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Rare-earth cobalt aluminides with $Y_2Co_3Ga_9$-type structure

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Two new rare-earth cobalt aluminides, $Gd_2Co_3Al_9$ and $Tb_2Co_3Al_9$, were synthesized. Their crystal structures and the structure of $Sm_2Co_3Al_9$ were refined from X-ray powder diffraction data: $Y_2Co_3Ga_9$ structure type, *oS*56, *Cmcm*, *a* = 12.8263(7), *b* = 7.5192(4), *c* = 9.4054(6) Å for the Sm-containing compound, *a* = 12.7883(8), *b* = 7.4955(5), *c* = 9.3711(6) Å for the Gd-containing compound, and *a* = 12.7606(9), *b* = 7.4783(5), *c* = 9.3332(6) Å for the Tb-containing compound. The structures are built from monoatomic R_4Al_6 layers (triangle mesh of *R* atoms and Al_3 triangles in ratio 2:1) and puckered Co_6Al_{12} layers (triangle mesh of Co and Al atoms in the ratio 1:2) alternating along [001].

Aluminide / Rare-earth metal / Cobalt / X-ray powder diffraction / Crystal structure

Introduction

86 representatives of the orthorhombic structure type $Y_2Co_3Ga_9$ (Pearson symbol *oS*56, space group *Cmcm*, *a* = 12.718, *b* = 7.383, *c* = 9.431 Å) [1] are known so far according to Pearson's Crystal Data [2]. The structure type forms in ternary systems of rare-earth elements or uranium with transition metals of group VIII and aluminum, gallium, or antimony (Table 1). Isotypic aluminides have been reported for all the rare-earth metals, except Eu, and transition metals of the Co subgroup (Co, Rh, Ir) or Pd. Gallides are also found with all the Partial disorder was observed in the structures of the compounds $Ho_2Rh_3Al_9$ and $Er_2Ir_3Al_9$ (structure type $Ho_2Rh_3Al_9$, Pearson symbol *oS*84-28, space group *Cmcm*, *a* = 13.168, *b* = 7.602, *c* = 9.337 Å) [3].

We present here the results of a structural investigation of three rare-earth cobalt aluminides of composition $R_2Co_3Al_9$ (*R* = Sm, Gd, Tb), two of which (*R* = Gd, Tb) were synthesized for the first time. The compound with Sm was reported in [4], however, only cell parameters were refined and the structure type assigned. For two other rare-earth cobalt aluminides (*R* = Y, Nd) complete structure determinations were carried out from X-ray single-crystal diffraction data [4,5].

Table 1 Ternary compounds with $Y_2Co_3Ga_9$-type structure (*oS*56, *Cmcm*) [2].

T \ *R*	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U
Aluminides																
Co	+				+	+		+[a]	+[a]							+
Rh	+	+	+	+	+	+		+	+	+	+[b]	+	+		+	+
Pd	+							+	+	+	+	+	+			
Ir	+	+	+	+	+	+		+	+	+	+	+[b]	+	+	+	+
Gallides																
Co	+				+	+		+	+	+	+	+	+	+	+	
Ru	+	+	+	+	+	+		+	+	+	+	+	+			
Rh	+		+			+	+	+	+	+	+	+	+	+		+
Ir	+		+			+	+	+	+	+	+	+	+	+		+
Antimonides																
Pd			+													

[a] this work; [b] partial disorder ($Ho_2Rh_3Al_9$-type structure).

Experimental

Alloys of nominal composition $R_{14.3}Co_{21.4}Al_{64.3}$ (R = Sm, Gd, Tb) were synthesized from high-purity metals ($R \geq$ 99.8 wt.%, Co $\geq$ 99.99 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. To achieve high efficiency of the interaction between the components the samples were melted twice. The ingots were annealed at 600ºC in evacuated quartz ampoules for 1 month and subsequently quenched in cold water. The losses during the preparation of the samples were less than 0.5 % of the total mass, which was 1 g for each alloy.

