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Crystal structures of the phases in the $DyNi_3Al_9$–$DyNi_3Ga_9$ system

Oleh LESKO[1], Nataliya MUTS[1]*, Yaroslav TOKAYCHUK[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
* *Corresponding author. Tel.: +380322600388; e-mail: nataliya.muts@lnu.edu.ua*

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The subsystem $DyNi_3Al_9$–$DyNi_3Ga_9$ was investigated by X-ray powder diffraction. Both boundary compounds crystallize with the partly ordered $DyNi_3Al_9$ type (Pearson symbol *hR*99, space group *R*32), which contains monoatomic layers with single rare-earth atoms and $(Al,Ga)_3$ triangles in the ratio 2:1. The solid solutions based on the ternary compounds were found to extend to the limiting compositions $DyNi_3(Al_{0.82}Ga_{0.18})_9$ (*a* = 7.2589(1), *c* = 27.4045(6) Å) and $DyNi_3(Al_{0.44}Ga_{0.56})_9$ (*a* = 7.24477(9), *c* = 27.4508(4) Å), respectively, at 600°C. Complete refinements were performed for several compositions. The samples contained in addition variable amounts of a $Ni_2(Al,Ga)_3$ phase with Ni_2Al_3-type structure and a new phase. The crystal structure of the new quaternary compound $Dy_{0.67}Ni_2(Al,Ga)_5$ was refined from X-ray powder diffraction data and was found to belong to the structure type $Sc_{0.6}Fe_2Si_{4.9}$ (Pearson symbol *hP*20, space group *P*6_3*/mmc*). The homogeneity range extends from the composition $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ to $Dy_{0.67}Ni_2(Al_{0.31}Ga_{0.69})_5$ at 600°C and the unit-cell parameters change from *a* = 4.19886(9), *c* = 15.8614(4) Å for the former to *a* = 4.17494(7), *c* = 15.9229(4) Å for the latter. It follows that the cell volume increases when Ga atoms are replaced by Al atoms.

Dy–Ni–Al–Ga system / X-ray diffraction / Crystal structure / Aluminides

Introduction

The Dy–Ni–Al and Dy–Ni–Ga systems are rich in intermetallic compounds; a total of 35 ternary phases have been reported [1-3]. Several isostructural phases form, such as the compounds with stoichiometry 1:1:4 (structure type $YNiAl_4$, Pearson symbol *oS*24, space group *Cmcm*), 1:3:2 (YCo_3Ga_2, *hP*18, *P6/mmm*), 1:1:2 ($MgCuAl_2$, *oS*16, *Cmcm*), 3:6:2 ($Ce_3Ni_6Si_2$, *cI*44, *Im*-3*m*), and 2:1:2 (W_2CoB_2, *oI*10, *Immm*). Our attention was drawn to the isostructural compounds formed in the Al- and Ga-rich regions, in particular $DyNi_3Al_9$, which crystallizes with a partially disordered (own) structure type (*hR*99, *R*32, *a* = 7.2723, *c* = 27.344 Å) [4], and $DyNi_3Ga_9$, which adopts the same structure type (*a* = 7.2455, *c* = 27.4346 Å) [5]. The aluminide was also found to crystallize with the related type $Yb_{0.67}Ni_2Al_6$ presenting a higher degree of disorder reflected in a smaller unit cell (*hP*11, *P*-6*m*2, *a* = 4.2008, *c* = 9.1262 Å) [6].

In this work, our aim was to synthesize and investigate samples along the line $DyNi_3Al_9$–$DyNi_3Ga_9$: determine the solubility of the fourth component (Ga or Al) in the ternary compounds with stoichiometry 1:3:9, search for new phases in the quaternary system and determine their crystal structure.

Experimental

Seven $DyNi_3Al_xGa_{9-x}$ samples (x = 0, 1.5, 2.25, 3.375, 5.625, 6.75, 9) were synthesized by arc-melting elements of the following purities: Dy ≥ 99.89 mass%, Ni ≥ 99.89 mass%, Al ≥ 99.985 mass%, and Ga ≥ 99.89 mass%. The mass of each sample was 1 g and the weight loss during the preparation was less than 1 % of the total mass. The alloys were annealed at 600°C for 126 d in evacuated quartz ampoules, and subsequently quenched in cold water.

Phase analysis and crystal structure refinements were performed using X-ray powder diffraction patterns recorded at room temperature on a DRON-2.0M diffractometer (Fe $K\alpha$ radiation, 2θ angular range 20-120°, step 0.05°) and a STOE Stadi P diffractometer (Cu $K\alpha_1$ radiation, 2θ angular range 6-110.625°, step 0.015°) using the program package FullProf Suite [7]. TYPIX database [8] was used to identify the structure types and standardize the structural parameters. The compositions of the samples and quaternary phases were analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with an X-Max^{N}20 detector.

3. Results and discussion

The results of the local EDX analyses of the $DyNi_3Al_xGa_{9-x}$ (x = 1.5, 2.25, 3.375, 5.625, 6.75) samples showed good agreement with the nominal composition (Table 1). Images of a polished surface of the $DyNi_3Al_{1.5}Ga_{7.5}$, $DyNi_3Al_{2.25}Ga_{6.75}$, $DyNi_3Al_{3.375}Ga_{5.625}$, $DyNi_3Al_{5.625}Ga_{3.375}$, and $DyNi_3Al_{6.75}Ga_{2.25}$ samples are shown in Fig. 1. The samples close to the boundary compounds contained important amounts of a $DyNi_3Al_9$-type phase, however, all the samples were found to be multiphase: the $DyNi_3Al_{1.5}Ga_{7.5}$, $DyNi_3Al_{2.25}Ga_{6.75}$, $DyNi_3Al_{3.375}Ga_{5.625}$, and $DyNi_3Al_{5.625}Ga_{3.375}$ samples contained two phases, and the $DyNi_3Al_{6.75}Ga_{2.25}$ sample contained three phases. An additional phase found in all the samples was a solid solution $Ni_2(Al,Ga)_3$, with Ni_2Al_3-type structure. The compound was found to dissolve very small amounts of the rare-earth element; the highest solubility of Dy was observed for the $DyNi_3Al_{3.375}Ga_{5.625}$ sample.

