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SOLID SOLUTIONS IN THE *R*NiIn–*R*NiGa (*R* = Pr, Ho) SYSTEMS

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The PrNiIn–PrNiGa and HoNiIn–HoNiGa systems were investigated by X-ray powder diffraction and energy dispersive X-ray analysis in full concentration ranges at 870 K. The existence of two limited solid solutions in each system was observed and changes of unit cells parameters of the phases in them were determined.
The crystal structure of $PrNiIn_{0.79}Ga_{0.21}$ phase was refined based on the experimental hkl reflections using the FullProf package: ZrNiAl-type structure, space group P-62m, Pearson symbol hP9, a = 0.74795(15), c = 0.39454(8) nm, R_{Bragg} = 0.077, R_f = 0.085.
Partial substitution of indium by gallium atoms was confirmed by structure refinement from single crystal X-ray diffraction data: $HoNiIn_{0.69}Ga_{0.31}$ phase crystallizes with ZrNiAl-type structure (P-62m, hP9, a = 0.73604(3), c = 0.37241(2) nm, R1 = 0.0096 for 205 F^2 values, 16 variables).

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

Introduction

The vast majority of *RE*–Ni–*X* systems (*RE* – rare earth, *X* is a *p*-element of the III–V group of the periodic table) contain compounds of equiatomic composition that have interesting magnetic and transport properties in a wide temperature range [1, 2]. Such compounds with indium have crystal structures belonging to the hexagonal ZrNiAl-type structure [3, 4], and with gallium – to the orthorhombic HoNiGa-type structure [5]. The properties of compounds PrNiIn, HoNiIn [6–10] and HoNiGa [11], among others ternary intermetallic compounds *RE*Ni*X*, have their own characteristics: HoNiIn order ferromagnetically below 20 K [8], PrNiIn does not order magnetically down to 1.5 K [10], while HoNiGa is paramagnet above 12 K [11]. Thermodynamic properties of hydrogen in *RE*NiIn (*RE* = La, Ce, Pr, Nd) ternary compounds strongly depend on the *RE* elements [12]. The Curie temperature in the $Gd_{1-x}Ho_xNiIn$ solid solution decreases linearly with increasing Ho content and temperature dependences of magnetization and heat capacity show that all compounds, except GdNiIn, undergo a phase transition at a low temperature of 7–9 K [13]. Therefore, it is relevant to study the interaction of

components in the PrNiIn–PrNiGa and HoNiIn–HoNiGa systems at 870 K in the full range of concentrations with mutual substitution of *p*-elements.

