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THE NdT_{1-x}Ge_xIn (*T* = Rh, Pd) SOLID SOLUTIONS

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The NdT_{1-x}Ge_xIn (*T* = Rh, Pd, *x* = 0–1) systems were investigated by X-ray powder diffraction and energy dispersive X-ray analysis. The existence of limited solid solutions with the ZrNiAl-type structure (space group *P*-62*m*) was observed:

NdRh_{1-0.5}Ge_{0.5}In: *a* = 0.75340–0.73139(7), *c* = 0.40280–0.42944(4) nm;

NdPd_{1-0.5}Ge_{0.5}In: *a* = 0.76825–0.73367(6), *c* = 0.40054–0.43309(4) nm.

The results of partial substitution of Rh atoms by Ge atoms were confirmed by single crystal X-ray analysis. NdRh_{0.7}Ge_{0.3}In phase crystallizes with ZrNiAl-type structure (*P*-62*m*, *hP*9, *a* = 0.74755(11), *c* = 0.41886(8) nm, *R*1 = 0.0183 for 360 *F*² values, 16 variables), which agrees well with the results of phase analysis and EDX data.

Keywords: indium, solid solution, powder method, single crystal, crystal structure.

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1. Introduction

The crystal structures of compounds with equiatomic composition, which are formed in the majority of rare-earth metal-transition metal-*p*-element systems, belong to hexagonal AlB₂-, ZrNiAl-, or rhombohedral KHg₂-, CaCuGe-, TiNiSi-type structure [1–7]. Almost all known compounds of this group exhibit interesting physical properties [8–17]. Replacement of palladium or rhodium with germanium in the CePd_{1-x}Ge_xIn and CeRh_{1-x}Ge_xIn systems has a significant effect on the structural characteristics and properties of solid solutions with ZrNiAl-type structure [18, 19].

The aim of this work is to study the effect of substitution of *d*-element (Pd or Rh) on Ge in NdTIn compounds (*T* = Rh, Pd) on the possibility of formation and structure of solid solutions.

2. Materials and experimental techniques

The interaction of components in the NdRh_{1-x}Ge_xIn and NdPd_{1-x}Ge_xIn systems was studied on samples, prepared by arc-melting of pure metals, all with stated purities better than 99.9 %.

Diffraction data were obtained using Guinier powder camera (Enraf-Nonius FR552, Cu *K*_{α1}-radiation), equipped with an image processing technique (FujiFilm, BAS-READER 1800) and Stoe Stadi P diffractometer (Cu *K*_{α1}-radiation). Phase analysis was performed

using Powder Cell [20] and STOE WinXPOW [21] programs, and structural calculations were performed using Fullprof package [22]. The result of X-ray powder diffraction data were confirmed by energy dispersive X-ray analysis (scanning electron microscope REMMA-102-02).

Single crystals were grown using a special heat treatment. Arc-melted samples of $\text{NdRh}_{0.7}\text{Ge}_{0.3}\text{In}$ were placed in small tantalum containers that were sealed in evacuated silica tubes as an oxidation protection. The ampoules were first heated in a Huttinger Elektronik high-frequency furnace (Freiburg, Typ TIG 1.5/300) to 1270 K at a speed of 5 °/h and held at that temperature for 120 h. Then the furnace was turned off to cool the samples to room temperature. After cooling, the samples could easily be separated from the tantalum container. No reaction of the container material was evident. As a result, irregularly shaped single crystals were obtained. They were investigated using the Laue method (precision camera, Mo $K\alpha$ -radiation) in order to check the quality for intensity data collection. Further investigation of the crystal structure was conducted using the single crystal method (Stoe IPDS-II diffractometer, Mo $K\alpha$ -radiation). The structure was solved in ZrNiAl-type structure and refined using the SHELXL-97 program suite [23]. The quantitative and qualitative composition of the single crystal was determined by EDX analysis (JEOL 5900LV scanning electron microscope) and closely matches the composition of the synthesized sample: 34 (1) at. % Nd : 23(1) at. % Rh : 11(1) at. % Ge : 33(1) at. % In.