The X-ray powder diffraction patterns revealed the existence of a new phase with $Sc_{0.6}Fe_2Si_{4.9}$-type structure (Pearson symbol *hP*20, space group *P*6$_3$*/mmc*) in the $DyNi_3Ga_9$ (trace amounts, 5.9(1) mass%), $DyNi_3Al_{2.25}Ga_{6.75}$ (17.2(2) mass%), $DyNi_3Al_{3.375}Ga_{5.625}$ (main phase, 84.8(7) mass%), $DyNi_3Al_{5.625}Ga_{3.375}$ (main phase, 77.2(6) mass%), and $DyNi_3Al_{6.75}Ga_{2.25}$ (43.0(5) mass%) samples (Table 2). The content of $Ni_2(Al,Ga)_3$ varied from 3(1) mass% for the $DyNi_3Al_{1.5}Ga_{7.5}$ sample to 22.8(2) mass% for $DyNi_3Al_{5.625}Ga_{3.375}$ sample. The change of the unit-cell parameters for the phase with Ni_2Al_3-type, as well as the results of EDX, indicate the solubility of Ga in the binary compound Ni_2Al_3 (the maximum solubility of Ga is 29.2(9) at.% according to EDX for the $DyNi_3Al_{1.5}Ga_{7.5}$ sample). Belyaina *et al.* [9], during their investigation of the phase equilibria in the Ni–Al–Ga system at 700°C, determined the presence of extended solid solutions of the isostructural compounds Ni_2Al_3 and Ni_2Ga_3. However, the compounds did not form a continuous solid solution at 700°C because of the existence of a two-phase field along the Ni_2Al_3–Ni_2Ga_3 line (~30-50 at.% Ga) [9]. The unit-cell parameters of the phase with Ni_2Al_3-type structure identified in the samples synthesized here are in good agreement with the parameters reported in the literature: Ni_2Al_3 (a = 4.0359, c = 4.8956 Å), $Ni_2(Al_{0.5}Ga_{0.5})_3$ (a = 4.0473, c = 4.8879 Å), $Ni_2(Al_{0.58}Ga_{0.42})_3$ (a = 4.0418, c = 4.8874 Å), and Ni_2Ga_3 (a = 4.0532, c = 4.8857 Å). X-ray diffraction patterns of the polycrystalline $DyNi_3Al_xGa_{9-x}$ (x = 0, 1.5, 2.25, 3.375, 5.625, 6.75, 9) samples are shown in Figs. 2-3.

The solubility of aluminum in the ternary compound $DyNi_3Ga_9$ and the solubility of gallium in $DyNi_3Al_9$ were established. The solid solution based on the $DyNi_3Ga_9$ compound was found to extend to the composition $DyNi_3(Al_{0.44}Ga_{0.56})_9$ and on the $DyNi_3Al_9$-side the limiting composition was $DyNi_3(Al_{0.82}Ga_{0.18})_9$. The atomic coordinates for the initial model ($DyNi_3Al_9$-type) for the crystal structure refinements were taken from the earlier determinatioms of $DyNi_3Ga_9$ [5] and $DyNi_3Al_9$ [4]. The atomic coordinates and isotropic displacement parameters for the solid solutions $DyNi_3(Al_xGa_{1-x})_9$ and $DyNi_3(Al_{1-x}Ga_x)_9$ with structure type $DyNi_3Al_9$ are listed in Tables 3 and 4. The occupancies of the Dy and Ga (or mixed Al/Ga) sites in Wyckoff positions 6*c*, 18*f*, 3*b* and 9*e* were refined, taking into consideration the fact that the sum of the occupancies of the Dy1 and Ga (or Al/Ga)7 sites, and of the Dy2 and Ga (or Al/Ga)2 sites must be equal to 1.

Table 1 Results of the EDX analysis of the $DyNi_3Al_xGa_{9-x}$ (x = 1.5, 2.25, 3.375, 5,625, 6.75) samples.

