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Structure of *R*Ni$_3$Al$_9$ (*R* = Y, Gd, Dy, Er) with Either Ordered or Partly Disordered Arrangement of Al-Atom Triangles and Rare-Earth-Metal Atoms

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Abstract

ErNi$_3$Al$_9$, $M_r = 586.22$, trigonal, new type, *hR*78, *R*32 – f^2edc^4 (No. 155), $a = 7.2716(5)$, $c = 27.346(3)$ Å, $V = 1252.2(2)$ Å^3, $Z = 6$, $D_x = 4.664$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 17.654$ mm^{-1}, $F(000) = 1614$, $T = 293$ K, $wR = 0.021$ for 785 contributing unique reflections. The structure is built up of three kinds of monoatomic layer perpendicular to **c**: Al-atom layers with triangular mesh, Ni-atom layers with triangular mesh and layers containing two rare-earth-metal atoms for one Al-atom triangle. GdNi$_3$Al$_9$ [$a = 7.3006(9)$, $c = 27.478(5)$ Å, $wR = 0.020$ for 791 reflections] is isotypic. YNi$_3$Al$_9$ [$a = 7.2894(7)$, $c = 27.430(5)$ Å, $wR = 0.035$ for 635 reflections] and DyNi$_3$Al$_9$ [$a = 7.2723(9)$, $c = 27.344(6)$ Å, $wR = 0.027$ for 682 reflections] crystallize in related structures with a partly disordered arrangement of Al-atom triangles and rare-earth-metal atoms. Similar monoatomic layers to those in ErNi$_3$Al$_9$ build up the orthorhombic structure of Y$_2$Co$_3$Al$_9$ (Y$_2$Co$_3$Ga$_9$ type). The stoichiometry 1:3:9 is related to that of R_2T_3Al$_9$ by replacing every second mixed layer of composition R_2Al$_3$ by an Al-atom layer (Al$_3$): $6RT_3\text{Al}_9 = 6R_2T_3\text{Al}_9 - 3R_2\text{Al}_3 + 3\text{Al}_3$.

Introduction

The Al-rich part of the rare-earth–transition metal–Al phase diagrams appears to be very complicated, with a large number of compounds of very similar composition. In the Y–Ni–Al system, for example, five compounds containing more than 50 at.% Al, have been identified (Rykhal' & Zarechnyuk, 1977; Gladyshevskii & Parthé, 1992). We report here the structures of four new rare-earth-metal–Ni aluminides, two of which are isotypic whereas the other two crystallize in partly disordered, closely related structures.

Experimental

Samples were prepared from high-purity elements (Y, Gd, Dy, Er ≥ 99.9%, Ni and Al ≥ 99.999%) by arc melting under argon atmosphere and annealed at 1073 K for two weeks in a silica tube under an argon atmosphere (400 mm Hg). Single crystals were mounted on a Philips PW1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator, ω–2θ scan mode. An absorption correction was made using *LSABS* (Blanc, Schwarzenbach & Flack, 1991), the anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Systematic absences led to the following possible space groups: *R*3, $R\bar{3}$, *R*32, *R*3*m* and $R\bar{3}m$ (*International Tables for Crystallography*, 1983, Vol. A). The structure of ErNi$_3$Al$_9$ was solved in space group *R*32 by *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987); one rare-earth-metal,

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Table 1. *Details of data collection and refinement for* $ErNi_3Al_9$, $GdNi_3Al_9$, YNi_3Al_9 *and* $DyNi_3Al_9$

Nominal composition	$Er_5Ni_{15}Al_{80}$	$Gd_5Ni_{15}Al_{80}$	$Y_5Ni_{15}Al_{80}$	$Dy_{15}Ni_{25}Al_{60}$
Weight loss (%)	0.1	0.1	0.6	0.1
Size of crystal* (mm)	0.066 × 0.066 × 0.038	0.056	0.040 × 0.048 × 0.064	0.096 × 0.056 × 0.040
Reflections for unit cell [2θ range (°)]	23 [20–39]	26 [16–37]	28 [16–37]	19 [20–37]
Sinθ/λ (Å^{-1})	0.08–0.70	0.08–0.70	0.08–0.70	0.08–0.70
hkl with antireflections	$-10 \le h \le 10$ $0 \le k \le 9$ $0 \le l \le 38$	$-10 \le h \le 10$ $0 \le k \le 9$ $0 \le l \le 38$	$-10 \le h \le 10$ $0 \le k \le 9$ $0 \le l \le 38$	$0 \le h \le 8$ $0 \le k \le 8$ $0 \le l \le 38$
Standard reflections (max. % *I* variation)	$\bar{1}\bar{1}6$ (0.8) $\bar{1}\bar{1}0$ (0.9)	$\bar{3}00$ (0.6) $00\overline{12}$ (1.3)	$\bar{3}00$ (0.9) $00\overline{12}$ (0.6)	$\bar{3}00$ (0.6) $\bar{1}\bar{1}6$ (0.7)
Collected reflections	2212	2268	2260	972
Unique reflections (R_{int})	785 (0.017)	803 (0.030)	797 (0.071)	795 (0.038)
μ (mm^{-1})	17.654	15.254	14.376	16.497
Transmission factors	0.383–0.539	0.545–0.552	0.444–0.556	0.457–0.545
Reflections with $\lvert F_{rel}\rvert > 3\sigma(\lvert F_{rel}\rvert)$	785	791	635	682
Refined parameters	43	43	43	43
Extinction $G \times 10^2$	2.37 (6)	2.34 (6)	1.5 (1)	5.29 (9)
Enantiomorph polarity x	1.01 (2)	−0.01 (2)	−0.03 (2)	1.07 (3)
Max. shift/e.s.d. × 10^3	0.3	0.3	0.2	0.2
Residual electron density (e Å^{-3})	+2.1 (−1.2)	+0.9 (−1.9)	+1.4 (−2.2)	+4.4 (−3.3)
S	2.15	1.22	1.24	1.79
R	0.021	0.025	0.045	0.049
wR, $w = 1/\sigma^2(\lvert F_{rel}\rvert)$	0.021	0.020	0.035	0.027