Materials and experimental techniques

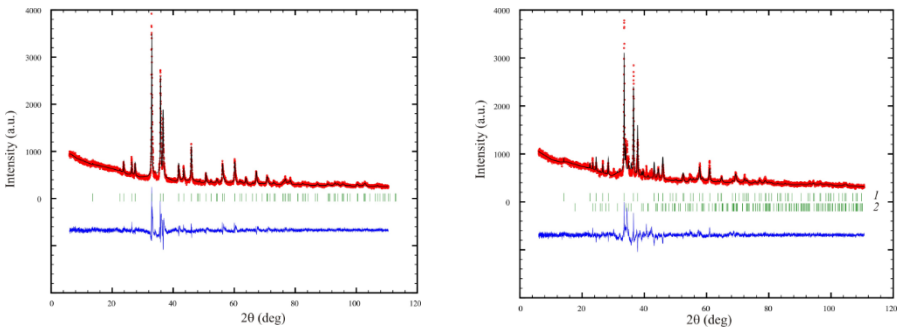
Polycrystalline samples of *RE*NiIn$_{1-x}$Ga$_x$ (*RE* = Pr, Ho) systems (up to 1.0 g), with *x* range from 0 to 1.0 in steps of 0.1, were prepared by arc melting of the pure elements (all with stated purities better than 99.9 %) under an argon atmosphere (purified using titanium sponge). The surface of praseodymium was mechanically cleaned immediately before weighing. The buttons were remelted twice to ensure homogeneity. Further all samples were sealed in evacuated quartz ampules and then annealed for one month at 870 K, followed by quenching in cold water without breaking the ampoules. The samples were analyzed by X-ray powder diffraction (XRD) using a DRON 2.0M (Fe *K*α radiation) and STOE STADI P (Cu *K*α1 radiation) diffractometers. Phase analysis was performed using Powder Cell [14] and STOE WinXPOW [15] programs. Structural calculations were performed using Fullprof package [16]. Some alloys were examined on a Tescan Vega 3 LMU scanning electron microscope (SEM) equipped with an Oxford Instruments SDD X-Max^{N20} detector. In the HoNiIn$_{1-x}$Ga$_x$ system, single crystals of an irregular shape with a metallic lustre were selected from annealed sample of HoNiIn$_{0.7}$Ga$_{0.3}$ composition. Intensity data for a single crystal of the composition: Ho:Ni:In:Ga – 34.0(2) at. % Ho, 32.3(2) at. % Ni, 25.2(2) at. % In, 8.5(2) at. % Ga (SEM Zeiss EVO MA 15) was collected at room temperature by use of a SuperNova Rigaku Oxford Diffraction diffractometer (Mo *K*α-radiation) at the Technical University of Dresden (Germany). The crystal structure was refined using the JANA 2006 software programs [17].

Results and discussions

Two limited solid solutions were detected in the PrNiIn–PrNiGa system based on the starting compounds under the study conditions (870 K). Up to 20 atomic % of indium is replaced by gallium in the PrNiIn compound with the formation of solid solution of the composition PrNiIn$_{1.0\text{-}0.4}$Ga$_{0\text{-}0.6}$ (ZrNiAl-type structure [18]: space group *P*-62*m*; *a* = 0.7552(1)–0.7336(3); *c* = 0.3963(1)–0.3938(2) nm, *V* = 0.1957(1)–0.1835(1) nm^3. On the other hand, only 3 atomic % of gallium is replaced by indium in the PrNiGa structure, forming a solid solution of the composition PrNiIn$_{0.1\text{-}0}$Ga$_{0.9\text{-}1.0}$ with a HoNiGa-type structure [5]: space group *Pnma*; *a* = 0.7451(2)–0.7438(2), *b* = 0.4565(1)–0.4552(1), *c* = 0.6833(2)–0.6818(1) nm, *V* = 0.2324(1)–0.2308(1) nm^3. Two samples with gallium content of 23–26 at. % contains a phase with approximate composition Pr$_{0.43}$Ni$_{0.18}$In$_{0.25}$Ga$_{0.14}$ of unknown structure. These data were confirmed by results of XRD and EDX analysis. Two XRD patterns of PrNiIn$_{0.7}$Ga$_{0.3}$ and PrNiIn$_{0.3}$Ga$_{0.7}$ samples are shown in Fig. 1.

Ternary compounds with equiatomic composition HoNiIn and HoNiGa partially dissolve the fourth component in the HoNiIn–HoNiGa system at 870 K. Limited solid solutions are formed of the following compositions: HoNiIn$_{1.0\text{-}0.4}$Ga$_{0\text{-}0.6}$ (ZrNiAl; *P*-62*m*; *a* = 0.74343(4)–0.72453(6); *c* = 0.37472(3)–0.37013(4) nm; *V* = 0.17936(2)–0.16826(3) nm^3) and HoNiGa$_{1.0\text{-}0.8}$In$_{0\text{-}0.2}$ (HoNiGa; *Pnma*; *a* = 0.68226(4)–0.68261(9); *b* = 0.42790(2)–0.42894(5); *c* = 0.73296(4)–0.73915(9) nm; *V* = 0.21398(2)–21642(5) nm^3). Some samples contain additional phases (up to 5%): Ho$_3$Ni$_6$Ga$_2$ (Ce$_3$Ni$_6$Si$_2$-type structure) [19] and (or) Ni$_2$In$_3$ (Ni$_2$Al$_3$-type structure) [20]. Fig. 2 shows the XRD pattern of a sample of composition HoNiIn$_{0.5}$Ga$_{0.5}$.

