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Crystal structure, thermal expansion and hydrogen sorption properties of the $\text{GdNi}_{5-x}\text{Ga}_x$ alloys

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Abstract. Alloys of the composition $\text{GdNi}_{5-x}\text{Ga}_x$ were prepared and their structural and hydrogen sorption properties were studied. It was found that nickel in GdNi_5 can be replaced by gallium up to the composition GdNi_2Ga_3 . The crystal structure of the alloys depends on the heat treatment. The hexagonal structure of the prototype compound (CaCu₅ type; space group *P6/mmm*) is preserved in all as-cast alloys. After annealing the alloys of the compositions GdNi_3Ga_2 and $\text{GdNi}_{2.5}\text{Ga}_{2.5}$ crystallize with a larger unit cell of the YCo₃Ga₂ type, but closely related to the structure of GdNi_5 . The linear coefficients of thermal expansion were determined between room temperature and 873 K by x-ray powder diffraction. All alloys exhibit expansion anisotropy; the expansion along the *a* axis being larger than along the *c* axis. Alloys have been exposed to hydrogen and were found to absorb up to 4.3 hydrogen atoms per alloy formula unit at room temperature. The hydrogen uptake depends on the structure and the composition of the alloy. Binary GdNi_5 and alloys with the larger unit cell are inert to hydrogen at pressures up to 20 MPa. The hydrogen equilibrium pressure and the hydrogen capacity decrease as the content of gallium increases. The entropy and the enthalpy have been calculated for the alloy–hydrogen systems that exhibit a desorption equilibrium plateau.

1. Introduction

Intermetallic compounds of the general composition AB_5 have been extensively investigated as possible hydrogen storage media. Primarily, this is because of the ability of LaNi_5 to absorb large amounts of hydrogen (up to 6.7 hydrogen atoms per formula unit), and exhibits an equilibrium plateau at moderate pressures at room temperature [1]. At present some of the LaNi_5 -based compounds are commercially traded as hydride-forming alloys and have a wide variety of applications including rechargeable nickel–metal hydride (Ni/MH) batteries.

The effect of replacement of either components in selected REB_5 compounds (RE = rare earth, B = 3d metal) on their structural, physical and hydrogen sorption properties have also been studied extensively. For example it was found that the hydrogen sorption properties and/or the crystal structure are strongly influenced when nickel is partially replaced by aluminium in the systems RENi_4Al [2] and $\text{RENi}_{5-x}\text{Al}_x$ (RE = La, Nd, Gd, Tb, Dy, Ho, Er) [3–10]. In all these systems the equilibrium pressure as well as the hydrogen capacity of the binary compound is drastically reduced by substitution. Some other examples of the influence of substitution on the magnetic and structural properties of AB_5 compounds can be found in the systems $\text{RECo}_{5-x}\text{Ga}_x$ [11], $\text{CeNi}_{5-x}\text{Ga}_x$ [12, 13], $\text{CeNi}_{5-x}\text{Cu}_x$ [14] and at the compositions RET_2Ga_3 (T = Co, Ni, Cu) [15–19].

There are some published data on the $\text{GdNi}_{5-x}\text{Ga}_x$ system, where it was reported that GdNi_4Ga [20] crystallizes with the CaCu₅ type of structure. It was also reported that GdNi_3Ga_2

crystallizes with a larger unit cell of the YCo_3Ga_2 type, that is closely related to the CaCu_5 structure [15, 17, 21]. The hydrogen sorption properties of GdNi_4Ga [20] and of the binary GdNi_5 [20, 22] have also been reported.

However, a systematic study of the structural and hydrogen sorption properties of the $\text{GdNi}_{5-x}\text{Ga}_x$ alloys has not been performed so far. The results reported here represent the continuation of our studies on structural characteristics, thermal expansion and hydrogen sorption properties of RENi_5 compounds where nickel has been partially replaced by other metals or metalloids.

2. Experiment

Samples of the weight of 1.2–1.7 g were prepared by argon arc melting from commercial available gadolinium, gallium (Johnson Matthey, UK) and nickel (Carlo Erba, Italy) of stated purity 3N, 4N and 2N5, respectively. Iron was the main impurity in nickel. Hydrogen used was of the purity 99.999% and was supplied by Jesenice, Slovenia. To ensure homogeneity the samples were turned upside down and remelted several times and then annealed at 1100 K. In order to prepare single-phase materials the total annealing time of 21 days was necessary for some alloys.

