

- HOVESTREYDT, E., ENGEL, N., KLEPP, K., CHABOT, B. & PARTHÉ, E. (1982). *J. Less-Common Met.* **85**, 247–274.
- JEITSCHKO, W. (1970). *Acta Cryst.* **B26**, 815–822.
- KRIPYAKEVICH, P. I., MARKIV, Y. YA. & MELNIK, E. V. (1967). *Dopov. Akad. Nauk Ukr. RSR Ser. A*(8), pp. 750–753.
- LIMA-DE-FARIA, J., HELLNER, E., LIEBAU, F., MAKOVICKY, E. & PARTHÉ, E. (1990). *Acta Cryst.* **A46**, 1–11.
- PARTHÉ, E. & CHABOT, B. (1984). In *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, edited by K. A. Gschneidner Jr & L. Eyring, Ch. 48, pp. 113–334. Amsterdam: North-Holland.
- RIHALI, R. M. & ZARECHNYUK, O. S. (1977). *Dopov. Akad. Nauk Ukr. RSR Ser. A*(4), pp. 375–377.
- RUNDQVIST, S. & JELLINEK, F. (1959). *Acta Chem. Scand.* **13**, 425–432.
- SCHWARZENBACH, D. (1966). Private communication.
- SPRENGER, H. & NICKL, J. J. (1972). *J. Less-Common Met.* **27**, 163–168.
- ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 265–268.
- ZAREMBA, V. I., KALYCHAK, YA. M., ZAVALII, P. YU. & SOBOLEV, A. N. (1989). *Dokl. AN USSR Ser. B*(2), pp. 38–40.

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

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**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

Table 1. Atomic positional and displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for YAlGe with space group  $Cmcm$ ; *e.s.d.'s* are given in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Wyckoff position	x	y	z	$U_{eq}$
Y	4(c)	0	0.3099 (2)	1/4	0.9 (1)
Ge	4(c)	0	0.6058 (3)	1/4	1.0 (1)
Al	4(a)	0	0	0	1.0 (4)

Table 2. Interatomic distances up to 3.5 Å in YAlGe; *e.s.d.'s* are given in parentheses

Y-2Ge	2.939 (3)	Ge-4Al	2.720 (1)
2Ge	3.014 (1)	2Y	2.939 (3)
Ge	3.090 (4)	2Y	3.014 (1)
4Al	3.181 (2)	Y	3.090 (4)
Al-4Ge	2.720 (1)		
2Al	2.8823 (5)		
4Y	3.181 (2)		

Table 3. New description of the  $UPt_2$  structure in space group  $Cmcm$  based on original data by Hatt & Williams (1959):  $a = 4.12$ ,  $b = 9.68$ ,  $c = 5.60$  Å

	Wyckoff position	x	y	z
U	4(c)	0	0.33	1/4
Pt(1)	4(c)	0	0.62	1/4
Pt(2)	4(a)	0	0	0

cycle was 0.00007.\* Final residual electron density  $+2.67$  ( $-5.33$ )  $e \text{\AA}^{-3}$ . The programs used to refine the structure are 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.

Refinements were tried with different ordering at the Al [4(a)] and Ge [4(c)] sites. The interchange of the Al and Ge sites led to very high  $R$  values ( $R = 0.236$  and  $wR = 0.286$ ) and unreasonable atomic displacement parameters. The refinement of the population parameters starting from statistical occupation by Al and Ge on both sites led to 100% occupations of Al at 4(a) and Ge at 4(c).

*Isotypic compounds:* All other  $RAI\text{Ge}$  compounds were also prepared by arc melting method under an Ar atmosphere. Our efforts to synthesize YbAlGe with YAlGe type were not successful. The samples

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53232 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

were annealed at 873 K for 100 h. The observed powder patterns were compared with simulated powder diagrams calculated using the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). The unit-cell parameters for  $RAI\text{Ge}$  ( $R = \text{La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Sc}$ ), given on the left side of Table 3, were refined from Guinier film data of the annealed samples (except for GdAlGe HT), which had been measured with a film reader using an internal Si standard ( $a = 5.4308$  Å) and the program *LATCON* (Schwarzenbach, 1966). The unit-cell parameters for YAlGe and SmAlGe were refined from the single-crystal data.

**Discussion.** The  $RAI\text{Ge}$  compounds crystallize with two structure types: the orthorhombic YAlGe type when  $R$  is a small rare-earth element and the tetragonal  $\alpha\text{-ThSi}_2$  type (or an ordered variant) when  $R$  is a large rare-earth element.

