

## Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>, a Quaternary Substitution Variant of the Hexagonal Fe<sub>2</sub>P type

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(Received 25 January 1990; accepted 24 April 1990)

**Abstract.** Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>,  $M_r = 551.55$ , hexagonal, *hP9*, (189) *P6̄2m* – *gfd*,  $a = 6.9481$  (6),  $c = 4.1565$  (5) Å,  $V = 173.78$  (3) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 5.270$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 37.55$  mm<sup>-1</sup>,  $F(000) = 248$ ,  $T = 300$  K,  $wR = 0.048$  for 474 contributing reflections. Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> is a new, quaternary substitution variant of the Fe<sub>2</sub>P or the ZrNiAl type.

**Introduction.** A comparison of the crystal structures of the ternary rare-earth–transition-element silicides or germanides with the corresponding isotypic aluminides shows that in certain cases the Al atoms do not simply substitute for the Si or Ge atoms, but occupy transition-element sites. The transition elements are then found on the former Si or Ge sites. Examples of such pairs of formulae of isotypic silicides or germanides and aluminides (see Parthé & Chabot, 1984) are: Sc<sub>2</sub>Co<sub>3</sub>Si – Sc<sub>2</sub>RuAl<sub>3</sub> (*hP12*, *P6̄3/mmc*); Sc<sub>6</sub>Ni<sub>16</sub>Si<sub>7</sub> – Sc<sub>6</sub>Ni<sub>7</sub>Al<sub>16</sub> (*cF116*, *Fm3̄m*); ScRu<sup>[4*t*]</sup>Ge – ZrNiAl<sup>[4*t*]</sup> (*hP9*, *P6̄2m*). In the case of ScRuGe and ZrNiAl the site occupation interchange is not evident from the chemical formula. Therefore one of the sites has been identified by a superscripted symbol which indicates the atom coordination (Lima-de-Faria, Hellner, Liebau, Makovicky & Parthé, 1990).

In order to find out more about this site-occupation interchange we decided to study the structures of the rare-earth–transition-element–aluminium germanides.

**Experimental.** The sample of nominal composition Y<sub>2</sub>NiAl<sub>2</sub>Ge<sub>2</sub> was prepared by arc melting under argon atmosphere (Y 99.9, Ni 99.99, Al 99.99 and Ge 99.99%). The weight loss was 0.04%. A needle-shaped single crystal [ $\pm(110)$ : 0.022 mm,  $\pm(1\bar{1}0)$ : 0.022 mm,  $\pm(001)$ : 0.088 mm] obtained from the as-cast sample was mounted on a Philips PW1100 automatic four-circle diffractometer, Mo *K* $\alpha$  radiation with graphite monochromator. The unit-cell parameters were refined from 2 $\theta$  values of 24 reflections (Mo *K* $\alpha$ ,  $\lambda = 0.71073$  Å,  $15 < 2\theta < 35^\circ$ ) using the program *LATCON* (Schwarzenbach, 1966). 1186 reflections were collected to  $(\sin\theta/\lambda) = 0.994$  Å<sup>-1</sup> ( $0 \leq h \leq 11$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 8$  and the anti-

reflections) in the  $\omega$ –2 $\theta$  scan mode, yielding 569 reflections ( $R_{\text{int}} = 0.053$ ). Two standard reflections,  $1\bar{2}1$  and  $20\bar{1}$ , were measured with maximum intensity variations 0.6 and 1.6% respectively. Absorption correction was made using the program *ABSORB* with max. and min. transmission factors of 0.30637 and 0.15765. The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No systematic absences; the following space groups are possible: *P6̄22*, *P6mm*, *P6̄m2*, *P6̄2m* and *P6/mmm* (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group *P6̄2m* by the *MULTAN87* program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). The refinement was based on  $|F|$  values using isotropic atomic displacement parameters and the program *CRYLSQ*. Seven variables refined to  $R = 0.062$  and  $wR = 0.048$  [ $w = 1/\sigma^2(|F_{\text{rel}}|)$ ,  $S = 1.919$ ] considering 474 contributing reflections with  $|F_{\text{rel}}| > 3\sigma(|F_{\text{rel}}|)$ . The max. shift/e.s.d. in the last cycle was 0.0002.\* Final residual electron density  $+7.2$  ( $-9.1$ ) e Å<sup>-3</sup>. The programs used to refine the structure were all from the *XTAL2.6* system (Hall & Stewart, 1989). 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 up to 3.5 Å in Table 2.