Sample, composition, at.%, [EDX composition, at.%]	Spectrum (see Fig. 1)	Average composition, at.%	Phase, [structure type]
$DyNi_3Al_{1.5}Ga_{7.5}$ $Dy_{7.7}Ni_{23.1}Al_{11.5}Ga_{57.7}$ [$Dy_{6.7}Ni_{23.0}Al_{12.5}Ga_{57.8}$]	1-5 6-10	$Dy_{7.1(4)}Ni_{22.2(3)}Al_{11(1)}Ga_{59.8(8)}$ $Dy_{0.8(7)}Ni_{35(2)}Al_{35(2)}Ga_{29.2(9)}$	$DyNi_3(Al_{0.25}Ga_{0.75})_9$ [$DyNi_3Al_9$] $Ni_2(Al,Ga)_3$ [Ni_2Al_3]
$DyNi_3Al_{2.25}Ga_{6.75}$ $Dy_{7.7}Ni_{23.1}Al_{17.3}Ga_{51.9}$ [$Dy_{7.3}Ni_{24.5}Al_{18.6}Ga_{49.6}$]	1-3 4-6	$Dy_{7.9(1)}Ni_{25.3(5)}Al_{17.7(2)}Ga_{49.1(6)}$ $Dy_{0.6(1)}Ni_{37.7(6)}Al_{42.9(2)}Ga_{18.8(3)}$	$DyNi_3(Al_{0.44}Ga_{0.56})_9$ [$DyNi_3Al_9$] $Ni_2(Al,Ga)_3$ [Ni_2Al_3]
$DyNi_3Al_{3.375}Ga_{5.625}$ $Dy_{7.7}Ni_{23.1}Al_{26.0}Ga_{43.2}$ [$Dy_{7.9}Ni_{23.8}Al_{22.2}Ga_{46.1}$]	1-3 4-6	$Dy_{9.0(5)}Ni_{24.8(1)}Al_{25(2)}Ga_{41.2(9)}$ $Dy_{1.5(9)}Ni_{37.7(3)}Al_{43.5(2)}Ga_{17.3(2)}$	$Dy_{0,67}Ni_2(Al_{0.40}Ga_{0.60})_5$ [$Sc_{0.6}Fe_2Si_{4.9}$] $Ni_2(Al,Ga)_3$ [Ni_2Al_3]
$DyNi_3Al_{5.625}Ga_{3.375}$ $Dy_{7.7}Ni_{23.1}Al_{43.3}Ga_{25.9}$ [$Dy_{7.1}Ni_{24.1}Al_{48.1}Ga_{20.7}$]	1-3 4-5	$Dy_{9.5(2)}Ni_{21.8(2)}Al_{44.6(5)}Ga_{24.1(8)}$ $Dy_{0.4(1)}Ni_{36(1)}Al_{59(1)}Ga_{4.6(3)}$	$Dy_{0,67}Ni_2(Al_{0.69}Ga_{0.31})_5$ [$Sc_{0.6}Fe_2Si_{4.9}$] Ni_2Al_3 [Ni_2Al_3]
$DyNi_3Al_{6.75}Ga_{2.25}$ $Dy_{7.7}Ni_{23.1}Al_{51.9}Ga_{17.3}$ [$Dy_{7.4}Ni_{23.6}Al_{54.3}Ga_{14.7}$]	3-5 6-8 9-11	$Dy_{9.1(1)}Ni_{21.9(8)}Al_{49.9(9)}Ga_{19.1(6)}$ $Dy_{7.8(4)}Ni_{24.3(8)}Al_{54.2(2)}Ga_{13.7(3)}$ $Dy_{0.7(3)}Ni_{36.3(9)}Al_{59.9(8)}Ga_{3.1(7)}$	$DyNi_3(Al_{0.82}Ga_{0.18})_9$ [$Sc_{0.6}Fe_2Si_{4.9}$] $DyNi_3Ga_9$ [$DyNi_3Al_9$] Ni_2Al_3 [Ni_2Al_3]

