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Structure of Orthorhombic $YNiAl_3$

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Abstract. Nickel yttrium trialuminide, $M_r = 228.56$, orthorhombic, new type, $oP20$, $Pnma - c^5$ (No. 62), $a = 8.156$ (1), $b = 4.0462$ (4), $c = 10.638$ (2) Å, $V = 351.06$ (6) Å^3, $Z = 4$, $D_x = 4.324$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 22.826$ mm^{-1}, $F(000) = 424$, $T = 293$ K, $wR = 0.057$ for 362 contributing unique reflections. The coordination numbers are Y 19, Ni 9 and Al 12. The $YNiAl_3$ structure is related to $YNiAl_2$ with an $MgCuAl_2$-type structure and $YNiAl_4$ with its own type. In all three structures the Y atoms are at the centres of pentacapped pentagonal prisms, the Ni atoms are at the centres of tricapped trigonal prisms of composition Y_2Al_4 and the Al atoms are at the centres of deformed cubes with four additional neighbours.

Introduction. The phase equilibria in the Y-poor part (< 34at.% Y) of the Y–Ni–Al system were investigated at 873, 1073 (Rykhal' & Zarechnyuk, 1977) and 1273 K (Rosen & Goebel, 1968). Based on crystal structure determinations, the compositions of the following phases are now known with certainty: YNi_2Al_3 (ordered $HoNi_{2.6}Ga_{2.4}$ type), $YNiAl_4$ ($YNiAl_4$ type), Y_3Ni_8Al (Ce_3Co_8Si type), $YNiAl_2$ ($MgCuAl_2$ type), $Y_3Ni_6Al_2$ ($Ce_3Ni_6Si_2$ type) and YNiAl (ZrNiAl type). The crystal structures of three other compounds have not yet been determined and their proposed stoichiometries remain to be verified: YNi_3Al_{16}, $Y_2Ni_3Al_7$ and YNi_3Al. It has been observed that the annealing temperature has a great influence on the number of compounds formed in the Al-rich part of the phase diagram. We annealed some Al-rich alloys at 773 K and found two new phases $YNiAl_3$ and $Y_4Ni_6Al_{23}$. We report here on the structure determination of the former; the latter structure being the subject of a separate publication (Gladyshevskii & Parthé, 1992).

Experimental. Single crystals were found in a sample of nominal composition $Y_{17}Ni_{25}Al_{58}$, prepared from Y (99.9%), Ni (99.99%) and Al (99.99%) by arc melting under an Ar atmosphere (weight loss 0.4%) and annealed at 773 K for two weeks in a silica tube under an Ar atmosphere (400 mm Hg). A single crystal of irregular shape (mean radius 0.022 mm) was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 20 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $16 < 2\theta < 34°$) using the

Table 1. *Atomic positional and displacement parameters for* $YNiAl_3$ *with space group Pnma*

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

	Wyckoff position	x	y	z	U_{eq} (Å^2 × 100)
Al(1)	4(*c*)	0.0540 (7)	¼	0.5835 (4)	0.6 (2)
Ni	4(*c*)	0.1070 (3)	¼	0.3569 (2)	0.71 (6)
Y	4(*c*)	0.1860 (2)	¼	0.0088 (2)	0.67 (4)
Al(2)	4(*c*)	0.3565 (7)	¼	0.7215 (5)	0.7 (2)
Al(3)	4(*c*)	0.3853 (8)	¼	0.2860 (5)	1.0 (2)

Table 2. *Interatomic distances in* $YNiAl_3$ (*up to* 4.0 Å *for* Y *atoms and* 3.7 Å *for* Ni, Al *atoms*)

E.s.d.'s are given in parentheses.

Y—2Al(1)	3.036 (4)	Al(1)— Ni	2.449 (5)
2Al(2)	3.055 (4)	2Ni	2.494 (3)
2Ni	3.091 (2)	Al(2)	2.627 (7)
Al(1)	3.158 (6)	2Al(1)	2.833 (5)
2Al(3)	3.170 (4)	Al(2)	2.871 (8)
Al(3)	3.284 (6)	2Al(3)	2.996 (5)
Al(2)	3.358 (5)	2Y	3.036 (4)
Al(3)	3.367 (5)	Y	3.158 (6)
Al(2)	3.637 (6)		
2Y	3.652 (2)	Al(2)—2Ni	2.501 (3)
Ni	3.719 (3)	Al(1)	2.627 (7)
Ni	3.759 (3)	Al(1)	2.871 (8)
		2Al(3)	2.907 (6)
Ni— Al(3)	2.362 (6)	2Al(3)	2.922 (6)
Al(3)	2.392 (7)	2Y	3.055 (4)
Al(1)	2.449 (5)	Y	3.358 (5)
2Al(1)	2.494 (3)	Y	3.637 (6)
2Al(2)	2.501 (3)		
2Y	3.091 (2)	Al(3)— Ni	2.362 (6)
		Ni	2.392 (7)
		2Al(2)	2.907 (6)
		2Al(2)	2.922 (6)
		2Al(1)	2.996 (5)
		2Y	3.170 (4)
		Y	3.284 (6)
		Y	3.367 (5)

