The Orthorhombic Crystal Structure of Ru_2Si_3, Ru_2Ge_3, Os_2Si_3 and Os_2Ge_3

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Single-crystal studies have indicated that the true symmetry of Ru_2Ge_3 is not tetragonal but orthorhombic. Space group *Pbcn* (No. 60); $a = 11·436$, $b = 9·238$ and $c = 5·716$ Å; $Z = 8$, $D_x = 9·23$ g cm^{-3}, F.W. 419·91, $F(000) = 1472$, μ(Mo $K\alpha$) = 40·4 cm^{-1}. The structure was solved by the Patterson method and refined to an R of 0·085. The compounds Ru_2Si_3, Os_2Si_3 and Os_2Ge_3 are isotypic. The Ru_2Ge_3 structure is related to the tetragonal Ru_2Sn_3 structure. Two unit cells of the latter placed side by side give the orthorhombic unit cell of Ru_2Ge_3 ($a/c = 2$). Whereas the positions of the transition element in both structures are nearly identical and of the β-tin type, there are differences between Sn and Ge sites and consequently different coordination polyhedra.

Introduction

Nowotny and coworkers (Nowotny, 1970) determined the crystal structures of a group of transition metal silicides, germanides, stannides and gallides of composition T_nB_{2n-m} (T = transition element, B = Si, Ge, Sn or Ga). These, for which Pearson (1970) has coined the descriptive term 'chimney-ladder' structures, are characterized by long tetragonal unit cells consisting of β-tin subcells of the transition elements stacked one on top of the other, and a helical arrangement of the B elements (Boller, 1974). There is a correlation between composition, cell length and partial valence electron concentration (Jeitschko & Parthé, 1967; Parthé, 1969; Parthé, 1974).

For the compounds with transition elements of the Fe group, only tetragonal Ru_2Sn_3 (Schwomma, Nowotny & Wittmann, 1964) can be properly grouped with the chimney-ladder structures. Ru_2Si_3, Ru_2Ge_3 (Schwomma, Nowotny & Wittmann, 1963a), Os_2Si_3 (Schwomma, Nowotny & Wittmann, 1963b) and Os_2Ge_3 (Flieher, Völlenkle & Nowotny, 1968) have a tetragonal unit cell with a base four times larger than that of Ru_2Sn_3. We decided to determine the crystal structures of Ru_2Si_3, Ru_2Ge_3, Os_2Si_3 and Os_2Ge_3 in order to study their possible relation to the chimney-ladder structures.

Experimental

Alloys of Ru_2Si_3, Ru_2Ge_3, Ru_2Sn_3 and Os_2Si_3 were prepared by arc-melting a mixture of the component elements under a purified argon atmosphere without further annealing. Their composition was checked by microprobe analysis. For example for a specimen of nominal composition Ru_2Ge_3 the quantitative analysis with use of the program *MAGIC* IV (Colby, 1970) gave 39·94 at.% Ru and 60·04 at.% Ge. Os_2Ge_3 was obtained as a by-product of the reaction of Os–Ge–S or Os–Ge–Se samples in quartz ampoules (900°, 40 days). Samples of nominal composition Os:Ge:Se =

9:9:2 formed, except for traces of unreacted Os, Os_2Ge_3 and GeSe, the latter, due to its high volatility, being quantitatively vapour-transported to the cooler parts of the quartz tube.

The powder diagrams of all these phases could be indexed with the large tetragonal cells given in the literature. However, a single-crystal photograph of Ru_2Ge_3 (diameter 0·3 mm) indicated orthorhombic, not tetragonal, symmetry. The systematic extinctions for reflexions with k odd for $0kl$, l odd for $h0l$ and $h+k$ odd for $hk0$ lead to the unique space group *Pbcn* (No. 60). The lattice parameters of Ru_2Ge_3 obtained by least-squares fit from diffractometer measured d values are $a = 11·436$ (5), $b = 9·238$ (4), $c = 5·716$ (2) Å.

