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# On the structural and thermodynamic properties of the $\text{RENi}_4\text{Ga}$ –hydrogen ( $\text{RE} \equiv \text{La, Ce, Nd and Sm}$ ) systems

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**Abstract.** The  $\text{RENi}_4\text{Ga}$  ( $\text{RE} \equiv \text{La, Ce, Nd and Sm}$ ) intermetallic compounds were prepared and studied by means of x-ray powder diffraction. All compounds are single phase and exhibit the same hexagonal symmetry ( $\text{CaCu}_5$  type; space group  $P6/mmm$ ) as do their prototype  $\text{RENi}_5$  binaries. The interaction with hydrogen was also studied. It was found that all ternary intermetallics react readily and reversibly with hydrogen to form hydrides with high hydrogen contents of up to four hydrogen atoms per alloy formula unit. The pressure composition desorption isotherms were measured. The entropy, the enthalpy and the Gibbs free energy of formation have been extracted from the equilibrium plateau in the pressure–composition desorption isotherms. The hydrogen capacity and the equilibrium pressure of the  $\text{RENi}_4\text{Ga}$ –hydrogen systems were compared with the corresponding values for their aluminium analogues and with the values for the  $\text{RENi}_5$ –hydrogen systems and briefly discussed. The hydride properties of gallium containing and aluminium containing compounds show great similarities whereby both series of ternary compounds form more stable hydrides and exhibit smaller hydrogen capacities than do the corresponding binaries.

## 1. Introduction

It is well known that many  $\text{RENi}_5$  intermetallics ( $\text{RE} \equiv$  rare earth including misch metal (Mm)) react reversibly and absorb large quantities of hydrogen. They have therefore attracted a great deal of attention as possible hydrogen storage materials. The exceptional representative  $\text{LaNi}_5$  forms  $\text{LaNi}_5\text{H}_{6.7}$  at room temperature and under 200 kPa of hydrogen [1]. Substitution of nickel in  $\text{RENi}_5$  by other metals or metalloids frequently drastically influences the crystal structure of the prototype  $\text{RENi}_5$ , as well as the thermodynamic characteristics of the corresponding  $\text{RENi}_5$ –hydride. For some examples one can mention the systems  $\text{LaNi}_{5-x}\text{Al}_x$ –hydrogen [2],  $\text{LaNi}_{5-x}\text{Sn}_x$ –hydrogen [3, 4],  $\text{LaNi}_{5-x}\text{Cu}_x$ –hydrogen [5],  $\text{CeNi}_{5-x}\text{Cu}_x$ –hydrogen [6],  $\text{MnNi}_{5-x}\text{Al}_x$ –hydrogen [7],  $\text{DyNi}_{5-x}\text{Al}_x$ –hydrogen [8],  $\text{TbNi}_{5-x}\text{Al}_x$ –hydrogen [9] and  $\text{HoNi}_{5-x}\text{Al}_x$ –hydrogen [10]. However, aluminium seems to be the best substituent in tailoring the metal–hydrogen system for a particular application [2, 11]. Accordingly, it was possible to prepare some  $\text{LaNi}_5$  based compounds that are today commercially used as hydrogen storage materials [12, 13] and as negative electrode in environmental friendly rechargeable nickel–metal hydride (Ni/MH) batteries [14, 15].

Since hydrogen sorption properties of gallium substituted  $\text{RENi}_5$  alloys have not been studied so far, and aluminium and gallium have similar atomic sizes and configuration of valence electrons, we were interested to perform structural and thermodynamic studies of selected  $\text{RENi}_4\text{Ga}$ –hydrogen systems. It should be pointed out the existence of some papers

on the  $\text{RENi}_3\text{Ga}_2$  ( $\text{RE} \equiv$  rare earth) [16–18] compounds and on the  $\text{RENi}_{5-x}\text{Ga}_x$  systems ( $\text{RE} \equiv$  La, Ce, Gd) [19, 20] dealing with their crystal structure and magnetic properties, but not at the  $\text{RENi}_4\text{Ga}$  stoichiometry. The only exception is the  $\text{CeNi}_4\text{Ga}$  compound, where the hexagonal structure of the  $\text{CaCu}_5$  type ( $a = 4.966 \text{ \AA}$ ,  $c = 4.072 \text{ \AA}$ ) is reported [20].