* Fragments cut from hexagonal plates: dimensions ±(100), ±(010), ±(001) or mean diameter.

one Ni and six Al sites were identified. For the Y and Dy compounds two additional atom sites, *i.e.* one rare-earth-metal and one Al site, were detected on a difference electron-density map. The structures were confirmed by least-squares refinements based on $|F|$ values, varying a scale factor, isotropic extinction, enantiomorph-polarity, atomic positional and atomic displacement parameters.

The programs used for the data reduction and structure refinement are all from the *XTAL*3.0 system (Hall & Stewart, 1990). Details of the data collection and refinement are listed in Table 1. The final atomic positional, the (equivalent) isotropic displacement and the refined population parameters are listed in Table 2.* The atomic coordinates of $ErNi_3Al_9$ and $GdNi_3Al_9$ were standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987), with directly comparable data sets being presented for YNi_3Al_9 and $DyNi_3Al_9$. The interatomic distances up to 4 Å in $ErNi_3Al_9$ are given in Table 3.

Refinements

For the structures of $DyNi_3Al_9$ and YNi_3Al_9 some distances *R*(1)—Al(7), *R*(2)—Al(2), Al(2)—Al(7) and Al(7)—Al(7) are too short to allow for full occupancy of these sites and the structure were thus assumed to be partly disordered. From crystal-chemical considerations (see *Description and related structures*) the population parameters of the *R*(1), *R*(2), Al(2) and Al(7) sites were constrained to make the occupancy sums of *R*(1) with Al(7) and *R*(2) with Al(2) each equal to unity, as indicated in the footnote to Table 2. Further, as the results from microprobe analysis indicated no deviation from the composition RNi_3Al_9, the sum of all site occupancies was constrained to this composition. The *R*(1), *R*(2), Al(2) and Al(7) sites were assigned isotropic displacement parameters, all the other sites being set anisotropic. The values of the resulting displacement parameters are entirely satisfactory, confirming the validity of the model. For $ErNi_3Al_9$ and $GdNi_3Al_9$ preliminary tests showed that the occupancies of the *R*(2) and Al(7) sites refined to values insignificantly different from zero. These sites were not included in the final refinement and anisotropic displacement parameters were refined for the *R*(1) and Al(2) sites.

Owing to the relationship of these structures to a hypothetical structure in space group $P\bar{6}m2$ described below, many of the refinable atomic coordinates have numerical values very close to simple rational fractions. Furthermore, the z parameters of the Al(4), Al(5) and Al(6) sites, which are symmetry-independent in space group $R32$, have related values: z, $\sim(\frac{1}{3} - z)$, $\sim(\frac{1}{3} + z)$. Least-squares refinements on $ErNi_3Al_9$, constraining one site or one set of sites at a time to the positions implied by the rational relations (with appropriately constrained anisotropic displacement parameters), all resulted in R factors and goodness-of-fit values higher than those obtained in a conventional refinement with isotropic displacement parameters and symmetry constraints corresponding only to the point symmetry of the special positions in space group $R32$. Thus it appears that in this case there is no advantage in including additional constraints.

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55872 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0339]

Table 2. *Atomic positional, displacement and population parameters for* $ErNi_3Al_9$, $GdNi_3Al_9$, YNi_3Al_9 *and* $DyNi_3Al_9$ *with space group* $R32$

The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$ ($Å^2 \times 10^2$). E.s.d.'s are given in parentheses.