X-ray powder diffraction patterns of the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and $Tb_2Co_3Al_9$ were obtained at room temperature on a Stoe Stadi P diffractometer with Cu $K\alpha_1$-radiation. The structures were refined by the Rietveld method starting from coordinates of the parent structure type $Y_2Co_3Ga_9$ [1] using the FullProf Suite program package [6] (Fig. 1). In the final cycles of the refinements 26 parameters were allowed to vary: sample shift, scale factor, three cell parameters, six profile parameters (pseudo-Voigt profile), eleven positional and three atomic displacement parameters and one texture parameter. Isotropic displacement parameters for the same chemical element were constrained to be equal. The background was defined by polynomial functions using a Fourier filtering technique. Experimental details and crystallographic data are listed in Table 2, atomic coordinates and isotropic displacement parameters are given in Table 3.

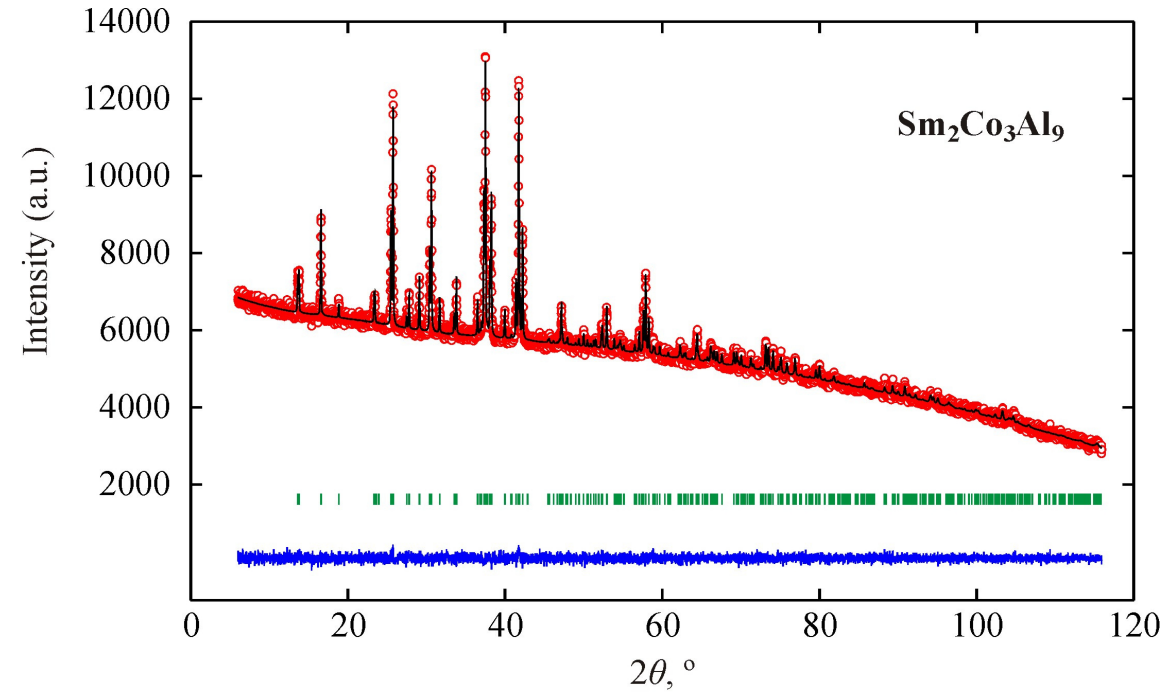
Results and discussion

Interatomic distances and coordination numbers of the atoms in the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and Tb_2Co_3Al are listed in Table 4, the corresponding coordination polyhedra are shown in Fig. 2. The rare-earth metal atoms are surrounded by eleven Al atoms, six Co atoms, and three R atoms forming hexagonal prisms (composition Al_6Co_6) with additional atoms in front of all the faces. The symmetry of this polyhedron is almost trigonal. The cobalt atoms from both Wyckoff positions are situated inside icosahedra (composition Al_8R_4, no Co-Co contacts), which can be reduced to cubes if only the Al atoms are considered. The aluminum atoms from three of the crystallographically independent sites (Al1, Al2, Al4) also centre icosahedra, however, built from the three elements (composition $Al_6Co_3R_3$ or $Al_8Co_2R_2$). The polyhedron around the aluminum atoms from the fourth site (Al3) contains 13 vertices ($Al_8Co_3R_2$) and can be derived from an icosahedron. Despite the different composition and degree of deformation of the coordination polyhedra of the Co and Al atoms, the average distance from the central atom to the

