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## Structure of $RNi_3Al_9$ ( $R = Y, Gd, Dy, Er$ ) with Either Ordered or Partly Disordered Arrangement of Al-Atom Triangles and Rare-Earth-Metal Atoms

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### Abstract

$ErNi_3Al_9$ ,  $M_r = 586.22$ , trigonal, new type,  $hR78$ ,  $R32 - f^2edc^4$  (No. 155),  $a = 7.2716$  (5),  $c = 27.346$  (3) Å,  $V = 1252.2$  (2) Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 4.664$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 17.654$  mm<sup>-1</sup>,  $F(000) = 1614$ ,  $T = 293$  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.  $GdNi_3Al_9$  [ $a = 7.3006$  (9),  $c = 27.478$  (5) Å,  $wR = 0.020$  for 791 reflections] is isotypic.  $YNi_3Al_9$  [ $a = 7.2894$  (7),  $c = 27.430$  (5) Å,  $wR = 0.035$  for 635 reflections] and  $DyNi_3Al_9$  [ $a = 7.2723$  (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  $ErNi_3Al_9$  build up the orthorhombic structure of  $Y_2Co_3Al_9$  ( $Y_2Co_3Ga_9$  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 ( $Al_3$ ):  $6RT_3Al_9 = 6R_2T_3Al_9 - 3R_2Al_3 + 3Al_3$ .

### 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 (Rykhali' & 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  $\geq 99.9\%$ , Ni and Al  $\geq 99.999\%$ ) 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,  $\omega$ - $2\theta$  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:  $R3$ ,  $R\bar{3}$ ,  $R32$ ,  $R3m$  and  $R\bar{3}m$  (*International Tables for Crystallography*, 1983, Vol. A). The structure of  $ErNi_3Al_9$  was solved in space group  $R32$  by MULTAN87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987); one rare-earth-metal,

Table 1. Details of data collection and refinement for  $\text{ErNi}_3\text{Al}_9$ ,  $\text{GdNi}_3\text{Al}_9$ ,  $\text{YNi}_3\text{Al}_9$  and  $\text{DyNi}_3\text{Al}_9$ 

Nominal composition	$\text{Er}_3\text{Ni}_{15}\text{Al}_{80}$	$\text{Gd}_3\text{Ni}_{15}\text{Al}_{80}$	$\text{Y}_3\text{Ni}_{15}\text{Al}_{80}$	$\text{Dy}_{15}\text{Ni}_{25}\text{Al}_{60}$
Weight loss (%)	0.1	0.1	0.6	0.1
Size of crystal* (mm)	$0.066 \times 0.066 \times 0.038$	0.056	$0.040 \times 0.048 \times 0.064$	$0.096 \times 0.056 \times 0.040$
Reflections for unit cell [ $2\theta$ range ( $^\circ$ )]	23 [20–39]	26 [16–37]	28 [16–37]	19 [20–37]
$\text{Sin}\theta/\lambda$ ( $\text{\AA}^{-1}$ )	0.08–0.70	0.08–0.70	0.08–0.70	0.08–0.70
$hkl$ with antireflections	$-10 \leq h \leq 10$ $0 \leq k \leq 9$ $0 \leq l \leq 38$	$-10 \leq h \leq 10$ $0 \leq k \leq 9$ $0 \leq l \leq 38$	$-10 \leq h \leq 10$ $0 \leq k \leq 9$ $0 \leq l \leq 38$	$0 \leq h \leq 8$ $0 \leq k \leq 8$ $0 \leq l \leq 38$
Standard reflections	$\bar{1}\bar{1}6$ (0.8)	$300$ (0.6)	$300$ (0.9)	$300$ (0.6)
(max. % $l$ variation)	$\bar{1}\bar{1}0$ (0.9)	$00\bar{1}\bar{2}$ (1.3)	$00\bar{1}\bar{2}$ (0.6)	$\bar{1}\bar{1}6$ (0.7)
Collected reflections	2212	2268	2260	972
Unique reflections ( $R_{\text{int}}$ )	785 (0.017)	803 (0.030)	797 (0.071)	795 (0.038)
$\mu$ ( $\text{mm}^{-1}$ )	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 $ F_{\text{rel}}  > 3\sigma( F_{\text{rel}} )$	785	791	635	682
Refined parameters	43	43	43	43
Extinction $G \times 10^3$	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. $\times 10^3$	0.3	0.3	0.2	0.2
Residual electron density ( $e \text{\AA}^{-3}$ )	+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
$wR$ , $w = 1/\sigma^2( F_{\text{rel}} )$	0.021	0.020	0.035	0.027

