Yb₇Al₅Ge₈, an Intergrowth of TiNiSi, AlB₂ and CsCl Type Columns

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Abstract. $Al_5Ge_8Yb_7$, $M_r = 1926 \cdot 907$, monoclinic, $mS40$, $C2/m - i^9da$, $a = 15 \cdot 958$ (3), $b = 4 \cdot 2871$ (6), $c = 12 \cdot 611$ (2) Å, $\beta = 95 \cdot 78$ (2)°, $V = 858 \cdot 4$ (2) Å^3, $Z = 2$, $D_x = 7 \cdot 455$ Mg m^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71073$ Å, $\mu = 51 \cdot 444$ mm^{-1}, $F(000) = 1622$, $T = 300$ K, $wR = 0 \cdot 044$ for 1002 contributing unique reflections. This new structure type can be considered as an intergrowth of TiNiSi, AlB₂ and CsCl type columns. The Ge coordination of the Al atom is mostly tetrahedral. The best chance of finding ternary rare-earth structures where Al and Ge atoms have different coordinations seems to occur with ternary compounds formed with small rare-earth elements.

Introduction. In the course of our studies of the structures of the ternary rare-earth aluminium germanides we tried to synthesize the equiatomic Yb compound. The sample gave a diffraction pattern of an unknown structure. We report here the results of our structure determination.

Experimental. The sample of nominal composition YbAlGe was prepared by reaction of the pure metals in a high-frequency furnace under argon atmosphere (Yb 99·9, Al 99·99 and Ge 99·99%). The reaction was observed at a temperature of about 773 K and the sample was left in the furnace at 1000 K for half an hour. The weight loss was less than 2%. A needle-shaped single crystal [±(100) : 0·008 mm, ±(010) : 0·088 mm, ±(001) : 0·008 mm] obtained from the as-cast sample 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 23 reflections ($20 < 2\theta < 40°$) using the program *LATCON* (Schwarzenbach, 1966). 2896 reflections were collected out to $(\sin\theta)/\lambda = 0 \cdot 703$ Å^{-1} ($-22 \le h \le 22$, $0 \le k \le 6$, $0 \le l \le 17$ and the antireflections) in the ω–2θ scan mode, yielding 1393 unique reflections ($R_{int} = 0 \cdot 047$). Two standard reflections (313 and 31$\bar{3}$) were measured with maximum intensity variations 1·5 and 0·9%, respectively. Absorption correction was made using the program *ABSORB* (Davenport, Spadaccini & Stewart, 1989) with max. and min. transmission factors of 0·4955 and 0·3737.

The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The systematic absences of the reflections led to three possible space groups: $C2$, Cm and $C2/m$ (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group $C2/m$ using the *MULTAN*87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). The final refinement was based on $|F|$ values and anisotropic atomic displacement parameters using the program *CRYLSQ* (Olthof-Hazekamp, 1989). 64 variables refined to $R = 0 \cdot 055$ and $wR = 0 \cdot 044$ [$w = 1/\sigma^2(|F_{rel}|)$], $S = 2 \cdot 141$, considering 1002 contributing unique reflections with $|F_{rel}| > 3\sigma(|F_{rel}|)$. Secondary-extinction correction parameter (Gaussian distribution of mosaic) was refined to $G = 0 \cdot 0034$ (4). The max. shift/e.s.d. in the last cycle was 0·0003, and the final residual electron density was $+8 \cdot 1$ ($-8 \cdot 9$) e Å^{-3}. The positions of the largest residual peak and hole are *ca* 1 Å apart and they are located at 0·2 Å from Yb(2) atoms. The comparatively large residual electron densities may be caused by constraints on U_{ij} of the heavy Yb atoms during the structure refinement. The programs used to refine the structure are all from the *XTAL*2.6 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 interatomic distances up to 3·9 Å in Table 2.

