Tb_{0.67}PdAl₃ and Gd_{1.33}Pt₃Al₈ with layers of rare-earth-metal atoms and Al-atom triangles

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The crystal structures of the ternary compounds Tb_{0.67}PdAl₃ (*hP*14-4.67, *P*6₃/*mmc*, *a* = 4.394(4), *c* = 9.372(6) Å) and Gd_{1.33}Pt₃Al₈ (*hR*51-14.00, *R*3̄*m*, *a* = 4.3090(14), *c* = 38.54(2) Å) were refined from X-ray single-crystal diffraction data. They contain monoatomic layers stacked along [001] with ordered or disordered distribution of rare-earth-metal atoms and Al-atom triangles. Together with the structures of Y₂Co₃Ga₉, Sc_{0.67}Fe₂Si₅, Er₄Pt₉Al₂₄, and ErNi₃Al₉, they form a family of intergrowth structures built up of three kinds of monoatomic layer. Analyzing the relative positions of the monoatomic layers, some basic stacking rules, which may help to predict new structures, are formulated.

Aluminide / Rare-earth metal / Noble metal / Single-crystal X-ray diffraction / Intergrowth layered structure

Introduction

The Al-rich parts of the phase diagrams of *R-T-Al* systems, where *R* is a rare-earth metal and *T* a *d*-element of group VIII, appear to be very complicated and a large number of ternary compounds containing >60 at.% Al have been reported [1]. Ternary aluminides crystallizing with 28 different structure types are listed in Table 1. Nine types among these, *i.e.* ErNi₃Al₉ [16], DyNi₃Al₉ [16], Sc_{0.67}Fe₂Si₅ [19], Gd_{1.33}Pt₃Al₈ [20], Er_{1.33}Pt₃Al₈ [21], Er₄Pt₉Al₂₄ [21], Y₄Pt₉Al₂₄ [21], Y₂Co₃Ga₉ [22], and Ho₂Rh₃Al₉ [23], are characterized by the presence of Al-atom triangles. These triangles and rare-earth-metal atoms are distributed in the ratio 1:2 in layers. Such compounds form in a rather narrow range of Al content (64.3-69.2 at.%) and their structures may be completely decomposed into monoatomic (one-atom thick) layers.

The aim of the present work was to study this group of ternary aluminides containing ordered or disordered layers with *R* atoms and Al₃ triangles, formulate some basic stacking rules for the layers, and search for new representatives with rare-earth metals and *d*-elements of group VIII.

Experimental

Alloys were synthesized from the elements (Tb ≥ 99.83 wt.%, Gd ≥ 99.86 wt.%, Pd ≥ 99.9 wt.%, Pt ≥ 99.9 wt.%, Al 99.998 wt.%) by arc melting in a

water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. The ingots were annealed at 600°C in quartz ampoules under vacuum for 1 month and subsequently quenched in cold water. The weight losses during the preparation of the samples were less than 0.5 % of the total mass, which was 1 g for each alloy.

Single crystals were extracted from alloys of nominal compositions Tb₁₁Pd₂₄Al₆₅ and Gd₁₄Pt₂₁Al₆₅ (in at.%). They were mounted on glass fibers and X-ray diffraction data were collected in the ω -2 θ scan mode at room temperature on a CAD-4T diffractometer (Mo *K* α radiation, λ = 0.71073 Å). An analytical absorption correction was applied. No significant variation of the intensities was observed during the data collections. Cell parameters were obtained by a least-squares refinement of the angles of 25 reflections for each crystal. For the Tb-containing crystal, the systematic extinctions (*hhl* and 00*l*: *l* = 2*n*+1) indicated as possible space groups *P*6₃*mc*, *P*6̄2*c*, and *P*6₃/*mmc* [27]. The structure was solved by direct methods in the centrosymmetric space group *P*6₃/*mmc*, using the SHELXS-97 program [28], leading to the composition Tb_{0.67}PdAl₃. A full-matrix least-squares refinement of the positional and anisotropic displacement parameters was performed on *F*² using the SHELXL-97 program [28]. Trial refinements in the noncentrosymmetric space groups *P*6₃*mc* and *P*6̄2*c* did not improve the results. In the case of the Gd-containing crystal, the atomic coordinates reported for Gd_{1.33}Pt₃Al₈ (space group

Table 1 Structure types of ternary aluminides of rare-earth metals and *d*-elements of group VIII containing >60 at.% Al [1].