X-ray powder diffraction patterns of the as-cast as well as the annealed alloys were obtained with a Philips MPD 1880 diffractometer. Monochromatic nickel filtered $\text{Cu K}\alpha$ radiation was employed. The diffraction patterns were scanned in steps of 0.02° (2θ) with a counting time of 2.5 s/step. The high temperature data at 473 K, 673 K and 873 K were taken with a Paar HTK-10 high temperature attachment in vacuum of less than 0.1 Pa. Before measurement the temperature of the sample was stabilized for 15 minutes and controlled with a Pt–PtRh(10%) thermocouple. The intensities were calculated with the ‘Lazy Pulverix’ program [23].

The pressure–composition–isotherm (PCI) measurements were carried out in a stainless-steel apparatus that enables work in a temperature range from 77 K 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. The 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 previously being completely saturated with hydrogen. The equilibrium pressure was measured after 15 minutes and the procedure was repeated until the pressure dropped to 10 kPa, when the remaining amounts of hydrogen were released by heating and measured. The hydride composition was calculated from the pressure–temperature–volume data.

3. Results and discussion

3.1. Structure

Alloys of the composition $\text{GdNi}_{5-x}\text{Ga}_x$ ($x = 0, 0.5, 1, 1.5, 2, 2.5$ and 3) were prepared and studied by x-ray powder diffraction. It was found that all alloys are single phase, but the as-cast and the annealed alloys exhibit sometimes different diffraction patterns. All as-cast alloys and annealed alloys with $x = 0, 0.5, 1, 1.5$ and 3 crystallize with the hexagonal structure of the CaCu_5 type (space group $P6/mmm$), i.e., the same structure as does the prototype binary GdNi_5 . The diffraction patterns of the remaining annealed alloys ($x = 2$ and 2.5) were indexed on the basis of the same space group, but with a larger unit cell of the YCo_3Ga_2 type which is closely related to the CaCu_5 type of structure. The unit cell parameters for all alloys are

Table 1. Crystallographic and thermodynamic data for the $GdNi_{5-x}Al_x$ -hydrogen system.

Composition	a (Å)	c (Å)	c/a	V (Å ³)	ΔH^a kJ (mol H ₂) ⁻¹	ΔS^a J (mol H ₂ K) ⁻¹	Literature
GdNi ₅	4.915	3.967	0.807	82.99			[20]
GdNi _{4.5} Ga _{0.5}	4.942	4.008	0.811	84.77			
GdNi _{4.5} Ga _{0.5} H _{4.32}					-21.93	-98.11	
GdNi ₄ Ga	4.967	4.041	0.814	86.34			[20]
GdNi ₄ GaH _{3.54}	5.107	4.120	0.807	93.06	-33.63	-116.40	[20]
GdNi _{3.5} Ga _{1.5}	5.020	4.054	0.808	88.48			
GdNi _{3.5} Ga _{1.5} H _{2.56}	5.172	4.131	0.799	95.70			
GdNi ₃ Ga ₂	5.047	4.057	0.804	89.50			
GdNi ₃ Ga ₂ H _{1.71}	5.176	4.105	0.793	95.24			
GdNi ₃ Ga ₂ ^b	8.756	4.135	0.472	274.55			
GdNi ₃ Ga ₂ ^c	5.055	4.135	0.818	91.51			
GdNi ₃ Ga ₂	8.748	4.135	0.804	274.05			[15]
GdNi _{2.5} Ga _{2.5}	5.133	4.043	0.788	92.25			
GdNi _{2.5} Ga _{2.5} H _{0.43}	5.198	4.049	0.779	94.74			
GdNi _{2.5} Ga _{2.5} ^b	8.903	4.090	0.459	280.75			
GdNi ₂ Ga ₃	5.207	4.024	0.773	94.49			
GdNi ₂ Ga ₃ H _x	5.210	4.028	0.773	94.69			

^a Determined at the ratio of two hydrogen atoms per alloy formula unit.

^b YCo₃Ga₂ type of structure.

^c YCo₃Ga₂ type, normalized parameter a .

