Y . For YCO_3 , upon hydrogenation two homogeneity domains are reported. The beta phase YCO_3D_y exists for $1 \leq y \leq 1.9$ and was described in the $R\bar{3}m$ space group by Benham et al. [24]. The authors also reported uniaxial volume expansion ($\delta a/a = -0.07\%$, $\delta c/c = 9.72\%$) for this phase that they attribute to the filling of the RM_2 units only stating that locally the RM_5 unit volume is almost unchanged upon hydrogenation. All deuterium was found to be located in the tetrahedral site $36i_1$ in agreement with the exclusive hydrogenation of RM_2 units. The gamma phase $\text{YCO}_3\text{D}_{3.8}$ was investigated by Bartashevich et al. [25]. Less anisotropic volume expansion was observed ($\delta a/a = 4.44\%$, $\delta c/c = 8.27\%$). In addition to the site $36i_1$ reported for the beta phase, they found significant occupation for sites $18h_2$ and $36i_2$ that they attribute to the RM_5 units. These two latter sites correspond to the most filled sites of the LaNi_5 hydride ($6m$ and $12n$, respectively, in the $P6/mmm$ space group). In addition, a small orthorhombic distortion comparable to that observed in RCO_5 hydrides [26] is reported. This distortion is supposed to take place within the RM_5 units by analogy to what is observed in the RCO_5 systems. According to these works, it is expected that the beta phase corresponds to the filling of the RM_2 units followed by the filling of the RM_5 units in the gamma phase. Thermodynamic and crystallographic data are given in Table 2 for various RM_3 compounds.

3. Pseudo-binary systems

Substitutions on metallic sublattice have been widely used to modify the hydrogenation properties of intermetallic compounds and particularly to adapt the plateau pressure when hydrogenated. Such effect can be expected for RM_3 compounds but relatively few works have been published on the structural properties of such pseudo-binary compounds. Wasylechko et al. [27] studied the effect of gallium substitution on a series of RNi_3 compounds ($\text{R}=\text{Y}$, Pr to Lu except Pm and Eu). They found that in the $\text{RNi}_{3-x}\text{Ga}_x$ system, increasing the x value induces a change from the PuNi_3 - to the CeNi_3 -type structure. The partial replacement of nickel or yttrium by other metals has been investigated by Burnasheva and Tarasov [28] for YNi_3 . All substituted compounds can be indexed in the PuNi_3 -type structure. Regarding hydrogen absorption, a decrease of the capacity is observed when Ni is replaced by Co, Mn, Cr, Fe, V or Al. Similarly, reduction of capacity is obtained when replacing yttrium by Ca, Sc or Ti. Possible replacement of nickel by aluminum was studied by Yartys' and Bulyk [29] for the RNi_3 system. Interestingly, they obtained a series of compounds $\text{R}_3\text{Ni}_8\text{Al}$ ($\text{R}=\text{Y}$, Nd , Sm , Gd and Tb) which adopts the $\text{Ce}_3\text{Co}_8\text{Si}$ -type structure. Capacities ranging from 0.57 to 0.97 H/M were reported under 1 bar of hydrogenation

pressure. Again the hydrogenation appears to process in two steps: the first one inducing anisotropic expansion of c parameter only, the second one involving isotropic volume increase.

Substitution of cobalt by nickel or iron in YCO_3 have been studied [30,31] without improving significantly the reversible capacities. Similarly, Verbetsky et al. reported on $\text{CeNi}_{2.2}\text{Mn}_{0.8}$ [11] and CeNi_2Co [9] under high hydrogen pressure. They found capacities about 1.7 wt.% but they did not observe any plateau. Concerning the structural properties of these pseudo-binary hydrides, they are often limited to cell parameter determination as reported on $\text{CeNi}_2\text{CoH}_x$ in Table 2. Substitution of cobalt by gallium was tempted by Yartys' et al. [32] on RCO_3 samples ($\text{R}=\text{Y}$ and Gd) for which capacities between 0.5 and 0.77 H/Metal were reported. Finally, Sivakumar et al. [33,34] investigated the system $\text{Zr}_x\text{Tb}_{1-x}\text{Fe}_{1.5}\text{Co}_{1.5}$ for $x=0.1$ and 0.2 and described sloping plateaus when hydrogenated.