The results reported here represent the continuation of our systematic study on the structural and hydrogen sorption properties of selected  $\text{RENi}_5$  compounds where nickel is partially replaced by other metals.

## 2. Experimental details

The starting materials used in this investigation were supplied by Johnson Matthey, UK (rare earth with purity of 99.9%; gallium with purity of 99.99%) and Carlo Erba, Italy (nickel, 99.5%; main impurity iron). The alloys of the composition  $\text{RENi}_4\text{Ga}$  ( $\text{RE} \equiv$  La, Ce, Nd, Sm) were prepared by arc melting under an argon atmosphere. To ensure homogeneity, the alloys were inverted and remelted several times. The weight loss of the material was checked and was found to be negligible. Good single phase material was obtained after annealing in vacuum at 1173 K for at least 5 days.

The x-ray powder diffraction patterns were obtained with a Philips PW 1050 diffractometer equipped with a graphite monochromator and nickel-filtered  $\text{Cu K}\alpha$  radiation. The intensities were calculated using the 'Lazy-Pulverix' program [21].

All alloys were exposed to hydrogen supplied by Jesenice, Slovenia (purity, 99.999%). The pressure–composition isotherm (PCI) measurements were carried out in a stainless-steel apparatus that enables work in a temperature range from 77 to 800 K, in vacuum and/or with hydrogen at pressures up to 20 MPa. Prior to PCI measurements the alloys were activated by heating under hydrogen (700 K, 10 MPa). After cooling, the absorbed hydrogen was removed by heating and evacuating. This procedure was repeated until the amount of released hydrogen remained constant. The desorption PCI measurements were made by releasing small quantities of hydrogen from the reactor with alloys prior to a complete saturation with hydrogen. The equilibrium pressure was measured after 15 min and the procedure repeated until the pressure dropped to 10 kPa, when the samples were heated and additional amounts of released hydrogen were measured. The composition was calculated from the pressure–temperature–volume data.

## 3. Results and discussion

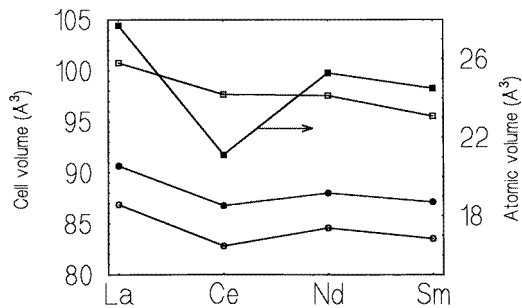
### 3.1. Crystal structure

Analysis of the x-ray powder diffraction data of the  $\text{RENi}_4\text{Ga}$  ( $\text{RE} \equiv$  La, Ce, Nd, Sm) alloys indicated that these single phase materials are of hexagonal symmetry and of the  $\text{CaCu}_5$  structure type (space group  $P6/mmm$ ). The relevant unit cell parameters of the  $\text{RENi}_4\text{Ga}$  compounds are given in table 1. The values of the binary  $\text{RENi}_5$  and the ternary  $\text{RENi}_4\text{Al}$  compounds with the same rare earth metals are also included for comparison. The unit cell parameters of the  $\text{RENi}_4\text{Ga}$  compounds are bigger than those of the corresponding binary compounds (table 1) since the atomic radius of Ga (1.41 Å) is larger than that of Ni (1.24 Å). Figure 1 illustrates the unit cell volumes for all three series of compounds. The atomic volumes for the pure rare earth metals (including  $\alpha$ -cerium) are shown for comparison [25]. In all cases the lanthanide contraction and the anomalous valence of cerium are clearly visible.