\* Fragments cut from hexagonal plates: dimensions  $\pm(100)$ ,  $\pm(010)$ ,  $\pm(001)$  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 *XTAL3.0* 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  $\text{ErNi}_3\text{Al}_9$  and  $\text{GdNi}_3\text{Al}_9$  were standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987), with directly comparable data sets being presented for  $\text{YNi}_3\text{Al}_9$  and  $\text{DyNi}_3\text{Al}_9$ . The interatomic distances up to 4 Å in  $\text{ErNi}_3\text{Al}_9$  are given in Table 3.

### Refinements

For the structures of  $\text{DyNi}_3\text{Al}_9$  and  $\text{YNi}_3\text{Al}_9$  some distances  $R(1)$ – $\text{Al}(7)$ ,  $R(2)$ – $\text{Al}(2)$ ,  $\text{Al}(2)$ – $\text{Al}(7)$  and  $\text{Al}(7)$ – $\text{Al}(7)$  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  $R(1)$ ,

$R(2)$ ,  $\text{Al}(2)$  and  $\text{Al}(7)$  sites were constrained to make the occupancy sums of  $R(1)$  with  $\text{Al}(7)$  and  $R(2)$  with  $\text{Al}(2)$  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  $R\text{Ni}_3\text{Al}_9$ , the sum of all site occupancies was constrained to this composition. The  $R(1)$ ,  $R(2)$ ,  $\text{Al}(2)$  and  $\text{Al}(7)$  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  $\text{ErNi}_3\text{Al}_9$  and  $\text{GdNi}_3\text{Al}_9$  preliminary tests showed that the occupancies of the  $R(2)$  and  $\text{Al}(7)$  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  $\text{Al}(2)$  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  $\text{Al}(4)$ ,  $\text{Al}(5)$  and  $\text{Al}(6)$  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  $\text{ErNi}_3\text{Al}_9$ , 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.

\* 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<sub>3</sub>Al<sub>9</sub>, GdNi<sub>3</sub>Al<sub>9</sub>, YNi<sub>3</sub>Al<sub>9</sub> and DyNi<sub>3</sub>Al<sub>9</sub> with space group R32

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

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

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

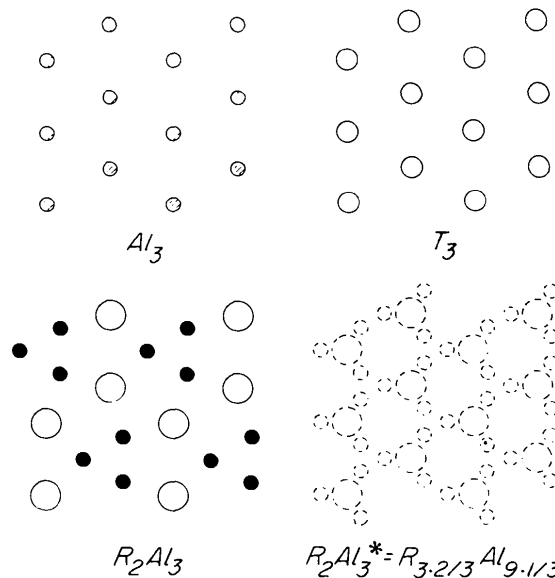


Fig. 1. Monoatomic layers observed in ErNi<sub>3</sub>Al<sub>9</sub>, hypothetical RNi<sub>3</sub>Al<sub>9</sub> and Y<sub>2</sub>Co<sub>3</sub>Al<sub>9</sub>: Al-atom layer with triangular mesh, *T*-atom layer with triangular mesh, *R*<sub>2</sub>Al<sub>3</sub> layer with ordered arrangement of *R* atoms (large circles) and Al-atom (small black circles) triangles, and *R*<sub>2</sub>Al<sub>3</sub>\* 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<sub>3</sub>Al<sub>9</sub>.