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program *LATCON* (Schwarzenbach, 1966). 1288 reflections were collected out to $(\sin\theta/\lambda) = 0.703$ Å^{-1} ($0 \le h \le 11$, $0 \le k \le 5$, $0 \le l \le 14$ and the anti-reflections) in the ω–2θ-scan mode, yielding 579 unique reflections ($R_{int} = 0.12$). Two standard reflections, 020 and 113, were measured with maximum intensity variations of 0.9 and 1.3%, respectively. Absorption correction was made using the program *LSABS* (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.4901 and 0.4804. 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: $Pn2_1a$ ($= Pna2_1$) and *Pnma* (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group *Pnma* by the program *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by the structure refinement, based on $|F|$ values, using the program *CRYLSQ* (Olthof-Hazekamp, 1990). 31 variables including anisotropic atomic displacement parameters refined to $R = 0.068$ and $wR = 0.057$ [$w = 1/\sigma^2(|F_{rel}|)$, $S = 1.382$] considering 362 contributing unique reflections with $|F_{rel}| > 4\sigma(|F_{rel}|)$. The maximum shift/e.s.d. in the last cycle was 0.00004. Final residual electron density +5.1 (−4.0) e Å^{-3}. The programs used to refine the structure are all from the *XTAL*3.0 system (Hall & Stewart, 1990). The atomic positional parameters were standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The atomic positional and displacement parameters are given in Table 1* and the interatomic distances in Table 2.

Discussion. A projection of the $YNiAl_3$ structure along [010] and the coordination polyhedra of the atoms are presented in Fig. 1. The structure is characterized by infinite isolated columns of base-sharing trigonal Y_2Al_4 prisms, each prism being centred by an Ni atom. Between these columns Al(3) atoms are found inside deformed cubic coordination polyhedra consisting of two Y and six Al atoms. The other Al atoms [Al(1) and Al(2)] are also at the centres of deformed cubes built up in this case of two Y, two Ni and four Al atoms. The Y atoms are at the centres of pentagonal prisms consisting of two Y, two Ni and six Al atoms. The three rectangular faces of the trigonal prism, four only of the cubes and the five of the pentagonal prism are capped. The Y atom has four more neighbours, two capping the pentagonal base planes and two located in the central plane. That means that Ni actually has coordination number 9 (6 + 3), Al has 12 (8 + 4) and Y has 19 (10 + 5 + 2 + 2).

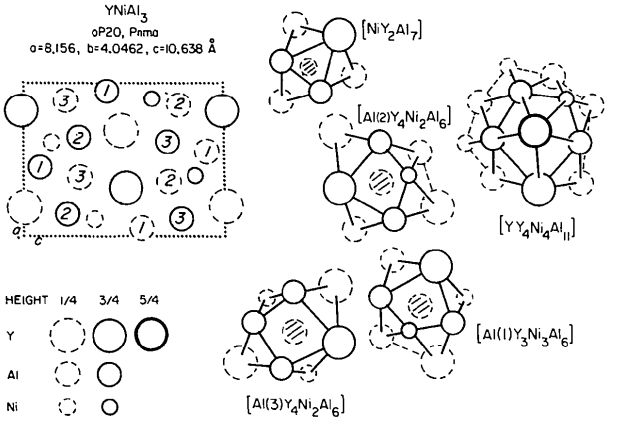

Fig. 1. Projection of the $YNiAl_3$ structure along [010] and the coordination polyhedra of the atoms. The numbers inside the circles corresponding to the Al atoms are the label numbers used in Table 1.