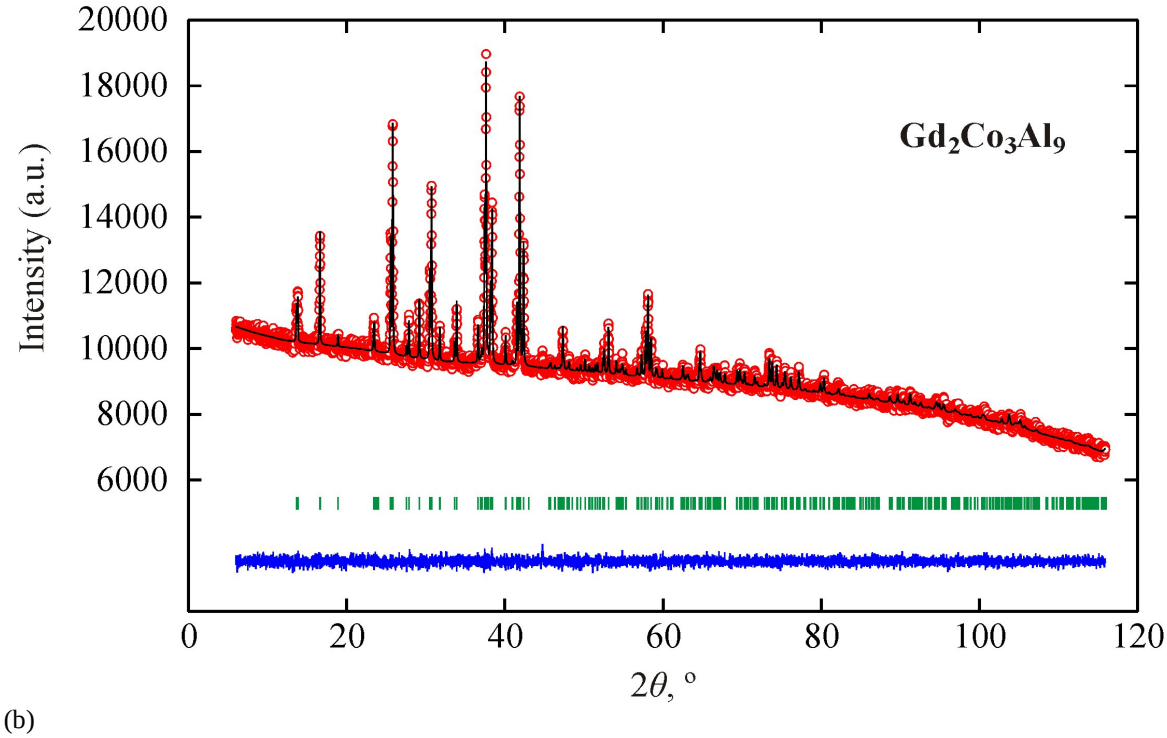
Table 2 Experimental details and crystallographic data for the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and $Tb_2Co_3Al_9$.

Compound		$Sm_2Co_3Al_9$	$Gd_2Co_3Al_9$	$Tb_2Co_3Al_9$
Formula weight M_r		720.33	734.13	737.48
Structure type			$Y_2Co_3Ga_9$	
Pearson symbol			*oS*56	
Space group			*Cmcm* (#63)	
Unit-cell parameters:	*a*, Å	12.8263(7)	12.7883(8)	12.7606(9)
	b, Å	7.5192(4)	7.4955(5)	7.4783(5)
	c, Å	9.4054(6)	9.3711(6)	9.3332(6)
Cell volume *V*, Å^3		907.09(9)	898.27(10)	890.65(10)
Formula units per cell *Z*			4	
Density D_X, g cm^{-3}		5.275	5.429	5.500
Preferred orientation: value / [direction]		0.988(5) / [011]	0.999(5) / [011]	0.995(5) / [011]
Scanning mode			$\theta/2\theta$	
Range 2θ, º			6-115.9	
Step size, °			0.015	
Profile parameters	*U*	0.040(4)	0.045(5)	0.053(5)
	V	-0.018(3)	-0.016(4)	-0.023(4)
	W	0.0131(7)	0.0123(7)	0.0138(8)
Shape parameter		0.642(13)	0.606(14)	0.587(14)
Asymmetry parameters		0.100(5), 0.0169(18)	0.064(6), 0.0141(19)	0.086(6), 0.0132(19)
Reliability factors:	R_B	0.0675	0.0694	0.0652
	R_F	0.1010	0.1060	0.0976
	R_p[a]	0.0111	0.863	0.0115
	R_{wp}[a]	0.0139	0.0108	0.0145
	χ^2	1.02	1.07	1.04

[a] Non-corrected for background.