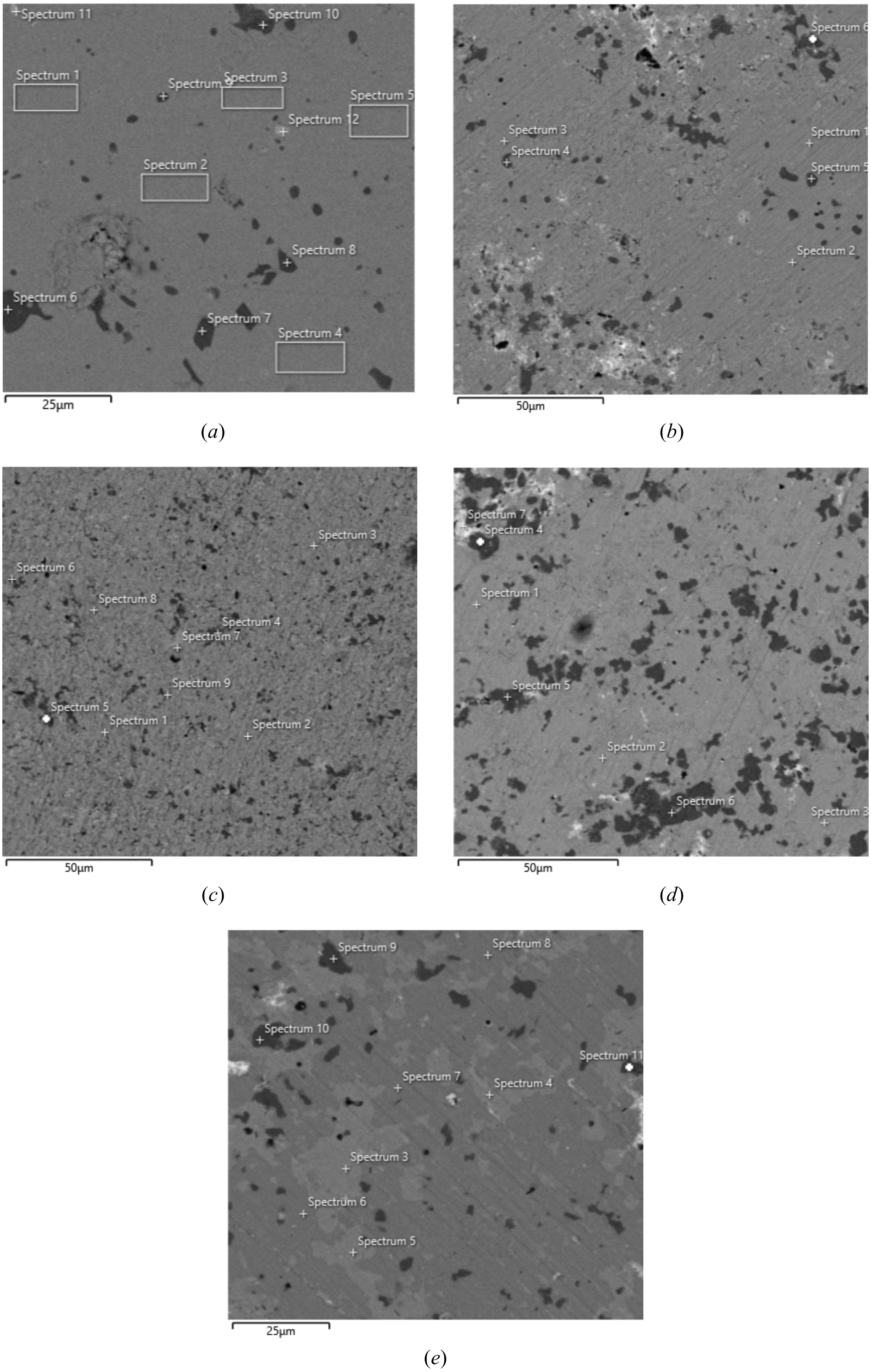

Fig. 1 Photos of a surface of the $DyNi_3Al_{1.5}Ga_{7.5}$ (*a*), $DyNi_3Al_{2.25}Ga_{6.75}$ (*b*), $DyNi_3Al_{3.375}Ga_{5.625}$ (*c*), $DyNi_3Al_{5.625}Ga_{3.375}$ (*d*), and $DyNi_3Al_{6.75}Ga_{2.25}$ (*e*) samples.

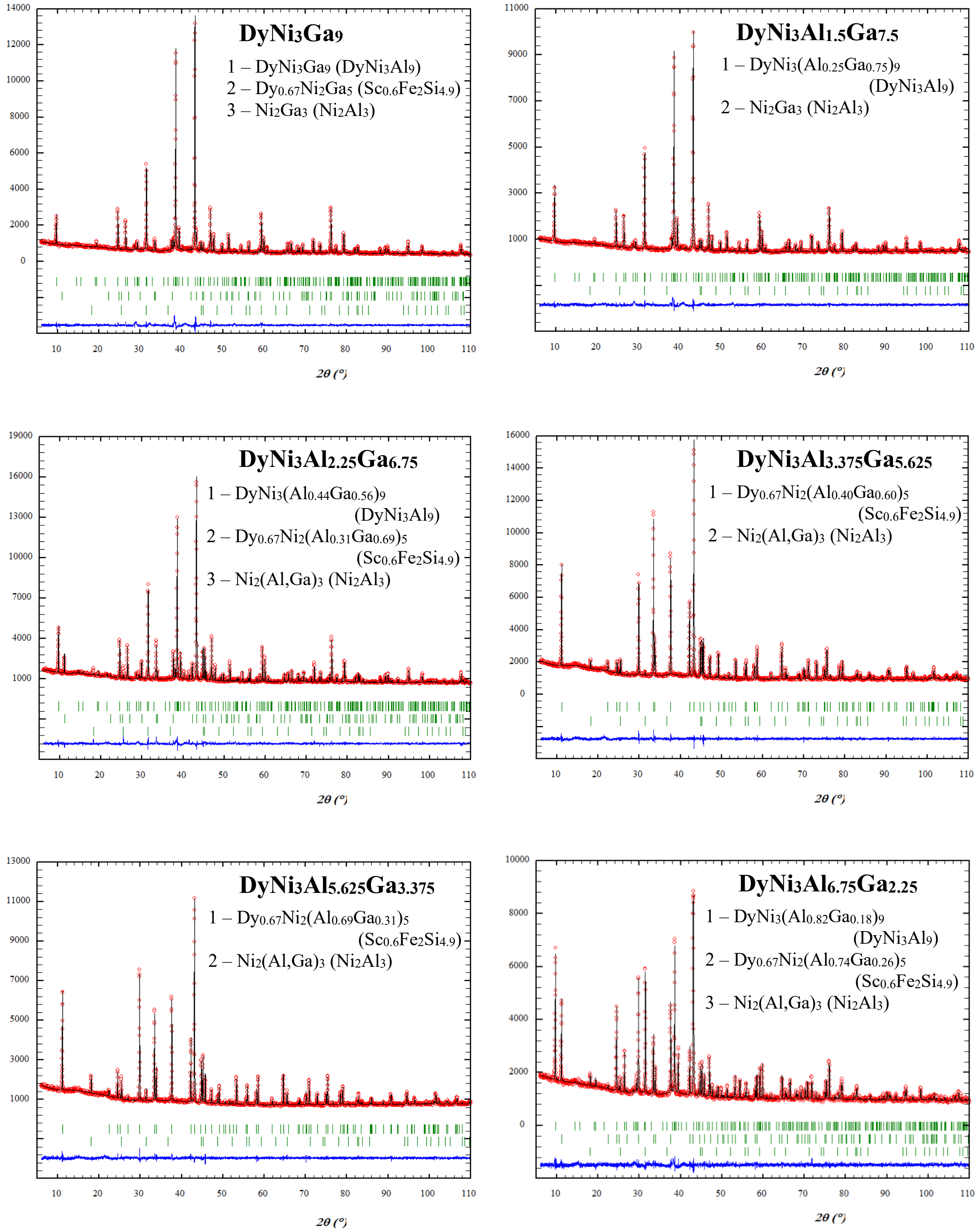

Fig. 2 Observed, calculated and difference (bottom) X-ray powder diffraction patterns for the $DyNi_3Ga_9$, $DyNi_3Al_{1.5}Ga_{7.5}$, $DyNi_3Al_{2.25}Ga_{6.75}$, $DyNi_3Al_{3.375}Ga_{5.625}$, $DyNi_3Al_{5.625}Ga_{3.375}$, and $DyNi_3Al_{6.75}Ga_{2.25}$ samples; Cu $K\alpha_1$ radiation.