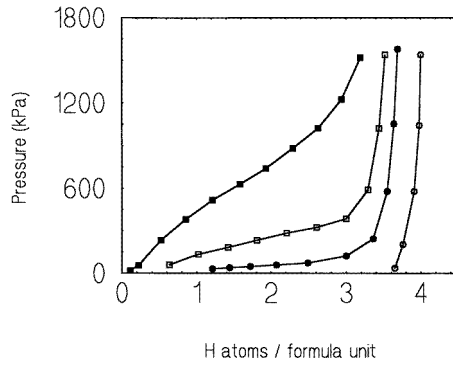
In the  $\text{CaCu}_5$  type of structure there exist two layers of atoms: the basal layer ( $z = 0$ )

**Table 1.** Crystallographic and hydrogen absorption data for the  $RENi_5$ ,  $RENi_4Ga$  and  $RENi_4Al$  ( $RE \equiv La, Ce, Nd, Sm$ ) compounds.

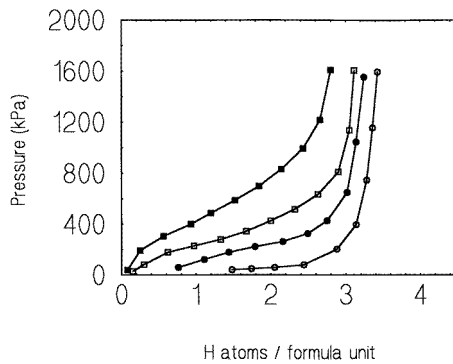
Composition	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$V_{hydride}/V_{alloy}$	$P_{eq}$ at 293 K (kPa)	Reference
$LaNi_5$	5.016	3.986	86.85			[22]
$LiNi_5H_{6.7}$					200	[1]
$LaNi_4Ga$	5.073(3)	4.069(3)	90.68(4)			p.w. <sup>a</sup>
$LaNi_4GaH_4$	5.280(3)	4.173(2)	100.75(4)	1.111	<15	p.w.
$LaNi_4Al$	5.066	4.070	90.55			[23]
$LaNi_4AlH_{4.3}$	5.319	4.235	103.76	1.146	<0.1	[23]
$CeNi_5$	4.887	4.003	82.79			[22]
$CeNi_5H_6$					4848	[24]
$CeNi_4Ga$	4.959(2)	4.047(3)	86.76(3)			p.w.
$CeNi_4GaH_{3.5}$	5.197(2)	4.176(3)	97.68(3)	1.126	47	p.w.
$CeNi_4Al$	4.943	4.085	86.47			[23]
$CeNi_4AlH_{3.7}$	5.227	4.186	99.05	1.145	<0.1	[23]
$NdNi_5$	4.956	3.976	84.57			[22]
$NdNi_5H_6$						[24]
$NdNi_4Ga$	5.006(3)	4.055(2)	88.00(4)			p.w.
$NdNi_4GaH_{3.6}$	5.220(2)	4.135(2)	97.57(3)	1.109	<25	p.w.
$NdNi_4Al$	5.004	4.067	88.19			[23]
$NdNi_4AlH_{4.0}$	5.229	4.183	99.05	1.123	<1	[23]
$SmNi_5$	4.927	3.975	83.56			[22]
$SmNi_5H_4$						[24]
$SmNi_4Ga$	4.980(2)	4.056(2)	87.11(3)			p.w.
$SmNi_4GaH_{3.4}$	5.196(3)	4.172(3)	95.54(4)	1.097	70	p.w.
$SmNi_4Al$	4.980	4.050	86.98			[23]
$SmNi_4AlH_{3.6}$	5.193	4.155	97.04	1.116	<10	[23]

<sup>a</sup> Present work.