Backscattered electron images of the surfaces of individual samples of the studied systems and composition of phases according to the results of the EDX analysis are shown in Fig. 3.



a *b*

Fig. 1. Experimental (circles), calculated (continuous line) and difference (lowest line) powder X-ray diffraction patterns of samples: *a* – $PrNiIn_{0.7}Ga_{0.3}$; *b* – $PrNiIn_{0.3}Ga_{0.7}$ (*1* – $PrNiIn_{0.4}Ga_{0.6}$; *2* – $PrNiIn_{0.1}Ga_{0.9}$) (Stoe Stadi P, Cu $K\alpha_1$-radiation).

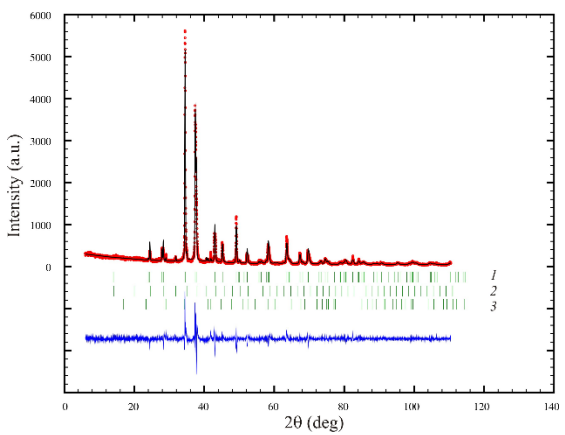


Fig. 2. Experimental (circles), calculated (continuous line) and difference (lowest line) powder X-ray diffraction patterns of $HoNiIn_{0.5}Ga_{0.5}$ sample (*1* – $HoNiIn_{0.5}Ga_{0.5}$; *2* – $Ho_3Ni_6Ga_2$; *3* – Ni_2In_3) (Stoe Stadi P, Cu $K\alpha_1$-radiation).

Within the solid solutions with a structure of the ZrNiAl and HoNiGa types we observed the expected decreasing lattice parameters with increasing gallium content (Fig. 4), since the sizes of *p*-elements (r_{Pr}= 0.1828, r_{Ho}= 0.1766, r_{Ni}= 0.1246, r_{In}= 0.1626, r_{Ga}= 0.1221 nm [21]) are a direct impact on the values of the unit cell parameters. Variations of the unit cell parameters in the solid solutions change similar to those in the *RE*NiIn–*RE*NiGa and *RE*CuIn–*RE*CuGa systems (*RE* = Y, La, Ce, Pr, Gd, Tb, Ho) [22–29].