The previously published tetragonal lattice constants for Ru_2Ge_3 were $a = 11·40_5$, $c = 9·27_0$ Å (Schwomma, Nowotny & Wittmann, 1963a) or $a = 5·709$, $c = 4·650$ Å (Raub & Fritzsche, 1962). The intensities of the Ru_2Ge_3 reflexions were recorded with graphite-monochromated Mo $K\alpha$ radiation and a Philips PW 1100 computer-controlled four-circle goniometer. The θ–2θ scan technique was employed to collect all nonequivalent intensities out to a limit of (sin θ)/λ = 0·9 Å^{-1}. Lorentz and polarization corrections were applied by the method of Levy & Ellison (1960). No absorption correction was used [μ(Mo $K\alpha$) = 40·4 cm^{-1}]. The structure determination was carried out with 607 independent reflexions.

Structure determination

A comparison with the smaller tetragonal structure of Ru_2Sn_3 indicated that there should be eight formula units Ru_2Ge_3 per orthorhombic cell. The structure was solved by the Patterson method. The atomic positions were refined with the *CRYLSQ* program in the X-RAY (1972) system. After four cycles varying the positional and isotropic thermal parameters for all atoms the value of $R = \sum |\Delta F|/\sum |F_{obs}|$ was 0·085. The scattering factors used were those given in the X-RAY (1972)

Fig. 1. Stereo drawing of one unit cell of Ru₂Ge₃ (*ORTEP*, Johnson, 1965). The origin has been shifted by $00\frac{1}{4}$ from the orthorhombic coordinate system of space group *Pbcn*. For clarity Ru atoms with $z=1$ have been omitted.

Table 1. *Observed and calculated structure factors for* Ru₂Ge₃

Reading from left to right the columns contain the values h, k, l, $|F_o|$ and $|F_c|$.

Table 2. *Atomic parameters in* Ru₂Ge₃ *and in* Ru₂Si₃

Isotropic temperature factors are expressed as $T=\exp\left[-8\pi^2 U(\sin\theta/\lambda)^2\right]$. E.s.d.'s are in parentheses.

		x		y		z		U	
	Position	Ru₂Ge₃	Ru₂Si₃	Ru₂Ge₃	Ru₂Si₃	Ru₂Ge₃	Ru₂Si₃	Ru₂Ge₃	Ru₂Si₃
Ru(1)	8(d)	0·2476 (3)	0·2472 (2)	0·1869 (4)	0·1864 (2)	0·2418 (8)	0·2401 (4)	0·1 (1)	0·2 (1)
Ru(2)	4(c)	0	0	0·0476 (5)	0·0451 (2)	0·25	0·25	0·1 (1)	0·3 (1)
Ru(3)	4(c)	0	0	0·5719 (6)	0·5748 (3)	0·25	0·25	0·1 (1)	0·3 (1)
Ge or Si(1)	8(d)	0·4260 (4)	0·4275 (9)	0·2774 (5)	0·2841 (9)	0·4658 (9)	0·4537 (16)	0·1 (1)	0·7 (2)
Ge or Si(2)	8(d)	0·3288 (4)	0·3253 (8)	0·4317 (6)	0·4350 (10)	0·0879 (11)	0·0934 (16)	0·1 (1)	−0·1 (2)
Ge or Si(3)	8(d)	0·1373 (4)	0·1366 (11)	0·4014 (5)	0·3994 (11)	0·3996 (11)	0·3946 (17)	0·4 (1)	0·9 (2)

Table 3. *Coordination distances* (Å) *in* Ru_2Ge_3 *and* Ru_2Si_3

The standard deviations of the least significant figures are in parentheses.

			Ru_2Si_3
Ru(1)–Ge(1)	2·552 (6)		
–Ge(1)′	2·559 (6)		
–Ge(2)	2·599 (6)		
–Ge(2)′	2·425 (7)	2·530	2·469
–Ge(2)″	2·664 (6)		
–Ge(3)	2·517 (6)		
–Ge(3)′	2·497 (7)		
Ru(2)–2Ge(1)	2·444 (6)		
–2Ge(2)	2·418 (5)	2·431	2·362
–2Ge(2)′	2·759 (5)		
–2Ge(1)′	2·908 (6)		
Ru(3)–2Ge(1)	2·418 (6)		
–2Ge(3)	2·384 (6)	2·454	2·377
–2Ge(3)′	2·559 (6)		
Ge(1)–Ru(1)	2·552 (6)		
–Ru(1)′	2·559 (6)		
–Ru(2)	2·444 (6)	2·493	2·415
–Ru(3)	2·418 (6)		
Ge(2)–Ru(1)	2·599 (6)		
–Ru(1)′	2·425 (7)		
–Ru(1)″	2·664 (6)	2·526	2·449
–Ru(2)	2·418 (5)		
Ge(3)–Ru(1)	2·517 (6)		
–Ru(1)′	2·497 (7)		
–Ru(3)	2·384 (6)	2·489	2·420
–Ru(3)′	2·559 (6)		