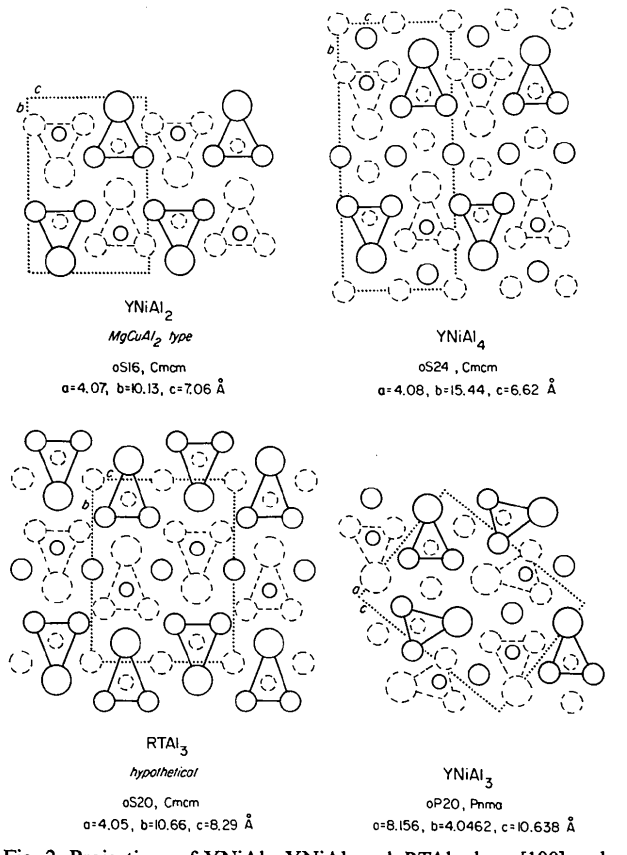

Fig. 2. Projections of $YNiAl_2$, $YNiAl_4$ and $RTAl_3$ along [100] and $YNiAl_3$ along [010]. Only the outlines of the trigonal prisms are indicated. Large circles Y or *R*, medium circles Al, and small circles Ni or *T*. The atoms drawn with full lines differ from those drawn with dashed lines by a shift of $\frac{1}{2}$ in height.

* Lists of structure factors and anisotropic displacement parameters has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54565 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *The occupation of the vertices in the pentagonal* (10*p*), *trigonal* (6*p*) *prisms and cubes* (8*cb*) *around the* Y, Ni *and* Al *atoms respectively, in the structures of* $YNiAl_2$, $YNiAl_3$, *hypothetical* $RTAl_3$ *and* $YNiAl_4$

The rectangular faces are centred by additional atoms (5*c*, 3*c*, 4*c*).

	Y coordination	Ni coordination	Al coordination
$YNiAl_2$	$\underbrace{2Ni+8Al}_{10p}+\underbrace{2Y+1Ni+2Al}_{5c}+2Y+2Ni$	$\underbrace{2Y+4Al}_{6p}+\underbrace{1Y+2Al}_{3c}$	$\underbrace{4Y+2Ni+2Al}_{8cb}+\underbrace{1Y+1Ni+2Al}_{4c}$
$YNiAl_3$	$\underbrace{2Y+2Ni+6Al}_{10p}+\underbrace{5Al}_{5c}+2Y+2Ni$	$\underbrace{2Y+4Al}_{6p}+\underbrace{3Al}_{3c}$	$\underbrace{2Y+2Ni+4Al}_{8cb}+\underbrace{1Y+1Ni+2Al}_{4c}$
			$\underbrace{2Y+2Ni+4Al}_{8cb}+\underbrace{2Y+2Al}_{4c}$
			$\underbrace{2Y+6Al}_{8cb}+\underbrace{2Y+2Ni}_{4c}$
$RTAl_3$	$\underbrace{2T+8Al}_{10p}+\underbrace{1T+4Al}_{5c}+2R$	$\underbrace{2R+4Al}_{6p}+\underbrace{1R+2Al}_{3c}$	$\underbrace{2R+2T+4Al}_{8cb}+\underbrace{2R+2Al}_{4c}$
			$\underbrace{4R+4Al}_{8cb}+\underbrace{2T+2Al}_{4c}$
$YNiAl_4$	$\underbrace{2Ni+8Al}_{10p}+\underbrace{5Al}_{5c}+2Y+2Ni$	$\underbrace{2Y+4Al}_{6p}+\underbrace{3Al}_{3c}$	$\underbrace{2Y+2Ni+4Al}_{8cb}+\underbrace{1Y+1Ni+2Al}_{4c}$
			$\underbrace{8Al}_{8cb}+\underbrace{3Y+1Ni}_{4c}$
			$\underbrace{4Y+4Al}_{8cb}+\underbrace{4Al}_{4c}$

The structural features of $YNiAl_3$ can be compared with those of $YNiAl_2$ (Rykhal', Zarechnyuk & Yarmolyuk, 1972) which has an $MgCuAl_2$-type structure (Perlitz & Westgren, 1943), $YNiAl_4$ with its own type (Rykhal' *et al.*, 1972) and a hypothetical $RTAl_3$ type; all of the structures are shown in a projection along the shortest axis in Fig. 2. Common to these structures is not only the formation of the infinite columns of Ni-centred trigonal Y_2Al_4 prisms, but also the pentagonal-prismatic coordination of the Y atoms and the deformed cubes around the Al atoms, as can be seen from Table 3.