Site			$ErNi_3Al_9$	$GdNi_3Al_9$	YNi_3Al_9	$DyNi_3Al_9$
Ni	18(*f*)	*x*	0.3331 (2)	0.3333 (2)	0.3332 (2)	0.3348 (4)
		y	0.0061 (2)	0.0060 (2)	0.0060 (2)	0.0027 (5)
		z	0.08522 (3)	0.08472 (2)	0.08486 (3)	0.08519 (4)
		U_{eq}	0.55 (3)	0.64 (3)	0.75 (4)	0.84 (7)
Al(1)	18(*f*)	*x*	0.3338 (6)	0.3335 (5)	0.3333 (6)	0.329 (1)
		y	0.3356 (6)	0.3370 (5)	0.3369 (5)	0.332 (1)
		z	0.09967 (8)	0.09845 (6)	0.09868 (9)	0.0996 (1)
		U_{eq}	0.86 (9)	0.88 (7)	0.9 (1)	1.0 (2)
Al(2)	9(*e*)	*x*	0.2097 (3)	0.2088 (3)	0.2087 (5)	0.210 (1)
		y	0	0	0	0
		z	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
		U_{eq}	0.65 (8)	0.76 (7)	0.64 (7)†	0.8 (1)†
		PP	1	1	0.937 (4)†	0.598 (2)†
Al(3)	9(*d*)	*x*	0.3333 (4)	0.3338 (3)	0.3341 (5)	0.3331 (9)
		y	0	0	0	0
		z	0	0	0	0
		U_{eq}	0.92 (8)	1.10 (7)	1.1 (1)	1.2 (2)
Al(4)	6(*c*)	*x*	0	0	0	0
		y	0	0	0	0
		z	0.0521 (1)	0.05164 (7)	0.0516 (1)	0.0518 (2)
		U_{eq}	0.63 (7)	0.80 (5)	0.90 (9)	1.0 (1)
R(1)	6(*c*)	*x*	0	0	0	0
		y	0	0	0	0
		z	0.16687 (1)	0.16685 (1)	0.16677 (5)	0.16670 (4)
		U_{eq}	0.51 (1)	0.54 (1)	0.70 (3)†	0.46 (2)†
		PP	1	1	0.969 (2)†	0.799 (1)†
Al(5)	6(*c*)	*x*	0	0	0	0
		y	0	0	0	0
		z	0.2818 (1)	0.28213 (7)	0.2821 (1)	0.2812 (2)
		U_{eq}	0.64 (6)	0.78 (5)	0.97 (9)	1.0 (1)
Al(6)	6(*c*)	*x*	0	0	0	0
		y	0	0	0	0
		z	0.3871 (1)	0.38648 (8)	0.3867 (1)	0.3863 (2)
		U_{eq}	0.79 (6)	0.91 (5)	0.98 (9)	0.8 (1)
R(2)	3(*b*)	*x*			0	0
		y			0	0
		z			$\frac{1}{2}$	$\frac{1}{2}$
		U			0.70 (3)†	0.46 (2)†
		PP	0	0	0.063 (4)†	0.402 (2)†
Al(7)	18(*f*)	*x*			0.202 (11)	0.213 (3)
		y			0.012 (12)	0.002 (3)
		z			0.159 (2)	0.1681 (7)
		U			0.64 (7)†	0.8 (1)†
		PP	0	0	0.031 (2)†	0.201 (1)†

† Isotropic displacement parameters with the following constraints: $U[R(2)] = U[R(1)]$, $U[Al(7)] = U[Al(2)]$, $PP[R(1)] + PP[Al(7)] = 1$, $PP[R(2)] + PP[Al(2)] = 1$, $PP[R(1)] + PP[R(2)]/2 = 1$.

Description and related structures

In order to understand the construction of the structure of $ErNi_3Al_9$ we will decompose it into monoatomic layers perpendicular to the threefold axes. Of the three different kinds of layer stacked along [001] of the triple-hexagonal cell, two have triangular meshes, but cannot be considered as close-packed since the interatomic distances are greater than 4 Å. One of these layers, shown in Fig. 1, is formed exclusively of Al atoms and the other exclusively of Ni (*T*) atoms. The third kind of layer contains rare-earth-metal and Al atoms in the ratio 2:3. The

Table 3. *Interatomic distances up to* 4 Å *in* $ErNi_3Al_9$, *with e.s.d.'s in parentheses*

Er(1)—3	Al(2)	2.977 (2)
3	Al(1)	3.039 (4)
3	Al(1)	3.050 (3)
	Al(4)	3.139 (3)
	Al(5)	3.142 (3)
3	Ni	3.273 (1)
3	Ni	3.278 (2)
Ni—	Al(3)	2.331 (1)
	Al(2)	2.419 (1)
	Al(1)	2.426 (5)
	Al(1)	2.470 (4)
	Al(1)	2.473 (5)
	Al(4)	2.566 (2)
	Al(5)	2.573 (2)
	Al(6)	2.615 (2)
	Er(1)	3.273 (1)
	Er(1)	3.278 (2)
Al(1)—	Ni	2.426 (5)
	Ni	2.470 (4)
	Ni	2.473 (5)
	Al(6)	2.717 (5)
	Al(4)	2.760 (3)
	Al(5)	2.762 (5)
	Al(2)	2.794 (3)
	Al(2)	2.796 (2)
	Er(1)	3.039 (4)
	Er(1)	3.050 (3)
	Al(3)	3.641 (3)
	Al(3)	3.644 (4)
	Al(3)	3.657 (4)
	Al(1)	3.664 (3)
	Al(2)	3.807 (5)
Al(2)—2	Ni	2.419 (1)
2	Al(2)	2.642 (3)
2	Al(1)	2.794 (3)
2	Al(1)	2.796 (5)
2	Er(1)	2.977 (2)
2	Al(6)	3.444 (3)
2	Al(1)	3.807 (5)
Al(3)—2	Ni	2.331 (1)
2	Al(5)	2.804 (2)
2	Al(4)	2.811 (3)
2	Al(6)	2.835 (2)
2	Al(1)	3.641 (3)
2	Al(1)	3.644 (4)
2	Al(1)	3.657 (4)
Al(4)—3	Ni	2.566 (2)
3	Al(1)	2.760 (3)
3	Al(3)	2.811 (3)
	Al(4)	2.848 (4)
	Er(1)	3.139 (3)
Al(5)—3	Ni	2.573 (2)
3	Al(1)	2.762 (5)
3	Al(3)	2.804 (2)
	Al(6)	2.880 (4)
	Er(1)	3.142 (3)
Al(6)—3	Ni	2.615 (2)
3	Al(1)	2.717 (5)
3	Al(3)	2.835 (2)
	Al(5)	2.880 (4)
3	Al(2)	3.444 (3)