At.% Al	Compound	Structure type	Pearson symbol	Space group	Ref.
76.9	RFe ₂ Al ₁₀ (<i>R</i> = Y, La-Nd, Sm, Gd-Lu), RRu ₂ Al ₁₀ (<i>R</i> = Y, La-Nd, Sm, Gd, Tb, Ho, Er), ROs ₂ Al ₁₀ (<i>R</i> = La, Pr, Nd)	YbFe ₂ Al ₁₀	<i>oS52</i>	<i>Cmcm</i>	[2]
76.1	R _{3.64} Os ₆ Al _{30.69} (<i>R</i> = Nd, Sm, Gd-Yb)	Y _{3.64} Re ₆ Al _{30.69}	<i>hP88-7.34</i>	<i>P6₃/mcm</i>	[3]
75.6	Y _{3.93} Os ₆ Al _{30.75}	Y _{3.93} Os ₆ Al _{30.75}	<i>hP90-8.63</i>	<i>P6₃/mcm</i>	[4]
75.5	NdRh ₄ Al _{15.37}	NdRh ₄ Al _{15.37}	<i>tP96-14.51</i>	<i>P4₂/nmc</i>	[5]
75.0	Ce ₂ Ru ₃ Al ₁₅	Ce ₂ Ru ₃ Al ₁₅	<i>hP80</i>	<i>P6₃/mcm</i>	[6]
75.0	Sm ₂ Os ₃ Al ₁₅	Sm ₂ Os ₃ Al ₁₅	<i>hP84-4.00</i>	<i>P6₃/mcm</i>	[7]
75.0	EuCo ₂ Al ₉	BaFe ₂ Al ₉	<i>hP12</i>	<i>P6/mmm</i>	[8]
72.7	RFe ₂ Al ₈ (<i>R</i> = La-Pr), RCo ₂ Al ₈ (<i>R</i> = Pr, Sm, Yb)	CeFe ₂ Al ₈	<i>oP44</i>	<i>Pbam</i>	[9]
72.6	CeRu _{2.83} Al _{10.17}	CeRu _{2.83} Al _{10.17}	<i>oI64-8.00</i>	<i>Imma</i>	[10]
70.4	R ₃ Ni ₅ Al ₁₉ (<i>R</i> = Y, Gd-Tm, Lu)	Gd ₃ Ni ₅ Al ₁₉	<i>oS108</i>	<i>Cmcm</i>	[11]
70.4	Pr ₂ Co ₆ Al ₁₉	U ₂ Co ₆ Al ₁₉	<i>mS108</i>	<i>C2/m</i>	[12]
70.0	La ₂ NiAl ₇	La ₂ NiAl ₇	<i>tI40</i>	<i>I4mm</i>	[13]
69.7	R ₄ Ni ₆ Al ₂₃ (<i>R</i> = Y, Ce, Sm, Gd, Yb)	Y ₄ Ni ₆ Al ₂₃	<i>mS66</i>	<i>C2/m</i>	[14]
69.5	LaNi _{1.44} Al _{5.56}	SrAu ₂ Ga ₅	<i>tP8</i>	<i>P4/mmm</i>	[15]
69.2	RNi ₃ Al ₉ (<i>R</i> = Gd, Er)	ErNi ₃ Al ₉	<i>hR78</i>	<i>R32</i>	[16]
69.2	RNi ₃ Al ₉ (<i>R</i> = Y, Dy, Yb)	DyNi ₃ Al ₉	<i>hR99-21.00</i>	<i>R32</i>	[16]
66.7	RNiAl ₄ (<i>R</i> = Y, Ce-Nd, Sm, Gd-Tm, Lu), CePdAl ₄	YNiAl ₄	<i>oS24</i>	<i>Cmcm</i>	[17]
66.7	RCoAl ₄ (<i>R</i> = La-Pr)	LaCoAl ₄	<i>oP12</i>	<i>Pmma</i>	[18]
65.2	R _{0.67} Pt ₂ Al ₅ (<i>R</i> = Y, Ce, Gd-Er)	Sc _{0.67} Fe ₂ Si ₅	<i>hP20-4.67</i>	<i>P6₃/mmc</i>	[19]
64.9	R _{1.33} Pt ₃ Al ₈ (<i>R</i> = Ce, Gd)	Gd _{1.33} Pt ₃ Al ₈	<i>hR51-14.00</i>	<i>R$\bar{3}$m</i>	[20]
64.9	Er _{1.33} Pt ₃ Al ₈	Er _{1.33} Pt ₃ Al ₈	<i>mS34-9.33</i>	<i>C2/m</i>	[21]
64.9	R ₄ Pd ₉ Al ₂₄ (<i>R</i> = Gd-Tm), R ₄ Pt ₉ Al ₂₄ (<i>R</i> = Gd-Lu)	Er ₄ Pt ₉ Al ₂₄	<i>aP37</i>	<i>P$\bar{1}$</i>	[21]
64.9	Y ₄ Pt ₉ Al ₂₄	Y ₄ Pt ₉ Al ₂₄	<i>aP51-14.00</i>	<i>P$\bar{1}$</i>	[21]
64.3	Y ₂ Co ₃ Al ₉ , R ₂ Rh ₃ Al ₉ (<i>R</i> = Y, La-Nd, Sm, Gd-Dy, Er, Tm, Lu), R ₂ Pd ₃ Al ₉ (<i>R</i> = Y, Gd-Tm), R ₂ Ir ₃ Al ₉ (<i>R</i> = Y, La-Nd, Sm, Gd-Ho, Tm-Lu)	Y ₂ Co ₃ Ga ₉	<i>oS56</i>	<i>Cmcm</i>	[22]
64.3	Ho ₂ Rh ₃ Al ₉ , Er ₂ Ir ₃ Al ₉	Ho ₂ Rh ₃ Al ₉	<i>oS84-28.00</i>	<i>Cmcm</i>	[23]
63.2	R ₃ Ru ₄ Al ₁₂ (<i>R</i> = Y, Ce-Nd, Sm, Gd-Tm), R ₃ Os ₄ Al ₁₂ (<i>R</i> = Y, Ce-Nd, Sm, Gd-Tm)	Gd ₃ Ru ₄ Al ₁₂	<i>hP38</i>	<i>P6₃/mmc</i>	[24]
62.5	RNi ₂ Al ₅ (<i>R</i> = La-Pr)	PrNi ₂ Al ₅	<i>oI16</i>	<i>Immm</i>	[25]
61.5	RFe ₄ Al ₈ (<i>R</i> = Y, La-Nd, Sm-Lu)	CeMn ₄ Al ₈	<i>tI26</i>	<i>I4/mmm</i>	[26]

R $\bar{3}$ m) in [20] were used as starting model and the structure was confirmed by a full-matrix least-squares refinement using SHELXL-97. The atomic coordinates of both structures were standardized by the program STRUCTURE TIDY [29]. Crystal data and details of the data collections and structure refinements for Tb_{0.67}PdAl₃ and Gd_{1.33}Pt₃Al₈ are given in Table 2.

