

## The Crystal Structures of $\text{Rh}_2\text{Si}$ and $\text{Rh}_5\text{Si}_3$ with some Notes on the Rh-Si System

INGVAR ENGSTRÖM

*Institute of Chemistry, University of Uppsala, Uppsala, Sweden*

The crystal structures of  $\text{Rh}_2\text{Si}$  and  $\text{Rh}_5\text{Si}_3$  have been refined from single crystal data. For  $\text{Rh}_2\text{Si}$  ( $C23$  type), the unit cell dimensions are  $a = 5.40_8 \text{ \AA}$ ,  $b = 3.93_0 \text{ \AA}$ , and  $c = 7.38_3 \text{ \AA}$ , and the atomic parameters are  $\text{Rh}_I$  in  $4(c)$ :  $x = 0.8393$ ,  $z = 0.0694$ ;  $\text{Rh}_{II}$  in  $4(c)$ :  $x = 0.9728$ ,  $z = 0.6991$ ;  $\text{Si}$  in  $4(c)$ :  $x = 0.2819$ ,  $z = 0.1052$ . For  $\text{Rh}_5\text{Si}_3$  ( $\text{Rh}_5\text{Ge}_3$ -type) the unit cell dimensions are  $a = 5.31_7 \text{ \AA}$ ,  $b = 10.13_1 \text{ \AA}$  and  $c = 3.89_5 \text{ \AA}$ , and the atomic parameters are  $\text{Rh}_I$  in  $2(c)$ ;  $\text{Rh}_{II}$  in  $4(g)$ :  $x = 0.1542$ ,  $y = 0.2158$ ;  $\text{Rh}_{III}$  in  $4(h)$ :  $x = 0.3297$ ,  $y = 0.3936$ ;  $\text{Si}_I$  in  $2(a)$ ;  $\text{Si}_{II}$  in  $4(h)$ :  $x = 0.3917$ ,  $y = 0.1505$ . A hexagonal phase with the composition  $\text{Rh}_{\sim 1.5}\text{Si}$  and the unit cell dimensions  $a = 11.85_1 \text{ \AA}$ ,  $c = 3.62_3 \text{ \AA}$  is reported.

An investigation of the silicides of the platinum metals has recently been reported by Finnie<sup>1</sup>, and the results for the rhodium-silicon system are in good agreement with those of the earlier investigation of Bhan and Schubert<sup>2</sup>. A further examination of the rhodium-silicon system has been made at this Institute and some new results have been obtained.

The present paper gives an account of some phase-analytical observations, and in addition the results of the crystal structure refinements of  $\text{Rh}_2\text{Si}$  and  $\text{Rh}_5\text{Si}_3$  are reported. The formation of these intermediate phases was reported earlier by Aronsson *et al.*<sup>3</sup> ( $\text{Rh}_2\text{Si}$ ) and Bhan and Schubert<sup>2</sup> ( $\text{Rh}_5\text{Si}_3$ ).

### EXPERIMENTAL

*Powder diffraction examination.* Alloys were prepared by arc-melting rhodium metal powder (Heraeus, claimed purity 99.9 %) and silicon powder (Pechiney and Cie, claimed purity 99.9 %). The arc-melted alloys were annealed in evacuated and sealed silica tubes at  $1100^\circ\text{C}$  for 8–14 days. Powder photographs were recorded in Guinier cameras using  $\text{CuK}\alpha$ -radiation with silicon ( $a = 5.4305 \text{ \AA}$ ) as an internal calibration standard. The lattice parameters are accurate to about 0.1 %.

*Single crystal examination.* Diffraction patterns were recorded in a Weissenberg camera using Nb-filtered  $\text{MoK}$ -radiation. The multiple film technique was used with thin iron foil interleaved between successive films. The intensities of the X-ray reflections were estimated visually by comparison with a standard intensity scale.

Table 1. Phase analytical observations on the Rh—Si system at 1100°C.

