Chemistry of Metals and Alloys

Chem. Met. Alloys 3 (2010) 35-41
Ivan Franko National University of Lviv
www.chemetal-journal.org

New compounds RNiAl$_3$ (R = Gd, Tb, Dy)

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Received April 28, 2010; accepted June 29, 2010; available on-line November 5, 2010

Three new and two already known rare-earth nickel aluminides RNiAl$_3$ (R = Y, Sm, Gd, Tb, and Dy) were synthesized by arc melting and their crystal structures were studied by X-ray powder diffraction. They are isotypic to YNiAl$_3$: Pearson symbol *oP*20, space group *Pnma*, a = 8.1532(5), b = 4.0426(2), c = 10.6349(7) Å for YNiAl$_3$, a = 8.1871(1), b = 4.09150(7), c = 10.7013(2) Å for SmNiAl$_3$, a = 8.164(2), b = 4.0680(9), c = 10.666(3) Å for GdNiAl$_3$, a = 8.1484(2), b = 4.05440(8), c = 10.6328(3) Å for TbNiAl$_3$, and a = 8.133(1), b = 4.0350(7), c = 10.611(2) Å for DyNiAl$_3$. A complete structure determination was carried out for SmNiAl$_3$. The structure type YNiAl$_3$ is built up of tricapped trigonal prisms centered by Ni atoms. It is compared with closely related structure types with the ratio R:Ni = 1:1, in particular MgCuAl$_2$ and YNiAl$_4$, which also have many representatives in R–Ni–Al systems.

Rare-earth nickel aluminide / X-ray powder diffraction / Crystal structure

Introduction

A large number of ternary compounds have been reported in the R–Ni–Al systems, where R is a rare-earth metal [1]. The structures of these aluminides belong to 17 different structure types. They are characterized by invariable compositions and complete ordering of the atoms in the structures, except for a few compounds with La$_2$NiAl$_7$-, SrAu$_2$Ga$_5$-, YNi$_2$Al$_3$-, and MgZn$_2$-type structures. Compounds with the two former types have point compositions, however, with partial Ni/Al atom disorder, whereas the compounds with the MgZn$_2$-type structure are characterized by complete Ni/Al atom disorder. The compounds with YNi$_2$Al$_3$-type structure posses narrow homogeneity ranges along lines with constant R content. Complete rows of isotypic rare-earth nickel aluminides do not exist for any structure type. Europium does not form any ternary compound with Ni and Al, and the heavy rare-earth elements form a larger number of compounds (61) than the light rare-earth elements (38).

Among the structures of aluminides with rare-earth metal and nickel there is a group of structure types, YNiAl$_4$, YNiAl$_3$, MgCuAl$_2$, ZrNiAl, LaNiAl, and W$_2$CoB$_2$, which are characterized by the ratio R:Ni = 1:1. The compositions of the compounds are located on the line between the binary compound RNi and aluminum. The orthorhombic MgCuAl$_2$ type [2] has the largest number of representatives (14 compounds) in the R–Ni–Al systems. The structures of the equiatomic rare-earth nickel aluminides belong to the hexagonal ZrNiAl [3] (13 compounds) and orthorhombic LaNiAl [4] (1 compound) types. It may be noted that high-pressure modifications of several equiatomic RNiAl intermetallics adopt the hexagonal MgZn$_2$ type [5] (10 compounds). Twelve, nine, and two representatives are known so far among rare-earth nickel aluminides for the orthorhombic structure types YNiAl$_4$ [6], W$_2$CoB$_2$ [7], and YNiAl$_3$ [8], respectively. The structure of YNiAl$_3$ has been determined by X-ray single-crystal diffraction [8], whereas for SmNiAl$_3$ cell parameters were recently refined from X-ray powder diffraction [9].

The aim of the present work was to search for new representatives of the structure type YNiAl$_3$ in R–Ni–Al systems.

Experimental

Samples of nominal composition RNiAl$_3$ were synthesized from the elements (purity of Y ≥ 99.76 wt.%, Sm ≥ 99.83 wt.%, Eu ≥ 99.81 wt.%, Gd ≥ 99.86 wt.%, Tb ≥ 99.83 wt.%, Dy ≥ 99.83 wt.%, Ni ≥

99.99 wt.%, and Al ≥ 99.998 wt.%) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The ingots were annealed at 600ºC under vacuum in quartz ampoules for 1 month and subsequently quenched in cold water. The weight loss during the preparation of the samples was less than 1 % of the total mass, which was 1 g for each alloy.