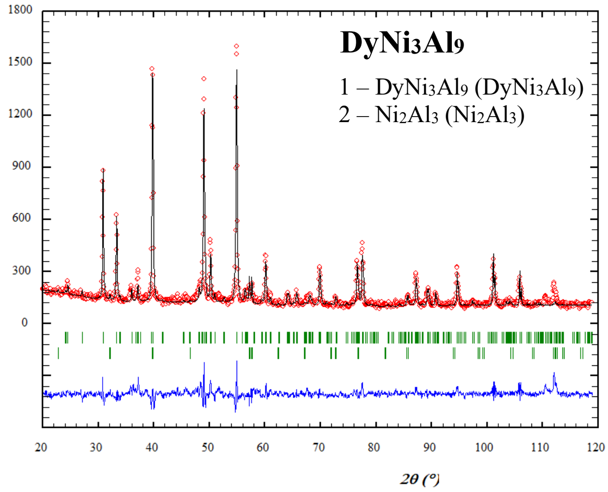

Fig. 3 Observed, calculated and difference (bottom) X-ray powder diffraction patterns for the $DyNi_3Al_9$ sample; Fe $K\alpha_1$ radiation.

Table 2 Results of the phase analysis of the $DyNi_3Al_xGa_{9-x}$ (x = 0, 1.5, 2.25, 3.375, 5,625, 6.75, 9) samples.

x	Sample	Phase [structure type], content, mass%	Unit-cell parameters, Å
0	$DyNi_3Ga_9$	$DyNi_3Ga_9$ [$DyNi_3Al_9$], 91.0(8)	a = 7.24541(11), c = 27.4342(5)
			a = 7.2455, c = 27.4346 [5]
		$Dy_{0,67}Ni_2Ga_5$ [$Sc_{0.6}Fe_2Si_{4.9}$], 5.9(1)	a = 4.152041(1), c = 15.972(1)
		Ni_2Ga_3 [Ni_2Al_3], 3.1(1)	a = 4.0523(3), c = 4.8874(5)
1.5	$DyNi_3Al_{1.5}Ga_{7.5}$	$DyNi_3(Al_{0.25}Ga_{0.75})_9$ [$DyNi_3Al_9$], 97(1)	a = 7.2439(1), c = 27.4435(6)
		Ni_2Ga_3 [Ni_2Al_3], 3(1)	a = 4.0402(2), c = 4.8843(4)
2.25	$DyNi_3Al_{2.25}Ga_{6.75}$	$DyNi_3(Al_{0.44}Ga_{0.56})_9$ [$DyNi_3Al_9$], 73(1)	a = 7.24477(9), c = 27.4508(4)
		$Dy_{0.67}Ni_2(Al_{0.31}Ga_{0.69})_5$* [$Sc_{0.6}Fe_2Si_{4.9}$], 17.2(2)	a = 4.17494(7), c = 15.9229(4)
		$Ni_2(Al,Ga)_3$ [Ni_2Al_3], 9.8(1)	a = 4.04044(8), c = 4.8866(1)
3.375	$DyNi_3Al_{3.375}Ga_{5.625}$	$Dy_{0,67}Ni_2(Al_{0.40}Ga_{0.60})_5$ [$Sc_{0.6}Fe_2Si_{4.9}$], 84.8(7)	a = 4.17888(7), c = 15.9092(3)
		$Ni_2(Al,Ga)_3$ [Ni_2Al_3], 15.2(5)	a = 4.03851(9), c = 4.8881(1)
5.625	$DyNi_3Al_{5.625}Ga_{3.375}$	$Dy_{0,67}Ni_2(Al_{0.69}Ga_{0.31})_5$ [$Sc_{0.6}Fe_2Si_{4.9}$], 77.2(6)	a = 4.19379(7), c = 15.8701(3)
		$Ni_2(Al,Ga)_3$ [Ni_2Al_3], 22.8(2)	a = 4.04350(9), c = 4.89311(13)
6.75	$DyNi_3Al_{6.75}Ga_{2.25}$	$DyNi_3(Al_{0.82}Ga_{0.18})_9$ [$DyNi_3Al_9$], 46.9(6)	a = 7.2589(1), c = 27.4045(6)
		$Dy_{0,67}Ni_2(Al_{0.74}Ga_{0.26})_5$ [$Sc_{0.6}Fe_2Si_{4.9}$], 43.0(5)	a = 4.19886(9), c = 15.8614(4)
		$Ni_2(Al,Ga)_3$ [Ni_2Al_3], 10.1(1)	a = 4.0489(1), c = 4.8957(2)
9	$DyNi_3Al_9$	$DyNi_3Al_9$ [$DyNi_3Al_9$], 96(6)	a = 7.2806(2), c = 27.393(2)
			a = 7.2723, c = 27.344 [4]
		Ni_2Al_3 [Ni_2Al_3], 4(2)	a = 4.0477(5), c = 4.9045(9)