Nominal composition of alloy	Observed phases	Unit cell dimensions (in Å)		Ref.
		This work (estimated accuracy $\pm 0.1$ %)	Literature data	
Rh <sub>2.0</sub> Si <sub>0.9</sub>	Rh(Si) and Rh <sub>2</sub> Si	$a = 3.80_5$ $a = 5.41_3, b = 3.93_1, c = 7.38_4$	Rh: $a = 3.8044$ (for pure rhodium) Rh <sub>2</sub> Si: $a = 5.40_8, b = 3.93_0, c = 7.38_3$	9 1,2,3
Rh <sub>2.2</sub> Si <sub>1.1</sub>	Rh <sub>2</sub> Si and Rh <sub>3</sub> Si <sub>3</sub>	$a = 5.41_0, b = 3.93_0, c = 7.38_8$ $a = 5.31_7, b = 10.12_4, c = 3.90_2$	Rh <sub>3</sub> Si <sub>3</sub> : $a = 5.30_9, b = 10.07_4, c = 3.88_8$	2
Rh <sub>2.0</sub> Si <sub>1.4</sub>	Rh <sub>3</sub> Si <sub>3</sub> and Rh <sub>1.5</sub> Si	$a = 5.31_7, b = 10.12_4, c = 3.90_2$ $a = 11.85_1, c = 3.62_3$		
Rh <sub>2.0</sub> Si <sub>1.7</sub>	Rh <sub>1.5</sub> Si *	$a = 11.85_1, c = 3.62_3$		

\* Additional lines in the powder pattern indicated the presence of small amounts of another phase, the structure of which did not belong to any of the RhSi modifications (B2, B20, B31) reported.

For the refinement of Rh<sub>2</sub>Si a single crystal fragment was selected from an arc-melted alloy annealed at 1100°C for 14 days. A powder photograph of the alloy showed weak reflections from Rh<sub>3</sub>Si<sub>3</sub> in addition to reflections from Rh<sub>2</sub>Si. Single crystal diffraction patterns were obtained with the [010] direction as the rotation axis and the zero layer was recorded. The intensities of 164 non-equivalent  $h0l$  reflections were measured. The 22 strongest reflections were omitted from the refinement because of extinction effects and are not included in the final  $R$  value quoted below.

Crystals of Rh<sub>5</sub>Si<sub>3</sub> obtained from arc-melted and sintered alloys were too small for use in a single crystal examination. Crystals were therefore prepared by heating a near single-phase alloy of Rh<sub>5</sub>Si<sub>3</sub> in an induction furnace at ~1200°C for 4 h. A powder pattern of the product showed that small amounts of a phase, here referred to as Rh<sub>1.5</sub>Si, were also present. All powder patterns of samples containing Rh<sub>5</sub>Si<sub>3</sub> and prepared at 1200°C demonstrated line-broadening effects and the unit cell dimensions do not have an accuracy better than ± 0.1 %. Single crystal patterns were obtained with the [001] direction as the rotation axis and the zero layer was recorded. The structure was refined from 120 non-equivalent  $F(hk0)$ -values.

*Structure refinement.* The atomic scattering factor tables given for Rh by Thomas and Umeda<sup>5</sup> and for Si by Tomiie and Stam<sup>6</sup> were used. The real part of the dispersion correction factor according to Dauben and Templeton<sup>7</sup> was included in the structure factor calculations.

The Lorentz and polarisation factor corrections, the structure factor calculations and the calculations of interatomic distances were carried out on the electronic digital computer BESK, with programmes available at BESK. Atomic parameters and individual isotropic temperature factors were refined using a least squares programme<sup>14</sup> for crystal structure refinements on the electronic digital computer FACIT. A weighting scheme

Table 2. X-Ray powder data for Rh<sub>2</sub>Si. (Guinier-type camera, CuK $\alpha$ -radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$p  F _{\text{calc}}^2 \times 10^{-3}$
101	0.0310	0.0312	w---	1.6
002	—	0.0436	—	0.4
011	0.0494	0.0494	m	11.4
102	0.0639	0.0639	m	20.3
111	0.0697	0.0697	st	41.9
200	—	0.0813	w---	2.6
201	—	0.0922	—	1.2
112	0.1023	0.1023	st+	131.3
103	0.1184	0.1184	st	65.3
210	0.1196	0.1198	st+	125.5
202	0.1249	0.1249	st	82.5
211	0.1306	0.1307	st+	203.8
013	0.1364	0.1366	st+	211.2
020	0.1537	0.1539	st	161.7
113	0.1568	0.1569	w	27.0
212	—	0.1634	—	13.8
004	—	0.1744	—	0.4
203	0.1794	0.1794	m	78.5
121	—	0.1851	—	1.9
301	0.1937	0.1938	m	62.3
104	—	0.1947	—	16.5
022	—	0.1975	—	0.5
{ 122	0.2178	{ 0.2178	w	{ 25.5
{ 213				
302	0.2263	0.2265	w-	18.4
311	—	0.2323	—	1.6
114	0.2329	0.2332	w-	20.2
220	—	0.2352	—	3.3
221	—	0.2461	—	1.6
204	0.2557	0.2557	w-	15.6
312	—	0.2650	—	0.8
123	0.2723	0.2723	m	86.7
222	0.2788	0.2788	m+	110.5
303	—	0.2810	—	7.0
105	0.2927	0.2928	w+	67.7
214	—	0.2942	—	2.0