Table 4 *List of observed* (I_o) *and calculated* (I_c) *intensities for a powder diagram of* Ru_2Ge_3

$I_o = (I_{sc}/LP)m$; $I_c = 10^{-5}F_c^2m$. I_{sc}: I collected on single crystal; m: multiplicity factor. Cu $K\alpha = 1·5418$ Å.

h	k	l	$10^3 \sin^2 \theta_c$	I_o	I_c
1	1	1	29·70	0·3	0·1
2	2	0	46·03	1·9	1·9
0	2	1	46·04	1·6	1·2
1	2	1	50·59	0·2	0·5
2	2	1	64·22	0·2	0·3
3	1	1	66·05	0·2	0·2
4	0	0	72·71	1·1	1·6
0	0	2	72·76	1·1	0·9
3	2	1	86·94	2·0	2·1
4	1	1	97·86	6·2	8·5
2	1	2	97·90	6·4	6·6
2	3	1	99·04	14·6	14·0
4	2	0	100·56	0·1	0·2
0	2	2	100·61	0·4	0·3
1	2	2	105·16	0·4	0·4
3	0	2	113·65	2·1	2·4
4	2	1	118·75	21·2	22·4
2	2	2	118·79	21·3	17·6
5	1	0	120·57	1·2	1·5
2	4	0	129·60	0·8	0·8
0	4	1	129·61	1·0	0·9
1	4	1	134·15	1·6	1·3
1	3	2	139·97	0·9	0·7
4	0	2	145·45	17·1	19·5
2	4	1	147·78	27·4	22·0
4	1	2	152·43	3·1	4·2
5	3	0	176·28	0·5	0·5
3	3	2	176·33	1·0	0·9
1	5	0	178·64	3·5	2·6
4	4	0	184·12	0·5	0·6
0	4	2	184·18	0·2	0·2

system. No anomalous dispersion was considered. Unit weights were used for all reflexions. The calculated and observed structure factors are given in Table 1. The final positional and thermal atomic parameters are listed in Table 2, the interatomic distances in Table 3. A powder intensity calculation for Ru_2Ge_3 (Yvon, Jeitschko & Parthé, 1969) is given in Table 4.

Isotypic compounds

Powder and single-crystal studies on Ru_2Si_3, Os_2Si_3 and Os_2Ge_3 indicate that these compounds are isotypic with Ru_2Ge_3. Their lattice constants are given in Table 5. In the case of Ru_2Si_3 the single crystal intensities were used to refine the positional parameters of
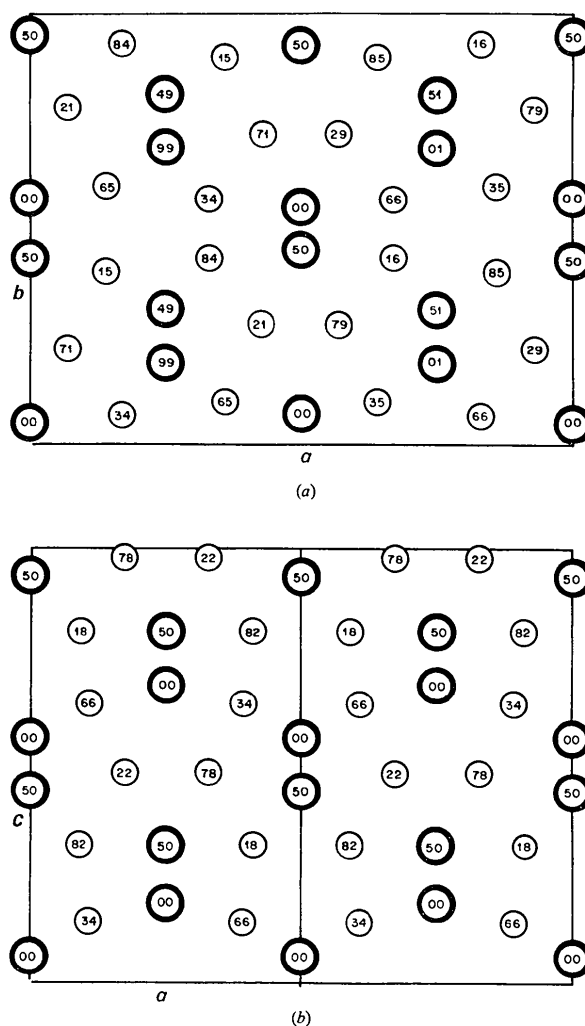