**Discussion.** The Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> structure, shown in Fig. 1, is a quaternary substitution variant of the Fe<sub>2</sub>P type (Rundqvist & Jellinek, 1959). In the same system a ternary Fe<sub>2</sub>P type substitution variant is already known with YNiAl (ZrNiAl type) which has, however, a 10% smaller *c/a* ratio (Rihali & Zarechnyuk, 1977). In the structure of Fe<sub>2</sub>P occur three different kinds of coordination polyhedra: a tetragonal pyramid (5*y*), a tetrahedron (4*t*) and a

\* Lists of structure factors and isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53218 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

trigonal prism (6p). The simplified crystal chemical formula of Fe<sub>2</sub>P considering only heteronuclear coordinations can be written as Fe<sub>3</sub><sup>[5p]</sup>-Fe<sub>3</sub><sup>[4t]</sup>P<sub>2</sub><sup>[6p]</sup>P<sup>[6p]</sup>, where the unprimed P represent the P atoms inside the edge-linked trigonal prism columns and the primed P the atoms which center the isolated trigonal prism columns. In analogy to the formula for Fe<sub>2</sub>P the simplified crystal chemical formula of the quaternary compound can be written as: Y<sub>3</sub><sup>[(1,4)py]</sup>Al<sub>3</sub><sup>[(2,2)t]</sup>Ge<sub>2</sub><sup>[6p,ni]</sup>Ni<sup>[6p,ni]</sup>. The large Y atoms occupy the pyramidal sites, Al atoms the tetrahedral sites, Ge atoms the unprimed prismatic sites and Ni, the smallest atom in the compound, the

primed prismatic site. The site occupation in Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> corresponds in essential parts to general trends which can be deduced from the following study of the nine ternary Fe<sub>2</sub>P substitution variants.

*The Fe<sub>2</sub>P type substitution variants.* At least nine different ternary derivatives of the Fe<sub>2</sub>P type with four different compositions are known: ABC, A<sub>6</sub>BC<sub>2</sub>, A<sub>3</sub>BC<sub>5</sub> and A<sub>3</sub>B<sub>4</sub>C<sub>2</sub>. Seven of the eight hexagonal structure types are shown in Fig. 1, in addition to the Fe<sub>2</sub>P and the Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> structures. In Fig. 2 is shown the only known orthorhombic Fe<sub>2</sub>P type derivative which is actually a deformation of the hexagonal equiatomic substitution variant. The site occupations of all these structure types, which are summarized in Table 3, are now described in detail below.

ZrNiAl: *hP9*, *P6̄2m* (Kripyakevich, Markiv & Melnik, 1967). This equiatomic structure type is quite common with ternary rare earth and transition-metal compounds; however, the element distribution on the tetrahedral and prismatic sites has not always been determined. It should be distinguished between two kinds of occupation variants of the ZrNiAl type.\* In the compound ZrNiAl itself the Al atoms occupy the tetrahedral sites and the Ni atoms all the prismatic sites. In the isotypic compound ScRuGe the transition element and the main group element positions are, however, interchanged (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982). These differences in the site occupation between silicides or germanides and aluminides are typical and have been

\* To compare the different occupation variants directly from the atom coordinates it is necessary to use only the standardized structure data. Note that an origin shift by 00½ leads to an interchange of the 3(f) and 3(g) Wyckoff positions.

Table 1. Atomic positional and displacement parameters for Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> with space group *P6̄2m*

The isotropic atomic displacement factors are expressed as  $T = \exp[-2\pi^2 U(\sin\theta/\lambda)^2]$ . E.s.d.'s are given in parentheses.