4. Ternary and quaternary systems

New interest in RM_3 -type alloys has been found in recent works on the system $\text{R}-\text{Mg}-\text{Ni}$. In the original paper [35], Kadir et al. report on the existence of RMg_2Ni_9 for various rare earths (La to Gd). They obtained this new phase by reaction of a mixture of MgNi_2 and RNi_5 intermetallic compounds or by direct reaction of the pure elements. They showed that such compounds adopt the PuNi_3 -type structure. Moreover, they found that the magnesium atoms lie in the site $6c$ of the $R\bar{3}m$ space group. Therefore, alloys RMg_2Ni_9 can be seen as ternary compounds built on the stacking of RNi_5 and MgNi_2 units. It is worth noting that contrary to binary compound CeNi_3 , CeMg_2Ni_9 adopts also the rhombohedral structure despite an intermediate valence state deduced from the variation of the cell parameters as a function of the rare earth. Many substitutions have then been then tempted either on the R site (by Ca, Y), on the Mg one (by Ca, Ti) or on the nickel sublattice (by Al or Mn) [20,36–39]. Several other ternary compounds like CaMg_2Ni_9 and YMg_2Ni_9 were obtained and adopt the same structure as that determined for LaMg_2Ni_9 . Kohno et al. [39] also reported on MgLa_2Ni_9 but did not mention if this latter compound adopts the PuNi_3 -type structure.

The system $\text{La}_{1-x}\text{Ce}_x\text{Y}_2\text{Ni}_9$ was investigated by Badour and co-workers [40,41] for various values of x ($0 \leq x \leq 1$). The compound LaY_2Ni_9 adopts the rhombohedral structure of PuNi_3 -type. A large amount of the lanthanum atoms occupies site $3a$ leading to a partially ordered ternary compound. Substitution by cerium involves anisotropic variations of the cell parameter with a decrease of a and an increase of c leading to an overall cell volume reduction of 2.4%. Increasing cerium content leads to a statistical distribution of the rare earths over the two available sites $3a$ and $6c$. Depending of the atomic radius

difference between yttrium and the pseudo-atom $R = (\text{La}_{1-x}\text{Ce}_x)$ either a partially ordered ternary or a randomly distributed pseudo-binary compound can be obtained.

All the compounds absorb hydrogen with various capabilities. The weight capacities vary from 0.33% for LaMg_2Ni_9 up to 1.87% for $(\text{La}_{0.65}\text{Ca}_{0.35})\text{Mg}_{1.32}\text{Ca}_{0.68}\text{Ni}_9$ (under 2 bar of hydrogen at 10 °C). For the system $\text{La}_{1-x}\text{Ce}_x\text{Y}_2\text{Ni}_9$ capacities between 0.9 wt.% for the pure Ce and 1.5 wt.% for the pure La compound are obtained at room temperature and close to atmospheric pressure [40,41]. Crystal structure of the deuteride $\text{CeY}_2\text{Ni}_9\text{D}_{7.7}$ was investigated recently by neutron diffraction [42]. Anisotropy observed under hydrogen loading is very important with $\delta a/a = -2.0\%$ whereas $\delta c/c$ reaches 27.5% and deuterium site occupancy is limited to RM_2 units only (Table 2). On the contrary, $\text{LaY}_2\text{Ni}_9\text{D}_{12.8}$ shows isotropic expansion of the cell and analysis of neutron diffraction data still in progress shows that both RM_3 and RM_2 units are occupied by deuterium.

5. Discussion

According to this review, very few binary or pseudo-binary compounds exhibit interesting storage properties under ambient temperature and pressure conditions. The peculiar case of RCO_3 and RNi_3 phases should be mentioned since hydrogenation proceeds in some cases through the existence of two hydride phases (beta and gamma). This behavior must be compared to that of cobalt substituted RM_3 compounds for which such two phase domains exist and are known to significantly enhance the cycle life by reducing the decrepitation process in electrochemical storage [43,44].