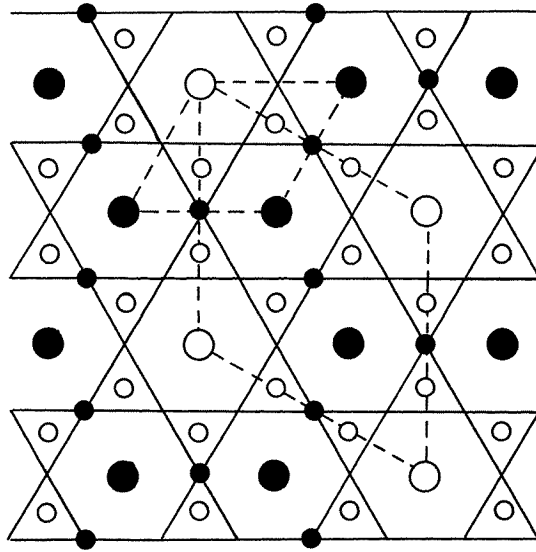


Figure 1. Projection along the c axis of the $GdNi_5$ (smaller) and the $GdNi_3Ga_2$ (larger) cell (dashed lines). $GdNi_5$: ● Gd (at $z = 0$), ○ Gd (at $z = 0$), ○ Ni (at $z = 0$), ● Ni (at $z = 1/2$), (+ Ni atoms); $GdNi_3Ga_2$: ● Gd (at $z = 0$), ○ Gd (at $z = 1/2$), ○ Ni (at $z = 0$), ● Ni (at $z = 1/2$), (+ Ga atoms) at all not-marked junctions of the $z = 1/2$ layer (solid lines).

given in table 1. Note that the parameter a of the smaller cell (a_s) is related to the value of the parameter a of the larger cell (a_L) as $a_s = a_L \times 3^{-1/2}$. The parameters c of both cells differ

Table 2. Atomic coordinates for GdNi₅ (space group *P6/mmm*, CaCu₅ type), GdNi₃Ga₂ (space group *P6/mmm*, YCo₃Ga₂ type) and GdNi_{2.5}Ga_{2.5} (space group *P6/mmm*, YCo₃Ga₂ type).

Atom	Position	Coordinates			Occupation
		<i>x</i>	<i>y</i>	<i>z</i>	
GdNi ₅					
Gd	1(1)	0	0	0	1
Ni	2(c)	1/3	2/3	0	1
Ni	3(g)	1/2	0	1/2	1
GdNi ₃ Ga ₂					
Gd	2(c)	1/3	2/3	0	1
Gd	1(b)	0	0	1/2	1
Ni	6(j)	0.28	0	0	1
Ni	3(g)	1/2	0	1/2	1
Ga	6(m)	0.19	0.38	1/2	1
GdNi _{2.5} Ga _{2.5}					
Gd	1(a)	0	0	0	0.3
Gd	2(c)	1/3	2/3	0	1
Gd	1(b)	0	0	1/2	0.7
Ni	6(j)	0.29	0	0	1
Ni	3(g)	1/2	0	1/2	0.5
Ga	3(g)	1/2	0	1/2	0.5
Ga	6(m)	0.19	0.38	1/2	1

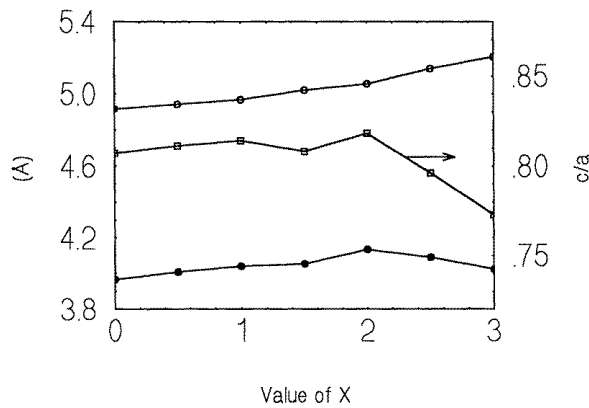


Figure 2. Variation of *a* (○) and *c* (●) parameter and the *c/a* ratio (□) of the GdNi_{5-x}Ga_x alloys.

by less than 2%. The corresponding data for GdNi₅ and GdNi₄Ga which have been published elsewhere [20] are included for comparison. The structural relationship of both structures is illustrated in figure 1 and the atomic coordinates [24] are listed in table 2. The calculated and observed intensity values for GdNi₃Ga₂ (YCo₃Ga₂ type) are given in table 3.