Discussion. A projection of the Yb₇Al₅Ge₈ structure along [010] is shown in the upper drawing of Fig. 1. The Yb₇Al₅Ge₈ type is a new structure type which can be considered as an intergrowth of TiNiSi, AlB₂ and CsCl type columns, all parallel to the [010] direction. All Yb atoms participate in the formation of one or more trigonal prisms. The columns formed

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Table 1. *Atomic positional and displacement parameters for* Yb₇Al₅Ge₈ *with space group C2/m; e.s.d.'s are given in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	$U_{eq}(\text{Å}^2 \times 100)$
Yb(1)	4(*i*)	0.01782 (8)	0	0.2983 (1)	0.87 (6)
Yb(2)	4(*i*)	0.15884 (8)	0	0.54329 (9)	0.84 (6)
Ge(1)	4(*i*)	0.1751 (2)	0	0.1050 (2)	0.9 (1)
Al(1)	4(*i*)	0.2242 (6)	0	0.3052 (7)	1.2 (4)
Ge(2)	4(*i*)	0.3484 (2)	0	0.6203 (2)	1.0 (2)
Ge(3)	4(*i*)	0.3877 (2)	0	0.3150 (2)	0.9 (1)
Ge(4)	4(*i*)	0.4468 (2)	0	0.1345 (2)	0.9 (1)
Al(2)	4(*i*)	0.6087 (6)	0	0.1671 (7)	1.1 (4)
Yb(3)	4(*i*)	0.81087 (8)	0	0.1358 (1)	0.97 (6)
Al(3)	2(*d*)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.9 (6)
Yb(4)	2(*a*)	0	0	0	0.74 (8)

Table 2. *Interatomic distances up to* 3.9 Å *in* Yb₇Al₅Ge₈

Yb(1)—2Ge(3)	3.007 (2)	Al(1)—Ge(1)	2.567 (9)
2Ge(4)	3.111 (2)	Ge(3)	2.599 (9)
2Ge(2)	3.125 (2)	2Ge(2)	2.653 (6)
2Al(2)	3.149 (7)	2Al(2)	3.222 (9)
Al(1)	3.286 (9)	Yb(3)	3.277 (9)
2Al(3)	3.361 (1)	Yb(1)	3.286 (9)
Yb(2)	3.616 (2)	2Yb(2)	3.318 (6)
Yb(2)	3.635 (2)	2Yb(3)	3.416 (7)
Ge(1)	3.671 (4)		
Yb(3)	3.707 (2)	Al(2)—2Ge(1)	2.550 (5)
Yb(4)	3.743 (1)	Ge(4)	2.575 (9)
		Ge(2)	2.70 (1)
Yb(2)—2Ge(3)	2.934 (2)	2Yb(1)	3.149 (7)
2Ge(2)	2.970 (2)	2Al(1)	3.222 (9)
Ge(2)	3.082 (3)	Yb(3)	3.291 (9)
Al(1)	3.277 (9)	2Yb(4)	3.363 (7)
2Al(1)	3.318 (6)	Ge(4)	3.82 (1)
2Al(3)	3.323 (1)		
Yb(1)	3.616 (2)	Al(3)—2Ge(3)	2.795 (3)
Yb(1)	3.635 (2)	2Ge(2)	2.983 (3)
2Yb(2)	3.859 (2)	4Yb(2)	3.323 (1)
		4Yb(1)	3.361 (1)
Yb(3)—2Ge(1)	3.045 (3)		
2Ge(4)	3.050 (2)	Ge(1)—2Al(2)	2.550 (5)
Ge(1)	3.067 (3)	Al(1)	2.567 (9)
2Ge(3)	3.263 (2)	Yb(4)	2.969 (3)
Al(2)	3.291 (9)	2Yb(3)	3.045 (3)
2Al(1)	3.416 (7)	Yb(3)	3.067 (3)
Yb(4)	3.617 (1)	Yb(1)	3.671 (4)
Yb(1)	3.707 (2)		
		Ge(2)—2Al(1)	2.653 (6)
Yb(4)—4Ge(4)	2.912 (2)	Al(2)	2.70 (1)
2Ge(1)	2.969 (3)	2Yb(2)	2.970 (2)
4Al(2)	3.363 (7)	Al(3)	2.983 (3)
2Yb(3)	3.617 (1)	Yb(2)	3.082 (3)
2Yb(1)	3.743 (1)	2Yb(1)	3.125 (2)
Ge(3)—Ge(4)	2.551 (4)	Ge(4)—Ge(3)	2.551 (4)
Al(1)	2.599 (9)	Al(2)	2.575 (9)
Al(3)	2.795 (3)	2Yb(4)	2.912 (2)
2Yb(2)	2.934 (2)	2Yb(3)	3.050 (2)
2Yb(1)	3.007 (2)	2Yb(1)	3.111 (2)
2Yb(3)	3.263 (2)	Al(2)	3.82 (1)