Results

Structure of Tb_{0.67}PdAl₃. The refined atomic coordinates, site occupancies, and displacement

parameters for the structure of Tb_{0.67}PdAl₃ are listed in Table 3. It represents a new structure type of ideal composition R_{0.67}TAl₃. The main feature of this structure is a statistical distribution of Tb atoms (position 2*c*) and Al₃ triangles (6*h*) within atomic layers of composition Tb_{0.67}Al. The occupancy of the site in Wyckoff position 6*h* cannot exceed 1/3 because higher occupancy would lead to the appearance of impossibly short Al-Al distances (~1.8 Å) in the structure. Therefore, during the structure refinement, the occupancy of the Al site in Wyckoff position 6*h* was fixed at the value 0.33, whereas the occupancy of the Tb site in 2*c* was refined as a free parameter. The composition of the crystal refined to Tb_{0.611(8)}PdAl₃.

Table 2 Experimental details and crystallographic data for Tb_{0.67}PdAl₃ and Gd_{1.33}Pt₃Al₈.

Refined composition		Tb _{0.611(8)} PdAl ₃	Gd _{1.33} Pt ₃ Al ₈
Formula weight, M_r		284.45	1010.26
Structure type		Tb _{0.67} PdAl ₃	Gd _{1.33} Pt ₃ Al ₈
Pearson symbol		<i>hP</i> 14-4.67	<i>hR</i> 51-14.00
Space group		<i>P</i> 6 ₃ / <i>mmc</i> (#194)	<i>R</i> 3̄ <i>m</i> (#166)
Unit-cell parameters:	a , Å c , Å	4.394(4) 9.372(6)	4.3090(14) 38.54(2)
Cell volume V , Å ³		156.7(2)	619.7(5)
Formula units per cell Z		2	3
Density D_x , g cm ⁻³		6.029	8.121
Absorption coefficient μ , mm ⁻¹		20.013	61.951
Crystal shape		prism	plate
Crystal size, mm		0.035×0.035×0.100	0.055×0.055×0.035
Color		metallic grey	metallic grey
# of reflections:	measured	1041	710
	independent	119	345
	with $I > 2\sigma(I)$	87	227
Reliability factor R_{int}		0.0813	0.0445
Range of h, k, l		$-6 \leq h \leq 5, -3 \leq k \leq 6, -13 \leq l \leq 13$	$-5 \leq h \leq 1, -5 \leq k \leq 2, -54 \leq l \leq 54$
Range θ , °		4.35-30.47	4.76-30.47
Reliability factors:	R wR S	0.0316 0.0650 1.353	0.0641 0.1398 1.355
# of reflections used in refinement		87	227
# of refined parameters		13	24
Weighting scheme		$w = 1/[(\sigma F_o)^2 + (0.0186P)^2 + 1.77P]$	$w = 1/[(\sigma F_o)^2 + (0.0610P)^2 + 97.70P]$
Residual electron density:	$\Delta\rho_{max}$, e Å ⁻³ $\Delta\rho_{min}$, e Å ⁻³	1.513 -2.029	6.357 -6.079

Table 3 Atomic coordinates, site occupancies, and displacement parameters (Å²) for Tb_{0.67}PdAl₃ (*hP*14-4.67, *P*6₃/*mmc*, $a = 4.394(4)$, $c = 9.372(6)$ Å).

Site	Wyckoff position	x	y	z	U_{eq}	Occupancy
Tb	2c	1/3	2/3	1/4	0.0074(7)	0.611(8)
Pd	2a	0	0	0	0.0097(6)	1
Al1	6h	0.134(2)	0.268(4)	1/4	0.014(3)	0.33
Al2	4f	1/3	2/3	0.5727(6)	0.0144(11)	1

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb	0.0079(8)	0.0079(8)	0.0065(8)	0.0039(4)	0	0
Pd	0.0103(8)	0.0103(8)	0.0087(9)	0.0051(4)	0	0
Al1	0.015(5)	0.032(9)	0.000(4)	0.016(5)	0	0
Al2	0.0066(15)	0.0066(15)	0.030(3)	0.0033(8)	0	0

The content of the unit cell and the coordination polyhedra in the structure of Tb_{0.67}PdAl₃ are shown in Fig. 1, and the interatomic distances within the coordination polyhedra are listed in Table 4. The Tb atoms center 20-vertex polyhedra [TbAl₁₁Pd₆Tb₃], which can be described as hexagonal prisms of composition Al₆Pd₆ with three Tb and five additional Al atoms capping the eight faces. The smaller atoms are characterized by icosahedral coordination: [PdAl₈Tb₄] (can also be described as a deformed cuboctahedron), [Al₁Al₈Pd₂Tb₂] and strongly

deformed [Al₂Al₆Pd₃Tb₃]. These polyhedra are very similar to those observed in the structure type Y₂Co₃Ga₉ [22], which is an ordered variant of the Tb_{0.67}PdAl₃ structure with fully ordered distribution of rare-earth-metal atoms and *p*-element-atom triangles. **Structure of Gd_{1.33}Pt₃Al₈.** Gd_{1.33}Pt₃Al₈ crystallizes with its own structure type; our refinements confirm the structural model proposed in [20]. The refined atomic coordinates, site occupancies, and displacement parameters are listed in Table 5. As for the structure of the Tb_{0.67}PdAl₃ compound, the main feature of the

Table 4 Interatomic distances for Tb_{0.67}PdAl₃ (*hP*14-4.67, *P*6₃/*mmc*, *a* = 4.394(4), *c* = 9.372(6) Å).