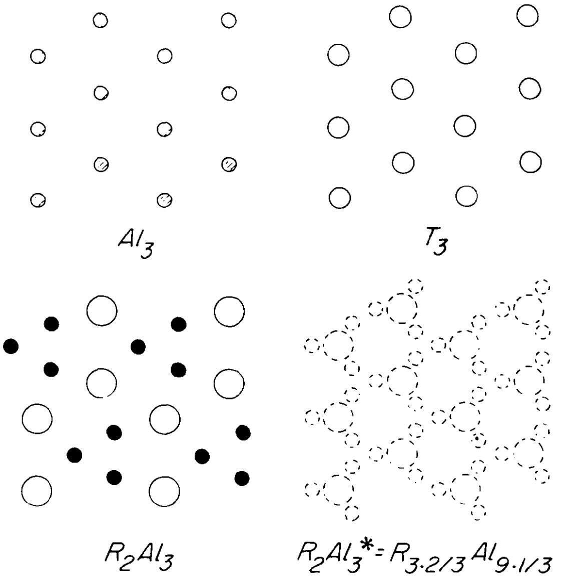
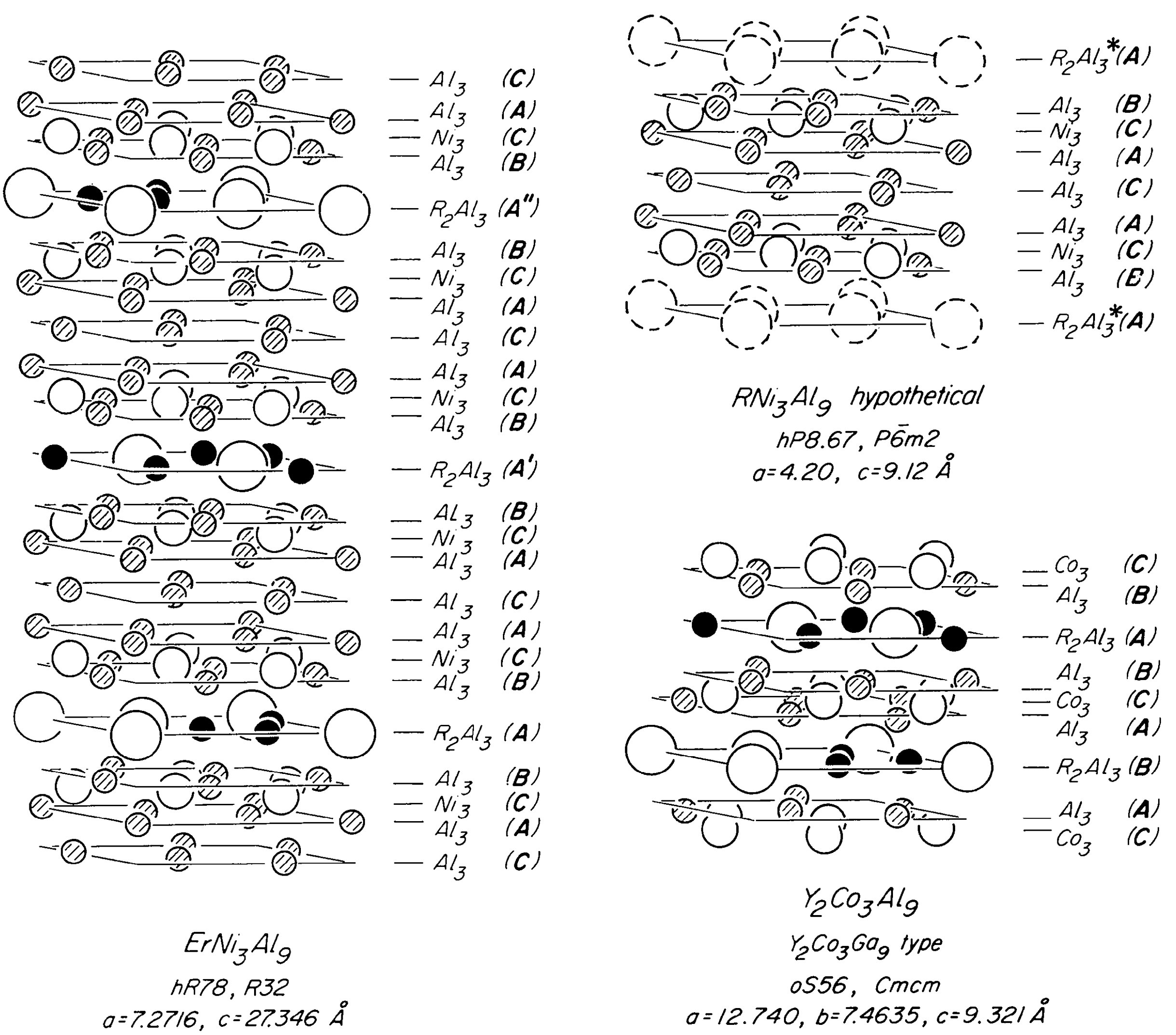