* composition from EDX analysis

The new compound $Dy_{0.67}Ni_2(Al,Ga)_5$ belongs to the structure type $Sc_{0.6}Fe_2Si_{4.9}$, and the atomic coordinates for the initial model were taken from [10]. The homogeneity range extends, at least, from the composition $Dy_{0.67}Ni_2(Al_{0.31}Ga_{0.69})_5$ to $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ at 600°C. The unit-cell parameters vary from a = 4.17494(7), c = 15.9229(4) Å, V = 240.355(8) Å^3 for $Dy_{0.67}Ni_2(Al_{0.31}Ga_{0.69})_5$ to a = 4.19886(9), c = 15.8614(4) Å, V = 242.178(9) Å^3 for $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$. It follows that the cell volume increases when Ga atoms are replaced by Al atoms. The unit-cell parameters for the $DyNi_3(Al_xGa_{1-x})_9$, $DyNi_3(Al_{1-x}Ga_x)_9$ and $Dy_{0.67}Ni_2(Al,Ga)_5$ phases are given in Fig. 4. Atomic coordinates and isotropic displacement parameters for the $Dy_{0.67}Ni_2(Al,Ga)_5$ phase with $Sc_{0.6}Fe_2Si_{4.9}$-type structure at the compositions $Dy_{0.67}Ni_2(Al_{0.40}Ga_{0.60})_5$, $Dy_{0.67}Ni_2(Al_{0.69}Ga_{0.31})_5$, and $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ are presented in Table 5. Details of the structural refinements on X-ray powder diffraction data for the $DyNi_3Al_xGa_{9-x}$ (x = 3.375, 5.625, and 6.75) samples annealed at 600°C are given in Table 6.

The structure of the new quaternary compound $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ contains $Dy_{0.67}(Al,Ga)$ layers built from Dy atoms (Wyckoff position 2c) and triangles, formed by a statistical mixture of Al and Ga atoms (position 6*h*), in the ratio 2:1. As in the case of the phases with $DyNi_3Al_9$-type structure the occupancies of the Dy and mixed Al/Ga sites in Wyckoff positions 2*c* and 6*h* were refined, fixing the sum of the occupancies of the Dy1 and (Al/Ga)1 atoms to 1.

Table 3 Atomic coordinates and displacement parameters for $DyNi_3Ga_9$, $DyNi_3(Al_{0.25}Ga_{0.75})_9$, and $DyNi_3(Al_{0.44}Ga_{0.56})_9$ (structure type $DyNi_3Al_9$, Pearson symbol *hR*99, space group *R*32).

Atom	Wyckoff position	Atomic coordinates			Occupancy	B_{iso}, Å^2
		x	*y*	*z*		
$DyNi_3Ga_9$ (*a* = 7.24541(11), *c* = 27.4342(5) Å)						
Dy1	6*c*	0	0	0.3332(4)	0.781(6)	0.46(9)
Dy2	3*b*	0	0	0	0.402(4)	0.46(9)
Ni	18*f*	0.3264(15)	0.0099(15)	0.08218(11)	1	0.64(9)
Ga1	18*f*	0.3287(14)	0.3384(11)	0.06637(1)	1	0.75(5)
Ga2	9*e*	0.212(2)	0	0	0.598(4)	0.75(5)
Ga3	9*d*	0.3483(14)	0	0.5000	1	0.75(5)
Ga4	6*c*	0	0	0.4510(4)	1	0.75(5)
Ga5	6*c*	0	0	0.2181(5)	1	0.75(5)
Ga6	6*c*	0	0	0.1154(5)	1	0.75(5)
Ga7	18*f*	-0.008(8)	0.198(4)	0.3296(11)	0.219(6)	0.75(5)
$DyNi_3(Al_{0.25}Ga_{0.75})_9$ (*a* = 7.2439(1), *c* = 27.4435(6) Å)						
Dy1	6*c*	0	0	0.3321(3)	0.783(6)	0.82(11)
Dy2	3*b*	0	0	0	0.386(3)	0.82(11)
Ni	18*f*	0.32106(14)	0.0038(14)	0.0821(1)	1	1.13(9)
Ga1/Al1	18*f*	0.3318(16)	0.3360(11)	0.0663(1)	0.830(9)/0.170(9)	1.16(9)
Ga2	9*e*	0.2106(18)	0	0	0.649(4)	1.10(5)
Ga3/Al3	9*d*	0.3439(13)	0	1/2	0.891(9)/0.109(9)	1.47(12)
Ga4/Al4	6*c*	0	0	0.4503(4)	0.614(2)/0.386(2)	0.74(5)
Ga5/Al5	6*c*	0	0	0.2168(5)	0.583(3)/0.417(3)	0.098(4)
Al6/Ga6	6*c*	0	0	0.1149(6)	0.725(2)/0.275(2)	2.81(5)
Ga7	18*f*	0.006(6)	0.194(4)	0.331(1)	0.170(3)	1.10(2)
$DyNi_3(Al_{0.44}Ga_{0.56})_9$ *a* = 7.24477(9), *c* = 27.4508(4) Å)						
Dy1	6*c*	0	0	0.33193(18)	0.759(1)	0.45(6)
Dy2	3*b*	0	0	0	0.230(7)	0.45(6)
Ni	18*f*	0.3328(9)	0.0152(9)	0.08237(11)	1	1.32(9)
Ga1/Al1	18*f*	0.3193(9)	0.3427(11)	0.06582(11)	0.561(2)/0.439(2)	0.43(4)
Ga2	9*e*	0.2042(18)	0	0	0.444(4)	0.43(4)
Ga3/Al3	9*d*	0.3395(13)	0	1/2	0.571(9)/0.429(9)	0.43(4)
Ga4/Al4	6*c*	0	0	0.4527(3)	0.384(2)/0.386(2)	0.43(4)
Ga5/Al5	6*c*	0	0	0.2180(4)	0.333(10)/0.667(10)	0.43(4)
Al6/Ga6	6*c*	0	0	0.1155(5)	0.726(10)/0.274(10)	0.43(4)
Ga7	18*f*	0.020(4)	0.201(3)	0.3267(7)	0.166(4)	0.43(4)

Table 4 Atomic coordinates and displacement parameters for $DyNi_3(Al_{0.82}Ga_{0.18})_9$ (structure type $DyNi_3Al_9$, Pearson symbol *hR*99, space group *R*32, *a* = 7.2589(1), *c* = 27.4045(6) Å).