	Wyckoff position	x	y	z	U (Å <sup>2</sup> × 100)
Al	3(g)	0.2268 (6)	0	½	0.40 (7)
Y	3(f)	0.5963 (2)	0	0	0.62 (2)
Ge	2(d)	½	⅔	½	0.67 (3)
Ni	1(a)	0	0	0	0.99 (6)

Table 2. Interatomic distances up to 3.5 Å in Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>

Y...Ni	2.805 (2)	Al...2Ni	2.608 (3)
4Ge	2.965 (1)	2Al	2.729 (5)
4Al	3.202 (1)	2Ge	2.762 (4)
2Al	3.303 (3)	4Y	3.202 (1)
		2Y	3.303 (3)
Ni...6Al	2.608 (3)	Ge...3Al	2.762 (4)
3Y	2.805 (2)	6Y	2.965 (1)

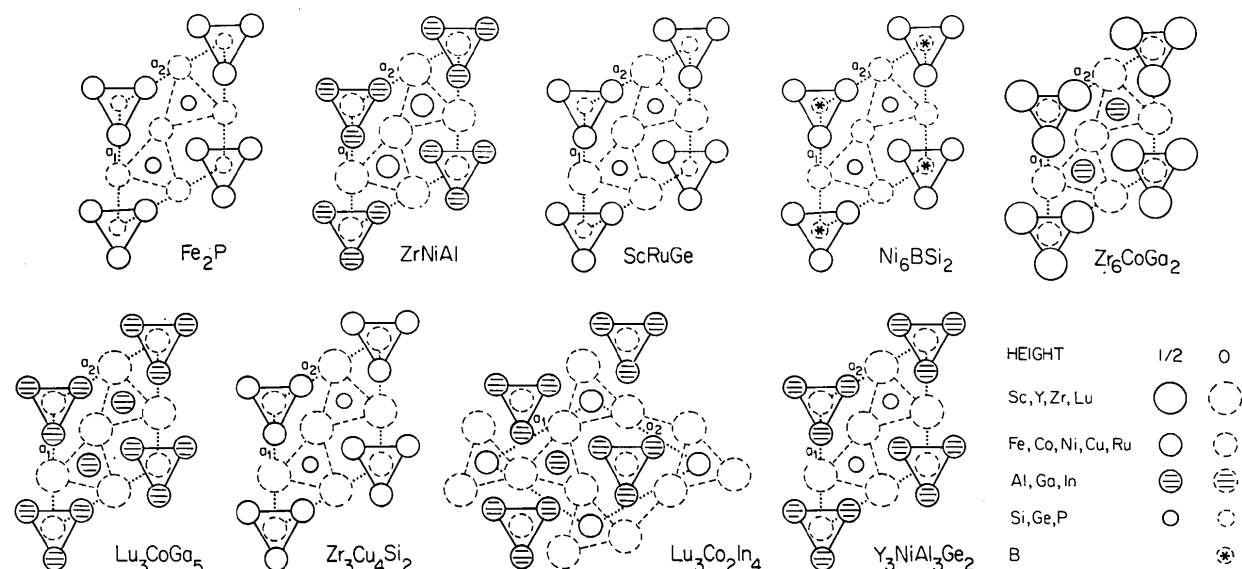


Fig. 1. The [0001] projections of Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>, Fe<sub>2</sub>P and seven of its ternary substitution variants.

verified whenever the atom distribution has really been investigated in detail (see Kripyakevich *et al.*, 1967; Hovestreydt *et al.*, 1982).

$\beta_1$ -K<sub>2</sub>UF<sub>6</sub>: *hP9*, *P6̄2m* (Zachariasen, 1948). This structure corresponds to Fe<sub>2</sub>P with the prismatic sites occupied in ordered fashion by the K and U atoms. K atoms occupy the unprimed P positions, U the primed P position and F all the Fe positions. In Fig. 1 are shown two isotypes which may be considered as crystallizing in the  $\beta_1$ -K<sub>2</sub>UF<sub>6</sub> anti-type: Ni<sub>6</sub>BSi<sub>2</sub> (Rundqvist & Jelinek, 1959) and Zr<sub>6</sub>CoCa<sub>2</sub> (Belyavina & Markiv, 1982). These two types differ in the occupation of the primed P site by a main group and transition element, respectively.

Lu<sub>3</sub>CoGa<sub>5</sub>: *hP9*, *P6̄2m* (Gladyshevskii, 1983). The Lu atoms occupy the pyramidal sites, Ga the tetrahedral sites and the unprimed P positions and Co the primed P position.