To obtain good reversible capacities, preparation of new ternary compounds as proposed first by Kadir with LaMg_2Ni_9 seems to be the most promising route. Preparation of RM_3 -type compounds can be easily achieved for a very large variety of elements if one considers all the possibility of intergrowth between various RM_3 and RM_2 units. The crystallographic structure adopted by the binary RM_2 parent unit does not seem to greatly influence the stabilization of the PuNi_3 -type structure since such compounds are obtained either with C36- MgNi_2 or C15- YNi_2 . According to that, many RM_2 compounds either hexagonal (C36 or C14 type) or cubic (C15 type) may be used in combination with RM_3 units to prepare new ternary compounds. It is also worth noting that compounds with cerium are easily stabilized into the rhombohedral PuNi_3 structure when substituted by lighter elements like Mg or Y. As a general rule, it seems that the occurrence of a given $\text{RR}'_2\text{M}_9$ compound is closely related to the stability of the individual RM_3 and $\text{R}'\text{M}_2$ phases in the CaCu_5 or Laves phase structures, respectively. This statement could be a useful guide to choose potential elements for the preparation of new ternary compounds.

Repertition of the R elements between the two available sites 3a and 6c has been studied for various compositions. However, only a few elements have been investigated (Y, Mg, Ca) and it is difficult to draw reliable conclusions. It can be considered that lighter element with smaller atomic radius occupy preferentially the site 6c. This is indeed the case for LaY_2Ni_9 , YMg_2Ni_9 or LaMg_2Ni_9 and that is in agreement with the larger space available around the site 3a. However, this is not true for some Ca-containing compounds for which this element is dispersed over the two sites or for CeY_2Ni_9 that is randomly distributed. Cerium is generally observed in intermediate valence state in these compounds with consequently a reduced atomic radius and further data will be helpful to understand such behavior.

Regarding hydrogen absorption properties, most rare earths can be chosen for the RM_3 units but cerium should be carefully used. In each case, cerium induces severe uniaxial expansion along the *c*-axis and leads to hydrogen occupation within the RM_2 blocks only, therefore strongly limiting the overall capacity. As commercial alloys are very often prepared from Ce-containing mischmetal such effects must be carefully evaluated before using this cheaper mixture of rare earths.

When known, the crystallographic structures of the hydrides show some common features. Within the RM_2 blocks, both sites $36i_1$ and $18h_3$ are preferentially occupied which correspond to R_2M_2 tetrahedral sites usually found occupied in RM_2 -type compounds. Concerning the RM_3 units, site occupancies are significant for sites $18h_1$ (or $18h_2$) and $36i_2$ which can be related to sites $6m$ (R_2M_2) and $12n$ (RM_3), respectively in the CaCu_5 -type structure ($P6/mmm$ space group). That leads to the conclusion that the intergrowth between these two types of units does not significantly modify the nature of the sites occupied by hydrogen. According to that, overall capacity can be estimated equal to the weighted sum of the individual units as already proposed by Dunlap et al. [2]. Therefore, the choice of MgNi_2 as RM_2 units should be avoided since this compound does not absorb significantly hydrogen [45]. Introduction of elements like Ca (CaNi_2 absorbs about 1.13 H/M) or YNi_2 (1.2 H/M) confirms this statement since compounds like $\text{Y}_{0.5}\text{Ca}_{0.5}\text{MgCaNi}_9$ or LaY_2Ni_9 exhibit much larger capacities than LaMg_2Ni_9 (0.2 H/M). However, the choice of YNi_2 for the RM_2 units remain questionable since this latter compound is known to undergo amorphisation when fully hydrogenated [46].

Considering thermodynamic properties, a linear relationship between the cell volume and the logarithm of the plateau pressure (as it was observed for many LaNi_5 -type compounds) has been proposed by Chen et al. [20] who tentatively draw such correlation for their compounds. However, some additional measurements show large scattering of the reported values preventing any reliable linear relationship. According to the structural studies, competi-

tion between ternary versus pseudo-binary nature of the intermetallic compounds and different hydrogen occupation rates of both RM_5 - and RM_2 -units will not allow to obtain such general correlation. However, it remains true that plateau pressure may be adapted by substitution effects on the metal sublattice for these compounds. Finally, most of the investigated ternary compounds were obtained from pure nickel on the M sites. However, Chen et al. [20] prepared the compounds $LaCaMgNi_6Al_3$ and $LaCaMgNi_6Mn_3$ showing that substitutions can be easily performed also on the nickel sites. Taken into account the improvement obtained by such substitutions in the hydrogenation behavior of some RM_5 compounds, it will be of interest to study such effects on the cycle life and decrepitation process.