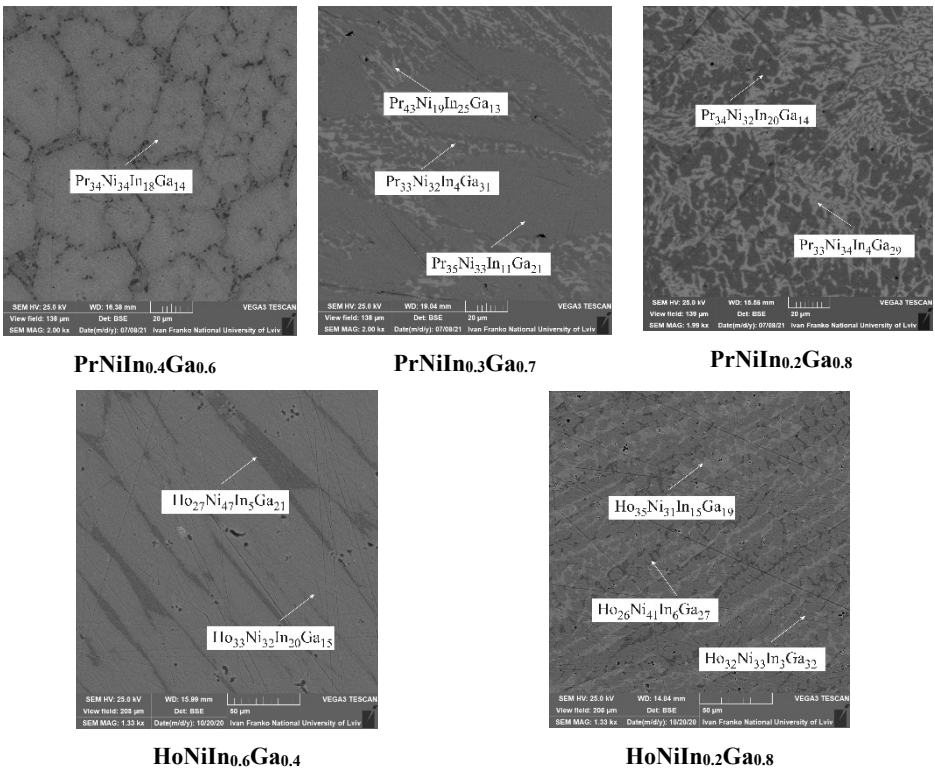
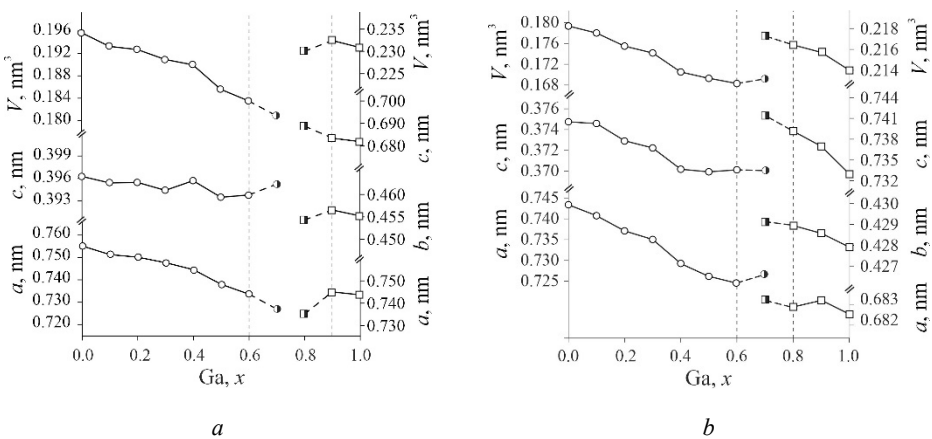


Fig. 3. Backscattered electron image of samples of the *RE*NiIn–*RE*NiGa systems (SEM Tescan Vega 3 LMU).



a *b*

Fig. 4. Variation of the unit cell parameters in the solid solutions: *a* – PrNiIn$_{1-x}$Ga$_x$ and *b* – HoNiIn$_{1-x}$Ga$_x$ (○ – ZrNiAl type, □ – HoNiGa type).

In order to confirm the substituting of indium atoms by gallium atoms the crystal structure of a sample with $PrNiIn_{0.7}Ga_{0.3}$ composition was refined from powder XRD data. Experimental reflections collected using a powder diffractometer STOE STADI P, Cu $K\alpha 1$ radiation. The details of the experiment and the results of refinement (FullProf package) are presented in Table. 1.