Table 3. X-Ray powder data for Rh<sub>5</sub>Si<sub>3</sub>. (Guinier-type camera, CuK $\alpha$ -radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>	$p  F ^2_{\text{calc}} \times 10^{-3}$
020	—	0.0232	—	0.8
110	—	0.0268	—	0
001	0.0390	0.0390	w— —	6.1
120	0.0442	0.0442	w— —	10.9
021	0.0622	0.0622	w—	15.0
111	0.0659	0.0659	m	41.5
130	0.0733	0.0732	m	41.0
121	0.0831	0.0833	st	171.7
200	—	0.0841	—	1.7
210	—	0.0899	—	2.4
040	—	0.0928	—	1.2
220	0.1069	0.1073	w	49.4
131	0.1122	0.1122	m	71.4
140	0.1141	0.1138	m	90.7
201	0.1231	0.1231	w— —	40.4
211	0.1290	0.1289	st+	373.9
041	0.1319	0.1318	st+	391.4
230	0.1365	0.1363	m—	170.2
221	0.1464	0.1463	m—	159.3
141	—	0.1528	—	2.2
002	0.1558	0.1562	m	268.4
150	—	0.1660	—	7.1
231	—	0.1753	—	1.1
240	0.1772	0.1769	w—	42.2
022	—	0.1794	—	1.0
112	—	0.1830	—	0
310	0.1947	0.1950	w	95.0
122	—	0.2004	—	13.9
151	—	0.2050	—	41.6
060	—	0.2087	—	0.1
320	—	0.2124	—	8.5
241	—	0.2159	—	0.2
{ 250		{ 0.2290		{ 40.7
{ 132	0.2298	{ 0.2294	m—	{ 53.0
{ 160		{ 0.2298		{ 99.0
311	—	0.2341	—	2.1
202	—	0.2403	—	2.3
330	—	0.2414	—	14.4
212	—	0.2461	—	3.2
042	—	0.2489	—	1.6
321	—	0.2514	—	3.9
222	0.2634	0.2634	w— —	66.0
251	—	0.2681	—	0
161	—	0.2688	—	4.6
142	0.2698	0.2700	w	122.2
331	—	0.2804	—	0.6
340	—	0.2820	—	3.9
{ 232	0.2927	{ 0.2924	m	{ 234.7
{ 260		{ 0.2928		{ 59.0

according to Cruickshank<sup>8</sup>,  $w = 1/(\alpha + |F_o| + c|F_o|^2)$  was used in the final stages of the refinements. The constants  $\alpha$  and  $c$  were approximately equal to  $2|F_{o,\text{min.}}|$  and  $2/|F_{o,\text{max.}}|$ , respectively.

Table 4. Observed X-ray powder data for Rh<sub>1.5</sub>Si. (Guinier-type camera, CuK $\alpha$ -radiation).

<i>hkl</i>	$\sin^2\Theta_{\text{obs}}$	$\sin^2\Theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>
110	0.0169	0.0169	w --
210	0.0394	0.0395	w --
{ 300	0.0508	{ 0.0508	st
{ 101		{ 0.0509	
111	0.0623	0.0622	w
{ 220	0.0678	{ 0.0677	w --
{ 201		{ 0.0679	
310	0.0732	0.0734	w +
211	0.0847	0.0848	w +
400	0.0900	0.0903	w
320	0.1071	0.1071	w +
221	0.1129	0.1130	m +
{ 410	0.1185	{ 0.1185	st +
{ 311		{ 0.1186	
401	0.1353	0.1355	m +
500	0.1407	0.1410	w
{ 330	0.1522	{ 0.1523	m
{ 321		{ 0.1525	
411	0.1635	0.1637	w --
510	0.1747	0.1749	w +
002	0.1814	0.1812	m
501	0.1858	0.1863	w --
331	0.1975	0.1976	w --
{ 511	0.2198	{ 0.2201	w
{ 520		{ 0.2200	
{ 212		{ 0.2206	
610	0.2417	0.2426	w --
{ 431	0.2542	{ 0.2540	w
{ 312		{ 0.2545	
{ 440	0.2704	{ 0.2708	w --
{ 402		{ 0.2714	
700	0.2763	0.2764	w --
520			
{ 611	0.2888	{ 0.2878	w --
{ 322		{ 0.2883	
620	0.2934	0.2934	w --
412	0.2997	0.2996	m +