3. Results and discussions

In the $\text{NdRh}_{1-x}\text{Ge}_x\text{In}$ and $\text{NdPd}_{1-x}\text{Ge}_x\text{In}$ systems partial solubility of Ge in compounds of equiatomic composition NdTIn ($T = \text{Rh}, \text{Pd}$) is observed with the formation of limited solid solutions with ZrNiAl-type structure. The limits of solid solutions were determined according to the results of X-ray phase and EDX analysis (Fig. 1) with such unit cell parameters: $\text{NdRh}_{1-0.5}\text{Ge}_{0.5}\text{In}$: $a = 0.7534\text{--}0.73139(7)$, $c = 0.4028\text{--}0.42944(4)$ nm and $\text{NdPd}_{1-0.5}\text{Ge}_{0.5}\text{In}$: $a = 0.76825\text{--}0.73367(6)$, $c = 0.40054\text{--}0.43309(4)$ nm.

Within the $\text{NdRh}_{1-0.5}\text{Ge}_{0.5}\text{In}$ solid solution, in addition to the main phase, some samples of the system contain small amounts of the NdRhIn_2 phase with the MgCuAl_2 -type structure [24], and $\text{NdPd}_{1-0.5}\text{Ge}_{0.5}\text{In}$ solid solution – NdPdIn_2 with the HfNiSi_2 -type structure [25], which agrees with phase equilibria diagram for the Nd–Pd–In system at 870 K [26]. Samples with a high germanium content (> 25 at. %) in both systems contain phases $\text{Nd}_2(T,\text{Ge})_2\text{In}$ (Mo_2FeB_2 -type structure) [27, 28], $\text{Nd}(T,\text{Ge})_2$ (AlB_2 -type structure) [29] and NdIn_3 (AuCu_3 -type structure) [30]. The phase $\text{Nd}_2(\text{Ge},T)_2\text{In}$ with the Mo_2FeB_2 -type structure, which is dominant in this concentration range of the Nd–Ge–In system [31], is in equilibrium with the main $R(T_{1-x}\text{Ge}_x)\text{In}$ phase with the ZrNiAl-type structure of the majority of samples.