The phase analysis was performed based on X-ray powder diffraction data collected on a DRON-2.0M diffractometer (Fe $K\alpha$ radiation), using the program POWDER CELL [10] and the database TYPIX [11].

The crystal structures of the new compounds were established by X-ray powder diffraction. Intensity data were collected on automatic diffractometers STOE STADI P (Cu $K\alpha_1$ radiation, λ = 1.5406 Å, in the angular range $6 \le 2\theta \le 90^\circ$ with the step 0.015º and scan time 250 s) and HZG-4a (Cu $K\alpha$ radiation, λ = 1.5418 Å, in the angular range $10 \le 2\theta \le 130^\circ$ with the step 0.05º and scan time 30 s). The structural parameters were refined by the Rietveld method, using the program DBWS-9807 [12]. The projections of the structures were drawn by the program ATOMS [13].

Results and discussion

The X-ray phase analysis of the alloys RNiAl$_3$ annealed at 600ºC showed that all the samples, with the exception of Eu, were single-phase samples, containing only the YNiAl$_3$-type phase. This phase is new for R = Gd, Tb, and Dy, whereas for Sm and Y it was known before. Europium, as in the case of other stoichiometries, does not form a corresponding ternary compound with aluminum and nickel.

Cell parameters for all the isotypic aluminides RNiAl$_3$ are listed in Table 1; they decrease with increasing atomic number of R from Sm to Dy. The refined cell parameters for YNiAl$_3$ and SmNiAl$_3$ are in good agreement with the literature data [8,9].

Details of the structural refinement (diffractometer STOE STADI P, pseudo-Voigt function) of the SmNiAl$_3$ compound are presented in Table 2. Atomic coordinates and displacement parameter are given in Table 3, and the interatomic distances and coordination polyhedra in Table 4. The experimental and calculated diffraction diagrams are shown in Fig. 1.

Table 1 Cell parameters of compounds RNiAl$_3$ with YNiAl$_3$-type structure.

Compound	a, Å	b, Å	c, Å	V, Å^3
SmNiAl$_3$ [a]	8.197	4.087	10.713	358.9
SmNiAl$_3$	8.1871(1)	4.09150(7)	10.7013(2)	358.47(1)
GdNiAl$_3$	8.164(2)	4.0680(9)	10.666(3)	354.2(2)
YNiAl$_3$ [b]	8.1560	4.0462	10.6380	351.06
YNiAl$_3$	8.1532(5)	4.0426(2)	10.6349(7)	350.52(4)
TbNiAl$_3$	8.1484(2)	4.05440(8)	10.6328(3)	351.28(1)
DyNiAl$_3$	8.133(1)	4.0350(7)	10.611(2)	348.4(1)

[a] literature data [9]
[b] literature (single-crystal) data [8]

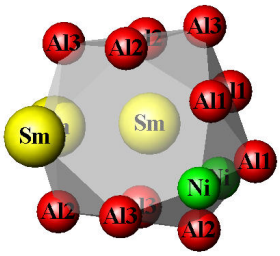
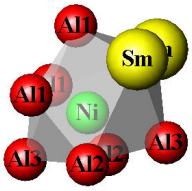
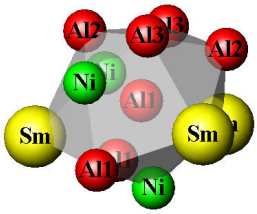
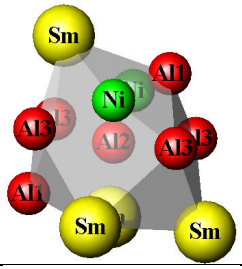
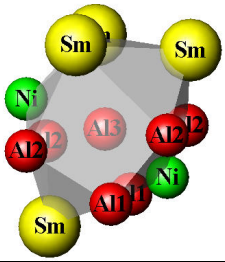
Table 2 Details of the structural refinement of SmNiAl$_3$.