Zr<sub>3</sub>Cu<sub>4</sub>Si<sub>2</sub>: *hP9*, *P6̄2m* (Sprenger & Nickl, 1972). The Zr atoms occupy the pyramidal sites, Cu the tetrahedral sites and the primed P position and Si the unprimed P positions.

Lu<sub>3</sub>Co<sub>2</sub>In<sub>4</sub>: *hP9*, *P6̄* (Zaremba, Kalychak, Zavalii & Sobolev, 1989). This structure has a different space group. The Lu atoms are on the pyramidal sites, Co occupy the primed P position and one of the unprimed P positions and In are found on the other unprimed P positions and on the tetrahedral sites. The formula in the original paper is given as Lu<sub>3</sub>Co<sub>2-x</sub>In<sub>4</sub> with  $x = 0.13$ ; however, the defects are of no importance for our discussion.

TiFeSi: *oI36*, *Ima2* (Jeitschko, 1970) (shown in Fig. 2). This is a deformation variant of ScRuGe with Ti atoms on the pyramidal, Fe on the tetrahedral and Si on the prismatic sites. However, the Si atoms are somewhat displaced from the ideal positions leading to a superstructure with lower symmetry.

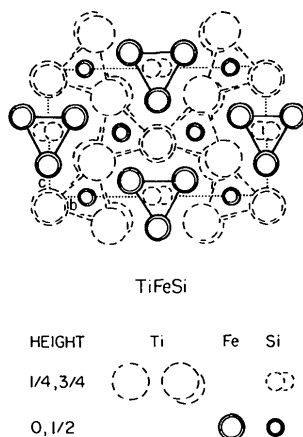


Fig. 2. The [100] projection of the orthorhombic TiFeSi structure.

Table 3. The atom distributions in the Fe<sub>2</sub>P type and its substitution variants

All structures except TiFeSi have Pearson code *hP9*. The space group is *P6̄2m* except for Lu<sub>3</sub>Co<sub>2</sub>In<sub>4</sub> (*P6̄*) and TiFeSi (*Ima2*). The Wyckoff positions of the last two compounds are not given here; however, for a comparison with the other substitution variants their atom distributions are referred here also to the Wyckoff positions in *P6̄2m*.

	Tetrahedral 3(g)	Pyramidal 3(f)	Prismatic sites 2(d) 1(a)	
Structures with space group <i>P6̄2m</i> - <i>gfda</i>				
Fe <sub>2</sub> P	Fe	Fe	P	P'
ZrNiAl	Al	Zr	Ni	Ni
ScRuGe	Ru	Sc	Ge	Ge
( $\beta_1$ -K <sub>2</sub> UF <sub>6</sub> )	(F)	(F)	(K)	(U)
Ni <sub>6</sub> BSi <sub>2</sub>	Ni	Ni	Si	B
Zr <sub>6</sub> CoGa <sub>2</sub>	Zr	Zr	Ga	Co
Lu <sub>3</sub> CoGa <sub>5</sub>	Ga	Lu	Ga	Co
Zr <sub>3</sub> Cu <sub>4</sub> Si <sub>2</sub>	Cu	Zr	Si	Cu
Y <sub>3</sub> NiAl <sub>3</sub> Ge <sub>2</sub>	Al	Y	Ge	Ni
Structures with lower symmetry				
Lu <sub>3</sub> Co <sub>2</sub> In <sub>4</sub>	In	Lu	Co + In	Co
TiFeSi	Fe	Ti	Si	Si

The following conclusions can be made in regard to general trends for the occupation of the different structure sites in the Fe<sub>2</sub>P type:

(a) The pyramidal site [3(f)] is always occupied by the largest element in the compound, such as, for example, a rare-earth element or early transition element. This is also correct for the  $\beta_1$ -K<sub>2</sub>UF<sub>6</sub>, Fe<sub>2</sub>P and Ni<sub>6</sub>BSi<sub>2</sub> structure types. This site is never occupied by Si, Ge, B, Al or Ga.

(b) The tetrahedral site [3(g)] is preferred by Al, Ga and In but never occupied by Si or Ge.