Atoms		δ , Å
Tb ^a	– 2 Al2	3.025(6)
	– 6 Al2	3.032(4)
	– 3 Al1 ^b	3.171(12)
	– 6 Pd	3.4532(19)
	– 3 Tb ^a	4.394(4)
Pd	– 2 Al1 ^b	2.555(7)
	– 6 Al2	2.627(3)
	– 4 Tb ^a	3.4532(19)
Al1 ^b	– 2 Pd	2.555(7)
	– 2 Al1 ^b	2.63(3)
	– 4 Al2	2.765(4)
	– 2 Tb ^f	3.171(12)
	– 2 Al2	3.384(9)
Al2	– 3 Pd	2.627(3)
	– 2 Al1 ^b	2.765(4)
	– 3 Al2	2.880(6)
	– 1 Tb ^a	3.025(6)
	– 2 Tb ^a	3.032(4)
	– 1 Al2	3.322(11)
	[– 3 Al1 ^b	3.384(9)]

^a occ. (Tb) = 0.611(8); ^b occ. (Al1) = 0.33**Table 5** Atomic coordinates, site occupancies, and displacement parameters (Å²) for Gd_{1.33}Pt₃Al₈ (*hR*51-14.00, *R*3̄*m*, *a* = 4.3090(14), *c* = 38.54(2) Å).

Site	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occupancy
Gd	6 <i>c</i>	0	0	0.26941(10)	0.0034(8)	0.67
Pt1	6 <i>c</i>	0	0	0.12093(5)	0.0037(6)	1
Pt2	3 <i>a</i>	0	0	0	0.0106(8)	1
Al1	18 <i>h</i>	0.539(4)	0.461(4)	0.3947(7)	0.011(5)	0.33
Al2	6 <i>c</i>	0	0	0.1872(4)	0.006(3)	1
Al3	6 <i>c</i>	0	0	0.3514(5)	0.010(3)	1
Al4	6 <i>c</i>	0	0	0.4437(4)	0.006(3)	1

Site	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Gd	0.0025(11)	0.0025(11)	0.0052(18)	0.0012(6)	0	0
Pt1	0.0039(7)	0.0039(7)	0.0033(9)	0.0020(3)	0	0
Pt2	0.0100(10)	0.0100(10)	0.0117(15)	0.0050(5)	0	0
Al1	0.007(7)	0.007(7)	0.007(11)	-0.005(9)	-0.006(5)	0.006(5)
Al2	0.006(5)	0.006(5)	0.005(6)	0.003(2)	0	0
Al3	0.006(5)	0.006(5)	0.017(10)	0.003(2)	0	0
Al4	0.007(4)	0.007(4)	0.003(7)	0.004(2)	0	0

structure of Gd_{1.33}Pt₃Al₈ is a statistical distribution of *R* atoms and Al₃ triangles within atomic layers of composition *R*_{0.67}Al. During the final cycles of the refinement, the occupancies of the corresponding sites were fixed at occ. = 0.67 for Gd in 6*c* and occ. = 0.33 for Al in 18*h*.

The content of the unit cell and the coordination polyhedra in the structure of Gd_{1.33}Pt₃Al₈ are shown in Fig. 2, and the interatomic distances within the coordination polyhedra are listed in Table 6. As in the

structure of Tb_{0.67}PdAl₃, the large atoms (Gd) center the 20-vertex polyhedra [GdAl₁₁Pt₆Gd₃] (hexagonal prisms of composition Al₆Pt₆ with three Gd and five additional Al atoms capping the eight faces). The coordination polyhedra around the Pt and Al atoms are icosahedra, or derivatives of these with one or two missing vertices: [Pt1Al₈Gd₂] (defect icosahedron or cuboctahedron), [Pt2Al₈Gd₄] (or cuboctahedron), [Al1Al₈Pt₂Gd₂], [Al2Al₆Pt₄Gd] (defect), [Al3Al₆Pt₃Gd₃], [Al4Al₆Pt₃Gd₂] (defect).

Table 6 Interatomic distances for Gd_{1.33}Pt₃Al₈ (*hR*51-14.00, *R* $\bar{3}m$, *a* = 4.3090(14), *c* = 38.54(2) Å).

Atoms		δ , Å	Atoms		δ , Å
Gd ^a	– 3 Al3	3.051(11)	Al2	– 1 Pt1	2.553(16)
	– 3 Al4	3.064(10)		– 3 Pt1	2.671(6)
	– 3 Al1 ^b	3.08(2)		– 3 Al4	2.845(11)
	– 1 Al3	3.160(19)		– 3 Al2	2.948(17)
	– 1 Al2	3.169(16)		– 1 Gd ^a	3.169(16)
	– 3 Pt1	3.319(3)		[– 3 Al1 ^b	3.61(3)]
	– 3 Pt2	3.501(3)	Al3	– 3 Pt2	2.583(5)
	– 3 Gd ^a	4.3090(14)		– 2 Al1 ^b	2.742(19)
Pt1	– 1 Al1 ^b	2.48(3)		– 3 Al3	2.851(18)
	– 3 Al4	2.521(3)		– 2 Gd ^a	3.051(11)
	– 1 Al2	2.553(16)		– 1 Gd ^a	3.160(19)
	– 3 Al2	2.671(6)		[– 3 Al1 ^b	3.43(3)]
	– 2 Gd ^a	3.319(3)		– 1 Al4	3.56(3)
Pt2	– 2 Al1 ^b	2.55(3)	Al4	– 3 Pt1	2.521(3)
	– 6 Al3	2.583(5)		– 3 Al2	2.845(11)
	– 4 Gd ^a	3.501(3)		– 2 Al1 ^b	2.88(2)
Al1 ^b	– 1 Pt1	2.48(3)		– 2 Gd ^a	3.064(10)
	– 1 Pt2	2.55(3)		– 1 Al3	3.56(3)
	– 2 Al1 ^b	2.66(6)			
	– 2 Al3	2.742(19)			
	– 2 Al4	2.88(2)			
	– 2 Gd ^a	3.08(2)			
	– 1 Al3	3.43(3)			
	– 1 Al2	3.61(3)			