*YAlGe and isotypic compounds.* A projection of the YAlGe structure along the short  $a$  axis is shown in the upper part of Fig. 1. The YAlGe structure is characterized by Ge centred trigonal prisms formed by 2Y and 4Al atoms. The simplified crystal chemical formula can be written as  $Y^{[(4,2)p]}Al^{[4s,4s]}Ge^{[(2,4)p]}$ . The structure is built up of infinite trigonal prism columns which are connected by sharing the Al edges forming prism sheets perpendicular to [010].

The YAlGe structure can be considered as a substitution variant of the  $UPt_2$  type (Hatt & Williams, 1959). The atomic positions of the  $UPt_2$  type were originally given in non-centrosymmetric space group *Ama2* with the  $z$  parameters of all atoms being 0.0 and 0.5 without any errors given. This structure contains, however, a symmetry centre and it is possible to describe exactly the same atom arrangement in space group  $Cmcm$  without origin shift, simply by interchanging the  $a$  and  $c$  axes. The new, centrosymmetric description of the  $UPt_2$  type is listed in Table

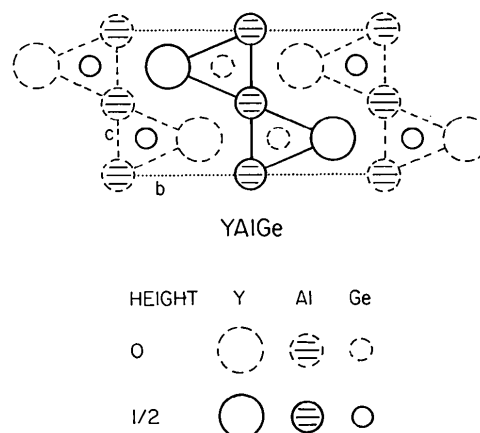


Fig. 1. The [100] projection of the YAlGe structure.

Table 4. Unit-cell parameters for RAlGe compounds

The structures from LaAlGe to GdAlGe HT have the tetragonal  $\alpha$ -ThSi<sub>2</sub> type (or an ordered variant): the structures from GdAlGe LT to ScAlGe are isotypic to orthorhombic YAlGe: the values on the right side preceded with an asterisk are from Raman & Steinfink (1967).

Compound	This work				Yanson (1975) and Raman & Steinfink (1967)			
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
LaAlGe	4.341 (1)		14.784 (8)	278.6 (2)	*4.307		*14.72	*273.0
CeAlGe	4.2889 (9)		14.721 (5)	270.8 (1)				
PrAlGe	4.2642 (4)		14.685 (2)	267.02 (6)	4.273		14.63	267.1
NdAlGe	4.233 (1)		14.638 (6)	262.2 (1)	4.272		14.66	267.2
SmAlGe	4.1957 (3)		14.588 (2)	256.79 (4)	4.188		14.52	254.5
EuAlGe	4.200 (1)		14.604 (6)	257.6 (1)				
GdAlGe HT	4.1521 (9)		14.415 (7)	248.5 (1)	4.152		14.42	248.6
					*4.148		*14.46	*248.7
GdAlGe LT	4.063 (2)	10.513 (4)	5.801 (4)	247.8 (2)				
TbAlGe	4.044 (3)	10.434 (8)	5.767 (3)	243.4 (2)	4.121	10.52	5.891	255.4
DyAlGe	4.035 (4)	10.396 (9)	5.752 (3)	241.3 (2)	4.091	10.46	5.874	251.4
HoAlGe	4.031 (4)	10.357 (9)	5.729 (3)	239.2 (2)	4.123	10.40	5.827	249.9
ErAlGe	4.010 (4)	10.314 (9)	5.704 (3)	235.9 (2)	4.101	10.34	5.840	247.6
TmAlGe	4.004 (3)	10.276 (8)	5.685 (3)	233.9 (2)	4.020	10.33	5.865	243.6
YbAlGe					4.307	10.57	5.935	270.2
LuAlGe	3.999 (4)	10.227 (9)	5.659 (4)	231.4 (2)				
YAlGe	4.0504 (5)	10.440 (1)	5.7646 (9)	243.77 (4)	4.200	10.62	5.908	263.5
ScAlGe	3.934 (2)	9.928 (4)	5.519 (2)	215.5 (1)				

3. It can be noted that the general atomic arrangement of the UPt<sub>2</sub> structure had been predicted as a possible  $R_2T$  structure by Le Roy, Moreau, Paccard & Parthé (1978) by applying a periodic unit-cell twinning operation to a cubic close-packed element structure ( $R$ ) and inserting smaller atoms ( $T$ ) in the trigonal prismatic holes formed (the space group had, however, erroneously been given as  $Pnma$  instead of  $Cmcm$ ).