Table 1

The details of the experiment and the crystal structure refinement results for $PrNiIn_{0.79}Ga_{0.21}$ phase

Sample composition	$PrNiIn_{0.7}Ga_{0.3}$
Empirical formula	$PrNiIn_{0.79}Ga_{0.21}$
Structure type	ZrNiAl
Space group, *Z*	*P*-62*m,* 3
Pearson symbol	*hP*9
Unit cell parameters, nm	a = 0.74795(15); c = 0.39454(8)
Cell volume, nm^3	V = 0.19115(7)
Diffractometer	STOE STADI P
Radiation; λ, nm	Cu $K\alpha_1$; 0.154060
Calculated density, g/cm^3	7.942
Absorption correction	1.6
Angular range 2θ, deg.	6.00–110.625
Step; scanning time, sec	0.015°; 40
Halfwidth parameters *U*; *V*; *W*	0.192(1); 0.089(1); 0.001(1)
Preferred orientation [100], G;	0.239(1)
R_p; R_{wp}; R_{Exp}	0.065; 0.089; 0.050
R_{Bragg}, R_F	0.077; 0.085

Table 2

Atomic coordinates and isotropic displacement parameters in the $PrNiIn_{0.79}Ga_{0.21}$ structure

Atom	Wyckoff site	*x*	*y*	*z*	$U_{eq.}\cdot 10^2$, nm^2
Pr	3*f*	0.58436(7)	0	0	0.0091(2)
Ni1	1*a*	0	0	0	0.0183(9)
Ni2	2*d*	1/3	2/3	1/2	0.0193(6)
*M**	3*g*	0.24882(10)	0	1/2	0.0105(3)

**M* = 0.79(1) In + 0.21(1) Ga

To confirm the substitution of indium by gallium atoms in the $HoNiIn_{1.0-0.4}Ga_{0-0.6}$ solid solution single-crystal studies were performed. Irregular shaped crystals were picked up from an annealed (870 K) sample of $Ho_{0.33}Ni_{0.33}In_{0.24}Ga_{0.10}$ composition. The crystal structure was solved and refined using the model of ZrNiAl-type structure reported for composition $HoNiIn_{0.69}Ga_{0.31}$ by program JANA 2006 [14]. All sites of the atoms in the structure are fully occupied. The mixture of indium and gallium atoms is located in a 3*g* site. Details of the crystallographic data and the structure refinements are listed in Table 3. Refined atomic coordinates and anisotropic displacement parameters in

the structure are listed in Table 4. The refined composition of single crystal correlates with the results of EDX analysis (SEM Zeiss EVO MA 15): 34.0(2) at. % Ho, 32.3(2) at. % Ni, 25.2(2) at. % In, 8.5(2) at. % Ga.

Table 3

The details of the experiment and the crystal structure refinement results for $HoNiIn_{0.69}Ga_{0.31}$ phase

Sample composition	$HoNiIn_{0.7}Ga_{0.3}$
Empirical formula	$HoNiIn_{0.69}Ga_{0.31}$
Structure type	ZrNiAl
Space group, *Z*	*P*-62*m*, 3
Pearson symbol	*hP*9
Unit cell parameters, nm	$a = 0.73604(3)$ $c = 0.37241(2)$
Cell volume, nm^3	$V = 0.17473(1)$
Diffractometer	SuperNova Rigaku Oxford Diffraction
Radiation; λ, nm	Mo *K*α; 0.071075
Temperature, K	299
Calculated density, g/cm^3	9.2571
Absorption coefficient, mm^{-1}	51.5
F(000)	416
θ range for data collection, deg.	3.2–30.6
hkl range	$-9 \le h \le 9$, $-10 \le k \le 9$, $-4 \le l \le 5$
Total reflections	1924
Independent reflections / parameters	205 / 16
Reflections with $I > 2\sigma(I)$	205
Goodness-of-fit on F^2	0.98
*R*1 / *wR*2 for $I > 2\sigma(I)$	0.0096/0.0243
*R*1 / *wR*2 for all data	0.0096/0.0243
Highest / lowest Δρ, $e/nm^3 \cdot 10^3$	0.57 / –0.53

Table 4

Atomic coordinates and anisotropic displacement parameters in the $HoNiIn_{0.69}Ga_{0.31}$ structure