^a occ. (Gd) = 0.67; ^b occ. (Al1) = 0.33 **Fig. 1** The unit cell and coordination polyhedra for atoms in the Tb_{0.67}PdAl₃ structure.

Fig. 2 The unit cell and coordination polyhedra for atoms in the $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$ structure.

Fig. 3 Monoatomic Al- and T -atom layers with triangular meshes.

Fig. 4 Monoatomic $R_{0.67}Al \equiv R_2Al_3 \equiv R_4Al_6$ layers: disordered and ordered distribution of R atoms and Al_3 triangles.

Fig. 5 Monoatomic Tb_{0.67}Al layers in the Tb_{0.67}PdAl₃ structure.

Discussion

Three kinds of monoatomic (one-atom thick) layer can be considered in the structure types Tb_{0.67}PdAl₃, Y₂Co₃Ga₉ [22], Sc_{0.67}Fe₂Si₅ [19], Gd_{1.33}Pt₃Al₈ [20], Er₄Pt₉Al₂₄ [21], $R_{0.67}Ni_2Al_6$ (hypothetic) [16], and ErNi₃Al₉ [16]. Two of them have triangular mesh, *i.e.* they possess the motif of close-packed layers, but the interatomic distances within the layers for aluminides (see Table 1) are ~ 4.3 Å. Such layers formed by p - (Al) or d -element atoms ($T = Co, Ni, Rh, Pd, Ir, Pt$) are shown in Fig. 3. The third kind of layer has the composition $R_{0.67}Al \equiv R_2Al_3 \equiv R_4Al_6$ (R = rare-earth metal). The R atoms and the centers of Al_3 triangles also form a triangular mesh (Fig. 4). These layers derive from close-packed R -atom layers by a statistical (disordered) or ordered replacement of one-third of the R atoms by Al_3 triangles. In case of ordered substitution, the translation unit for such layers will be

three times larger (new parameters: $\mathbf{a}' = 2\mathbf{a} + \mathbf{b}$, $\mathbf{b}' = -\mathbf{a} + \mathbf{b}$, see Fig. 4). The monoatomic layers are stacked along the crystallographic direction [001] in all the above mentioned structure types, *i.e.* they are perpendicular to the 6-fold axes in the hexagonal structures and 3-fold axes in the trigonal (rhombohedral) structures. The ratio of different layers, the stacking sequence and the degree of ordering in the R_2Al_3 layers distinguish the different structure types. The interatomic distances within triangles (~ 2.65 Å) are the shortest Al-Al contacts in the structures indicating strong interaction.

For the comparison and discussion of the above mentioned structures we use the conventional symbols introduced to define the stacking sequence of monoatomic layers in close-packed structures: position **A** with coordinates $x = 0, y = 0$, **B** with $x = 2/3, y = 1/3$ and **C** with $x = 1/3, y = 2/3$ (referring to the small hexagonal translation unit).

Fig. 6 Monoatomic Pd- and Al-atom layers in the Tb_{0.67}PdAl₃ structure.

The hexagonal unit cell of Tb_{0.67}PdAl₃ contains eight monoatomic layers along the crystallographic direction [001]: two layers of composition Tb_{0.67}Al (at $z = 1/4$ and $3/4$), two Pd layers ($z = 0$ and $1/2$) and four Al layers ($z = 0.0726, 0.4274, 0.5726$, and 0.9274). The composition of the compound can be written as $2\text{Tb}_{0.67}\text{Al} + 2\text{Pd} + 4\text{Al} = 2\text{Tb}_{0.67}\text{PdAl}_3$. In Figs. 5 and 6, the Tb_{0.67}Al layer at $z = 1/4$ has been assigned the relative stacking position **C**, whereas the Tb_{0.67}Al layer at $z = 3/4$ is shifted to position **B**; both Pd layers ($z = 0$ and $1/2$) are located in the relative position **A**, two of the Al layers ($z = 0.0726$ and 0.4274) in **B**, and the remaining Al layers ($z = 0.5726$ and 0.9274) in position **C**. Hence, the structure of the Tb_{0.67}PdAl₃ compound is characterized by the following stacking sequence of monoatomic layers: **A**(Pd)-**B**(Al)-**C**(Tb_{0.67}Al)-**B**(Al)-**A**(Pd)-**C**(Al)-**B**(Tb_{0.67}Al)-**C**(Al). Standardization of the symbols assigned to the relative positions of the monoatomic layers so that the Tb_{0.67}Al layer at $z = 1/4$ is located in position **A**, leads to the following stacking sequence: **B**(T)-**C**(Al)-**A**(R_{0.67}Al)-**C**(Al)-**B**(T)-**A**(Al)-**C**(R_{0.67}Al)-**A**(Al) (Fig. 7).