The YAlGe type is also formed with other RAlGe compounds when  $R$  is a small rare-earth element. The compounds and their unit-cell parameters are listed on the left side of Table 4.

The crystal structure which we found for YAlGe, as well as the unit cells of the isotypic compounds, are different from those reported by Yanson (1975) [cited by Gladyshevskii & Bodak (1982) and Bodak & Gladyshevskii (1985)]. The crystal structure of DyAlGe has, according to Yanson, space group  $Cmc2_1$ , while we found the centrosymmetric  $Cmcm$ . In addition there are essential differences in the atom coordinations, both structures not being clearly related geometrically. The unit-cell parameters and the cell volumes of all phases with DyAlGe type, given on the right side of Table 4, are larger by 4–8% than the values of the corresponding phases with YAlGe type. It is difficult to exclude with certainty, the existence of another modification. However, the DyAlGe structure type proposed by Yanson (1975) seems to be doubtful because one calculates unreasonably short  $R$ —Al distances: Y—Al, 2.38; Tb—Al, 2.34; Dy—Al, 2.33; Ho—Al, 2.34; Er—Al, 2.33; Tm—Al, 2.29; Yb—Al, 2.43 Å. No such short distances occur in our YAlGe structure (see Table 2), nor should be found in the isotypic compounds.

RAlGe compounds with  $\alpha$ -ThSi<sub>2</sub> type (or an ordered variant). We can confirm the results of

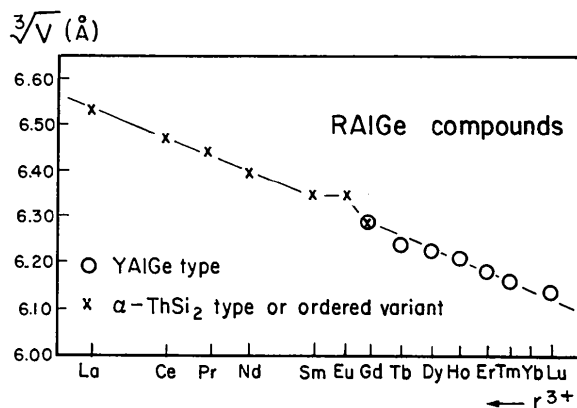


Fig. 2. Plot of the cube roots of the unit-cell volumes of the RAlGe phases versus the trivalent radii of the rare-earth elements. The phases with the  $\alpha$ -ThSi<sub>2</sub> type (or an ordered variant) are presented by crosses and the phases with the YAlGe type by open circles.

Yanson (1975), that powder diffraction patterns corresponding to the  $\alpha$ -ThSi<sub>2</sub> type ( $tI12$ ,  $I4_1/amd-ea$ ) (Brauer & Mitius, 1942) are observed with RAlGe compounds when  $R$  is a large rare-earth element. The possible ordering of the Al and Ge atoms on the Si sites was not studied. An ordered substitution variant of the  $\alpha$ -ThSi<sub>2</sub> type is known as the LaPtSi type ( $tI12$ ,  $I4_1md-a^3$ ) (Klepp & Parthé, 1982). The unit-cell parameters we found are given on the left side of Table 4. In addition to the phases already reported by Yanson (1975) and Raman & Steinfink (1967), we also investigated CeAlGe and EuAlGe. In the case of GdAlGe two structures were found: the  $\alpha$ -ThSi<sub>2</sub> type (or an ordered variant) above 1300 (10) K and the YAlGe type below that temperature. The phase transition temperature was determined from differential thermal analysis.

The unit-cell volumes of the  $RAI\text{Ge}$  phases decrease with increasing atomic number of the rare-earth elements as expected from the lanthanide contraction. In Fig. 2 are plotted the cube roots of the unit-cell volumes of the  $RAI\text{Ge}$  phases versus the trivalent ionic rare-earth radii  $r^{3+}$  (Templeton & Dauben, 1954). The cube roots of the unit-cell volumes for the phases with  $\alpha\text{-ThSi}_2$  type diffraction pattern and for the phases with the  $YAI\text{Ge}$  type follow the same linear function of  $r^{3+}$ . The only deviation from the linearity is observed with  $\text{EuAlGe}$ .