Comparing the structures $YNiAl_2$ and $YNiAl_4$ one notes the same arrangement of sheets of infinite trigonal-prism columns perpendicular to the [010] direction which are, in the case of $YNiAl_4$, separated by an extra layer of Al atoms. To construct a hypothetical model of an $RTAl_3$ structure we retained the sheet of infinite trigonal-prism columns perpendicular to [001] of $YNiAl_2$ and added Al sites in the cubic interstices. This led to a *C*-centred orthorhombic structure model with unit-cell values as given in Fig. 2; *R* atoms are at the centres of pentagonal prisms of composition T_2Al_8 and *T* atoms are at the centres of trigonal R_2Al_4 prisms as in $YNiAl_2$ and $YNiAl_4$. The reason why this hypothetical structure is not formed might be related to the waist contact which exists between *T* and *R* atoms (Parthé & Hovestreydt, 1985), the three rectangular faces of the trigonal prisms being capped by two Al and one *R* atom. Waist contacts between Ni and Y atoms do not exist in the primitive orthorhombic $YNiAl_3$ structure. Waist contacts exist in the $YNiAl_2$ structure; however, with this low Al content it does not appear to be possible to find an arrangement without such *T*—*R* bonds.

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Structure of Monoclinic $Y_4Ni_6Al_{23}$

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Abstract. Hexanickel tetrayttrium tricosaaluminide, $M_r = 1328.45$, monoclinic, new type *mS*66, *C*2/*m* – $i^{16}c$, $a = 15.836$ (2), $b = 4.0681$ (7), $c = 18.311$ (2) Å, $\beta = 112.97$ (1)°, $V = 1086.1$ (2) Å^3, $Z = 2$, $D_x = 4.062$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 16.896$ mm^{-1}, $F(000) = 1246$, $T = 293$ K, $wR = 0.058$ for 648 contributing unique reflections. The structure of $Y_4Ni_6Al_{23}$ is closely related to $YNiAl_4$ and $U_4Ni_5Al_{18}$, all having similar coordination polyhedra around Y (U) and Ni atoms. $YNiAl_4$-type slabs can be intergrown with another kind of slab to form the $U_4Ni_5Al_{18}$ structure. In $Y_4Ni_6Al_{23}$ the same slabs but in a different proportion are intergrown to form packets which are stacked without common atoms.

Introduction. In the Y–Ni–Al system eight compounds are known with less than 34 at.% Y (Rykhal' & Zarechnyuk, 1977). For six of them the crystal structures have been determined previously (for details see Bodak & Gladyshevskii, 1985). We report here the determination of the crystal structure of a new Al-rich compound with a composition not mentioned in the phase-diagram paper.

Experimental. Single crystals were found in a sample of nominal composition $Y_5Ni_{15}Al_{80}$. It was prepared from Y (99.9%), Ni (99.99%) and Al (99.99%) by arc melting under an argon atmosphere (weight loss 0.4%) and annealed at 773 K for two weeks in a silica tube under a 400 mm Hg argon atmosphere. A needle-shaped single crystal [± (100) 0.032, ± (010) 0.128, ± (001) 0.016 mm] was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 26 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $16 < 2\theta < 30°$) using the program *LATCON* (Schwarzenbach, 1966). 2330 reflections were collected out to $(\sin\theta/\lambda) = 0.603$ Å^{-1} ($-18 \le h \le 18$, $0 \le k \le 4$, $0 \le l \le 22$ and the anti-reflections) in the ω–2θ-scan mode, yielding 1130 unique reflections ($R_{int} = 0.12$). Two standard reflections, 020 and 0$\bar{2}$0, were measured with maximum intensity variations 0.9 and 1.3% respectively. Absorption correction was made using the program *LSABS* (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.7616 and 0.5521. 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: *C*2, *Cm* and *C*2/*m* (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group *C*2/*m* by the *MULTAN*87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by a structure refinement, based on $|F|$ values using the program *CRYLSQ* (Olthof-Hazekamp, 1990). 101 variables including anisotropic atomic displacement parameters refined to $R = 0.073$ and $wR = 0.058$ [$w = 1/\sigma^2(|F_{rel}|)$, $S = 1.537$] considering 648 contributing unique reflections with $|F_{rel}| > 4\sigma(|F_{rel}|)$. The maximum shift/e.s.d. in the last cycle was 0.0001. Final residual electron density +5.7 (−4.5) e Å^{-3}. The programs used to refine the structure are all from the *XTAL*3.0 system (Hall & Stewart, 1990). The atomic positional parameters were standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The atomic posi-

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