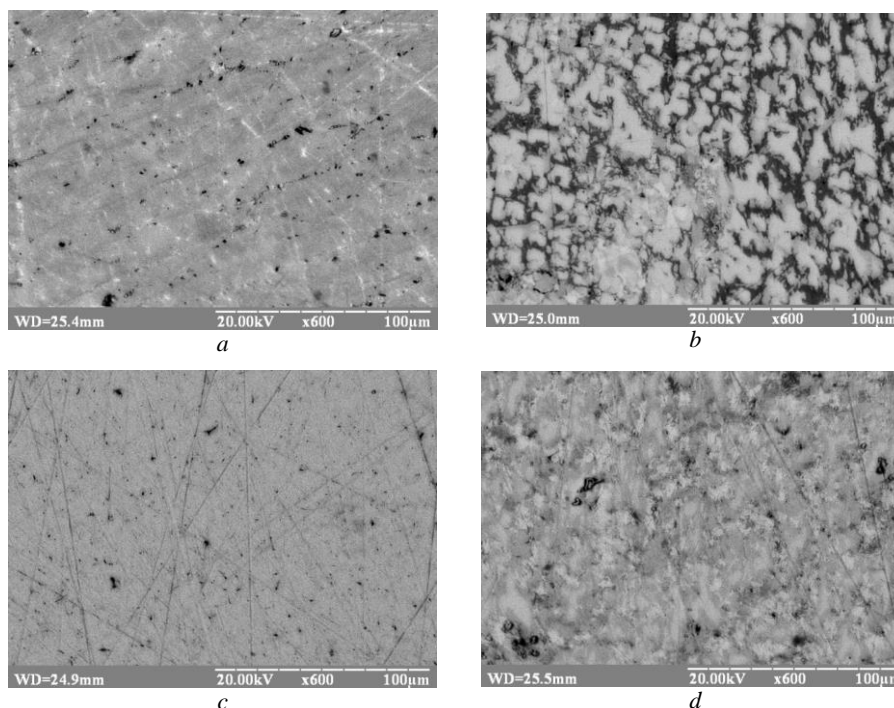


Fig. 1. Scanning electron micrographs of polished samples of the $\text{NdRh}_{1-x}\text{Ge}_x\text{In}$ (*a, b*) and $\text{NdPd}_{1-x}\text{Ge}_x\text{In}$ (*c, d*) systems: *a* – $\text{NdRh}_{0.5}\text{Ge}_{0.5}\text{In}$ (gray phase (*main*) – $\text{Nd}_{0.34}\text{Rh}_{0.16}\text{Ge}_{0.19}\text{In}_{0.31}$, dark phase – pores); *b* – $\text{NdRh}_{0.1}\text{Ge}_{0.9}\text{In}$ (light gray phase – $\text{Nd}_{0.39}\text{Rh}_{0.0}\text{Ge}_{0.42}\text{In}_{0.19}$, gray phase – $\text{Nd}_{0.27}\text{Rh}_{0.17}\text{Ge}_{0.51}\text{In}_{0.05}$, dark phase – $\text{Nd}_{0.25}\text{Rh}_{0.01}\text{Ge}_{0.05}\text{In}_{0.69}$); *c* – $\text{NdPd}_{0.5}\text{Ge}_{0.5}\text{In}$ (gray phase (*main*) – $\text{Nd}_{0.33}\text{Pd}_{0.17}\text{Ge}_{0.17}\text{In}_{0.33}$); *d* – $\text{NdPd}_{0.1}\text{Ge}_{0.9}\text{In}$ (gray phase – $\text{Nd}_{0.31}\text{Pd}_{0.16}\text{Ge}_{0.53}\text{In}_{0.0}$, light gray phase – $\text{Nd}_{0.39}\text{Pd}_{0.0}\text{Ge}_{0.43}\text{In}_{0.18}$, white phase – $\text{Nd}_{0.27}\text{Pd}_{0.02}\text{Ge}_{0.10}\text{In}_{0.61}$, dark phase – pores) (scanning electron microscope REMMA-102-02)

In order to confirm the crystal structure of solid solutions, one sample in each system was studied by powder X-ray analysis.

In $\text{NdRh}_{1-x}\text{Ge}_x\text{In}$ system, the crystal structure was refined for the main phase of the $\text{NdRh}_{0.5}\text{Ge}_{0.5}\text{In}$ sample (Fig. 2) based on the experimental hkl reflections using the FullProf package [22]: $\text{NdRh}_{0.55}\text{Ge}_{0.45}\text{In}$ (ZrNiAl-type structure [34], space group $P-62m$, $a = 0.74012(2)$ nm, $c = 0.43446(2)$ nm; $V = 0.20610(1)$ nm³; $R_{\text{Bragg}} = 0.0861$; $R_f = 0.0823$; phase content – 95 wt. %). Content of $\text{Nd}_2(\text{Rh,Ge})_2\text{In}$ phase (Mo_2FeB_2 -type structure, space group $P4/mbm$, $a = 0.74259(1)$ nm; $c = 0.41539$ nm) was 4 wt. %, and NdIn_3 phase (AuCu_3 -type structure, space group $Pm-3m$, $a = 0.4674(1)$ nm) – 1 wt. %. Structural parameters were not refined. The atomic parameters in the $\text{NdRh}_{0.55}\text{Ge}_{0.45}\text{In}$ structure are shown in the Table. 1.

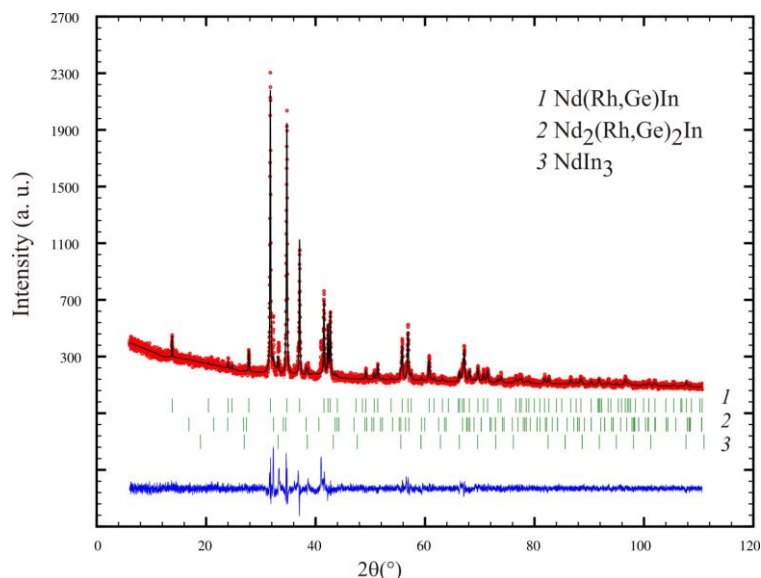


Fig. 2. Observed, calculated and difference X-ray patterns of the NdRh_{0.5}Ge_{0.5}In alloy (Stoe Stadi P, Cu K α_1 -radiation)