## RESULTS AND DISCUSSION

*Some notes on the Rh—Si system.* The unit cell dimensions obtained for metal-rich phases in two-phase regions of the Rh—Si system are given in Table 1. It can be seen from the table that the edge of the cubic unit cell for Rh(Si) does not differ significantly from that given for pure rhodium ( $a = 3.8044 \text{ \AA}$ )<sup>9</sup>. This indicates that the solubility of silicon in rhodium is very small. The table shows that there is no appreciable variation in the cell dimensions of Rh<sub>2</sub>Si and Rh<sub>5</sub>Si<sub>3</sub> and it is concluded that at the temperature of preparation the homogeneity range of each phase is narrow. The cell dimensions are also in good agreement with those in earlier publications.

Table 5. Interatomic distances in Rh<sub>2</sub>Si. (Distances shorter than 3.75 Å are listed).

Rh <sub>I</sub>	— 2 Rh <sub>I</sub>	: 2.81 <sub>7</sub> (2)
	— 6 Rh <sub>II</sub>	: 2.76 <sub>2</sub> (2), 2.79 <sub>6</sub> (2), 2.80 <sub>3</sub> , 2.82 <sub>7</sub>
	— 5 Si	: 2.41, 2.42, 2.44(2), 3.03
Rh <sub>II</sub>	— 6 Rh <sub>I</sub>	: 2.76 <sub>2</sub> (2), 2.79 <sub>6</sub> (2), 2.80 <sub>3</sub> , 2.82 <sub>7</sub>
	— 4 Rh <sub>II</sub>	: 2.80 <sub>6</sub> (2), 3.54 <sub>9</sub> (2)
	— 6 Si	: 2.47(2), 2.47, 2.80(2), 3.43
Si	— 5 Rh <sub>I</sub>	: 2.41, 2.42, 2.44(2), 3.03
	— 6 Rh <sub>II</sub>	: 2.47(2), 2.47, 2.80(2), 3.43
	— 4 Si	: 3.44(2), 3.45(2)

At the nominal composition Rh<sub>~1.5</sub>Si a new intermediate phase was found. Powder and single crystal data showed that the symmetry is hexagonal, and the unit cell dimensions are given in Table 1. The structure of the new phase has not yet been determined. It should be noted, however, that the *a*-axis is three times that reported by Bhan and Schubert<sup>2</sup> for Rh<sub>3</sub>Si<sub>2+</sub> (B8-type).

X-Ray powder data for Rh<sub>2</sub>Si, Rh<sub>5</sub>Si<sub>3</sub> and Rh<sub>1.5</sub>Si are presented in Tables 2–4. Only diffraction lines for which  $\sin^2\theta < 0.30$  are given.

Table 6. Interatomic distances in Rh<sub>5</sub>Si<sub>3</sub>. (Distances shorter than 4 Å are listed).