Space group		*Pnma*
Cell parameters:	a, Å	8.1871(1)
	b, Å	4.09150(7)
	c, Å	10.7013(2)
Cell volume V, Å^3		358.47(1)
Formula units per cell Z		4
Density D_x, g cm^{-3}		5.376
FWHM parameters U, V, W		0.012(4), 0.027(3), 0.0064(5)
Mixing parameter η		0.769(7)
Asymmetry parameter C_M		0.002(5)
Texture parameter G		0.966(1) [010]
Number of reflections		185
Number of refined parameters		26
Reliability factors R_B, R_p, R_{wp}		0.0912, 0.0058, 0.0077
Goodness of fit S		0.49

Table 3 Atomic coordinates and isotropic displacement parameters for SmNiAl$_3$: structure type YNiAl$_3$, *oP*20, *Pnma*, a = 8.1871(1), b = 4.09150(7), c = 10.7013(2) Å.

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
Sm	4*c*	0.1858(1)	1/4	0.0121(2)	0.68(3)
Ni	4*c*	0.1033(4)	1/4	0.3530(3)	0.81(1)
Al(1)	4*c*	0.0613(8)	1/4	0.5872(5)	0.93(2)
Al(2)	4*c*	0.3618(13)	1/4	0.7271(9)	0.94(3)
Al(3)	4*c*	0.3821(13)	1/4	0.2744(10)	1.14(3)

Table 4 Interatomic distances and coordination polyhedra in SmNiAl$_3$.

Atoms		δ, Å	Polyhedron
Sm	-2 Al(1)	3.020(5)	
	-2 Al(2)	3.103(7)	
	-2 Ni	3.173(3)	
	-1 Al(3)	3.235(11)	
	-1 Al(1)	3.253(7)	
	-2 Al(3)	3.311(9)	
	-1 Al(2)	3.373(10)	
	-1 Al(3)	3.377(11)	
	-2 Sm	3.675(1)	
	-1 Al(2)	3.686(10)	
Ni	-1 Al(3)	2.267(11)	
	-1 Al(3)	2.433(11)	
	-2 Al(2)	2.466(6)	
	-1 Al(1)	2.530(6)	
	-2 Al(1)	2.532(4)	
	-2 Sm	3.173(3)	
Al(1)	-1 Ni	2.530(6)	
	-2 Ni	2.532(4)	
	-1 Al(2)	2.572(12)	
	-1 Al(2)	2.880(12)	
	-2 Al(3)	2.901(9)	
	-2 Al(1)	2.946(6)	
	-2 Sm	3.020(5)	
	-1 Sm	3.253(7)	
Al(2)	-2 Ni	2.466(6)	
	-1 Al(1)	2.572(12)	
	-1 Al(1)	2.880(12)	
	-2 Al(3)	2.903(11)	
	-2 Al(3)	2.929(11)	
	-2 Sm	3.103(7)	
	-1 Sm	3.373(10)	
	-1 Sm	3.686(10)	
Al(3)	-1 Ni	2.267(11)	
	-1 Ni	2.433(11)	
	-2 Al(1)	2.901(9)	
	-2 Al(2)	2.903(11)	
	-2 Al(2)	2.929(11)	
	-1 Sm	3.235(11)	
	-2 Sm	3.311(9)	
	-1 Sm	3.377(11)	