The structures of the R₂T₃Al₉ compounds ($T = \text{Co}, \text{Rh}, \text{Pd}, \text{Ir}$) adopting the Y₂Co₃Ga₉ type have cell parameters c similar to that of Tb_{0.67}PdAl₃ and contain eight monoatomic layers stacked in the same way along [001]: **B**(T₆)-**C**(Al₆)-**A**(R₄Al₆)-**C**(Al₆)-**B**(T₆)-**A**(Al₆)-**C**(R₄Al₆)-**A**(Al₆) (Fig. 8). However, contrary to Tb_{0.67}PdAl₃, in the structure of R₂T₃Al₉ the R atoms and Al₃ triangles are distributed in an ordered way, leading to orthorhombic symmetry with a six times larger cell volume. Thus, the Y₂Co₃Ga₉ type is an ordered derivative of Tb_{0.67}PdAl₃. The group-subgroup relation for the corresponding space groups is the following: $P6_3/mmc$ (**a**, **b**, **c**) $\xrightarrow{\text{lib}}$ $P6_3/mcm$ (**a'** = $2\mathbf{a} + \mathbf{b}$, **b'** = $-\mathbf{a} + \mathbf{b}$, **c'** = **c**) $\xrightarrow{\text{I}}$ $Cmcm$ (**a''** = $2\mathbf{a}' + \mathbf{b}'$, **b''** = **b'**, **c''** = **c'**) [27]. Complete ordering of R atoms and Al₃ triangles is not possible in the intermediate superstructure with three-fold cell volume and space group $P6_3/mcm$, since only one Wyckoff position is available for the rare-earth-metal

atoms. Orthorhombic Ho₂Rh₃Al₉ is a partly disordered variant of Y₂Co₃Ga₉.

The R_{0.67}Pt₂Al₅ compounds belonging to the hexagonal Sc_{0.67}Fe₂Si₅ type and the trigonal (rhombohedral) Gd_{1.33}Pt₃Al₈-type compounds also contain disordered R_{0.67}Al layers. The unit cell of the Sc_{0.67}Fe₂Si₅ type contains 14 monoatomic layers along the crystallographic direction [001] (Fig. 9): two R_{0.67}Al layers, four T layers and eight Al layers. The composition of the corresponding compounds may be written in the following way: $2R_{0.67}\text{Al} + 4T + 8\text{Al} = 2R_{0.67}T_2\text{Al}_5$. The Sc_{0.67}Fe₂Si₅ type is described by the stacking sequence **A**(Al)-**B**(T)-**C**(Al)-**A**(R_{0.67}Al)-**C**(Al)-**B**(T)-**A**(Al)-**B**(Al)-**A**(T)-**C**(Al)-**B**(R_{0.67}Al)-**C**(Al)-**A**(T)-**B**(Al). Ordered derivatives of the Sc_{0.67}Fe₂Si₅ type are not yet known.

The unit cell of the structure of Gd_{1.33}Pt₃Al₈ contains six R_{0.67}Al layers, nine T and eighteen Al layers along the crystallographic direction [001] (Fig. 10). The composition is $6R_{0.67}\text{Al} + 9T + 18\text{Al} = 3R_{1.33}T_3\text{Al}_8$, and the 33 monoatomic layers are stacked in the following way in the triple hexagonal cell: **A**(T)-**C**(Al)-**B**(R_{0.67}Al)-**C**(Al)-**A**(T)-**B**(Al)-**A**(Al)-**B**(T)-**C**(Al)-**A**(R_{0.67}Al)-**C**(Al)-**B**(T)-**A**(Al)-**C**(R_{0.67}Al)-**A**(Al)-**B**(T)-**C**(Al)-**B**(Al)-**C**(T)-**A**(Al)-**B**(R_{0.67}Al)-**A**(Al)-**C**(T)-**B**(Al)-**A**(R_{0.67}Al)-**B**(Al)-**C**(T)-**A**(Al)-**C**(Al)-**A**(T)-**B**(Al)-**C**(R_{0.67}Al)-**B**(Al). In fact, the structure of Gd_{1.33}Pt₃Al₈ is an intergrowth of Tb_{0.67}PdAl₃- and Sc_{0.67}Fe₂Si₅-type slabs (in the ratio 1:1) delimited by the R_{0.67}Al layers. Such an intergrowth leads to rhombohedral symmetry. Triclinic Er₄Pt₉Al₂₄ is an ordering variant of Gd_{1.33}Pt₃Al₈ (R atoms and Al₃ triangles are distributed orderly) and its cell contains along the stacking direction $[\bar{1}01]$ 11 monoatomic layers in the sequence: **C**(T₃)-**B**(Al₃)-**A**(R₂Al₃)-**B**(Al₃)-**C**(T₃)-**A**(Al₃)-**C**(Al₃)-**A**(T₃)-**B**(Al₃)-**C**(R₂Al₃)-**B**(Al₃) (Fig. 11). The transformation from the triple hexagonal cell of Gd_{1.33}Pt₃Al₈ to the triclinic cell of Er₄Pt₉Al₂₄ is following: **a'** = $2\mathbf{a} + \mathbf{b}$, **b'** = $\mathbf{a} + 2\mathbf{b}$, **c'** = $2\mathbf{a}/3 + \mathbf{b}/3 + \mathbf{c}/3$.

Fig. 7 Stacking of monoatomic layers along [001] and $R_{0.67}M$ layers in the Tb_{0.67}PdAl₃ structure.