Atom	Wyckoff site	*x*	*y*	*z*	$U_{eq.} \cdot 10^2$, nm^2
Ho	3*f*	0.59037(5)	0	0	0.0126(1)
Ni1	1*a*	0	0	0	0.0252(5)
Ni2	2*d*	1/3	2/3	1/2	0.0111(3)
*M**	3*g*	0.25344(7)	0	1/2	0.0112(2)
Atom	U_{11}	U_{22}	U_{33}	U_{12}	
Ho	0.0126(1)	0.0139(2)	0.0118(2)	0.0069(1)	
Ni1	0.0184(6)	0.0184(6)	0.0388(9)	0.0092(3)	
Ni2	0.0104(3)	0.0104(3)	0.0126(4)	0.0052(2)	
*M**	0.0105(2)	0.0099(3)	0.0131(3)	0.0049(2)	

$U_{13} = U_{23} = 0$;
**M* = 0.69(1) In + 0.31(1) Ga.

The shortest distances for the $PrNiIn_{0.79}Ga_{0.21}$ phase are *M*–Ni1 (0.2712 nm), for $HoNiIn_{0.69}Ga_{0.31}$ phase are *M*–Ni1 (0.2636 nm), both slightly shorter than In–Ni1 distances in ternary compounds: 0.2863 and 0.2665 nm for PrNiIn and HoNiIn

structures, respectively. This is natural for the replacement of atoms with larger size (In) by atoms with smaller size (Ga). The interatomic distances of atoms in the structures of the studied solid solutions are given in Table 5.

Table 5

Shortest interatomic distances (nm) in the structures of *RE*NiIn$_{1-x}$Ga$_x$ (*RE* = Pr, Ho) systems

Compound / Atoms	PrNiIn [30]	PrNiIn$_{0.79}$Ga$_{0.21}$	HoNiIn [8]	HoNiIn$_{0.69}$Ga$_{0.31}$
R–*M*	0.30380	0.31922(9)	0.31227	0.31012(5)
R–Ni1	0.32351	0.31088(8)	0.30221	0.30150(4)
R–Ni2	0.30107	0.29920(5)	0.29260	0.29025(1)
Ni1–*M*	0.28630	0.27120(6)	0.26655	0.26357(4)
Ni2–*M*	0.28001	0.28619(7)	0.28068	0.27943(3)
Ni–Ni	0.39546	0.39454(8)	0.37346	0.37241(2)
M–*M*	0.35861	0.32234(11)	0.32945	0.32310(6)

In these structures, the mixtures of *p*-elements *M* (In/Ga) atoms are located in the centres of distorted tetragonal prisms, formed by six rare earth and two nickel atoms, which form columns along the *c* direction (Fig. 5). Nickel atoms are in the centres of trigonal prisms formed by rare earth atoms.

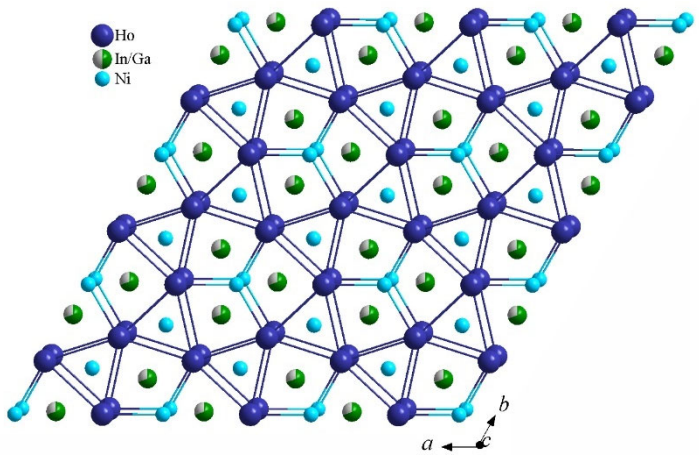


Fig. 5. Trigonal and tetragonal prisms along *c* direction in the HoNiIn$_{0.69}$Ga$_{0.31}$ structure.