Fig. 1. Monoatomic layers observed in $ErNi_3Al_9$, hypothetical RNi_3Al_9 and $Y_2Co_3Al_9$: Al-atom layer with triangular mesh, *T*-atom layer with triangular mesh, R_2Al_3 layer with ordered arrangement of *R* atoms (large circles) and Al-atom (small black circles) triangles, and $R_2Al_3^*$ layer with disordered arrangement of single *R* atoms (PP = $\frac{2}{3}$) and Al-atom triangles (PP = $\frac{1}{3}$). Subscripts in the notation of the layers refer to the multiplicity in the translation unit perpendicular to the *c* axis in $ErNi_3Al_9$.

Al atoms of these layers, Al(2) in Wyckoff site 9(*e*), form equilateral triangles with edge length of 2.64 Å, *i.e.* the shortest Al—Al distance observed in the structure. The centres of the triangles, together with the rare-earth-metal atoms, form a triangular mesh similar to those of the other two kinds of layer. It is thus possible to use the notation introduced for the stacking of close-packed layers to denote the stacking sequence of the triangular networks along **c**. In the $ErNi_3Al_9$ structure five Al-atom layers are stacked in the sequence *BACAB*, with an inter-layer distance of ~1.3–1.45 Å. The Ni layers, with the atoms at the relative position *C*, are inserted between the Al *A*- and *B*-layers. Such ~5.5 Å-thick packets of seven monoatomic layers are separated by one mixed Er–Al layer. The triangular mesh formed by the rare-earth-metal atoms and the centres of the Al(2) triangles corresponds to the relative position *A*. The content of one triple-hexagonal unit cell is shown on the left-hand side of Fig. 2. It can be seen that the stacking sequence $Al_3(B)$–$Ni_3(C)$–$Al_3(A)$–$Al_3(C)$–$Al_3(A)$–$Ni_3(C)$–$Al_3(B)$–$Er_2Al_3(A)$ is repeated three times in the translation unit *c*. The rhombohedral lattice arises as a result of the relative shift of the Al-atom triangles in consecutive Er_2Al_3 layers (*A*, *A'*, *A''*).

The coordinates of the atoms in the monoatomic layers between $z = 0$ and $z \simeq \frac{1}{6}$ in $ErNi_3Al_9$ are listed



$ErNi_3Al_9$
hR78, R32
a=7.2716, c=27.346 Å

RNi_3Al_9 hypothetical
hP8.67, $P\bar{6}m2$
a=4.20, c=9.12 Å

$Y_2Co_3Al_9$
$Y_2Co_3Ga_9$ type
oS56, Cmcm
a=12.740, b=7.4635, c=9.321 Å

Fig. 2. Stacking of monoatomic layers along [001] in $ErNi_3Al_9$, hypothetical RNi_3Al_9 and $Y_2Co_3Al_9$. Small circles correspond to Al, medium circles to Ni(Co) and large circles to Er(Y) atoms (for RNi_3Al_9 dashed large circles to $\frac{2}{3}$ *R* atoms and $\frac{1}{3}$ Al-atom triangles). Black circles in the drawings of $ErNi_3Al_9$ and $Y_2Co_3Al_9$ represent the Al atoms which form isolated triangles in the R_2Al_3 layers. Solid lines delimit sections corresponding to the translation unit of the $ErNi_3Al_9$ structure.