(c) The B, Si, Ge and P atoms are found only on prismatic sites. In general the smallest element in the compound occupies the primed prismatic site.

(d) The late transition elements have no particular preference and depending on their alloying partners may occupy any of the four sites.

We wish to acknowledge the help of Mrs Birgitta Künzler with the preparation of the drawings. This study was supported by the Swiss National Science Foundation under contract 20-28490.90.

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*Acta Cryst.* (1990). **C46**, 2276–2279

## Structure of YAlGe and Isotypic Rare-Earth–Aluminium Germanides

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(Received 25 January 1990; accepted 10 May 1990)

**Abstract.** YAlGe,  $M_r = 188.48$ , orthorhombic,  $oS12$ , (63)  $Cmcm - c^2a$ ,  $a = 4.0504$  (5),  $b = 10.440$  (1),  $c = 5.7646$  (9) Å,  $V = 243.77$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 5.136$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 37.481$  mm<sup>-1</sup>,  $F(000) = 336$ ,  $T = 300$  K,  $wR = 0.049$  for 153 contributing unique reflections. This new structure type, a substitution variant of the UPt<sub>2</sub> type, is characterized by sheets of Ge centred trigonal prisms formed by Y and Al atoms via common Al edges. The YAlGe type is found with RAlGe compounds when R is a small rare-earth element [ $R = \text{Gd}$  (low-temperature modification), Tb, Dy, Ho, Er, Tm, Lu and Sc]. With large rare-earth elements [ $R = \text{La}$ , Ce, Pr, Nd, Sm, Eu and Gd (high-temperature modification)] the tetragonal  $\alpha$ -ThSi<sub>2</sub> type (or an ordered variant) is observed.

**Introduction.** The equiatomic rare-earth aluminium silicides and germanides have been studied by Yanson (1975), who reported the  $\alpha$ -ThSi<sub>2</sub> type for the large rare-earth elements and a new type, the so-called DyAlGe type, for small rare-earth elements. However, the R–Al distances for compounds with the ‘DyAlGe type’ show unreasonably short values. This gave us an incentive for a reinvestigation of the structures of the RAlGe compounds.

**Experimental.** YAlGe. A sample of nominal composition YAlGe was prepared by arc melting under argon atmosphere (Y 99.9, Al 99.99 and Ge 99.99%). The weight loss was 0.2%. A needle-

shaped single crystal [ $\pm(100)$ : 0.048 mm,  $\pm(010)$ : 0.005 mm,  $\pm(001)$ : 0.005 mm], obtained from the as-cast sample, was mounted on a Philips PW1100 automatic four-circle diffractometer, Mo  $K\alpha$  radiation with graphite monochromator. The unit-cell parameters were refined from  $2\theta$  values of 23 reflections (Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $15 < 2\theta < 35^\circ$ ) using the program LATCON (Schwarzenbach, 1966). 906 reflections were collected out to  $(\sin\theta/\lambda) = 0.702$  Å<sup>-1</sup> ( $0 \leq h \leq 5$ ,  $0 \leq k \leq 14$ ,  $0 \leq l \leq 8$  and the anti-reflections) in the  $\omega$ - $2\theta$  scan mode, yielding 215 unique reflections ( $R_{\text{int}} = 0.11$ ). Two standard reflections ( $\bar{1}30$  and  $1\bar{1}\bar{2}$ ) were measured with maximum intensity variations of 1.06 and 4.4% respectively. Absorption correction was made using the program ABSORB with max. and min. transmission factors of 0.7077 and 0.5322. The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The systematic absences of the reflections led to the three possible space groups  $Cmcm$ ,  $Cmc2_1$  and  $Ama2$  (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group  $Cmcm$  using the MULTAN87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). The final refinement was based on  $|F|$  values and anisotropic atomic displacement parameters using the program CRYLSQ (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). There are 13 variables refined to  $R = 0.068$  and  $wR = 0.049$  [ $w = 1/\sigma^2(|F_{\text{ref}}|)$ ,  $S = 2.091$ ], considering 153 contributing reflections with  $|F_{\text{ref}}| > 3\sigma(|F_{\text{ref}}|)$ . The max. shift/e.s.d. in the last