Table 1

Atomic parameters of NdRh_{0.55}Ge_{0.45}In structure

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>
Nd	3 <i>f</i>	0.5896(5)	0	0
In	3 <i>g</i>	0.2382(7)	0	1/2
<i>M1</i> *	1 <i>a</i>	0	0	0
<i>M2</i> **	2 <i>d</i>	1/3	2/3	1/2

M1* = 0.95(4)Rh + 0.05(4)Ge; *M2* = 0.36(5)Rh + 0.64(5)Ge, B_{Overall} = 1.71(9).

The crystal structure of the main phase of NdPd_{0.5}Ge_{0.5}In sample (Fig. 3) was refined based on experimental *hkl* reflections using the FullProf software package [22]: NdPd_{0.56}Ge_{0.44}In (ZrNiAl-type structure [34], space group *P-62m*, *a* = 0.73984(6) nm, *c* = 0.43661(3) nm; *V* = 0.20696(3) nm³; *R*_{Bragg} = 0.0661; *R*_f = 0.0637; phase content – 97 wt. %). Content of Nd₂(Pd,Ge)₂In phase (Mo₂FeB₂-type structure, space group *P4/mbm*, *a* = 0.7688(3) nm; *c* = 0.3989(2) nm) was 2 wt. %, and NdIn₃ phase (AuCu₃-type structure, space group *Pm-3m*, *a* = 0.4656(1) nm) – 1 wt. %. Structural parameters were not refined. The atomic sites and isotropic displacement parameters in the NdPd_{0.56}Ge_{0.44}In structure are shown in Table 2.

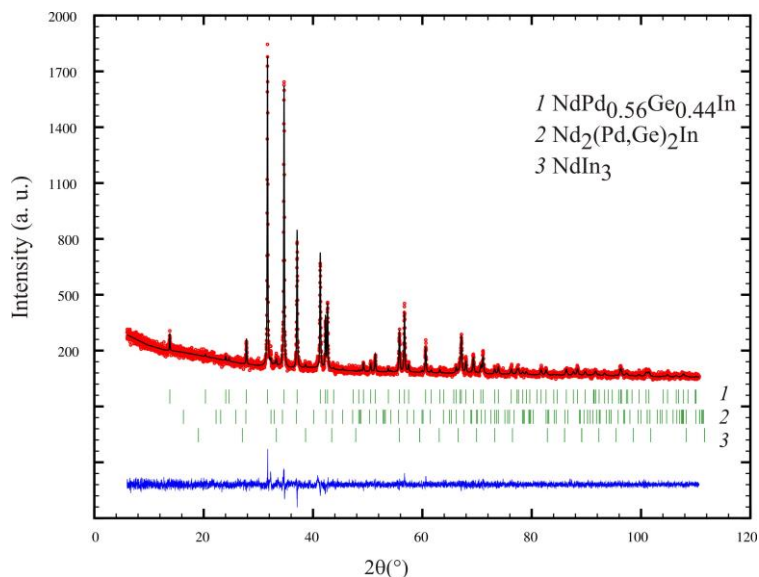


Fig. 3. Observed, calculated and difference X-ray patterns of the $\text{NdPd}_{0.5}\text{Ge}_{0.5}\text{In}$ alloy (Stoe Stadi P, $\text{Cu } K\alpha_1$ -radiation)

Table 2

Atomic and thermal displacement parameters of $\text{NdPd}_{0.56}\text{Ge}_{0.44}\text{In}$ structure

Atom	Wyckoff site	x	y	z	U_{Iso}
Nd	$3f$	0.5866(4)	0	0	0.0112(5)
In	$3g$	0.2413(6)	0	1/2	0.0153(7)
$M1^*$	$1a$	0	0	0	0.0143(17)
$M2^{**}$	$2d$	1/3	2/3	1/2	0.0222(17)

* $M1 = 0.96(5)\text{Pd} + 0.04(5)\text{Ge}$; ** $M2 = 0.36(5)\text{Pd} + 0.64(5)\text{Ge}$.