Table 4. *Positional coordinates of the atoms in the monoatomic layers between* $z = 0$ *and* $z \simeq \frac{1}{6}$ *in* $\mathrm{ErNi_3Al_9}$ *and* $\mathrm{DyNi_3Al_9}$

		$\mathrm{ErNi_3Al_9}$				$\mathrm{DyNi_3Al_9}$		
		x	y	z		x	y	z
$R_2\mathrm{Al_3}(A)$	2Er(1)	0	0	0.1669	1.6Dy(1)	0	0	0.1667
		$\frac{2}{3}$	$\frac{1}{3}$	0.1665		$\frac{2}{3}$	$\frac{1}{3}$	0.1666
					0.4Dy(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$
					1.2Al(7)	0.213	0.002	0.1681
						0.998	0.211	0.1681
						0.789	0.787	0.1681
						0.878	0.331	0.1652
						0.669	0.546	0.1652
						0.454	0.122	0.1652
	3Al(2)	0.5430	$\frac{2}{3}$	$\frac{1}{6}$	1.8Al(2)	0.543	$\frac{2}{3}$	$\frac{1}{6}$
		$\frac{1}{3}$	0.8764	$\frac{1}{6}$		$\frac{1}{3}$	0.877	$\frac{1}{6}$
		0.1236	0.4570	$\frac{1}{6}$		0.123	0.457	$\frac{1}{6}$
$\mathrm{Al_3}(B)$	3Al(1)	0.0018	0.6662	0.0997	3Al(1)	0.003	0.671	0.0996
		0.6644	0.9982	0.0997		0.668	0.997	0.0996
		0.3338	0.3356	0.0997		0.329	0.332	0.0996
$\mathrm{Ni_3}(C)$	3Ni	0.9939	0.3270	0.0852	3Ni	0.9973	0.3321	0.0852
		0.6730	0.6669	0.0852		0.6679	0.6652	0.0852
		0.3331	0.0061	0.0852		0.3348	0.0027	0.0852
$\mathrm{Al_3}(A)$	1Al(4)	0	0	0.0521	1Al(4)	0	0	0.0518
	1Al(5)	$\frac{2}{3}$	$\frac{1}{3}$	0.0515	1Al(5)	$\frac{2}{3}$	$\frac{1}{3}$	0.0521
	1Al(6)	$\frac{1}{3}$	$\frac{2}{3}$	0.0538	1Al(6)	$\frac{1}{3}$	$\frac{2}{3}$	0.0530
$\mathrm{Al_3}(C)$	3Al(3)	0	0.3333	0	3Al(3)	0	0.3331	0
		0.6667	0.6667	0		0.6669	0.6669	0
		0.3333	0	0		0.3331	0	0

in Table 4. The values of the x and y coordinates of the atoms forming layers with a triangular mesh are equal or close to the values 0, $\frac{1}{3}$ or $\frac{2}{3}$, with deviations which can be analysed in relation to the arrangement of the Al-atom triangles. Thus, the Ni atom near $\frac{1}{3}$ 0 0.0852 is displaced mainly in the direction of the y axis ($y = 0.0061$), away from a nearly superposed Al(2) atom ($\frac{1}{3}$ 0.8764 $\frac{1}{6}$) of the nearest $R_2\mathrm{Al_3}$ layer. The Al(1) atom near $\frac{1}{3}$ $\frac{1}{3}$ 0.0997 is displaced in the same direction ($y = 0.3356$) from two rare-earth-metal atoms towards one of the sides of the nearest Al-atom triangle. The slightly higher value of the z coordinate of the Al(6) site in the layer at $z \simeq 0.052$ corresponds to a displacement towards the closest, directly superposed Al-atom triangle.

The $\mathrm{ErNi_3Al_9}$ type corresponds to a homogeneous distribution of Al-atom triangles throughout the structure. The structure of $\mathrm{GdNi_3Al_9}$ is isotypic to that of $\mathrm{ErNi_3Al_9}$. However for the Y, and in particular for the Dy compound, a partly disordered arrangement of rare-earth-metal atoms and Al-atom triangles was observed. Each point of the triangular mesh of the $R_2\mathrm{Al_3}$ layers is either occupied by a rare-earth-metal atom or is the centre of an Al-atom triangle (see Fig. 1). For the Dy compound the sites $R(1)$ and $R(2)$ were found to have an occupation of 80 and 40%, respectively; for the Y compound corresponding values were 97 and 6%. It would seem reasonable that no disorder occurs inside the $R_2\mathrm{Al_3}$ layers, but that the overall disorder reflects a non-homogeneous stacking of these layers. It can be seen from Table 4, where the coordinates of the atoms in the five consecutive monoatomic layers are listed, that a slight deviation from coplanarity is observed for the atoms of the Al(7) site.

The stoichiometry 1:3:9 corresponds to the highest possible content of Al-atom triangles in the R–Al layers, since for a content above this limit unacceptably short distances between atoms from neighbouring triangles would appear (~1.5 Å), as can be seen from Fig. 1. For a structure with maximum disorder of R atoms and Al-atom triangles, both R sites would have a 67% occupation and sites Al(2) and Al(7) a 33% occupation. The resulting structure has space group $P\bar{6}m2$ with a smaller unit cell ($\frac{1}{9}$ of the volume of the triple-hexagonal cell). On the structure drawing on the right-hand side of Fig. 2 only R atoms have been drawn in the $R_2\mathrm{Al_3}$ layers in order not to overload the drawing. The unit-cell vectors can be derived from those of the $\mathrm{ErNi_3Al_9}$ type by the following transformation:

$$\mathbf{a}_{1(\mathrm{hyp})} = 2\mathbf{a}_1/3 + \mathbf{a}_2/3 \qquad a_{(\mathrm{hyp})} = a/3^{1/2}$$
$$\mathbf{a}_{2(\mathrm{hyp})} = -\mathbf{a}_1/3 + \mathbf{a}_2/3 \qquad c_{(\mathrm{hyp})} = c/3$$
$$\mathbf{c}_{(\mathrm{hyp})} = \mathbf{c}/3 \qquad V_{(\mathrm{hyp})} = V/9.$$