of Al(3)-centered Yb cubes (as in CsCl) and the columns formed of Ge(3)- and Ge(4)- centered Yb prisms (as in AlB₂) can be recognized easily. The TiNiSi type columns in Yb₇Al₅Ge₈ have been shaded and can be compared with the shaded part of the lower drawing which represents two unit cells of TiNiSi itself (Shoemaker & Shoemaker, 1965).

The peculiarities of the new structure can be explained by the fact that Ge and Al atoms prefer different coordination polyhedra, *i.e.* a trigonal rare-earth or rare-earth–aluminium prism for the Ge atom, but a different polyhedron, often a rare-earth cube for the Al atom. This difference is already evident with the structures of the equiatomic *R*Ge and *R*Al compounds. The first have the CrB or FeB type where all the small Ge atoms are at the centers of trigonal prisms formed by the large rare-earth atoms, while the latter crystallize with the DyAl or CeAl type (Bècle & Lemaire, 1967) in which the Al atom is far removed from the center of the trigonal prism. This tendency allows the understanding of the atom ordering in the TiNiSi type column of Yb₇Al₅-Ge₈. We note a Ge(2)-centered rather regular Yb₄Al₂ prism, the Al(1) atoms thus participating in the formation of the trigonal prisms. This prism corresponds to the Si-centered Ti₄Ni₂ prism in TiNiSi. The Ge(1) atom is at the centre of a deformed Yb₄Al₂ prism. The coordination of the Al atoms is best described by considering the geometrical arrangement of the Ge neighbors. The Al(1) and the Al(2) atoms in the TiNiSi type column are both at
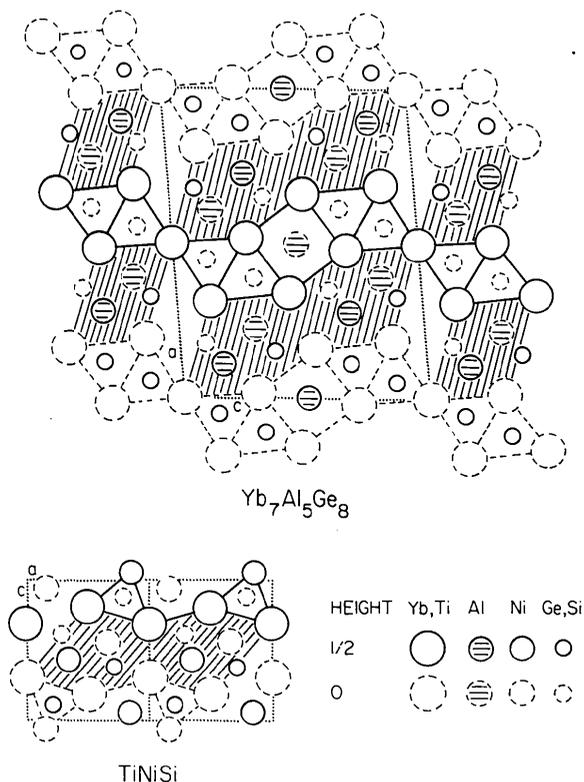
Fig. 1. Projection of the Yb₇Al₅Ge₈ structure along [010] (upper drawing) and of two unit cells of TiNiSi along [010] (lower drawing). The TiNiSi type columns in Yb₇Al₅Ge₈ and the corresponding part in the TiNiSi structure are shaded.

the centers of Ge tetrahedra, while the Al(3) atom at the center of the rare-earth cube is also at the center of a square of Ge atoms.