(a)

(b)

Fig. 2. (a) Projection of Ru_2Ge_3 along short c axis. Shift of origin by 00¼ from the orthorhombic coordinate system of space group $Pbcn$. Thicker circles correspond to Ru atoms. The inscribed numbers are the values $100z$ of the atoms. (b) Projection of two unit cells of Ru_2Sn_3 along **b**. Shift of origin of $00\frac{15}{16}$ from the tetragonal coordinate system of space group $P\bar{4}c2$.
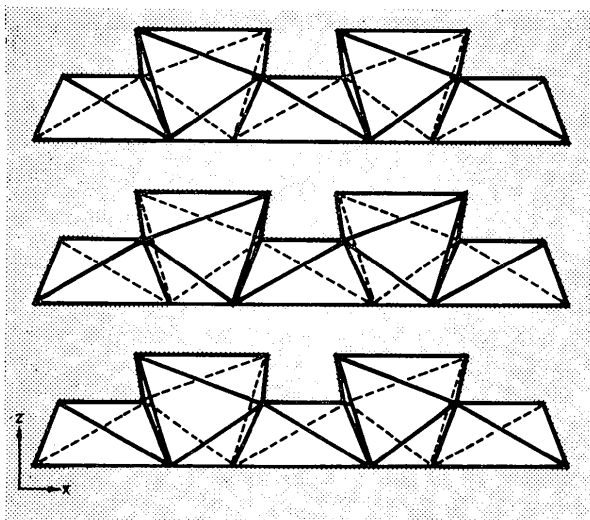
the atoms ($R_{400} = 0 \cdot 08$). The results are also given in Table 2 and show that there are no essential differences from Ru_2Ge_3.

Table 5. *Lattice constants of compounds with* Ru_2Ge_3 *structure type* (*space group Pbcn*)

Compound	a (Å)	b (Å)	c (Å)	D_x (g cm^{-3})
Ru_2Si_3	11·057 (4)	8·934 (3)	5·533 (2)	6·96
Ru_2Ge_3	11·436 (5)	9·238 (4)	5·716 (2)	9·23
Os_2Si_3	11·124 (4)	8·932 (3)	5·570 (2)	11·15
Os_2Ge_3	11·544 (5)	9·281 (4)	5·783 (2)	12·82
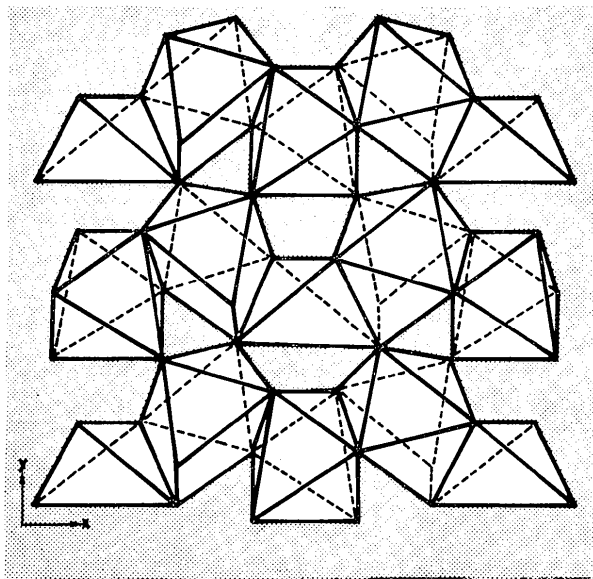
(a)

(b)

Fig. 3. (a) The coordination polyhedra of Ge atoms around the Ru atoms in Ru_2Ge_3 which are located in or close to the plane of projection ($z = 0$) shown in Fig. 2(a). (b) The deformed tetrahedra and the octahedra formed by Sn atoms around the Ru atoms at $y = 0$ shown in Fig. 2(b).