Fig. 8 Stacking of monoatomic layers along [001] and R_4M_6 layers in an Y₂Co₃Ga₉-type structure.

Fig. 9 Stacking of monoatomic layers along [001] and $R_{0.67}M$ layers in an $\text{Sc}_{0.67}\text{Fe}_2\text{Si}_5$ -type structure.

Monoclinic $\text{Er}_{1.33}\text{Pt}_3\text{Al}_8$ (transformation from $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$: $\mathbf{a}' = 2\mathbf{a} + \mathbf{b}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = -2\mathbf{a}/3 - \mathbf{b}/3 + \mathbf{c}/3$) and triclinic $\text{Y}_4\text{Pt}_9\text{Al}_{24}$ (transformation from $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$ as for $\text{Er}_4\text{Pt}_9\text{Al}_{24}$) differ from $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ by a partly disordered distribution of R atoms and Al_3 triangles.

Along the translation period c of the triple hexagonal cell of the trigonal (rhombohedral) structure type ErNi_3Al_9 there are 24 monoatomic layers: three $R_2\text{Al}_3$, six T_3 and fifteen Al_3 , consequently, the composition of the compound is $3R_2\text{Al}_3 + 6T_3 + 15\text{Al}_3 = 6RT_3\text{Al}_9$. The stacking sequence of the monoatomic layers repeats three times in the unit cell (Fig. 12): **B**(Al_3)-**A**(Al_3)-**B**(T_3)-**C**(Al_3)-**A**($R_2\text{Al}_3$)-**C**(Al_3)-**B**(T_3)-**A**(Al_3), and the rhombohedral Bravais lattice is the result of a relative shift of the Al_3 triangles in consecutive $R_2\text{Al}_3$ layers. Trigonal (rhombohedral) DyNi_3Al_9 differs from ErNi_3Al_9 by the distribution of R atoms and Al_3 triangles: in the ErNi_3Al_9 structure it is fully ordered, whereas in the structure of DyNi_3Al_9 it is partially disordered. The structure types ErNi_3Al_9 and DyNi_3Al_9 derive from a hypothetical hexagonal structure of composition $R_{0.67}\text{Ni}_2\text{Al}_6$ ($hP11\text{-}2.33$, $P\bar{6}m2$, $a \approx 4.20$, $c \approx 9.12$ Å [16]) with maximal disorder of R atoms and Al_3 triangles. The unit cell volume of the $R_{0.67}\text{Ni}_2\text{Al}_6$

structure is nine times smaller than the volume of the triple hexagonal cells of the ErNi_3Al_9 and DyNi_3Al_9 types ($\mathbf{a}' = 2\mathbf{a}/3 + \mathbf{b}/3$, $\mathbf{b}' = -\mathbf{a}/3 + \mathbf{b}/3$, $\mathbf{c}' = \mathbf{c}/3$).

The stacking sequences of the monoatomic layers in the structure types discussed above are summarized in [Table 7](#). For each type of layer, $R_{0.67}\text{Al} \equiv R_2\text{Al}_3 \equiv R_4\text{Al}_6$, $T \equiv T_3 \equiv T_6$, $\text{Al} \equiv \text{Al}_3 \equiv \text{Al}_6$, the symbols of their relative positions (**A**, **B**, **C**) and the Jagodzinski-Wyckoff symbols (***h***, ***c***) [29] are listed. Based on the analysis of the known structures, some general rules for the stacking of the monoatomic layers in structures containing layers with ordered or disordered distribution of *R* atoms and Al_3 triangles can be deduced:

- an $R_{0.67}\text{Al}$ layer is always located in hexagonal stacking (**h**) between two Al layers;
- a T layer is always located in cubic stacking (**c**) between two Al layers;
- $R_{0.67}\text{Al}$ and T layers are bridged by a single Al layer in cubic (**c**) stacking;
- T layers are separated by one or several Al layers in hexagonal (**h**) stacking.

The degree of hexagonal stacking (hexagonality) increases with increasing Al content: 25% of hexagonal stacking for Tb_{0.67}PdAl₃ and Y₂Co₃Ga₉-type aluminides (64.3 at.% Al), 36.4% for Gd_{1.33}Pt₃Al₈

Table 7 Stacking sequences of monoatomic layers in structures containing $R_{0.67}Al$ layers.

Structure type	Stacking sequence ^a																								
Tb _{0.67} PdAl ₃ , Y ₂ Co ₃ Ga ₉	R	M	T	M	R	M	T	M	R	M	T	M	R	M	T	M	R	M	T	M	R	M	T	M	R
	C	A	B	C	A	C	B	A	C	A	B	C	A	C	B	A	C	A	B	C	A	C	B	A	C
	h	c	c	c	h	c	c	c	h	c	c	c	h	c	c	c	h	c	c	c	h	c	c	c	h
Sc _{0.67} Fe ₂ Si ₅	T	M	M	T	M	R	M	T	M	M	T	M	R	M	T	M	M	T	M	R	M	T	M	M	T
	B	A	B	A	C	B	C	A	B	A	B	C	A	C	B	A	B	A	C	B	C	A	B	A	B
	c	h	h	c	c	h	c	c	h	h	c	c	h	c	c	h	h	c	c	h	c	c	h	h	c
Gd _{1.33} Pt ₃ Al ₈ , Er ₄ Pt ₉ Al ₂₄	M	R	M	T	M	R	M	T	M	M	T	M	R	M	T	M	R	M	T	M	M	T	M	R	M
	B	C	B	A	C	B	C	A	B	A	B	C	A	C	B	A	C	A	B	C	B	C	A	B	A
	c	h	c	c	c	h	c	c	h	h	c	c	h	c	c	c	h	c	c	h	h	c	c	h	c
R _{0.67} Ni ₂ Al ₆ , ErNi ₃ Al ₉	M	M	T	M	R	M	T	M	M	M	T	M	R	M	T	M	M	M	T	M	R	M	T	M	M
	B	A	B	C	A	C	B	A	B	A	B	C	A	C	B	A	B	A	B	C	A	C	B	A	B
	h	h	c	c	h	c	c	h	h	h	c	c	h	c	c	h	h	h	c	c	h	c	c	h	h