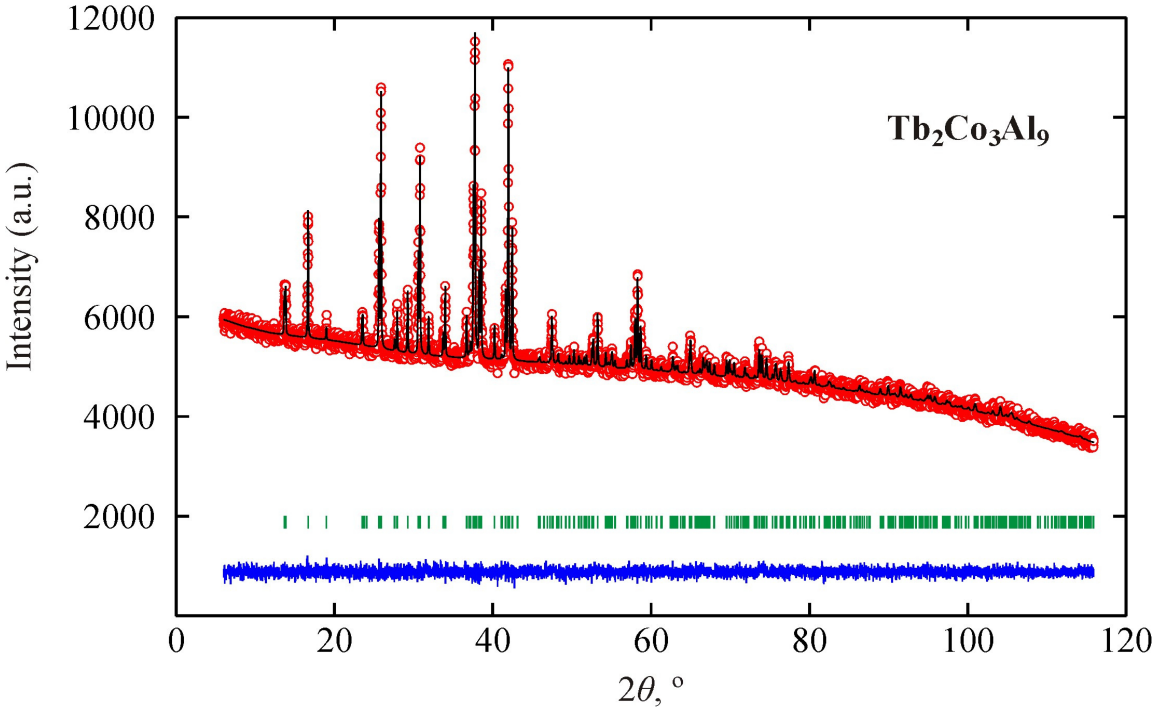


(a)



(b)

Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the $Sm_{14.3}Co_{21.4}Al_{64.3}$ (a), $Gd_{14.3}Co_{21.4}Al_{64.3}$ (b), and $Tb_{14.3}Co_{21.4}Al_{64.3}$ (c) samples (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections from the $R_2Co_3Al_9$ compounds.



(c)

Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the $Sm_{14.3}Co_{21.4}Al_{64.3}$ (a), $Gd_{14.3}Co_{21.4}Al_{64.3}$ (b), and $Tb_{14.3}Co_{21.4}Al_{64.3}$ (c) samples (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections from the $R_2Co_3Al_9$ compounds (*continued*).