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  $\text{ErNi}_3\text{Al}_9$  structure five Al-atom layers are stacked in the sequence *BACAB*, with an inter-layer distance of  $\sim 1.3\text{--}1.45$  Å. The Ni layers, with the atoms at the relative position *C*, are inserted between the Al *A*- and *B*-layers. Such  $\sim 5.5$  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  $\text{Al}_3(\text{B})\text{--Ni}_3(\text{C})\text{--Al}_3(\text{A})\text{--Al}_3(\text{C})\text{--Al}_3(\text{A})\text{--Ni}_3(\text{C})\text{--Al}_3(\text{B})\text{--Er}_2\text{Al}_3(\text{A})$  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  $\text{Er}_2\text{Al}_3$  layers (*A*, *A'*, *A''*).

The coordinates of the atoms in the monoatomic layers between  $z = 0$  and  $z = \frac{1}{6}$  in  $\text{ErNi}_3\text{Al}_9$  are listed

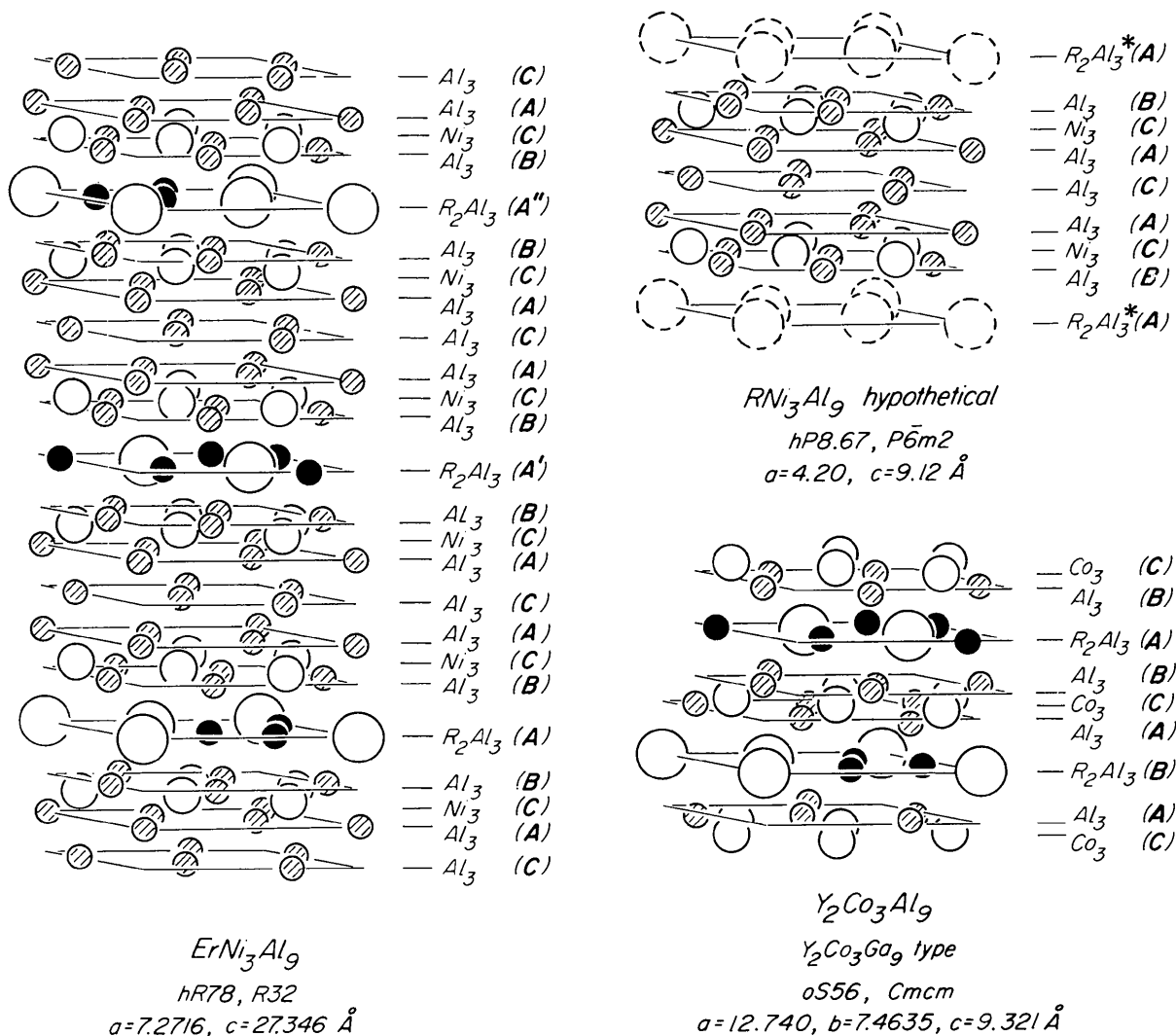


Fig. 2. Stacking of monoatomic layers along [001] in  $\text{ErNi}_3\text{Al}_9$ , hypothetical  $\text{RNi}_3\text{Al}_9$  and  $\text{Y}_2\text{Co}_3\text{Al}_9$ . Small circles correspond to Al, medium circles to Ni(Co) and large circles to Er(Y) atoms (for  $\text{RNi}_3\text{Al}_9$  dashed large circles to  $\frac{2}{3}$  R atoms and  $\frac{1}{3}$  Al-atom triangles). Black circles in the drawings of  $\text{ErNi}_3\text{Al}_9$  and  $\text{Y}_2\text{Co}_3\text{Al}_9$  represent the Al atoms which form isolated triangles in the  $\text{R}_2\text{Al}_3$  layers. Solid lines delimit sections corresponding to the translation unit of the  $\text{ErNi}_3\text{Al}_9$  structure.

Table 4. Positional coordinates of the atoms in the monoatomic layers between  $z = 0$  and  $z \approx \frac{1}{6}$  in ErNi<sub>3</sub>Al<sub>9</sub> and DyNi<sub>3</sub>Al<sub>9</sub>

		ErNi <sub>3</sub> Al <sub>9</sub>			DyNi <sub>3</sub> Al <sub>9</sub>			
		$x$	$y$	$z$		$x$	$y$	$z$
$R_2Al_3(A)$	2Er(1)	0	0	0.1669	1.6Dy(1)	0	0	0.1667