In our opinion, dimensional factor is the main factor affecting the formation of solid solutions. The chemical nature of germanium and d -metals influences less. The closeness of the atomic sizes ($r_{\text{Rh}} = 0.1345 \text{ nm}$, $r_{\text{Pd}} = 0.1376 \text{ nm}$, $r_{\text{Ge}} = 0.1369 \text{ nm}$) [32] has a direct impact on both the possibility of replacing d -metals with germanium and on the values of the unit cell parameters (Fig. 4). The unit cell parameter a decreases and the unit cell parameter c slightly increases within solid solutions. The change in the values of a parameter is influenced by the crystallographic peculiarities of the ZrNiAl -type structure. Substitution of d -metals (Rh i Pd) by Ge occurs in sites $2d$ ($1/3 \ 2/3 \ 1/2$) of space group $P-62m$, which leads to the compression of trigonal prisms around the atoms of the statistical mixture M , and the parameter a slightly decreases. A similar situation is observed in $\text{CePd}_{1-x}\text{Ge}_x\text{In}$ [18], $\text{CeRh}_{1-x}\text{Ge}_x\text{In}$ [19] and $\text{CePt}_{1-x}\text{Ge}_x\text{In}$ [33] systems, where substitution of the d -metal by germanium also occurs in the site $2d$ ($1/3 \ 2/3 \ 1/2$).

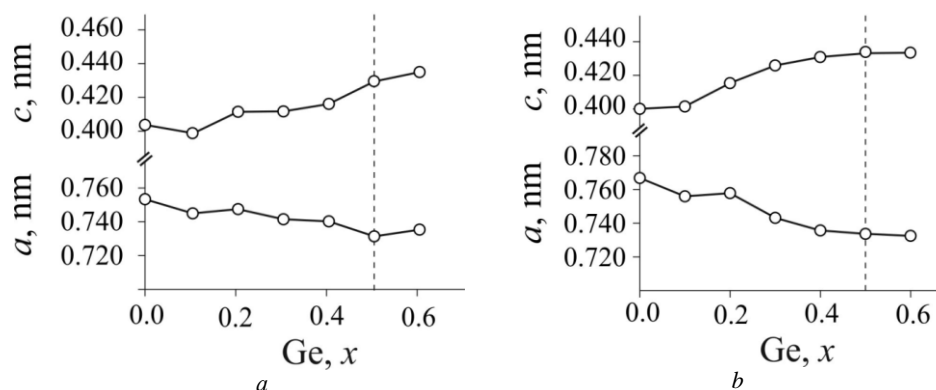


Fig. 4. Change of the unit cell parameters in solid solutions:
 a – NdRh_{1-x}Ge_xIn; b – NdPd_{1-x}Ge_xIn

The results of partial substitution of Rh atoms by Ge atoms were confirmed by single crystal X-ray analysis. The structure was solved and refined using programs from the SHELX-97 package [23].

NdRh_{0.7}Ge_{0.3}In phase crystallizes with ZrNiAl-type structure [34]: *P*-62*m*, *hP*9, *a* = 0.74755(11), *c* = 0.41886(8) nm, *R*1 = 0.0183 for 360 *F*² values, 16 variables, Table 3), which agrees well with the results of phase analysis and EDX data (JEOL 5900LV scanning electron microscope).