Table 3 Atomic coordinates and isotropic displacement parameters for the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and $Tb_2Co_3Al_9$ ($Y_2Co_3Ga_9$ structure type, *oS*56, *Cmcm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
			$Sm_2Co_3Al_9$		
Sm	8*g*	0.33820(16)	0.3331(4)	1/4	0.89(7)
Co1	8*e*	0.3281(5)	0	0	0.58(11)
Co2	4*a*	0	0	0	0.58(11)
Al1	16*h*	0.1661(7)	0.1680(12)	0.0698(6)	0.76(13)
Al2	8*g*	0.1018(8)	0.4424(12)	1/4	0.76(13)
Al3	8*f*	0	0.334(2)	0.5408(9)	0.76(13)
Al4	4*c*	0	0.126(2)	1/4	0.76(13)
			$Gd_2Co_3Al_9$		
Gd	8*g*	0.33831(17)	0.3330(4)	1/4	0.77(8)
Co1	8*e*	0.3282(5)	0	0	0.46(11)
Co2	4*a*	0	0	0	0.46(11)
Al1	16*h*	0.1662(7)	0.1680(12)	0.0681(6)	0.67(12)
Al2	8*g*	0.1027(8)	0.4424(12)	1/4	0.67(12)
Al3	8*f*	0	0.333(2)	0.5451(10)	0.67(12)
Al4	4*c*	0	0.130(2)	1/4	0.67(12)
			$Tb_2Co_3Al_9$		
Tb	8*g*	0.33880(17)	0.3331(4)	1/4	0.46(7)
Co1	8*e*	0.3287(5)	0	0	0.34(11)
Co2	4*a*	0	0	0	0.34(11)
Al1	16*h*	0.1682(7)	0.1652(13)	0.0696(7)	1.59(14)
Al2	8*g*	0.1018(9)	0.4436(13)	1/4	1.59(14)
Al3	8*f*	0	0.331(2)	0.5438(10)	1.59(14)
Al4	4*c*	0	0.128(2)	1/4	1.59(14)

Table 4 Interatomic distances and coordination numbers of atoms for the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and $Tb_2Co_3Al_9$.

Atoms		δ, Å			Coordination number
		$Sm_2Co_3Al_9$	$Gd_2Co_3Al_9$	$Tb_2Co_3Al_9$	
R	– 2 Al1	3.008(6)	2.982(6)	2.984(7)	20
	– 1 Al4	3.026(11)	3.038(11)	3.016(11)	
	– 2 Al1	3.036(8)	3.035(8)	3.002(9)	
	– 1 Al2	3.037(10)	3.023(10)	3.010(10)	
	– 2 Al1	3.047(8)	3.046(8)	3.025(9)	
	– 2 Al3	3.124(8)	3.084(9)	3.073(9)	
	– 1 Al2	3.142(10)	3.123(10)	3.135(12)	
	– 2 Co2	3.3780(17)	3.3662(18)	3.3516(18)	
	– 2 Co1	3.413(4)	3.404(4)	3.402(4)	
	– 2 Co1	3.438(2)	3.426(2)	3.416(2)	
	– 1 *R*	4.151(3)	4.135(3)	4.114(3)	
	– 2 *R*	4.388(4)	4.376(4)	4.372(4)	
Co1	– 2 Al1	2.518(10)	2.507(10)	2.478(10)	12
	– 2 Al2	2.555(5)	2.541(4)	2.532(5)	
	– 2 Al3	2.564(9)	2.564(9)	2.558(9)	
	– 2 Al1	2.582(9)	2.570(9)	2.587(10)	
	– 2 *R*	3.413(4)	3.404(4)	3.402(4)	
	– 2 *R*	3.438(2)	3.426(2)	3.416(2)	
Co2	– 2 Al4	2.535(6)	2.537(6)	2.522(6)	12
	– 2 Al3	2.541(15)	2.532(15)	2.509(15)	
	– 4 Al1	2.562(9)	2.552(9)	2.560(9)	
	– 4 *R*	3.3780(17)	3.3662(18)	3.3516(18)	
Al1	– 1 Co1	2.518(10)	2.507(10)	2.478(10)	12
	– 1 Co2	2.562(9)	2.552(9)	2.560(9)	
	– 1 Co1	2.582(9)	2.570(9)	2.587(10)	
	– 1 Al3	2.679(12)	2.678(12)	2.695(12)	
	– 1 Al4	2.741(8)	2.739(8)	2.742(8)	
	– 1 Al2	2.795(11)	2.792(11)	2.808(12)	
	– 1 Al1	2.807(12)	2.781(12)	2.792(13)	
	– 1 Al1	2.847(12)	2.823(12)	2.767(12)	
	– 1 *R*	3.008(6)	2.982(6)	2.984(7)	
	– 1 *R*	3.036(8)	3.035(8)	3.002(9)	
	– 1 *R*	3.047(8)	3.046(8)	3.025(9)	
	– 1 Al1	3.390(8)	3.409(8)	3.367(9)	
Al2	– 2 Co1	2.555(5)	2.541(4)	2.532(5)	12
	– 1 Al2	2.611(15)	2.627(14)	2.598(16)	
	– 1 Al4	2.714(16)	2.685(16)	2.694(17)	
	– 2 Al1	2.795(11)	2.792(11)	2.808(12)	
	– 2 Al3	2.899(13)	2.872(13)	2.869(13)	
	– 1 *R*	3.037(10)	3.023(10)	3.010(10)	
	– 2 Al3	3.138(10)	3.169(10)	3.149(11)	
	–1 *R*	3.142(10)	3.123(10)	3.135(12)	
Al3	– 1 Co2	2.541(15)	2.532(15)	2.509(15)	13
	– 2 Co1	2.564(9)	2.564(9)	2.558(9)	
	– 1 Al3	2.61(2)	2.64(2)	2.66(2)	
	– 2 Al1	2.679(12)	2.678(12)	2.695(12)	
	– 2 Al2	2.899(13)	2.872(13)	2.869(13)	
	– 2 *R*	3.124(8)	3.084(9)	3.073(9)	
	– 2 Al2	3.138(10)	3.169(10)	3.149(11)	
	– 1 Al4	3.151(13)	3.156(13)	3.935(19)	