6. Conclusions

New families of compounds can be obtained by preparing materials from the intergrowth of RM_5 -type compounds with RM_2 units adopting the $PuNi_3$ -type structure. In all cases, the aim of such preparation is to take profit from the properties of RM_5 - and RM_2 -type units to obtain compounds with enhanced behavior towards hydrogen absorption. For the RM_5 part, rare earth- and nickel-based alloys are obvious candidates according to their good storage properties. However, cerium content should be carefully evaluated. For the RM_2 part, one should think about compounds with high capacities even if they suffer from passivation or slow activation. Associated with $LaNi_5$ -type alloys in the $PuNi_3$ -type structure, these drawbacks may be overcome and could lead to potential materials for hydrogen storage. Moreover, substitution of nickel by other transition metals may also be used to further improve the characteristic of these materials toward hydrogenation properties.

References

- [1] D.T. Cromer, C.E. Olsen, *Acta Crystallogr.* 12 (1959) 689.
- [2] B.D. Dunlap, P.J. Viccaro, G.K. Shenoy, *J. Less-Common Met.* 74 (1980) 75.
- [3] K.H.J. Buschow, A.S. Van der Goot, *J. Less-Common Met.* 22 (4) (1970) 419.
- [4] T. Takeshita, W.E. Wallace, R.S. Craig, *Inorg. Chem.* 13 (1974) 2283.
- [5] V.A. Yartys', *Koord. Khim.* 18 (4) (1992) 401.
- [6] H. Oesterreicher, J. Clinton, H.F. Bittner, *Mater. Res. Bull.* 11 (1976) 1241.
- [7] V.V. Burnasheva, V.A. Yartys', S.P. Solov'ev, N.V. Fadeeva, K.N. Semenenko, *Soviet Phys. Crystallogr.* translated from *Kristallografiya* 27 (4) (1982) 409.
- [8] K.H.J. Buschow, R.M. Van Essen, *Solid State Commun.* 32 (1979) 1241.
- [9] S.A. Lushnikov, S.N. Klyamkin, V.N. Verbetsky, *J. Alloys Comp.* 330–332 (2002) 574.
- [10] R.M. Van Essen, K.H.J. Buschow, *J. Less-Common Met.* 70 (1980) 189.
- [11] V.N. Verbetsky, S.N. Klyamkin, A.Y. Kovriga, A.P. Bespalov, *Int. J. Hydrogen Energy* 21 (11–12) (1996) 997.
- [12] V.V. Burnasheva, B.P. Tarasov, K.N. Semenenko, *Russ. J. Inorg. Chem.* 27 (12) (1982) 1722.
- [13] V.V. Burnasheva, B.P. Tarasov, *Zh. Neorg. Khim.* 27 (8) (1982) 1906.
- [14] M. Yamaguchi, *J. Less-Common Met.* 106 (1985) 165.
- [15] S.K. Malik, W.E. Wallace, T. Takeshita, *Solid State Commun.* 28 (12) (1978) 977.
- [16] C.A. Bechman, A.J. Goudy, T. Takeshita, W.E. Wallace, R.S. Craig, *Inorg. Chem.* 15 (9) (1976) 2184.
- [17] S.K. Malik, F. Pourarian, W.E. Wallace, *J. Magn. Mater.* 40 (1–2) (1983) 27.
- [18] J.-C. Achard, A. Percheron-Guégan, H. Diaz, F. Briaucourt, F. Demany, in: *2nd International Congress on Hydrogen in Metals*, Paris, 1977, p. 1E12.
- [19] A.F. Andresen, *Structural studies of hydrides by neutron diffraction*, in: A.F. Andresen, A.J. Maeland (Eds.), *Hydrides for Energy Storage*, Pergamon, Oxford, 1978, p. 61.
- [20] J. Chen, H.T. Takeshita, H. Tanaka, N. Kuriyama, T. Sakai, I. Uehara, M. Haruta, *J. Alloys Comp.* 302 (1–2) (2000) 304.
- [21] V.A. Yartys', V.V. Burnasheva, K.N. Semenenko, N.V. Fadeeva, S.P. Solov'ev, *Int. J. Hydrogen Energy* 7 (12) (1982) 957.
- [22] V.A. Yartys', O. Isnard, ILL Experimental Report, Experiment Number 5-24-144, 2001.
- [23] V.A. Yartys', O. Isnard, A.B. Riabov, L.G. Akselrud, in: *Proceedings of the International Symposium on Metal Hydrogen System, Fundamental and Applications*, Annecy, *Journal of Alloys and Compounds*, 1–6 September 2002.
- [24] M.J. Benham, S. Bennington, D.K. Ross, D. Noreus, M. Yamaguchi, *Z. Phys. Chem. Neue Folge* 163 (1989) 283.
- [25] M.I. Bartashevich, A.N. Pirogov, V.I. Voronin, M. Yamaguchi, I. Yamamoto, T. Goto, *J. Alloys Comp.* 231 (1–2) (1995) 104.
- [26] F.A. Kuijpers, *Philips Research Report Suppl. 2*, University of Delft, Delft, 1973.
- [27] L.O. Wasylechko, A.A. Fedorchuk, Y.N. Grin, *J. Alloys Comp.* 219 (1–2) (1995) 222.
- [28] V.V. Burnasheva, B.P. Tarasov, *Russ. J. Inorg. Chem.* 29 (1984) 1136.
- [29] V.A. Yartys', I.I. Bulyk, *Z. Phys. Chem. Bd.* 179 (1993) 275.
- [30] A. Tauber, A.S.R.D. Finnegan, F. Rothwarf, W.E. Wallace, in: C.E. Lundin (Ed.), *Proceedings of the 12th Rare Earth Research Conference*, 1976, p. 1073.
- [31] M. Yamaguchi, Y.F.I. Yamamoto, T. Goto, *Z. Phys. Chem. NF* 163 (1989) 677.
- [32] V.A. Yartys', O.M.S.I.I. Bulyk, N.I. Yomasczuk, *J. Alloys Comp.* 189 (1992) L27.
- [33] R. Sivakumar, K.V.S.R.R.S. Ramaprabhu, B. Mayer, P.C. Schmidt, *J. Alloys Comp.* 302 (2000) 146.
- [34] R. Sivakumar, K.V.S.R.R.S. Ramaprabhu, B. Mayer, P.C. Schmidt, *Int. J. Hydrogen Energy* 25 (2000) 861.
- [35] K. Kadir, I. Uehara, T. Sakai, *J. Alloys Comp.* 257 (1997) 115.
- [36] K. Kadir, N. Kuriyama, T. Sakai, I. Uehara, L. Eriksson, *J. Alloys Comp.* 284 (1–2) (1999) 145.
- [37] K. Kadir, T. Sakai, I. Uehara, *J. Alloys Comp.* 287 (1–2) (1999) 264.
- [38] K. Kadir, T. Sakai, I. Uehara, *J. Alloys Comp.* 302 (1–2) (2000) 112.
- [39] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M. Yamamoto, M. Kanda, *J. Alloys Comp.* 311 (2) (2000) L5.
- [40] R. Baddour-Hadjean, L. Meyer, J.-P. Pereira-Ramos, M. Latroche, A. Percheron-Guégan, *Electrochem. Acta* 46 (15) (2001) 2385.
- [41] R. Baddour-Hadjean, J.-P. Pereira-Ramos, M. Latroche, A. Percheron-Guégan, *J. Alloys Comp.* 330–332 (2002) 782.
- [42] M. Latroche, *J. Solid State Chem.* (in preparation).