Rh <sub>I</sub>	— 2 Rh <sub>I</sub>	: 3.89 <sub>5</sub>
	— 4 Rh <sub>II</sub>	: 2.85 <sub>2</sub> (2), 2.99 <sub>8</sub> (2)
	— 4 Rh <sub>III</sub>	: 2.83 <sub>5</sub>
	— 2 Si <sub>I</sub>	: 2.66
	— 4 Si <sub>II</sub>	: 2.53
Rh <sub>II</sub>	— 2 Rh <sub>I</sub>	: 2.85 <sub>2</sub> , 2.99 <sub>8</sub>
	— 4 Rh <sub>II</sub>	: 2.74 <sub>8</sub> (2), 3.89 <sub>5</sub> (2)
	— 6 Rh <sub>III</sub>	: 2.81 <sub>5</sub> (2), 2.82 <sub>8</sub> (2), 3.79 <sub>8</sub> (2)
	— 2 Si <sub>I</sub>	: 2.33, 3.42
	— 4 Si <sub>II</sub>	: 2.41(2), 2.76(2)
Rh <sub>III</sub>	— 2 Rh <sub>I</sub>	: 2.83 <sub>5</sub>
	— 4 Rh <sub>II</sub>	: 2.81 <sub>5</sub> (2), 2.82 <sub>8</sub> (2)
	— 5 Rh <sub>III</sub>	: 2.81 <sub>2</sub> , 3.89 <sub>5</sub> (2), 3.94 <sub>2</sub> (2)
	— 2 Si <sub>I</sub>	: 2.40(2)
	— 4 Si <sub>II</sub>	: 2.37, 2.49, 2.85, 3.02
Si <sub>I</sub>	— 2 Rh <sub>I</sub>	: 2.66
	— 4 Rh <sub>II</sub>	: 2.33(2), 3.42(2)
	— 4 Rh <sub>III</sub>	: 2.40
	— 2 Si <sub>I</sub>	: 3.90
	— 4 Si <sub>II</sub>	: 3.23
Si <sub>II</sub>	— 2 Rh <sub>I</sub>	: 2.53
	— 4 Rh <sub>II</sub>	: 2.41(2), 2.76(2)
	— 4 Rh <sub>III</sub>	: 2.37, 2.49, 2.85, 3.02
	— 2 Si <sub>I</sub>	: 3.23
	— 5 Si <sub>II</sub>	: 3.25, 3.34(2), 3.90(2)

The structure determinations of Rh<sub>2</sub>Si and Rh<sub>5</sub>Si<sub>3</sub>. The structure type for Rh<sub>2</sub>Si was verified from comparison with the data for Ru<sub>2</sub>Si<sup>4</sup> and nothing was found during the refinement of the structure that contradicted the choice of the space-group *Pnma*.

From the observed intensity data for Rh<sub>5</sub>Si<sub>3</sub> it was evident that the structure-type proposed earlier<sup>2</sup> was correct. During the refinement of the structure there was nothing which indicated that a space-group other than *Pbam* should be chosen.

The results of the structure determinations are given below. Interatomic distances are listed in Tables 5 and 6.

### Rh<sub>2</sub>Si

Space-group: *Pnma* ( $D_{2h}^{16}$ ),  $Z = 4$  (Structure type *C* 23).  
 $a = 5.40_8$  Å,  $b = 3.93_0$  Å,  $c = 7.38_3$  Å,  $U = 156.9$  Å<sup>3</sup>.

Atom	Position	Isotropic temp.factor					
		$x$	$\sigma(x)$	$z$	$\sigma(z)$	$B$	$\sigma(B)$
Rh <sub>I</sub>	4(c)	0.8393	0.0004	0.0694	0.0003	0.42	0.02
Rh <sub>II</sub>	4(c)	0.9728	0.0004	0.6991	0.0003	0.36	0.02
Si	4(c)	0.2819	0.0018	0.1052	0.0011	0.6	0.1

Final  $R$ -value = 0.093.

### Rh<sub>5</sub>Si<sub>3</sub>

Space-group: *Pbam* ( $D_{2h}^9$ ),  $Z = 2$ , (Structure type Rh<sub>5</sub>Ge<sub>3</sub>).  
 $a = 5.31_7$  Å,  $b = 10.13_1$  Å,  $c = 3.89_5$  Å,  $U = 209.8$  Å<sup>3</sup>.