The parameter *a* and the volumes of the annealed alloys increase monotonically with the increased amount of gallium, provided that the values for the larger cell are normalized by division by a factor of 3^{1/2}. The parameter *c* and the *c/a* ratio exhibit maximal values at *x* = 2 (figure 2). This must be explained by movement of larger Gd atoms into the *z* = 1/2 plane which takes place at *x* = 2 (table 2).

In the GdNi₅ structure (CaCu₅ type) there exist two crystallographically inequivalent

Table 3. Calculated (I_c) and observed (I_0) intensity values for $GdNi_3Ga_2$ (YCo_3Ga_2 type of structure).

hkl	d	I_c	I_0
100	7.5829	0.5	n.o.
110	4.3780	4.7	6
001	4.1350	1.1	1
200	3.7915	4.7	3
101	3.6303	14.8	15
111	3.0061	10.1	10
210	2.8661	1.2	2
201	2.7945	50.3	59
300	2.5276	27.6	38
211	2.3556	100.0	100
220	2.1890	52.8	61
301	2.1566	61.3	64
310	2.1031	0.2	n.o.
002	2.0675	45.6	36
102	1.9947	0.0	n.o.
221	1.9346	26.8	30
400	1.8957	6.8	9
311	1.8746	0.9	1
112	1.8695	1.3	2
202	1.8152	1.2	1
320	1.7395	10.3	9
401	1.7233	0.3	n.o.
212	1.6768	0.5	1
410	1.6547	5.3	6
321	1.6035	6.3	21
302	1.6003	13.4	
411	1.5363	6.4	8
500	1.5166	1.5	1
222	1.5031	31.4	28
312	1.4744	0.1	n.o.
330	1.4593	6.2	8
420	1.4330	0.1	n.o.
501	1.4238	18.9	18
402	1.3973	4.6	6
003	1.3783	0.1	n.o.
331	1.3761	1.7	2
510	1.3619	1.0	1
103	1.3561	1.0	1
421	1.3540	12.2	14
322	1.3311	7.9	7
113	1.3147	0.9	1
203	1.2954	4.3	18
511	1.2936	12.6	
412	1.2919	4.8	
600	1.2638	8.4	10
430	1.2466	5.8	3
213	1.2422	12.6	12
502	1.229	1.4	1
520	1.2142	0.4	1
303	1.2102	8.6	8

n.o., not observed.

nickel sites; 2(c) in the basal plane layer at $z = 0$ of mixed atoms (Gd + Ni), and 3(g) in the interleaving layer (Kagome net) at $z = 1/2$. A detailed intensity analysis was carried out and it was determined that in all alloys with the CaCu₅ type of structure gallium atoms replace nickel atoms preferentially in the Kagome net. The only exception is GdNi₂Ga₃ (as-cast) where it was found that substitution of gallium for nickel takes place over the two available crystallographic sites, but after annealing it also proceeds within the Kagome net, only.

As mentioned before, after annealing at 1100 K, a structural change occurs for the alloys with $x = 2$ and 2.5. The crystal structure of GdNi₃Ga₂ (YCo₃Ga₂ type) has already been reported by several authors [15, 17, 21]. However, they do not quite agree over the atomic positions within the crystal lattice of GdNi₃Ga₂. Routsis *et al* [17] proposed a crystal lattice containing gallium atoms in the $z = 1/2$ plane, but with no rare earth atoms in this plane. Buschow *et al* [21] and Fremy *et al* [15] proposed a structure containing rare earth atoms within the $z = 1/2$ plane, but with gallium atoms either in the $z = 1/2$ plane or in the basal plane, respectively. Our results of intensity calculations indicated that the GdNi₃Ga₂ structure is fully ordered, whereby Ga atoms are distributed over the $z = 1/2$ plane only (although at different crystallographic positions than in [17] and [21]), while 1/3 of Gd atoms from the basal plane are shifted into the $z = 1/2$ plane as reported in [15] and [22]. However, the alloy containing more gallium (GdNi_{2.5}Ga_{2.5}) has less Gd atoms in the $z = 1/2$ plane than GdNi₃Ga₂ (table 2). This suggests that the atomic arrangement in this structure type is very composition sensitive.