Table 4 Interatomic distances and coordination numbers of atoms for the compounds $Sm_2Co_3Al_9$, $Gd_2Co_3Al_9$, and $Tb_2Co_3Al_9$ (*continued*).

Al4	– 2 Co2	2.535(6)	2.537(6)	2.522(6)	
	– 2 Al2	2.714(16)	2.685(16)	2.694(17)	
	– 4 Al1	2.741(8)	2.739(8)	2.742(8)	12
	– 2 *R*	3.026(11)	3.038(11)	3.016(11)	
	– 2 Al3	3.151(13)	3.156(13)	3.134(13)	

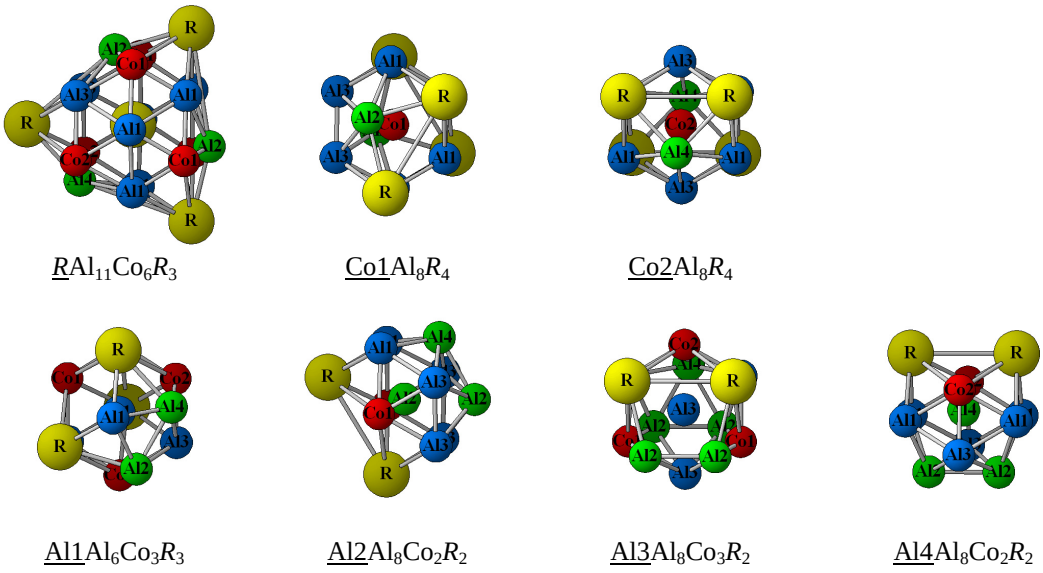


Fig. 2 Coordination polyhedra for atoms in the $R_2Co_3Al_9$ structure.

vertices remains almost the same (~ 2.83 Å). However, the particular ordering of the Co and Al atoms is important for the stability of the phase. This is supported by the absence of sites with statistical mixtures of Co and Al, and the absence of significant homogeneity ranges for the $Y_2Co_3Ga_9$-type compounds.