The structural features of $Yb_7Al_5Ge_8$ will be compared with those of related ternary compounds. A number of ternary rare-earth aluminium silicides are known. However, owing to the similarity of the scattering factors of Al and Si the distinction between Al and Si sites is not without problems. We, therefore, restrict our comparison to ternary compounds containing only Al and Ge. In addition to $Yb_7Al_5Ge_8$ the following rare-earth aluminium germanides are known:

RAlGe compounds with large rare-earth elements have the tetragonal α-ThSi$_2$ type of an ordered variant ($tI12$, $I4_1/amd$ or $I4_1md$). This structure is characterized by Al-centered and Ge-centered rare-earth prisms. With smaller rare-earth elements, the orthorhombic YAlGe type ($oS12$, $Cmcm$), a UPt$_2$ substitution variant, is formed (Zhao & Parthé, 1990). One finds here Ge-centered Y_2Al_4 trigonal prisms and Al-centered Ge squares like the Al(3)-centered Ge squares in $Yb_7Al_5Ge_8$.

RAl$_2$Ge$_2$ compounds (Zarechnyuk, Muravyeva & Gladyshevskii, 1970) with CaAl$_2$Si$_2$ type ($hP5$, $P\bar{3}m1$) (Gladyshevskii, Kripyakevich & Bodak, 1967; see also Klüfers, Mewis & Schuster, 1979), an antitype of Ce$_2$O$_2$S (Zachariasen, 1948). The latter type is a substitution variant of the A form of La$_2$O$_3$ with its unusual seven coordination of the La atoms. In the RAl$_2$Ge$_2$ compounds the original La (or Ce) site is occupied by the Ge atoms which have three rare-earth and four Al neighbors. Al atoms are at the centers of Ge tetrahedra like Al(1) and Al(2) in $Yb_7Al_5Ge_8$. The rare-earth atoms are at the centers of deformed Ge octahedra. In this structure there are not enough rare-earth atoms to form trigonal prisms or cubes.

Most of the phases of CaAl$_2$Si$_2$ type can be considered as Zintl phases. They are normal valence compounds with VEC$_A$, the partial valence electron concentration in respect to the anion A, equal to eight. The tetrahedra are linked such that there are 12 $C'AC'$ links per tetrahedron. The anionic tetrahedron complex with classification code $^0 8/12$ (Parthé & Chabot, 1990) consists of edge-linked Al-centered Ge tetrahedra which form a sheet perpendicular to [00.1]. For the rare-earth aluminium germanides, except for $Eu^{2+}Al_2Ge_2$ and $Yb^{2+}Al_2Ge_2$, VEC$_A$ is larger than eight and they can thus no longer be considered as Zintl phases.

$Sc_{11}Al_2Ge_8$ ($tI84$, $I4/mmm$) (Zhao & Parthé, 1991), a substitution variant of the $Ho_{11}Ge_{10}$ type. In this structure some of the Ge atoms are at the centers of trigonal Sc prisms. The Al atoms are not at the centers of trigonal prisms, cubes or tetrahedra, instead there are tightly bound squares of Al atoms.

The following do not really belong to this list of rare-earth compounds; however, they are mentioned here because Eu and Sr or Ca compounds are often isotypic. We shall consider only the Ge coordination around the Al atoms.

$Ca_3Al_2Ge_2$, $Sr_3Al_2Ge_2$ and $Ba_3Al_2Ge_2$ ($oI14$, $Immm$) (Widera, Eisenmann, Schäfer & Turban, 1976) with a substitution variant of the Ta$_3$B$_4$ type. In this structure type both Al and Ge atoms are at the centers of trigonal prisms.

$Ca_3Al_2Ge_3$ ($oP32$, $Pnma$) (Cordier & Schäfer, 1982) is a normal valence compound where all Al atoms have four tetrahedral Ge neighbors. This structure can also be classified as a Zintl phase with an anionic tetrahedron complex and classification code $^0 8/7$.