		$\frac{1}{3}$	$\frac{1}{3}$	0.1665	0.4Dy(2)	$\frac{1}{3}$	$\frac{1}{3}$	0.1666
					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	$\frac{1}{6}$
$Al_3(B)$	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
$Ni_3(C)$	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
$Al_3(A)$	1Al(4)	0	0	0.0521	1Al(4)	0	0	0.0518
	1Al(5)	$\frac{1}{3}$	$\frac{1}{3}$	0.0515	1Al(5)	$\frac{1}{3}$	$\frac{1}{3}$	0.0521
	1Al(6)	$\frac{1}{3}$	$\frac{1}{3}$	0.0538	1Al(6)	$\frac{1}{3}$	$\frac{1}{3}$	0.0530
$Al_3(C)$	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  $R_2Al_3$  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  $z \approx 0.052$  corresponds to a displacement towards the closest, directly superposed Al-atom triangle.

The ErNi<sub>3</sub>Al<sub>9</sub> type corresponds to a homogeneous distribution of Al-atom triangles throughout the structure. The structure of GdNi<sub>3</sub>Al<sub>9</sub> is isotypic to that of ErNi<sub>3</sub>Al<sub>9</sub>. 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  $R_2Al_3$  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  $R_2Al_3$  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 ( $\sim 1.5$  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 ( $\frac{1}{3}$  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  $R_2Al_3$  layers in order not to overload the drawing. The unit-cell vectors can be derived from those of the ErNi<sub>3</sub>Al<sub>9</sub> type by the following transformation:

$$\begin{aligned} \mathbf{a}_{1(\text{hyp})} &= 2\mathbf{a}_1/3 + \mathbf{a}_2/3 & a_{(\text{hyp})} &= a/3^{1/2} \\ \mathbf{a}_{2(\text{hyp})} &= -\mathbf{a}_1/3 + \mathbf{a}_2/3 & c_{(\text{hyp})} &= c/3 \\ \mathbf{c}_{(\text{hyp})} &= \mathbf{c}/3 & V_{(\text{hyp})} &= V/9. \end{aligned}$$

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 ErNi<sub>3</sub>Al<sub>9</sub> ( $c/3$ ).