Atom	Wyckoff position	Atomic coordinates			Occupancy	B_{iso}, Å^2
		x	*y*	*z*		
Dy1	6*c*	0	0	0.3335(7)	0.660(3)	1.18(9)
Dy2	3*b*	0	0	0	0.578(6)	1.18(9)
Ni	18*f*	0.319(3)	0.009(3)	0.08177(11)	1	1.30(11)
Al1	18*f*	0.342(4)	0.339(3)	0.0665(2)	1	0.04(9)
Ga2	9*e*	0.211(8)	0	0	0.422(6)	0.04(9)
Al3	9*d*	0.348(3)	0	0.5	1	0.04(9)
Al4	6*c*	0	0	0.4434(9)	1	0.04(9)
Al5	6*c*	0	0	0.217(2)	1	0.04(9)
Al6	6*c*	0	0	0.117(1)	1	0.04(9)
Ga7	18*f*	-0.0088(11)	0.206(7)	0.335(2)	0.340(3)	0.75(5)

Table 5 Atomic coordinates and displacement parameters for $Dy_{0.67}Ni_2(Al_{0.40}Ga_{0.60})_5$, $Dy_{0.67}Ni_2(Al_{0.69}Ga_{0.31})_5$ and $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ (structure type $Sc_{0.6}Fe_2Si_{4.9}$, Pearson symbol *hP*20, space group $P6_3/mmc$).

Atom	Wyckoff position	Atomic coordinates			Occupancy	B_{iso}, Å^2
		x	*y*	*z*		
$Dy_{0.67}Ni_2(Al_{0.40}Ga_{0.60})_5$ (a = 4.17888(7), c = 15.9092(3) Å)						
Dy1	2*c*	1/3	2/3	1/4	0.67	0.78(4)
Ni	4*f*	1/3	2/3	0.60945(8)	1	1.25(5)
Ga1/Al1	6*h*	0.5395(5)	0.0789(10)	1/4	0.25(2)/0.08(2)	1.31(11)
Ga2/Al2	4*f*	1/3	2/3	0.04615(11)	0.23(2)/0.77(2)	1.31(7)
Ga3/Al3	4*e*	0	0	0.13434(8)	0.891(9)/0.109(9)	1.50(5)
$Dy_{0.67}Ni_2(Al_{0.69}Ga_{0.31})_5$ (a = 4.19379(7), c = 15.8701(3) Å)						
Dy1	2*c*	1/3	2/3	1/4	0.67	0.46(4)
Ni	4*f*	1/3	2/3	0.60972(10)	1	1.06(6)
Ga1/Al1	6*h*	0.5363(8)	0.0726(15)	1/4	0.18(3)/0.15(3)	1.65(17)
Ga2/Al2	4*f*	1/3	2/3	0.04652(19)	0.03(1)/0.97(1)	1.46(11)
Ga3/Al3	4*e*	0	0	0.13611(13)	0.48(2)/0.52(2)	1.61(8)
$Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ (a = 4.19886(9), c = 15.8614(4) Å)						
Dy1	2*c*	1/3	2/3	1/4	0.67	0.34(8)
Ni	4*f*	1/3	2/3	0.61020(15)	1	0.87(9)
Al1/Ga1	6*h*	0.5352(14)	0.070(3)	1/4	0.14(3)/0.19(3)	2.2(4)
Al2	4*f*	1/3	2/3	0.0458(3)	1	0.93(15)
Al3/Ga3	4*e*	0	0	0.1359(2)	0.64(2)/0.36(2)	1.53(17)

Table 6 Experimental details of the structure refinements of the $DyNi_3Al_xGa_{9-x}$ (x = 3.375, 5.625, 6.75) samples (diffractometer STOE Stadi P, Cu $K\alpha_1$ radiation).

Sample		$DyNi_3Al_{3.375}Ga_{5.625}$	$DyNi_3Al_{5.625}Ga_{3.375}$	$DyNi_3Al_{6.75}Ga_{2.25}$
Phase composition		$Dy_{0.67}Ni_2(Al_{0.40}Ga_{0.60})_5$	$Dy_{0.67}Ni_2(Al_{0.69}Ga_{0.31})_5$	$Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$
Structure type		$Sc_{0.6}Fe_2Si_{4.9}$		
Pearson symbol		*hP*20		
Space group		$P6_3/mmc$		
Cell parameters:	*a*, Å	*a* = 4.17888(7),	*a* = 4.19379(7),	*a* = 4.19886(9),
	c, Å	*c* = 15.9092(3)	*c* = 15.8701(3)	*c* = 15.8614(4)
Cell volume *V*, nm^3		240.602(7)	241.726(7)	242.178(9)
Formula units per unit cell *Z*		2		
Density D_x, g/cm^3		10.004	8.803	8.419
Preferred orientation [direction]		0.988(2) [110]	0.999(2) [110]	1.000(3) [110]
θ range (°) [step]		6-110.625° [0.015]		
Number of measured reflections		6976		
Number of refined parameters		32	26	49
FWHM parameters:	*U*	0.038(1),	0.023(1),	0.024(1),
	V	-0.014(1),	-0.011(1),	-0.013(1),
	W	0.0118(3)	0.0108(3)	0.0116(3)
Mixing parameter η		0.472(6)	0.434(8)	0.592(8)
Asymmetry parameters		0.085(2)	0.091(3)	0.081(2)
Reliability factors:	R_B, R_F	2.77, 2.80,	4.62, 4.56,	5.92, 5.45,
	R_p, R_{wp}	2.57, 3.27,	2.85, 3.67,	2.64, 3.38,
	R_{exp}, χ^2	2.87, 1.42	3.17, 1.48	2.82, 1.47