**Figure 1.** The unit cell volumes for the  $RENi_5$  (○) and  $RENi_4Ga$  (●) alloys, the  $RENi_4Ga$  hydrides ( $RE \equiv La, Ce, Nd, Sm$ ) (□) and the atomic volumes for pure rare earth metals (■).

containing nickel (2(c) sites) and rare earth atoms (1(a) sites); and the equatorial layer ( $z = 1/2$ ) containing nickel atoms only (3(g) sites). A detailed x-ray intensity analysis was carried out and the atomic coordinates have been determined. It was found that the replacement of gallium atoms for nickel atoms takes place statistically and preferentially



**Figure 2.** PCI for the  $\text{LaNi}_4\text{Ga}$ -hydrogen system. (○) 293 K, (●) 353 K, (□) 388 K, (■) 428 K.



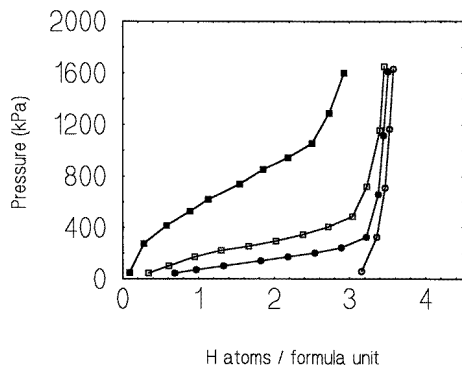
**Figure 3.** PCI for the  $\text{CeNi}_4\text{Ga}$ -hydrogen system. (○) 293 K, (●) 313 K, (□) 333 K, (■) 353 K.

within the equatorial layer. The unit cell expansion that is larger along the  $c$ -axis than along the  $a$ -axis also indicates that larger gallium atoms substitute smaller nickel atoms preferentially within the interleaving layer only. It should be noted that the values of unit cell parameters for  $\text{CeNi}_4\text{Ga}$  are in good agreement with the results reported by Tang *et al* [20].

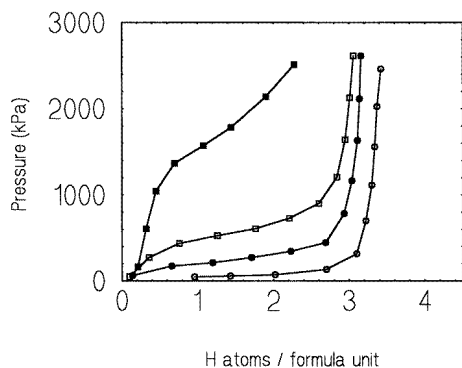
### 3.2. Thermodynamic properties

In order to determine the thermodynamic properties of the  $\text{RENi}_4\text{Ga}$ -hydrogen systems the alloys were exposed to hydrogen gas at different pressures and temperatures. All alloys were easily activated, and were found to absorb large quantities of hydrogen. The unit cell parameters for the hydrides were determined and are given in table 1 and the unit cell volumes are illustrated in figure 1. Hydrogen uptake increases the unit cell volume of the host alloy for up to 12.6%.

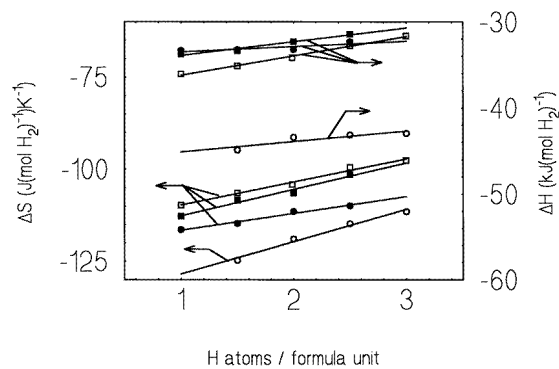
Figures 2–5 illustrate the results of the PCI measurements. The thermodynamic parameters entropy,  $\Delta S$ , and enthalpy,  $\Delta H$ , were determined (table 2) from the equilibrium pressures, at a ratio of two hydrogen atoms per alloy formula unit. The corresponding values were calculated using the least-square fit of the Van't Hoff equation  $\ln p_{eq} = \Delta H/RT - \Delta S/R$ , where  $p_{eq}$  = plateau pressure,  $\Delta H$  = reaction enthalpy,  $R$  = universal gas constant,  $T$  = temperature and  $\Delta S$  = reaction entropy. The enthalpy and