Table 3

Crystallographic data and structure refinement of NdRh_{0.7}Ge_{0.3}In

Empirical formula	NdRh _{0.7} Ge _{0.3} In
Unit-cell parameters, nm	<i>a</i> = 0.74755(11) <i>c</i> = 0.41886(8)
Cell volume, nm ³	0.20271(6)
Calculated density, g/cm ³	8.669
Absorption coefficient, mm ⁻¹	34.554
F(000)	450
θ range for data collection, deg	3.15–34.78
<i>hkl</i> range	±12, ±12, ±6
Total reflections	3158
Independent reflections / parameters	360/16
Reflections with <i>I</i> > 2σ(<i>I</i>)	330
Goodness-of-fit on <i>F</i> ²	0.936
<i>R</i> 1 / <i>wR</i> 2 for <i>I</i> > 2σ(<i>I</i>)	0.0183 / 0.0285
<i>R</i> 1 / <i>wR</i> 2 for all data	0.0241 / 0.0291
Extinction coefficient	0.0074(5)
Highest / lowest Δρ, e/nm ³ ·10 ³	1.055 and –1.618

Table 4

Atomic and thermal displacement parameters of NdRh_{0.7}Ge_{0.3}In structure

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Nd	3 <i>f</i>	0.58960(7)	0	0	0.0130(1)
In	3 <i>g</i>	0.24508(7)	0	1/2	0.0127(1)
<i>M</i> *	2 <i>d</i>	1/3	2/3	1/2	0.0123(4)
Rh2	1 <i>a</i>	0	0	0	0.0145(2)
Atom		<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂
Nd		0.0110(2)	0.0129(2)	0.0187(2)	0.0065(1)
In		0.0113(2)	0.0122(3)	0.0149(3)	0.0061(1)
<i>M</i> *		0.0114(4)	0.0114(4)	0.0142(6)	0.0057(2)
Rh2		0.0145(3)	0.0145(3)	0.0144(6)	0.0073(1)

**M* = 0.55(3)Rh + 0.45(3)Ge; *U*₂₃=*U*₁₃=0.

Table 5

Interatomic distances (*a*) and coordination numbers of atoms
in NdRh_{0.7}Ge_{0.3}In structure

Atom		<i>a</i> , nm	CN	Atom		□, □nm	CN
Nd–	1 <i>M</i> *	0.3068(1)	17	Rh2–	6In	0.2783(1)	9
	4Rh2	0.3081(1)			3Nd	0.3068(1)	
	2In	0.3320(1)		In–	2Rh2	0.2783(1)	12
	4In	0.3396(1)			2 <i>M</i>	0.2879(1)	
	4Nd	0.3914(1)			2In	0.3173(1)	
	2Nd	0.4189(1)			2Nd	0.3320(1)	
<i>M</i> –	3In	0.2879(1)	9	4Nd	0.3396(1)		
	6Nd	0.3081(1)					

**M* = 0.55(3) Rh + 0.45(3) Ge.

The shortest distances in this structure are between In–Rh2 ($\delta = 0.2783$ nm), which are slightly smaller than the sum of the radii of the corresponding atoms ($r_{\text{In}} + r_{\text{Rh}} = 0.301$ nm). All other distances between atoms are greater than the sum of the radii of the atoms ($r_{\text{Nd}} = 0.1821$ nm, $r_{\text{Rh}} = 0.1345$ nm, $r_{\text{Pd}} = 0.1376$ nm, $r_{\text{Ge}} = 0.1369$ nm, $r_{\text{In}} = 0.1663$ nm [32]) and indicate the absence of covalent interaction between them.

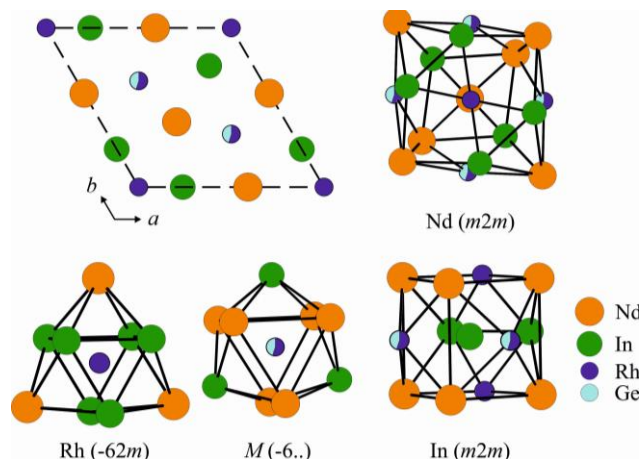


Fig. 5. Projection of the $\text{NdRh}_{0.7}\text{Ge}_{0.3}\text{In}$ structure along c axis and coordination polyhedra of atoms

4. Conclusions

The existence of substitutional solid solutions $\text{NdRh}_{1-0.5}\text{Ge}_{0-0.5}\text{In}$ and $\text{NdPd}_{1-0.5}\text{Ge}_{0-0.5}\text{In}$ with ZrNiAl-type structure (space group $P-62m$) was established and the change in the unit cell parameters was refined.