Cobalt and aluminum atoms in $R_2Co_3Al_9$ form triangle-mesh puckered layers where Co monoatomic layers are sandwiched between two Al monoatomic layers (Fig. 3), the thickness of the slabs being approximately 1.33 Å. The resulting slabs (composition Co_6Al_{12}) alternate along [001] with monoatomic layers that contain rare-earth and additional aluminum atoms in the ratio 2:3 (R_4Al_6). The latter layers can be derived from triangle-mesh *R*-atom layers, where every third *R* atom is replaced by an Al-atom triangle (ratio of *R* atoms to Al_3 triangles 2:1). The translation along the *c* direction contains two layers of each kind, $2R_4Al_6 + 2Co_6Al_{12} = 4R_2Co_3Al_9$, and the stacking of the layers of trigonal symmetry leads to overall orthorhombic symmetry.

Five other basic structure types for ternary aluminides contain similar layers, but in different proportions and/or stacking sequences: $Tb_{0.67}PdAl_3$ [7], $Sc_{0.67}Fe_2Si_5$ [8], $Yb_2Pt_6Al_{15}$ [9], $Gd_{1.33}Pt_3Al_8$ [10], and $Er_4Pt_9Al_{24}$ [11]. The $Tb_{0.67}PdAl_3$ type contains the same number of layers, but due to stacking faults concerning the relative shift of the layers containing rare-earth metal atoms and Al-atom triangles; the overall symmetry is hexagonal with a small average unit cell (*hP*14-4.67, $P6_3/mmc$). The $Tb_{0.67}PdAl_3$ type is a "fully" disordered variant of $Y_2Co_3Ga_9$, whereas the $Ho_2Rh_3Al_9$ type represents an intermediate situation with partial disorder of R atoms and Al3 triangles. The $Sc_{0.67}Fe_2Si_5$- and $Yb_2Pt_6Al_{15}$-type structures, as well as $Gd_{1.33}Pt_3Al_8$- and $Er_4Pt_9Al_{24}$-type structures, form two other couples of disordered and ordered stacking of similar layers, but with the ratio $2(R_4Al_6)$: $4(T_6Al_{12})$ and $2(R_4Al_6):3(T_6Al_{12})$, respectively. Also for these ratios, partly disordered variants are known, $Er_{1.33}Pt_3Al_8$ and $Y_4Pt_9Al_{24}$, respectively [11].

Table 5 presents the unit-cell parameters for known rare-earth cobalt aluminides with $Y_2Co_3Ga_9$-type structure. As expected, the unit-cell parameters decrease with decreasing atomic radii of the rare-earth element.