The atomic coordinates in space group $P\bar{6}m2$ are listed in Table 5 (the standardization has applied an origin shift of 00$\frac{1}{2}$ after the cell transformation). An ordered structure with the Al-atom triangles in all layers directly superposed would have space group $P\bar{6}2m$, and a cell volume corresponding to $\frac{1}{3}$ of the volume of the triple-hexagonal cell of $\mathrm{ErNi_3Al_9}$ ($c/3$).

It can be noted from Table 1 that the nominal composition of the Dy-based sample had a lower concentration of Al and a higher concentration of rare-earth metal ($\mathrm{Dy_{15}Ni_{25}Al_{60}}$) than the samples pre-

Table 5. *Positional coordinates in space group* $P\bar{6}m2$ *for a hypothetical* RNi$_3$Al$_9$ *structure with maximum disorder of R atoms and* Al-*atom triangles, calculated from the parameters of* DyNi$_3$Al$_9$

Corresponding sites in DyNi$_3$Al$_9$ are indicated in the last column.

Site		x	y	z	PP	Site in DyNi$_3$Al$_9$
Al(1)	3(*j*)	0.211	$\bar{x}$	0	$\frac{1}{3}$	Al(2,7)
Al(2)	2(*i*)	$\frac{2}{3}$	$\frac{1}{3}$	0.201		Al(1)
Ni	2(*h*)	$\frac{1}{3}$	$\frac{2}{3}$	0.244		Ni
Al(3)	2(*g*)	0	0	0.343		Al(4,5,6)
Al(4)	1(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$		Al(3)
R	1(*a*)	0	0	0	$\frac{2}{3}$	*R*(1,2)

pared for the Er, Gd and Y compounds. It is perhaps for this reason that a strongly disordered structure was observed in this system. Also the composition of the Y-based ingot was probably further from the stoichiometry 1:3:9 than the Er- and Gd-based ones, since the weight loss was larger in this case.

A related structure was recently observed in the Y–Co–Al system, *i.e.* Y$_2$Co$_3$Al$_9$ (Gladyshevskii, Cenzual & Parthé, 1992) which crystallizes in the Y$_2$Co$_3$Ga$_9$ structure type (Grin' *et al.*, 1984). It can be seen from the drawing on the right-hand side of Fig. 2 that this structure is built up of Al, Co(T) and mixed R_2Al$_3$ layers, similar to those observed in ErNi$_3$Al$_9$, but stacked in different proportions. In this case consecutive R_2Al$_3$ layers are separated by packets of only two Al and one Co atom layer. The stacking sequence in Y$_2$Co$_3$Al$_9$, written in a similar way to ErNi$_3$Al$_9$, is: Al$_3$(B)–Co$_3$(C)–Al$_3$(A)–R_2Al$_3$(B)–Al$_3$(A)–Co$_3$(C)–Al$_3$(B)–R_2Al$_3$(A). The Al-atom triangles in consecutive R_2Al$_3$ layers are rotated by 60° and shifted (B, A) so that the overall symmetry is lowered to orthorhombic (space group *Cmcm*). The stacking sequence of the seven layers between two consecutive R_2Al$_3$(B) layers is exactly the same as the one observed between two consecutive Al$_3$(C) layers in ErNi$_3$Al$_9$, *i.e. ACBABCA*. Thus, it is possible to convert the Y$_2$Co$_3$Al$_9$ structure into the ErNi$_3$Al$_9$ structure (ignoring the relative shift of the Al-atom triangles) by replacing the R_2Al$_3$(B) layers by Al$_3$(C) layers. The compositions of the two structures reflect this substitution: $6RT_3\text{Al}_9 = 6R_2T_3\text{Al}_9 - 3R_2\text{Al}_3 + 3\text{Al}_3$. Furthermore, ErNi$_3Al_9$ can be considered as a vacancy derivative of the Y$_2$Co$_3$Al$_9$ structure where the rare-earth-metal atoms of every second mixed layer have been removed. The Al-atom triangles of these layers expand to form a regular triangular mesh in stacking position C.

The Y$_2$Co$_3$Al$_9$ structure can be considered as an intergrowth of Th$_3$Pd$_5$-type slabs of composition Al$_3$Y$_2$Al$_3$ and CsCl-type slabs of composition CoAl (see Gladyshevskii, Cenzual & Parthé, 1992). Th$_3$Pd$_5$-type slabs, formed by a R_2Al$_3$ layer surrounded by two Al-atom layers, are also found in the ErNi$_3$Al$_9$ type; however, the atoms of the Ni-atom layer inside the CsCl-type slabs are displaced towards one of the surrounding Al-atom layers, in the direction of the nearest layer containing the rare-earth-metal atoms.