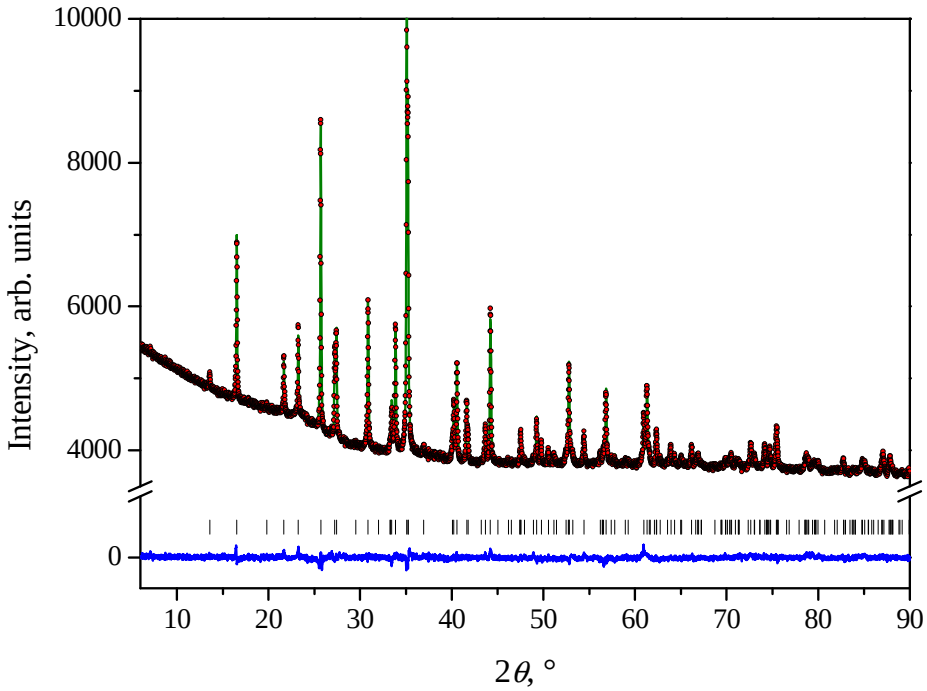


Fig. 1 Observed (dots), calculated (line) and difference (bottom) X-ray diffraction powder patterns (Cu $K\alpha_1$ radiation) for the sample SmNiAl$_3$.

A projection of the structure of the compound SmNiAl$_3$ along the crystallographic direction [010] is presented in Fig. 2. The structure is built up of tricapped trigonal prisms Sm_2Al_7 (Sm_2Al_4 prisms with three additional Al atoms capping the rectangular faces) centered by Ni atoms. Each polyhedron shares two vertices, two edges, and two triangular bases with other polyhedra. Considering the Sm_2Al_4 trigonal prisms without capping atoms, isolated infinite columns of base-sharing prisms along [010] can be emphasized. Additional Al atoms (site Al(3)) are located inside deformed cubic coordination polyhedra, consisting of two Sm and six Al atoms (see Table 4). The other Al atoms (sites Al(1) and Al(2)) also center deformed cubes, formed in this case by two Sm, two Ni and four Al atoms. Four faces of these deformed cubes are capped by different kinds of atom (1Sm + 1Ni + 2Al for the site Al(1), 2Sm + 2Al for Al(2), and 2Sm + 2Ni for Al(3)). The Sm atoms are at the centers of pentagonal prisms consisting of two Sm, two Ni and six Al atoms. Five rectangular faces of these prisms are capped exclusively by Al atoms.

The structural features of the compounds RNiAl$_3$ (YNiAl$_3$-type structure) can be compared with those of RNiAl$_4$ (YNiAl$_4$), RNiAl$_2$ (MgCuAl$_2$), RNiAl (LaNiAl and ZrNiAl), and R_2Ni$_2$Al (W_2CoB_2). These closely related structures are characterized by the ratio R:Ni = 1:1. They have one short translation period and are built up of two alternating atomic layers perpendicular to that direction. The structures are shown in a projection along the shortest axis in Fig. 3.

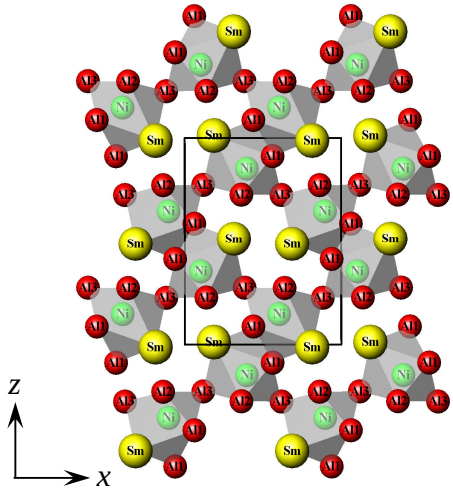


Fig. 2 Ni-centered tricapped trigonal prisms Sm_2Al_7 in the structure of the compound SmNiAl$_3$.

Comparing these structures one notes the similar environment of the Ni atoms, which are located inside straight trigonal prisms with an equatorial mirror plane (the prism axis being parallel to the direction of the short translation period). For the structures of the types YNiAl$_4$, YNiAl$_3$, and MgCuAl$_2$, the trigonal prisms have the composition R_2Al$_4$. In the case of the LaNiAl-type structure, the Ni atoms occupy two distinct sites, which center prisms of composition