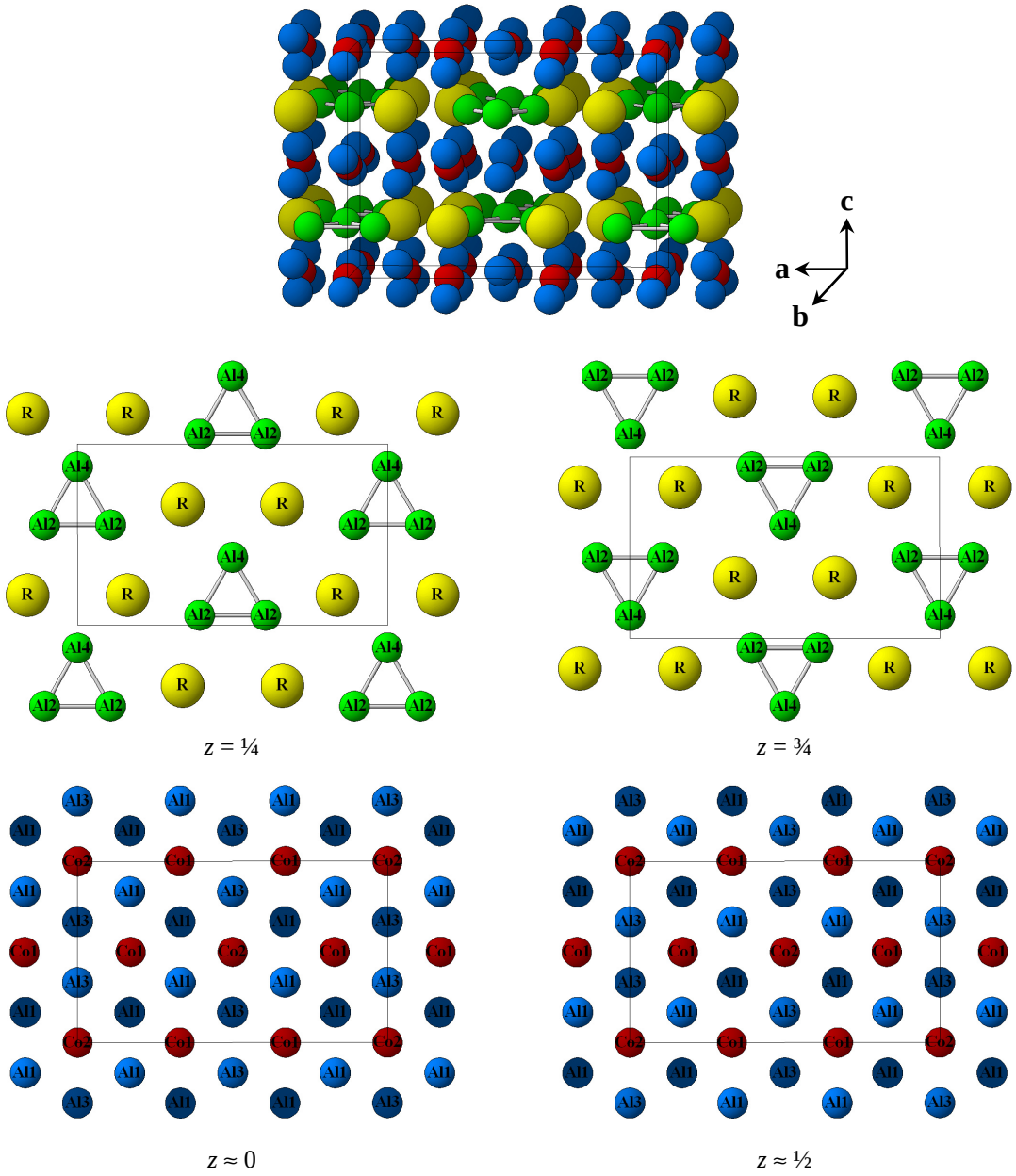


Fig. 3 Perspective view of the structure of $R_2Co_3Al_9$ ($Y_2Co_3Ga_9$ type) and projection of the R_4Al_6 and Co_6Al_{12} layers along [001].

Table 5 Unit-cell parameters of $R_2Co_3Al_9$ compounds with $Y_2Co_3Ga_9$-type structure.

Compound	*a*, Å	*b* Å	*c*, Å	*V*, Å^3	Reference
$Nd_2Co_3Al_9$	12.8911	7.5594	9.4703	922.9	[4]
$Sm_2Co_3Al_9$	12.823	7.511	9.402	905.5	[4]
	12.8263(7)	7.5192(4)	9.4054(6)	907.09(9)	this work
$Gd_2Co_3Al_9$	12.7883(8)	7.4955(5)	9.3711(6)	898.27(10)	this work
$Tb_2Co_3Al_9$	12.7606(9)	7.4783(5)	9.3332(6)	890.65(10)	this work
$Y_2Co_3Al_9$	12.740	7.4635	9.321	886.3	[5]

Conclusions

Two new rare-earth cobalt aluminides, $Gd_2Co_3Al_9$ and $Tb_2Co_3Al_9$, continue the row of isotypic compounds with $Y_2Co_3Ga_9$-type structure. The structures are ordered and can be decomposed into two kinds of layer with triangle mesh. The stacking of the layers leads to a structure with overall orthorhombic symmetry.

Acknowledgements

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