Conclusions

The existence of a new compound with the formula $Dy_{0.67}Ni_2(Al,Ga)_5$ was established based on X-ray powder diffraction and energy-dispersive X-ray spectroscopy. The new compound belongs to the structure type $Sc_{0.6}Fe_2Si_{4.9}$ (Pearson symbol *hP*20, space group $P6_3/mmc$). The homogeneity range includes the composition range from $Dy_{0.67}Ni_2(Al_{0.31}Ga_{0.69})_5$ to $Dy_{0.67}Ni_2(Al_{0.74}Ga_{0.26})_5$ at 600°C. The structure of the new compound contains $Dy_{0.67}(Al,Ga)$ layers built from Dy atoms and triangles, formed by a statistical mixture of Ga and Al atoms, in the ratio 2:1.

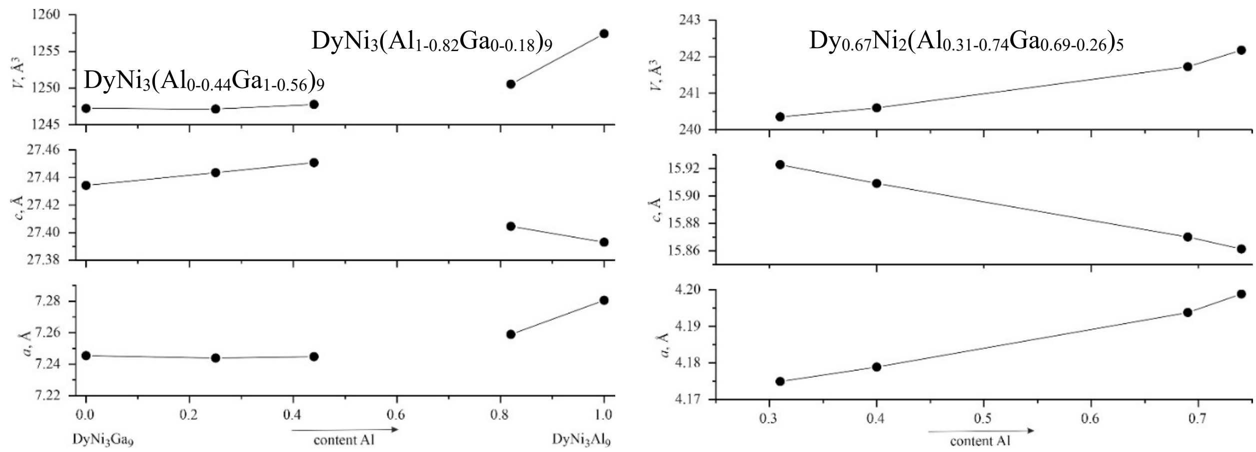

Fig. 4 Unit-cell parameters for the solid solutions $DyNi_3(Al_xGa_{1-x})_9$, $DyNi_3(Al_{1-x}Ga_x)_9$, and $Dy_{0.67}Ni_2(Al,Ga)_5$.

The solid solution based on the $DyNi_3Ga_9$ compound in the system Dy–Ni–Al–Ga extends to the composition $DyNi_3(Al_{0.44}Ga_{0.56})_9$ and the solubility of Ga in $DyNi_3Al_9$ to the composition $DyNi_3(Al_{0.82}Ga_{0.18})_9$.

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References

[1] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2023/24.

[2] L.O. Vasilechko, Yu.N. Grin', *Inorg. Mater.* 32 (1996) 512-515.

[3] R.M. Rykhal', O.S. Zarechnyuk, V.M. Mandzin, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* 6 (1980) 77-79.

[4] R. Gladyshevskii, K. Cenzual, H.D. Flack, E. Parthé, *Acta Crystallogr. B* 49 (1993) 468-474.

[5] V. Topertser, N. Muts, Ya. Tokaychuk, P. Demchenko, R. Gladyshevskii, *XIV Int. Conf. Crystal Chem. Intermetallic Compd.*, Lviv, Ukraine, September 2019, pp. 22-26.

[6] O. Matselko, S. Pukas, Yu. Lutsyshyn, R. Gladyshevskii, D. Kaczorowski, *J. Solid State Chem.* 198 (2013) 50-56.

[7] J. Rodríguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.

[8] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types TYPIX*, Springer Verlag, Berlin, 1993, Vols. 1-4, 1596 p; electronic version 1996.

[9] N.M. Belyaina, V.Y. Markiv, O.I. Nakonechna, F. Lozovyi, *J. Alloys Compd.* 593 (2014) 41-49.

[10] B.Ya. Kotur, M. Bruvo, *Sov. Phys. Crystallogr.* 36 (1991) 787-789.