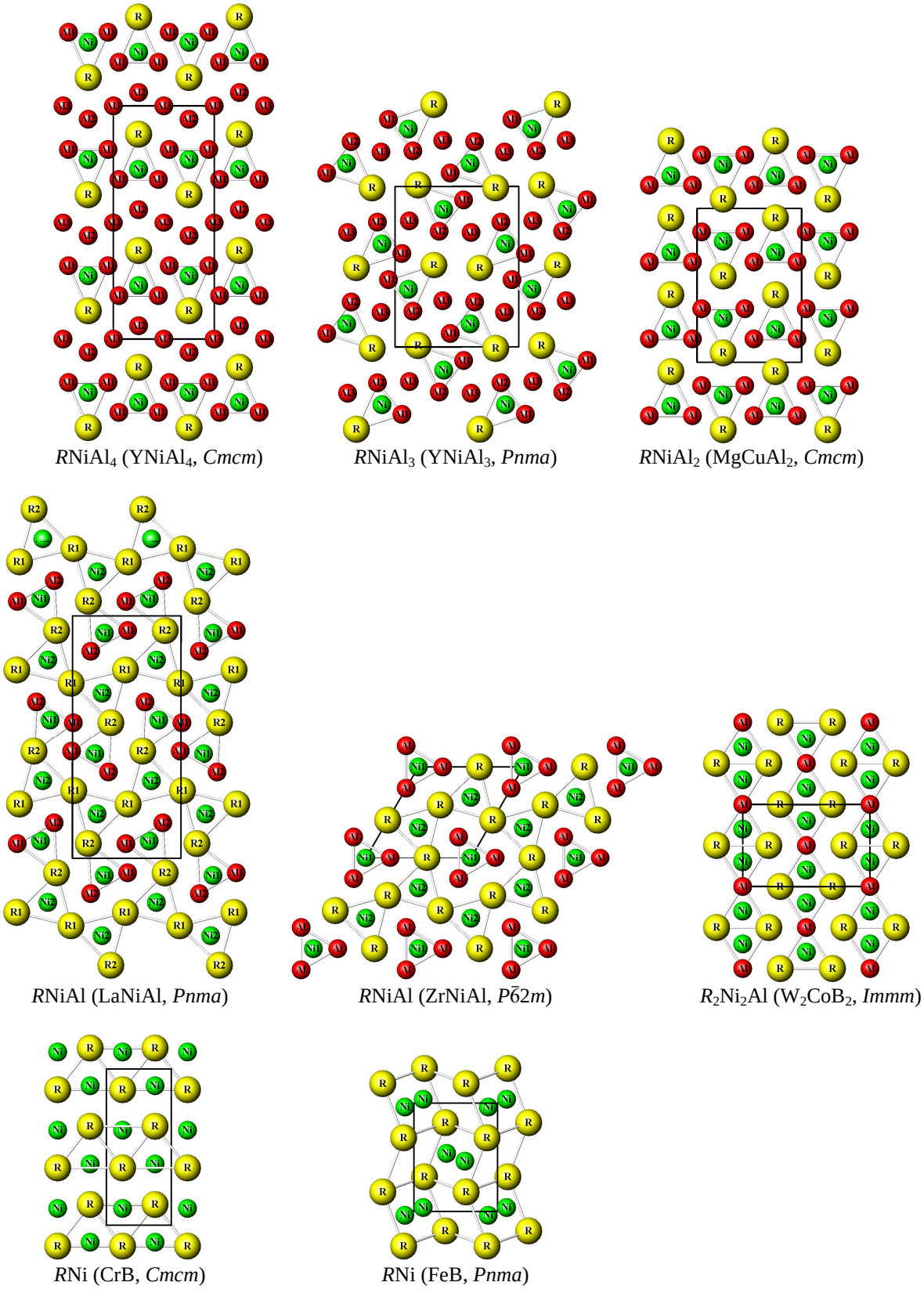


Fig. 3 Projections of the structures of rare-earth nickel aluminides: RNiAl$_4$ along [100], RNiAl$_3$ – [010], RNiAl$_2$ – [100], RNiAl – [010] and [001], R_2Ni$_2$Al – [100], and RNi – [100] and [010]; structure type and space group are indicated in parentheses.

R_2Al_4 and R_6, respectively (R_4Al_2 in average for two Ni sites). In the ZrNiAl-type structure the Ni atoms are at the center of prisms consisting of six R atoms (multiplicity 2 for the Ni site) or six Al atoms (multiplicity 1). Consequently, the average composition of the Ni-centered trigonal prisms is R_4Al_2 for this type. In the last structure, of W_2CoB_2 type, the Ni atoms center prisms of composition R_4Al_2.