Conclusions

Interaction of the components in the systems PrNiIn$_{1-x}$Ga$_x$ and HoNiIn$_{1-x}$Ga$_x$ at 870 K was investigated by means of X-ray phase analysis in full concentration range. The formation of the solid solutions of substitution of different lengths with the structures of the initial ternary compounds was detected and variations of the unit cells parameters of the solid solutions were studied. The mutual substitution of In/Ga atoms was confirmed by structural single crystal studies.

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РЕЗЮМЕ

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ТВЕРДІ РОЗЧИНИ В СИСТЕМАХ *R*NiIn–*R*NiGa (*R* = Pr, Ho)

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Методами рентгенівського фазового та, частково, локального рентгеноспектрального аналізів досліджено взаємодію компонентів у системах $PrNiIn_{1-x}Ga_x$ і $HoNiIn_{1-x}Ga_x$ при 870 K у повному концентраційному інтервалі.

Полікристалічні зразки (по 11 в кожній системі) масою до 1,0 г виготовлено електродуговим сплавлянням компактних металів високої чистоти в атмосфері очищеного аргону. Гомогенізували сплави шляхом відпалювання у вакуумованих кварцових ампулах при 870 K протягом місяця. Дослідження проведено з використанням методу порошкової рентгенівської дифракції. Окремі сплави досліджували на скануючих електронних мікроскопах Tescan Vega 3 LMU та Zeiss EVO MA 15. Масиви монокристальних даних одержано на дифрактометрі SuperNova Rigaku Oxford Diffraction (Mo *Kα*-випромінювання) в Технічному університеті Дрездена, (Німеччина).

У досліджених системах встановлено розчинність *p*-елемента (In або Ga) у вихідних сполуках еквіатомного складу, визначено межі твердих розчинів і уточнено значення параметрів елементарної комірки для них: $PrNiIn_{1.0\text{-}0.4}Ga_{0\text{-}0.6}$ (СТ ZrNiAl; ПГ *P*-62*m*; *a* = 0,7552(1)–0,7336(3); *c* = 0,3963(1)–0,3938(2) нм, *V* = 0.1957(1)–0.1835(1) nm^3); $PrNiIn_{0.1\text{-}0}Ga_{0.9\text{-}1.0}$ (СТ HoNiGa; ПГ *Pnma*; *a* = 0,7451(2)–0,7438(2), *b* = 0,4565(1)–0,4552(1), *c* = 0,6833(2)–0,6818(1) нм, *V* = 0.2324(1)–0.2308(1) nm^3); $HoNiIn_{1.0\text{-}0.4}Ga_{0\text{-}0.6}$ (СТ ZrNiAl; ПГ *P*-62*m*; *a* = 0,74343(4)–0,72453(6); *c* = 0,37472(3)–0,37013(4) нм; *V* = 0,17936(2)–0,16826(3) нм^3); $HoNiGa_{1.0\text{-}0.8}In_{0\text{-}0.2}$ (СТ HoNiGa; ПГ *Pnma*; *a* = 0,68226(4)–0,68261(9); *b* = 0,42790(2)–0,42894(5); *c* = 0,73296(4)–0,73915(9) нм; *V* = 0,21398(2)–0,21642(5) нм^3).

Кристалічну структуру фази $PrNiIn_{0,79}Ga_{0,21}$ уточнено методом порошку: СТ ZrNiAl; ПГ *P*-62*m*; *a* = 0,74795(15), *c* = 0,39454(8) нм, R_{Bragg} = 0,077, R_f = 0,085.

Структурне дослідження фази $HoNiIn_{0,69}Ga_{0,31}$ проведено на основі монокристальних даних, і кристалічну структуру уточнено по моделі структурного типу ZrNiAl; ПГ *P*-62*m*; *a* = 0,73604(3), *c* = 0,37241(2) нм, *R*1 = 0,0096, 205 незалежних відбить *hkl*, 16 параметрів.

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

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