Since Ru_2Sn_3 is isoelectronic with Ru_2Ge_3 we decided to check its crystal structure, which as noted above was reported to crystallize with a tetragonal unit cell half as big as the Ru_2Ge_3 cell. Single-crystal studies on Ru_2Sn_3 indicated that the previously given structure data were correct (Schwomma, Nowotny & Wittmann, 1964).

Discussion

A stereo drawing of one unit cell of Ru_2Ge_3 is shown in Fig. 1. The structure is related to that of Ru_2Sn_3. This similarity is demonstrated in Fig. 2(a) and (b). Fig. 2(a) shows a projection of the Ru_2Ge_3 structure along the short c axis. In the corresponding drawing for Ru_2Sn_3 one finds a projection along the b axis of two tetragonal unit cells placed side by side. The Ru sites are practically identical in both structures; however there are important differences between the Ge and the Sn sites and consequently different coordination polyhedra are formed.

In Figs. 3(a) and (b) are shown the coordination polyhedra of Ge or Sn atoms around the Ru atoms which are located on or close to the plane of projection shown in Fig. 2(a) ($z \sim 0$) and (b) ($y = 0$). In Ru_2Ge_3 [Fig. 3(a)] there is a seven-coordination figure around Ru(I), a deformed tetrahedron around Ru(II) and an octahedron around Ru(III) whereas in Ru_2Sn_3 [Fig. 3(b)] only tetrahedra and octahedra occur. If one also includes four more neighbours slightly further away the coordination around Ru(II) may be described as a deformed Archimedian antiprism. An even bigger difference with the coordination polyhedra can be noted if the polyhedra in the next parallel plane, with Ru atoms at $z \sim \frac{1}{2}$ and $y = \frac{1}{2}$, respectively, are compared. In Ru_2Ge_3 one has the same three polyhedra but in Ru_2Sn_3 only octahedra. The arrangement of the polyhedra in Ru_2Ge_3 is such that, perpendicular to the plane of projection, columns of connected identical polyhedra are formed, the Archimedian antiprisms being connected by a common face, the octahedra by a common edge and the seven-coordination figure also by a common face. All the Ge atoms have four-coordination but it is tetrahedral only in the case of Ge(II). The unusual coordination of Ge(I) and Ge(III), visible in Fig. 1, is identical with the coordination of all Sn atoms in Ru_2Sn_3. The average interatomic distances in the polyhedra of Ru_2Si_3 are listed in the last column of Table 3. They can be compared with values obtained by Engström (1970) from more metal-rich Ru silicides. One notes that the distances in Ru_2Si_3 are approximately 0·1 Å shorter. This trend toward a shortening of M–Si distances with increasing Si content has already been noted by Engström.

The reduction of Si(Ge)-coordination with composition of elements of group VIII can be explained according to Hladyschewski (1971) by the ability of transitional elements to accept from Si(Ge) a part of their valence electrons in the unfilled d levels. As a result, the real value of κ ($\kappa = R_T/R_{Si(Ge)}$, where R_T

and $R_{Si(Ge)}$ are the atomic radii of T and Si(Ge) respectively) increases. This increase helps the formation of compounds whose structures have smaller coordination numbers.

It is characteristic of all phases with the Ru₂Ge₃ type that their a/c ratio is 2. If this ratio were exactly 2, the transition element partial structure would be strictly tetragonal and of the β-tin type. In this respect the Ru₂Ge₃ type structures belong to the chimney-ladder structures although it seems as yet impossible to explain the deviations of the B element sites from those normally found in chimney-ladder structures.