In all the structures mentioned above the Ni-centered trigonal prisms form infinite columns (common triangular faces). It can be seen from Fig. 3 that the columns are isolated in the YNiAl$_4$-, YNiAl$_3$-, and MgCuAl$_2$-type structures. The two first structures contain additional Al atoms. In the LaNiAl- and ZrNiAl-type (R_6 prisms) structures, the infinite columns share one and three prism edges, respectively. The columns of Al$_6$ prisms in the ZrNiAl-type structures are isolated. In the case of the W_2CoB_2-type structure the infinite columns of Ni-centered trigonal prisms are connected *via* one edge and one rectangular face. As can be seen from Table 5, all the structure types described here (except LaNiAl) have representatives in the {Y, Sm, Gd, Tb, Dy}–Ni–Al systems.

Trigonal prismatic coordination is also characteristic of the Ni atoms in the structures of the binary equiatomic compounds RNi. The two common structure types are orthorhombic CrB [14] (R = La-Sm, Gd, Tb) and FeB [15] (Y, Gd, Dy-Lu). In the structures of these types the prisms are formed exclusively by R atoms (see Fig. 3). In the case of the FeB type the prisms axes are not parallel, and infinite columns of Ni-centered trigonal prisms are formed *via* common rectangular faces.

In the structures of the ternary aluminides described above, the Ni-centered trigonal prisms have the average composition R_2Al_4 for an Al content of 66.7-50.0 at.%, R_4Al_2 for 33.3-20.0 at.% Al, and R_6 for the binary compounds RNi. The corresponding information is summarized in Table 6.

Table 5 Crystallographic data for ternary compounds in the R–Ni–Al (R = Y, Sm-Dy) systems with the ratio R:Ni = 1:1.

Compound	Structure type	Pearson symbol	Space group	Y	Sm	Eu	Gd	Tb	Dy
RNiAl$_4$	**YNiAl$_4$**	*oS*24	*Cmcm*	+	+	–	+	+	+
RNiAl$_3$	**YNiAl$_3$**	*oP*20	*Pnma*	+	+	–	+	+	+
RNiAl$_2$	**MgCuAl$_2$**	*oS*16	*Cmcm*	+	+	–	+	+	+
RNiAl	**ZrNiAl**	*hP*9	*P*$\bar{6}$2*m*	+	+	–	+	+	+
R_2Ni$_2$Al	**W$_2$CoB$_2$**	*oI*10	*Immm*	+	+	–	+	+	+

Table 6 Compositions of Ni-centered trigonal prisms in the structures of compounds with the ratio R:Ni = 1:1 in the systems R–Ni–Al (R = rare-earth metal).

Structure type	Al content, at.%	Compositions of Ni-centered prisms	Average composition of Ni-centered prisms
YNiAl$_4$	66.7	R_2Al_4	**R_2Al_4**
YNiAl$_3$	60.0	R_2Al_4	**R_2Al_4**
MgCuAl$_2$	50.0	R_2Al_4	**R_2Al_4**
LaNiAl	33.3	1 R_2Al_4 + 1 R_6	**R_4Al_2**
ZrNiAl	33.3	2 R_6 + 1 Al$_6$	**R_4Al_2**
W$_2$CoB$_2$	20.0	R_4Al_2	**R_4Al_2**
CrB	0	R_6	**R_6**
FeB	0	R_6	**R_6**

Conclusions

Three new ternary compounds RNiAl$_3$ (R = Gd, Tb, and Dy) were found to crystallize with YNiAl$_3$-type structures (Pearson symbol *oP*20, space group *Pnma*). The isotypic structure of SmNiAl$_3$ was confirmed by a complete structure refinement on X-ray powder diffraction data. No corresponding ternary aluminide could be obtained with Eu.

The YNiAl$_3$ type contains Ni-centered tricapped trigonal prisms. Ni-centered trigonal prisms are also observed in the closely related structures of ternary aluminides with rare-earth metal and nickel that belong to the types YNiAl$_4$, MgCuAl$_2$, LaNiAl, ZrNiAl, and W$_2$CoB$_2$. In these structures, characterized by the ratio R:Ni = 1:1, the average composition of the trigonal prisms changes from R_2Al_4 to R_4Al_2 with decreasing Al content.

Acknowledgements

This work was supported by the Ministry of Ukraine for Education and Science under the grant No. 0109U002070.

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