The substitution in the GdNi_{5-x}Ga_x system can be briefly described as follows. In all annealed alloys, regardless of the structure changes, the replacement of nickel atoms by gallium atoms proceeds within the Kagome net. At the composition GdNi₃Ga₂ an ordering of gallium (nickel) atoms within the Kagome net accompanied by a shift of one third of Gd atoms from the basal plane (position 1(a)) along the c axis into the Kagome plane (position 1(b)) takes place at the same time (figure 1). This is true at the GdNi_{2.5}Ga_{2.5} composition too, whereby the remaining nickel atoms (position 3(g)) are gradually replaced by gallium atoms. A shift of about 1/3 of Gd atoms, but this time from the Kagome plane back into the basal plane (from position 1(b) into 1(a)), also takes place. The replacement of nickel by gallium continues until all nickel in the Kagome plane is replaced by gallium corresponding thus to the composition GdNi₂Ga₃.

The unit cell parameters of GdNi₃Ga₂ reported here agree well with the values given in literature (table 1). It should also be mentioned that similar structural changes are common in the RET_{5-x}M_x (T = Ni, Co, M = Al, Ge) systems [5–10, 12, 21]. On the other hand replacement of 3d transition metal with other transition metals results in continuous solid solution with the CaCu₅ type of structure [14, 25].

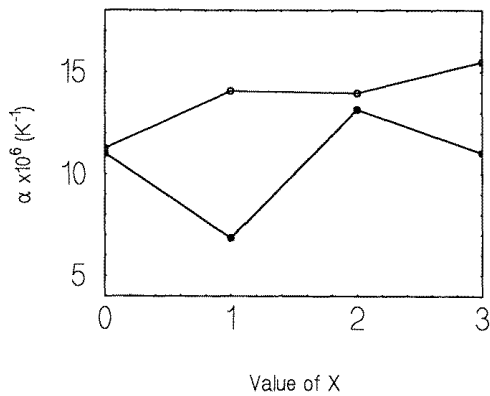
3.2. Thermal expansion

Thermal expansion of the crystal lattice of annealed alloys with $x = 0, 1, 2$ and 3 was studied. Therefore the unit cell parameters were accurately determined (standard error less than ± 0.001 Å) over temperature range between room temperature and 873 K (table 4).

The data for the as-cast alloy with $x = 2$ (smaller unit cell) were also determined and are included in table 4 for comparison. All alloys are stable within the studied temperature range and both unit cell parameters increase with temperature. The linear thermal expansion coefficients α_a and α_c of the lattice parameters a and c respectively were evaluated from the standard formula $x_T = x_{T_0} [1 + \alpha_{T_0} (T - T_0)]$ where x_T = lattice parameter at temperature T and x_{T_0} = lattice parameter at room temperature T_0 . The corresponding values of coefficients are also included in table 4 and illustrated in figure 3. The thermal expansion of the crystal lattice is

Table 4. Unit cell parameters (293–873 K) and expansion coefficients for the annealed $GdNi_{5-x}Ga_x$ alloys.

Compound	Parameter	Temperature (K)				Expansion coefficient ($10^{-6} K^{-1}$)		
		293	473	673	873	α_a	α_c	α_c/α_a
GdNi ₅	<i>a</i>	4.915	4.922	4.934	4.950	11.26	11.02	0.979
	<i>c</i>	3.967	3.975	3.984	3.992			
GdNi ₄ Ga	<i>a</i>	4.967	4.986	4.996	5.004	14.07	6.85	0.487
	<i>c</i>	4.041	4.043	4.053	4.057			
GdNi ₃ Ga ₂	<i>a</i>	8.756	8.778	8.804	8.826	13.98	13.17	0.942
	<i>c</i>	4.135	4.145	4.155	4.167			
GdNi ₂ Ga ₃	<i>a</i>	5.207	5.223	5.235	5.255	15.48	11.04	0.713
	<i>c</i>	4.024	4.032	4.039	4.051			
GdNi ₃ Ga ₂ ^a	<i>a</i>	5.047	5.055	5.061	5.075	8.88	20.99	2.364
	<i>c</i>	4.057	4.083	4.094	4.100			