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#### References

- BODAK, O. I. & GLADYSHEVSKII, E. I. (1985). *Ternary Systems Containing Rare Earth Metals*, pp. 46–121. Lvov: Vishcha Shkola Publishing House. (In Russian.)
- BRAUER, G. & MITIUS, A. (1942). *Z. Anorg. Allg. Chem.* **249**, 325–412.
- DEBAERDEMAEKER, T., GERMAIN, G., MAIN, P., TATE, C. & WOOLFSON, M. M. (1987). *MULTAN87. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- GELATO, L. M. & PARTHÉ, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
- GLADYSHEVSKII, E. I. & BODAK, O. I. (1982). *Crystal Chemistry of Intermetallic Compounds of the Rare Earth Metals*, p. 148. Lvov: Vishcha Shkola Publishing House. (In Russian.)
- HALL, S. R. & STEWART, J. M. (1989). Editors. *XTAL2.6 User's Manual*. Univs. of Western Australia, Australia, and Maryland, USA.
- HATT, B. A. & WILLIAMS, G. I. (1959). *Acta Cryst.* **12**, 655–657.
- KLEPP, K. & PARTHÉ, E. (1982). *Acta Cryst.* **B38**, 1105–1108.
- LE ROY, J., MOREAU, J.-M., PACCARD, D. & PARTHÉ, E. (1978). *Acta Cryst.* **B34**, 9–13.
- RAMAN, A. & STEINFINK, H. (1967). *Inorg. Chem.* **6**, 1789–1791.
- SCHWARZENBACH, D. (1966). Private communication.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). *CRYLSQ. The XRAY76 system*. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
- TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Am. Chem. Soc.* **76**, 5237–5239.
- YANSON, T. I. (1975). *Autoreferat Diss. Kand. Khim.* (Nauk, Lvov), pp. 10–12. (Abstract of thesis, in Russian.)
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

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## Structure of Copper(II) Hydroxide, $\text{Cu}(\text{OH})_2$

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**Abstract.**  $\text{Cu}(\text{OH})_2$ , mineral name spertiniite,  $M_r = 97.578$ , orthorhombic,  $Cmc2_1$ ,  $a = 2.9471$  (5),  $b = 10.593$  (1),  $c = 5.2564$  (7) Å,  $V = 164.1$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.949$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 124.62$  cm<sup>-1</sup>,  $F(000) = 188$ ,  $T = 295$  K,  $R$  is 0.042 for 417 unique observed reflections. The general features of the structure determined in the centrosymmetric space group  $Cmcm$  from X-ray powder data [Jaggi & Oswald (1961). *Acta Cryst.* **14**, 1041–1045] could be confirmed. An analysis of the thermal displacement parameters of the O atoms, however, shows that the correct space group is non-centrosymmetric,  $Cmc2_1$ . Therefore, the resulting Cu—O coordination polyhedron is square pyramidal or strongly (4 + 1 + 1) distorted octahedral, but not (4 + 2) octahedral. In addition, the H-atom positions could be localized from difference Fourier syntheses. Cu—O distances are 1.948 (3) and 1.972 (3) Å within the equatorial

plane of the square pyramid, the apical distance is 2.356 (5) Å and the Cu atom is displaced by 0.134 Å from the equatorial plane. Assuming octahedral coordination the next vertex distance is 2.915 (5) Å resulting in a (4 + 1 + 1) configuration. Chains of octahedra are formed by sharing equatorial edges along [100]. These chains build up corrugated layers perpendicular to the  $b$  axis by sharing edges of apical and equatorial OH<sup>-</sup> ions. The layers are connected via hydrogen bonds of the type O(1)—H(1)⋯O(1') with distances O(1)⋯O(1') = 2.904 (4), H(1)⋯O(1') = 1.92 (2) Å and the angle around H(1) is 167 (2)°.

**Introduction.** The structure of  $\text{Cu}(\text{OH})_2$  was first solved with powder diffraction X-ray data by Jaggi & Oswald (1961) in the space group  $Cmcm$ , and it was described as a layered structure type related to lepidocrocite,  $\gamma\text{-FeOOH}$ . The decomposition of