The coordination polyhedra observed in the structure of ErNi$_3$Al$_9$ are relatively irregular. The Ni atoms centre distorted Al$_8$ cubes and the Er atoms mixed 17-vertex polyhedra built up of five overlaying triangles and two capping atoms. The coordination number of the Al sites ranges from 8 to 11, the atoms in site Al(3) centring regular Al$_6$ trigonal prisms with Ni atoms capping the two triangular faces. The coordinations of sites R(2) and Al(7) in the partly disordered structures can be assumed to be similar to those of sites R(1) and Al(2), respectively.

Enantiomorph polarity

The values obtained for the enantiomorph-polarity parameter x (Bernardinelli & Flack, 1985), see Table 1, show that for each of the four crystals, it was clearly possible to distinguish between the coordinate set of Table 2 and the corresponding inverted set. The crystals of GdNi$_3$Al$_9$ and YNi$_3$Al$_9$ have the same arrangement as ($x = 0$), and the crystals of ErNi$_3$Al$_9$ and DyNi$_3$Al$_9$ have the inverted arrangement to ($x = 1$), the coordinates of Table 2. In order to facilitate comparison, non-inverted coordinates have been presented here for the Er and Dy compounds.

As the space group of all of these structures is $R32$, it would be tempting to say that the enantiomorphism or handedness of the crystals has been determined by the use of x. However, the high degree of pseudo-symmetry mentioned above puts this interpretation in doubt. Indeed, starting with all the atomic sites that can be present in the RNi$_3$Al$_9$ compounds, and reflecting them in a mirror plane perpendicular to [001] (present in the hypothetical structure in space group $P\bar{6}m2$), one finds that the atomic coordinate sets of the initial and mirror-image sites superimpose very closely, and with atoms of the same species, for all sites. The magnitude of the contribution of each site to the enantiomorphism will depend both on the deviation of the real from the idealized coordinates derived from the hypothetical $P\bar{6}m2$ structure and on the occupation of the sites. Thus Al(3) contributes next to nothing being very close to the site $\frac{1}{3}$ 0 0, and Ni, Al(1), Al(4), Al(5) and Al(6) slightly more. However, the contribution to the enantiomorphism of the pairs R(1)–R(2) and Al(2)–Al(7) depends principally on the difference in the occupation of these sites and will diminish as the occupations tend to equality. In this way the enantiomorphism in the Dy compound is much less marked than in the other three. One sees then that the enantiomorphism is a minor component in the non-centrosymmetric properties of these compounds. Alone it cannot account for the e.s.d.'s obtained for x. Clearly the polarity, or more precisely the non-enantiomorphic component of the non-centrosymmetric part of the electron density, is the predominant component which has been determined by x.

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Structure of $Gd_3Ru_4Al_{12}$, a New Member of the $EuMg_{5.2}$ Structure Family with Minority-Atom Clusters

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Abstract

$Gd_3Ru_{4+x}Al_{12-x}$ [$x = 0.13$ (2)], $M_r = 1209.44$, hexagonal, $hP38$, $P6_3/mmc$ – kh^2gfba (No. 194), $a = 8.8142$ (6), $c = 9.5692$ (9) Å, $V = 643.8$ (1) Å^3, $Z = 2$, $D_x = 6.239$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 20.330$ mm^{-1}, $F(000) = 1056$ (1), $T = 293$ K, $wR = 0.023$ for 338 contributing unique reflections. $Gd_3Ru_4Al_{12}$ is a substitution variant of the $Sc_3Ni_{11}Ge_4$ structure which is a partly disordered variant of the $Sc_3Ni_{11}Si_4$ type, all three structures being ternary substitution derivatives of the $EuMg_{5.2}$ or $ErZn_5$ types. Contrary to the related structure types, in $Gd_3Ru_4Al_{12}$ both Wyckoff sites 2(a) and 2(b) have full occupation, *i.e.* an ordered arrangement of alternate Ru and Al atoms is observed along the c axis. The structure of $Gd_3Ru_4Al_{12}$ is built up of two kinds of layers perpendicular to [001]: planar layers of composition Gd_3Al_4 and puckered layers of composition Ru_4Al_8. Similar layers are found in cubic $Hf_6Ni_7Al_{16}$, a ternary substitution variant of Th_6Mn_{23}, as well as in hexagonal Sr_9Mg_{38} and $BaLi_4$.

Introduction

The Gd–Ru–Al system has not been studied and no ternary compounds have been reported so far. Of the related systems with different transition metals from the Fe, Co or Ni groups, the largest number of phases have been identified in the Gd–Ni–Al system (Rykhal', Zarechnyuk & Marych, 1978; Gladyshevskii & Parthé, 1992; Gladyshevskii, Cenzual, Flack & Parthé, 1993). Of the eleven reported compounds, five form in the narrow concentration region from 7.7 to 16.7 at.% Gd and from 58.3 to 70.4 at.% Al. We identified a phase in the corresponding region of the Gd–Ru–Al system and determined its crystal structure.

Experimental

Crystals were found in a sample of nominal composition $GdRu_2Al_3$, prepared from high-purity elements

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