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References

BOLLER, H. (1974). *Mh. Chem.* **105.** In the press.
COLBY, J. W. (1970). *MAGIC IV. A Computer Program for Quantitative Electron Microprobe Analysis.* Bell Telephone Laboratories, Inc. Allentown, Pennsylvania.
ENGSTRÖM, I. (1970). *Structural Chemistry of Platinum Metal Silicides.* Abstracts of Uppsala Dissertations in Science, Uppsala.

FLIEHER, G., VÖLLENKLE, H. & NOWOTNY, H. (1968). *Mh. Chem.* **99,** 2408–2415.
HLADYSCHEWSKI, E. I. (1971). *Kristallochimia Silicidov i Germanidov.* Moscow: Metallurgia.
JEITSCHKO, W. & PARTHÉ, E. (1967). *Acta Cryst.* **22,** 417–430.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
LEVY, H. A. & ELLISON, R. D. (1960). *Acta Cryst.* **13,** 270–271.
NOWOTNY, H. (1970). In *The Chemistry of Extended Defects in Non-metallic Solids,* edited by LE ROY EYRING and M. O'KEEFE, pp. 223–237. Amsterdam: North-Holland.
PARTHÉ, E. (1969). In *Developments in the Structural Chemistry of Alloy Phases,* edited by B. GIESSEN, pp. 49–63. New York: Plenum.
PARTHÉ, E. (1974). *24th Intern. Congr. Pure and Applied Chemistry,* Hamburg **3,** 139–158.
PEARSON, W. B. (1970). *Acta Cryst.* B**26,** 1044–1046.
RAUB, E. & FRITZSCHE, W. (1962). *Z. Metallk.* **53,** 779–781.
SCHWOMMA, O., NOWOTNY, H. & WITTMANN, A. (1963a). *Mh. Chem.* **94,** 681–685.
SCHWOMMA, O., NOWOTNY, H. & WITTMANN, A. (1963b). *Mh. Chem.* **94,** 924–926.
SCHWOMMA, O., NOWOTNY, H. & WITTMANN, A. (1964). *Mh. Chem.* **95,** 1538–1543.
X-RAY (1972). Technical Report Tr-192 of the Computer Science Center, Univ. of Maryland, June 1972.
YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1969). *A Fortran IV Program for the Intensity Calculation of Powder Patterns,* 1969 version. Université de Genève, Laboratoire de Cristallographie aux Rayons X.

Structural Investigations of Ylides. V.* The Crystal and Molecular Structure of 3-Ethyl-1,2,5-trimethyl-3*H*-benzo[*c*][1,2,5]triazepino[1,2-*a*]cinnoline-1,2,3,5-tetracarboxylate

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Although not itself an ylide, the title compound is formed directly from an ylide by 1,5-dipolar cycloaddition of dimethyl acetylenedicarboxylate. The crystals are triclinic, space group $A\bar{1}$, with $Z=4$, $a=15\cdot245$, $b=10\cdot212$, $c=17\cdot612$ Å, $\alpha=89\cdot81$, $\beta=117\cdot65$, $\gamma=90\cdot47°$. The structure was solved by direct methods from 2747 independent reflexions collected on a diffractometer, and has been refined by least-squares calculations to a final R of 0·060. The analysis confirms that the ylide behaves as a 6π-electron 1,5-dipole in its reactions with esters of acetylenedicarboxylic acid.

Introduction

1,3-Dipolar cycloaddition of azomethine imines is well known (Huisgen, 1963). Thus the benzocinnolinium ylide (I) (Gait, Rance, Rees & Storr, 1972a) yields the adduct (II) when treated with dimethyl acetylenedicar-

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* Part IV: Cameron, Hair & Morris (1974). *Acta Cryst.* B**30,** 221–225.

boxylate in dimethylformamide at 70°C for 30 min. However, under identical reaction conditions the derivative (III) does not give analogous products, yielding instead a compound to which the structure (VI) has been tentatively assigned (Gait, Rance, Rees & Storr, 1972b). Moreover, when the reaction of (III) is carried out at room temperature over 24 h, a second isomeric adduct, assigned the structure (IV), is isolated together with (VI). The adduct (IV) rearranges under