Substitution of Rh or Pd atoms by Ge atoms was confirmed by single-crystal studies of the $\text{NdRh}_{0.7}\text{Ge}_{0.3}\text{In}$ phase (ZrNiAl-type structure, space group $P-62m$, $hP9$, $a = 0.74755(11)$, $c = 0.41886(8)$ nm, $R1 = 0.0183$, 16 parameters).

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ТВЕДРІ РОЗЧИННИ $\text{NdT}_{1-x}\text{Ge}_x\text{In}$ ($T = \text{Rh}, \text{Pd}$)**Г. Ничипорук^{1*}, Н. Домінюк^{1,2}, М. Горяча^{1,2}, Р. Пьоттген², В. Заремба¹**¹*Львівський національний університет імені Івана Франка,
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Системи $\text{NdT}_{1-x}\text{Ge}_x\text{In}$ ($T = \text{Rh}, \text{Pd}$, $x = 0\div 1$) досліджено рентгенівським методом порошку і локального рентгеноспектрального аналізу.

Зразки для досліджень синтезовано електродуговим сплавлянням шихти металів чистотою не менше 99,9 мас. % основного компонента і відпалено у вакуумованих кварцових ампулах упродовж місяця. Поверхню неодиму очищено від оксидів безпосередньо перед зважуванням і сплавлянням. Масиви дифракційних даних отримано з використанням порошкової камери Гіньє (Enraf-Nonius FR552, $\text{Cu } K\alpha_1$ -випромінювання) і дифрактометра Stoe Stadi P ($\text{Cu } K\alpha_1$ -випромінювання).

Синтез монокристалів виконано спеціальною термічною обробкою зразка складу $\text{NdRh}_{0,7}\text{Ge}_{0,3}\text{In}$ у вакуумованій танталовій ампулі у високочастотній печі Huttinger Elektronik, Freiburg, Тур TIG 1.5/300. Структуру нової фази розв'язано та уточнено з використанням комплексу програм SHELXL-97.

Визначено, що у досліджених системах утворюються обмежені тверді розчини заміщення зі структурою типу ZrNiAl (просторова група $P-62m$): $\text{NdRh}_{1-0,5}\text{Ge}_{0-0,5}\text{In}$ ($a = 0,75340\text{--}0,73139(7)$; $c = 0,40280\text{--}0,42944(4)$ нм; $V = 0,1980\text{--}0,1989(1)$ нм³) і $\text{NdPd}_{1-0,5}\text{Ge}_{0-0,5}\text{In}$ ($a = 0,76825\text{--}0,73367(6)$ нм; $c = 0,40054\text{--}0,43309(4)$ нм; $V = 0,2013\text{--}0,2018(1)$ нм³). У межах твердих розчинів, подібно до систем $\text{CePd}_{1-x}\text{Ge}_x\text{In}$, $\text{CeRh}_{1-x}\text{Ge}_x\text{In}$ і $\text{CePt}_{1-x}\text{Ge}_x\text{In}$, параметр елементарної комірки a зменшується, а параметр c – незначно збільшується, що зумовлено особливостями структур типу ZrNiAl . Методом порошку з використанням програми FullProf уточнено кристалічну структуру фаз $\text{NdRh}_{0,55}\text{Ge}_{0,45}\text{In}$ і $\text{NdPd}_{0,56}\text{Ge}_{0,44}\text{In}$.

Часткове заміщення атомів Rh атомами Ge підтверджено структурними дослідженнями монокристалів фази $\text{NdRh}_{0,7}\text{Ge}_{0,3}\text{In}$ (структурний тип ZrNiAl , просторова група $P-62m$, символ Пірсона $hP9$, $a = 0,74755(11)$; $c = 0,41886(8)$ нм; $R1 = 0,0183$; 16 параметрів).

Ключові слова: індій, твердий розчин, метод порошку, метод монокристала, кристалічна структура.

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