^a As-cast alloy.**Figure 3.** Coefficients of linear thermal expansion along the *a* (○) and the *c* (●) axes of the $GdNi_{5-x}Ga_x$ alloys.

anisotropic being larger along the *a* axis than along the *c* axis ($\alpha_a > \alpha_c$). The expansion along the *a* axis increases more or less with the increased content of gallium, while the expansion along the *c* axis exhibits a minimum at $x = 1$ and a maximum at $x = 2$. However, expansion coefficients of the smaller unit cell at the composition $GaNi_3Ga_2$ (as-cast alloy) show an about 2.5-fold larger expansion along the *c* axis than along the *a* axis. The latter could be attributed to the structural transformation (ordering of Ni/Ga atoms and a shift of rare earth atoms into the $z = 1/2$ plane) which starts to take place and is completed after 3 weeks at 1100 K.

The above findings, as well as the behaviour of the c/a ratio and the *c* parameter mentioned before, suggest that the interleaving (Kagome) layer possesses self-consistent properties, and plays the major role in the stabilization process of these phases.

3.3. Hydride properties

All alloys have been exposed to hydrogen gas at different pressures and temperatures. Generally, the alloys with the $CaCu_5$ type of structure, except for $GdNi_5$ and $GdNi_2Ga_3$, were

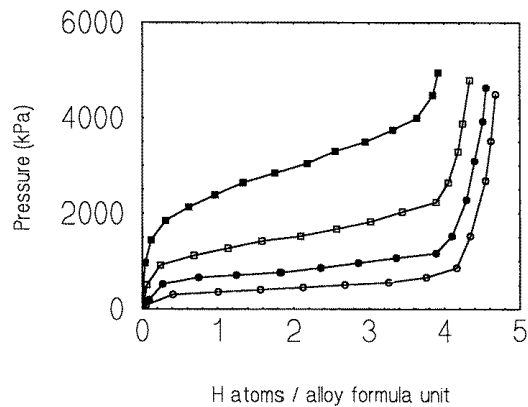


Figure 4. PCI for the $\text{GdNi}_{4.5}\text{Ga}_{0.5}$ -hydrogen system. 255 K (\circ), 273 K (\bullet), 293 K (\square), 313 K (\blacksquare).

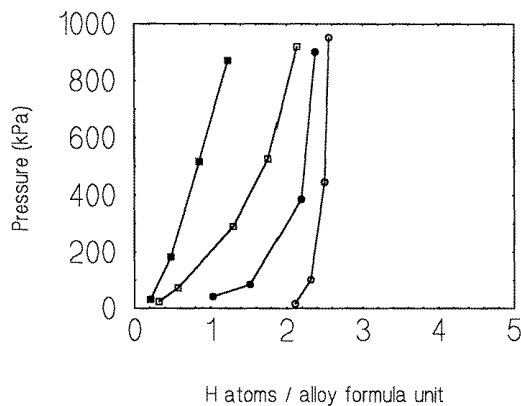


Figure 5. PCI for the $\text{GdNi}_{3.5}\text{Ga}_{1.5}$ -hydrogen system. 293 K (\circ), 353 K (\bullet), 393 K (\square), 421 K (\blacksquare).

easily activated and were found to absorb up to 4.3 hydrogen atoms per alloy formula unit ($\text{GdNi}_{4.5}\text{Ga}_{0.5}$) at room temperature. GdNi_2Ga_3 does not absorb any measurable amounts of hydrogen, but the slight increase in lattice parameters (table 1) after hydrogenation indicates that small amounts have been absorbed. Binary GdNi_5 and the annealed alloys with the YCo_3Ga_2 type of structure (GdNi_3Ga_2 and $\text{GdNi}_{2.5}\text{Ga}_{2.5}$) do not show any significant hydrogen absorption under the experimental conditions applied during the course of this study (< 700 K, < 20 MPa).