^a R – layer of composition $R_{0.67}Al \equiv R_2Al_3 \equiv R_4Al_6$ (R = rare-earth metal), $T - T \equiv T_3 \equiv T_6$ (T = Co, Ni, Rh, Pd, Ir, Pt), $M - M \equiv M_3 \equiv M_6$ (M = Al); **A**, **B**, **C** – relative shift of the layer perpendicular to the stacking direction; **h**, **c** – Jagodzinski-Wyckoff symbol

Fig. 10 Stacking of monoatomic layers along [001] and $R_{0.67}M$ layers in the $Gd_{1.33}Pt_3Al_8$ structure.

Fig. 11 Stacking of monoatomic layers along [001] and R_2M_3 layers in the $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ structure.

Table 8 Members of the homologous series $R_{0.67}T_nM_{2n+m}$.

Structure type	Space group	Slabs			Ideal composition
		$R_{0.67}M$	MTM	M	
Tb _{0.67} PdAl ₃	$P6_3/mmc$	2	2	—	$2R_{0.67}TM_3$
Y ₂ Co ₃ Ga ₉	$Cmcm$	$2(R_4M_6)$	$2(M_6T_6M_6)$	—	$12R_{0.67}TM_3 \equiv 4R_2T_3M_9$
Sc _{0.67} Fe ₂ Si ₅	$P6_3/mmc$	2	4	—	$2R_{0.67}T_2M_5$
Gd _{1.33} Pt ₃ Al ₈	$R\bar{3}m$	6	9	—	$6R_{0.67}T_{1.5}M_4 \equiv 3R_{1.33}T_3M_8$
Er ₄ Pt ₉ Al ₂₄	$P\bar{1}$	$2(R_2M_3)$	$3(M_3T_3M_3)$	—	$6R_{0.67}T_{1.5}M_4 \equiv R_4T_9M_{24}$
$R_{0.67}\text{Ni}_2\text{Al}_6$	$P\bar{6}m2$	1	2	1	$R_{0.67}T_2M_6$
ErNi ₃ Al ₉	$R32$	$3(R_2M_3)$	$6(M_3T_3M_3)$	$3(M_3)$	$9R_{0.67}T_2M_6 \equiv 6RT_3M_9$

(64.9 at.% Al), 42.9% for Sc_{0.67}Fe₂Si₅-type aluminides (65.2 at.% Si), and 50% for $R_{0.67}\text{Ni}_2\text{Al}_6$ and ErNi₃Al₉ (69.2 at.% Al).

Since a T layer is always surrounded by two Al (M) layers, it is possible to consider slabs formed by three consecutive layers Al- T -Al (MTM slabs). The structure types Tb_{0.67}PdAl₃, Y₂Co₃Ga₉, Sc_{0.67}Fe₂Si₅, Gd_{1.33}Pt₃Al₈, Er₄Pt₉Al₂₄, $R_{0.67}\text{Ni}_2\text{Al}_6$, and ErNi₃Al₉ form a homologous series with the general formula $R_{0.67}T_nM_{2n+m}$, based on the stacking of three different structural slabs. Two of them are identical to the monoatomic $R_{0.67}M$ and M layers discussed above, whereas the third one is the MTM slab. In the structure of Tb_{0.67}PdAl₃ (as well as in Y₂Co₃Ga₉) $R_{0.67}M$ (R_4M_6) and MTM ($M_6T_6M_6$) slabs alternate in the ratio 1:1. In the Sc_{0.67}Fe₂Si₅-type structure consecutive $R_{0.67}M$ layers are separated by two MTM slabs. In the

structure of $R_{0.67}\text{Ni}_2\text{Al}_6$ (ErNi₃Al₉) there is an additional M (M_3) layer between consecutive MTM ($M_3T_3M_3$) slabs, whereas in the structure of Gd_{1.33}Pt₃Al₈ (Er₄Pt₉Al₂₄) each $R_{0.67}M$ (R_2M_3) slab is situated between a single and a double MTM ($M_3T_3M_3$) slab. Structural features of the members of the homologous series $R_{0.67}T_nM_{2n+m}$ are summarized in [Table 8](#).

Conclusions

The Al-rich part of the R - T -Al systems (R – rare-earth metal, T – d -element of group VIII; > 60 at.% Al) contains a large number of compounds crystallizing with structures that can be decomposed into monoatomic layers with triangular (or derived) mesh.

Fig. 12 Stacking of monoatomic layers along [001] and R_2M_3 layers in the ErNi_3Al_9 structure.

Three kinds of layer are observed, among which the $R_{0.67}\text{Al}$ layer, which can be derived from a close-packed R -atom layer by a disordered or ordered replacement of one-third of the R atoms by Al_3 triangles. Probably, in the real structures the layers are ordered and the observed disorder is being due to stacking faults. Simple stacking rules could be derived, which may help to predict new structures.

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