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 (Dy<sub>15</sub>Ni<sub>25</sub>Al<sub>60</sub>) than the samples pre-

Table 5. Positional coordinates in space group  $P\bar{6}m2$  for a hypothetical  $RNi_3Al_9$  structure with maximum disorder of  $R$  atoms and Al-atom triangles, calculated from the parameters of  $DyNi_3Al_9$

Corresponding sites in  $DyNi_3Al_9$  are indicated in the last column.

Site	$x$	$y$	$z$	PP	Site in $DyNi_3Al_9$
Al(1)	$3(j)$	$0.211$	$\bar{x}$	0	Al(2,7)
Al(2)	$2(i)$	$\frac{1}{2}$	$\frac{1}{2}$	0.201	Al(1)
Ni	$2(h)$	$\frac{1}{2}$	$\frac{1}{2}$	0.244	Ni
Al(3)	$2(g)$	0	0	0.343	Al(4,5,6)
Al(4)	$1(d)$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	Al(3)
$R$	$1(a)$	0	0	0	$R(1,2)$

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.*  $Y_2Co_3Al_9$  (Gladyshevskii, Cenzual & Parthé, 1992) which crystallizes in the  $Y_2Co_3Ga_9$  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  $ErNi_3Al_9$ , 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  $Y_2Co_3Al_9$ , written in a similar way to  $ErNi_3Al_9$ , 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  $60^\circ$  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  $ErNi_3Al_9$ , *i.e.*  $ACBABCA$ . Thus, it is possible to convert the  $Y_2Co_3Al_9$  structure into the  $ErNi_3Al_9$  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:  $6RT_3Al_9 = 6R_2T_3Al_9 - 3R_2Al_3 + 3Al_3$ . Furthermore,  $ErNi_3Al_9$  can be considered as a vacancy derivative of the  $Y_2Co_3Al_9$  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  $Y_2Co_3Al_9$  structure can be considered as an intergrowth of  $Th_3Pd_5$ -type slabs of composition  $Al_3Y_2Al_3$  and CsCl-type slabs of composition CoAl (see Gladyshevskii, Cenzual & Parthé, 1992).  $Th_3Pd_5$ -type slabs, formed by a  $R_2Al_3$  layer surrounded by two Al-atom layers, are also found in the

$ErNi_3Al_9$  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  $ErNi_3Al_9$  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  $GdNi_3Al_9$  and  $YNi_3Al_9$  have the same arrangement as ( $x = 0$ ), and the crystals of  $ErNi_3Al_9$  and  $DyNi_3Al_9$  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  $RNi_3Al_9$  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  $\frac{1}{2} 0 0$ , 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<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub>, a New Member of the EuMg<sub>5.2</sub> Structure Family with Minority-Atom Clusters

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#### Abstract

Gd<sub>3</sub>Ru<sub>4+x</sub>Al<sub>12-x</sub> [ $x = 0.13$  (2)],  $M_r = 1209.44$ , hexagonal,  $hP38$ ,  $P6_3/mmc - kh^2g fba$  (No. 194),  $a = 8.8142$  (6),  $c = 9.5692$  (9) Å,  $V = 643.8$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 6.239$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 20.330$  mm<sup>-1</sup>,  $F(000) = 1056$  (1),  $T = 293$  K,  $wR = 0.023$  for 338 contributing unique reflections. Gd<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub> is a substitution variant of the Sc<sub>3</sub>Ni<sub>11</sub>Ge<sub>4</sub> structure which is a partly disordered variant of the Sc<sub>3</sub>Ni<sub>11</sub>Si<sub>4</sub> type, all three structures being ternary substitution derivatives of the EuMg<sub>5.2</sub> or ErZn<sub>5</sub> types. Contrary to the related structure types, in Gd<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub> 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<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub> is built up of two kinds of layers perpendicular to [001]: planar layers of composition Gd<sub>3</sub>Al<sub>4</sub> and puckered layers of composition Ru<sub>4</sub>Al<sub>8</sub>. Similar layers are found in

cubic Hf<sub>6</sub>Ni<sub>7</sub>Al<sub>16</sub>, a ternary substitution variant of Th<sub>6</sub>Mn<sub>23</sub>, as well as in hexagonal Sr<sub>9</sub>Mg<sub>38</sub> and BaLi<sub>4</sub>.

#### 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 (Rykhali', 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<sub>2</sub>Al<sub>3</sub>, prepared from high-purity elements

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