- [43] M. Latroche, A. Percheron-Guégan, Y. Chabre, *J. Alloys Comp.* 293–295 (1999) 637.
- [44] M. Latroche, Y. Chabre, A. Percheron-Guégan, O. Isnard, B. Knosp, *J. Alloys Comp.* 330–332 (2002) 787.
- [45] J.J. Reilly, R.H. Wiswall Jr., *Inorg. Chem.* 7 (1968) 2254.
- [46] M. Latroche, V. Paul-Boncour, A. Percheron-Guégan, *Z. Phys. Chem.* 179 (1993) 261.
- [47] J.F. Smith, D.A. Hansen, *Acta Crystallogr.* 19 (1965) 1019.
- [48] K.H.J. Buschow, R.M. Van Essen, *Solid State Commun.* 32 (1979) 1241.
- [49] A.J. Goudy, Thesis, University of Pittsburgh, PA, 1976, p. 1.
- [50] M. Yamaguchi, T.O.H. Ikeda, T. Katayama, T. Goto, *J. Less-Common Met.* 106 (1985) 165.
- [51] V.V. Burnasheva, V.V. Klimeshin, V.A. Yartys', K.N. Semenenko, *Inorganic Materials*, translated from *Izv. Akad. Nauk SSSR, Neorg. Mater.* 15 (1979) 627.