$Ba_4Al_8Ge_{15}$ ($cP54$, $Pm\bar{3}n$) (Eisenmann, Schäfer & Zagler, 1986) forms a clathrate structure where each Al has four tetrahedral Ge neighbors.

$Ba_{10}Al_3Ge_7$ ($hP40$, $P6_3/mcm$) (Widera & Schäfer, 1977) has a propeller-like Al$_3$Ge$_7$ anion complex where each Al atom has a triangular Ge-atom coordination.

The limited structure results indicate that if the rare-earth content is sufficiently high the Ge atom will be most likely at the center of a trigonal prism. The Al atom also may be occasionally at the center of a trigonal prism, but only if the rare-earth partner is large, otherwise it prefers a different coordination such as a cube. The Ge coordination of the Al atom is mostly tetrahedral; however, it can be a square or a triangle. The best chance of finding ternary rare-earth structures where Al and Ge atoms have different coordinations seems to occur with ternary compounds formed with small rare-earth elements.

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Sc$_{11}$Al$_2$Ge$_8$, a Ternary Substitution Variant of the Tetragonal Ho$_{11}$Ge$_{10}$ Type

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Abstract. Sc$_{11}$Al$_2$Ge$_8$, M_r = 1129·20, tetragonal, $tI84$, $I4/mmm - n^2mjh^2e^2d$, a = 10·419 (1), c = 14·974 (2) Å, V = 1625·6 (3) Å^3, Z = 4, D_x = 4·614 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 19·738 mm^{-1}, $F(000)$ = 2052, T = 300 K, wR = 0·045 for 369 contributing unique reflections. Sc$_{11}$Al$_2$Ge$_8$ is a new ternary substitution variant of the Ho$_{11}$Ge$_{10}$ type with the Al atoms substituting for the Ge atoms on one crystallographic site.

Introduction. From the study of the crystal structures of the binary or ternary rare-earth–transition-metal–non-metal compounds, with the non-metal being Si or Ge, it is known that the Al atoms, when introduced as a third or fourth component, do not always simply substitute for Si or Ge atoms but often prefer sites with different coordinations. To obtain more information on the site occupations of the Al atoms it was considered of interest to study the structures of rare-earth aluminium germanides.

Experimental. The sample of nominal composition Sc$_2$Al$_2$Ge was prepared by arc melting under argon atmosphere (Sc 99·99, Al 99·99 and Ge 99·99%). The weight loss was 0·6%. A single crystal with irregular shape (mean radius: 0·008 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 cell parameters were refined from 2θ values of 22 reflections (Mo $K\alpha$, λ = 0·71073 Å, $15 < 2\theta < 35°$) using the program *LATCON* (Schwarzenbach, 1966). 2696 reflections were collected out to $(\sin\theta)/\lambda$ = 0·702 Å^{-1} $(0 \le h \le 14, 0 \le k \le 14, 0 \le l \le 20$ and the antireflections) in the ω–2θ scan mode, yielding 721 unique reflections $(R_{int}$ = 0·13). Two standard reflections (330 and 006) were measured with maximum intensity variations of 1·05 and 1·2%, respectively. A spherical absorption correction was made using the program *ABSORB* (Davenport, Spadaccini & Stewart, 1989) with max. and min. transmission factors of 0·7468 and 0·7407. The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). From the resemblance of the unit cell and the possible space groups $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, $I4/mmm$ (*International Tables for Crystallography*, 1983, Vol. A), we were led to assume that the structure is isotypic to the Ho$_{11}$Ge$_{10}$ type (Smith, Johnson & Tharp, 1967). The space group $I4/mmm$, the Wyckoff position and the atom coordinates of Ho$_{11}$Ge$_{10}$ were used as starting values for the refinement. The refinement was based on $|F|$ values and isotropic atomic displacement parameters using the program *CRYLSQ* (Olthof-Hazekamp, 1989). During the first step of the refinement it was found that the displacement parameter of the Ge atoms at the 8(h) position was very high and there was a large hole at this position on the difference electron density map. This led us to place Al atoms in this site. The final refinement of the structure confirmed the substitution. 22 variables refined to R = 0·059 and wR = 0·045 [w = 1/