Our results on hydrogen sorption properties of GdNi_5 are not in agreement with the results reported in literature. In [22] was reported absorption of three hydrogen atoms per formula unit and an equilibrium pressure of 12 MPa at 396 K. Based on our results presented in this paper and in [20] a clear tendency that hydrogen capacity and the equilibrium pressure increase with the decrease of the gallium concentration is present. Therefore, we assume that GdNi_5 exhibits a much higher hydrogen equilibrium pressure and a significant higher hydrogen capacity from the values given in [22].

The pressure-composition isotherms (PCI) of desorption are shown in figures 4–6. For the $\text{GdNi}_{4.5}\text{Ga}_{0.5}$ -hydrogen system that exhibits well defined plateau pressures, the enthalpy, ΔH

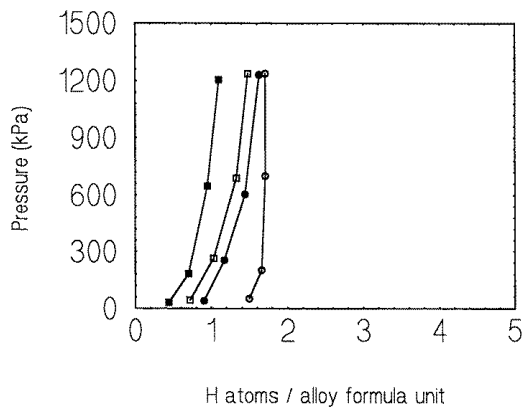


Figure 6. PCI for the GdNi_3Ga_2 -hydrogen system. 293 K (○), 428 K (●), 453 K (□), 493 K (■).

and the entropy, ΔS were calculated from the least-squares fit of the Van't Hoff equation $\ln p_{eq} = \Delta H/RT - \Delta S/R$ where p_{eq} = plateau pressure, ΔH = reaction enthalpy, ΔS = reaction entropy, R = universal gas constant, T = temperature (table 1). The results for GdNi_4Ga [20] are also included. The unit cell parameters for the hydrides stable at room temperature are listed in table 1.

A brief analysis of the relevant data indicates on the following features of the $\text{GdNi}_{5-x}\text{Ga}_x$ -hydrogen systems. Hydrogen uptake increases the unit cell volume of the host alloy for up to 8%. In the hydride-forming alloys the hydrogen capacity and the hydrogen equilibrium pressures decrease as the concentration of gallium increases. The latter findings are well in agreement with the model proposed by Gschneidner *et al* [26]. In their model the hydrogen plateau pressure decreases as the unit cell size increases, but the hydrogen capacity decreases as the number of unpaired nickel 3d electrons decreases. Thus, as gallium is substituted for nickel the cell volume increases, and the equilibrium pressure decreases. At the same time the nickel 3d electrons become increasingly paired up (gallium acts as an electron donor into the system) decreasing the hydrogen capacity.

It is also obvious that the tetrahedra of the larger unit cell (alloys with $x = 2$ and 2.5 after annealing) are more distorted and built up of a different kind of atom than those of the smaller cell. So the structure transformation seems to play a major role in hydrogen absorption properties of the $\text{RENi}_{5-x}\text{Ga}_x$ alloys. However, for a more general conclusion on the influence of the structure type on the hydrogen sorption properties of this class of alloys a detailed analysis of relevant data has to be made.

4. Conclusion

A study on the structural and hydride sorption properties of the $\text{GdNi}_{5-x}\text{Ga}_x$ alloys indicates that substitution of gallium for Ni in GdNi_5 proceeds up to GdNi_2Ga_3 . The hexagonal CaCu_5 crystal structure type of GdNi_5 is retained in the whole ternary region. After annealing for at least 21 d at 1100 K and at the composition GdNi_3Ga_2 and $\text{GdNi}_{2.5}\text{Ga}_{2.5}$, a larger unit cell of the YCo_3Ga_2 type that is closely related to CaCu_5 was observed. The linear thermal expansion coefficients between room temperature and 873 K exhibit anisotropy being larger along the a axis than along the c axis. Hydrogen desorption properties of the alloys $\text{GdNi}_{5-x}\text{Ga}_x$ indicated that ternary alloys within the composition range $\text{GdNi}_{4.5}\text{Ga}_{0.5}$ and $\text{GdNi}_{3.5}\text{Ga}_{1.5}$

absorb remarkable amounts of hydrogen. The hydrogen capacity and the equilibrium pressure decrease with the increased content of gallium.

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