**Figure 4.** PCI for the  $NbNi_4Ga$ -hydrogen system. (○) 293 K, (●) 333 K, (□) 353 K, (■) 388 K.



**Figure 5.** PCI for the  $SmNi_4Ga$ -hydrogen system. (○) 293 K, (●) 333 K, (□) 353 K, (■) 388 K.



**Figure 6.** The entropy,  $\Delta S$ , and the enthalpy,  $\Delta H$ , as a function of hydrogen uptake for (○)  $LaNi_4Ga$ , (●)  $CeNi_4Ga$ , (□)  $NdNi_4Ga$ , (■)  $SmNi_4Ga$ .

the entropy, as a function of the hydrogen uptake, are shown for all compounds in figure 6. The Gibbs free energy of formation ( $\Delta G$ ) was calculated according to  $\Delta G = \Delta H - T\Delta S$  and the corresponding values for room temperature are also included in table 2.

**Table 2.** Thermodynamic parameters for the RENi<sub>4</sub>Ga–hydrogen (RE ≡ La, Ce, Nd, Sm) systems at the ratio of two hydrogen atoms per alloy formula unit.

Composition	$\Delta H$ (kJ/mol H <sub>2</sub> )	$\Delta S$ (J/mol H <sub>2</sub> K <sup>-1</sup> )	$\Delta G$ at 293 K (kJ/mol H <sub>2</sub> )
LaNi <sub>4</sub> Ga	-43.42	-118.89	-8.59
CeNi <sub>4</sub> Ga	-33.22	-111.41	-0.58
NdNi <sub>4</sub> Ga	-34.19	-104.92	-3.45
SmNi <sub>4</sub> Ga	-32.29	-106.42	-1.11

A brief analysis of the relevant data permits us to extract the following thermodynamic features of the investigated systems:

- (i) a decrease in hydrogen desorption equilibrium pressure compared to the values for the corresponding RENi<sub>5</sub>–hydrogen systems.
- (ii) a decrease in hydrogen capacity compared to the values for the corresponding RENi<sub>5</sub>–hydrogen systems;
- (iii) a maximum hydrogen capacity of four hydrogen atoms per alloy formula unit at room temperature observed for LaNi<sub>4</sub>Ga;
- (iv) similar hydrogen desorption equilibrium pressures and hydrogen capacities to the corresponding aluminium analogues;
- (v) a general decrease of all relevant thermodynamic values with the increasing atomic number of the rare earth metal, with a discrepancy frequently observed by the cerium containing alloy.

#### 4. Conclusion

The structural study of the RENi<sub>4</sub>Ga (RE ≡ La, Ce, Nd, Sm) alloys revealed their single phase nature with the hexagonal symmetry of the CaCu<sub>5</sub> type. All these alloys react readily with hydrogen to form stable hydrides at room temperature with remarkable contents of hydrogen. The relevant thermodynamic properties for the RENi<sub>4</sub>Ga–hydrogen systems were extracted from the PCI curves and indicate that the hydrogen capacity and the hydrogen equilibrium pressure decrease, compared to the corresponding RENi<sub>5</sub>–hydrogen systems. The changes of the thermodynamic parameters follow the trend usually observed moving along the rare earth metal series. Although the gallium containing alloys exhibit similar thermodynamic characteristics as their aluminium analogues the latter remain still superior as hydrogen storage materials especially due to the much lower cost of aluminium.

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