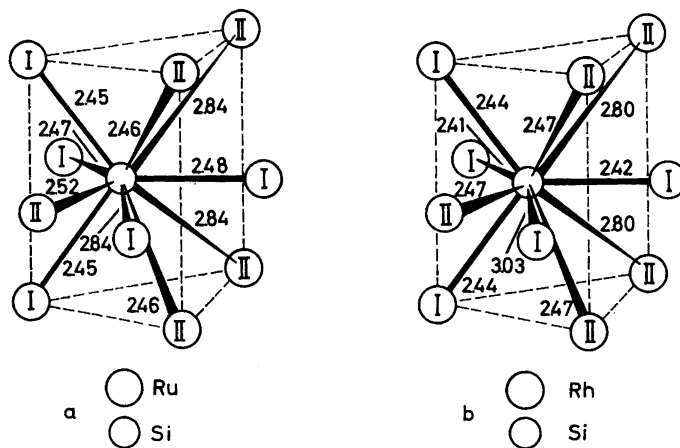
Atom	Position	Isotropic temp.factor					
		$x$	$\sigma(x)$	$y$	$\sigma(y)$	$B$	$\sigma(B)$
Rh <sub>I</sub>	2(c)	—	—	—	—	0.23	0.06
Rh <sub>II</sub>	4(g)	0.1542	0.0006	0.2158	0.0004	0.12	0.04
Rh <sub>III</sub>	4(h)	0.3297	0.0007	0.3936	0.0004	0.27	0.04
Si <sub>I</sub>	2(a)	—	—	—	—	0.5	0.3
Si <sub>II</sub>	4(h)	0.3917	0.0025	0.1505	0.0015	0.6	0.2

Final  $R$ -value = 0.074

*Discussion.* The structure types exhibited by Rh<sub>2</sub>Si and Rh<sub>5</sub>Si<sub>3</sub> have been discussed earlier by Geller<sup>10</sup>, in connection with the isomorphous germanides, Rh<sub>2</sub>Ge and Rh<sub>5</sub>Ge<sub>3</sub>. A comparison of the interatomic distances in these isomorphous silicides and germanides is given in Table 7. The average Rh—Rh distances listed in the table are nearly equal for the silicides and the germanides and are appreciably greater than the Goldschmidt metal diameter. The difference between the average Rh—Ge and Rh—Si distances is about 0.05 Å, which is equal to the difference between the tetrahedral covalent radii for germanium

Table 7. Comparison of interatomic distances in  $\text{Rh}_2\text{Si}$ ,  $\text{Rh}_2\text{Ge}$ ,  $\text{Rh}_5\text{Si}_3$  and  $\text{Rh}_5\text{Ge}_3$ 

Compound	Rh—Rh distances	Average distances
$\text{Rh}_2\text{Si}$	$\text{Rh}_\text{I}$ — 8 Rh: 2.76(2), 2.80(2), 2.80, 2.82(2), 2.83	2.80
	$\text{Rh}_\text{II}$ — 8 Rh: 2.76(2), 2.80(2), 2.80, 2.81(2), 2.83	2.80
$\text{Rh}_2\text{Ge}$	$\text{Rh}_\text{I}$ — 8 Rh: 2.75, 2.81(2), 2.81(2), 2.85, 2.88(2)	2.83
	$\text{Rh}_\text{II}$ — 8 Rh: 2.75, 2.80(2), 2.81(2), 2.81(2), 2.85	2.81
$\text{Rh}_5\text{Si}_3$	$\text{Rh}_\text{I}$ — 8 Rh: 2.84(4), 2.85(2), 3.00(2)	2.88
	$\text{Rh}_\text{II}$ — 8 Rh: 2.75(2), 2.82(2), 2.83(2), 2.85, 3.00	2.83
	$\text{Rh}_\text{III}$ — 7 Rh: 2.81, 2.82(2), 2.83(2), 2.84(2)	2.83
$\text{Rh}_5\text{Ge}_3$	$\text{Rh}_\text{I}$ — 8 Rh: 2.89(4), 2.95(2), 3.00	2.93
	$\text{Rh}_\text{II}$ — 8 Rh: 2.72(2), 2.78(2), 2.89(2), 2.95, 3.00	2.84
	$\text{Rh}_\text{III}$ — 7 Rh: 2.72(2), 2.87, 2.89(2), 2.89(2)	2.84
Rh—Si and Rh—Ge distances		
$\text{Rh}_2\text{Si}$	Si — 10 Rh: 2.41, 2.42, 2.44(2), 2.47(2), 2.47, 2.80(2), 3.03	2.58
$\text{Rh}_2\text{Ge}$	Ge — 10 Rh: 2.46, 2.47, 2.49(2), 2.50(2), 2.57, 2.83(2), 3.00	2.61
$\text{Rh}_5\text{Si}_3$	$\text{Si}_\text{I}$ — 8 Rh: 2.33(2), 2.40(4), 2.66(2)	2.45
	$\text{Si}_\text{II}$ — 10 Rh: 2.37, 2.41(2), 2.49, 2.53(2), 2.76(2), 2.85, 3.02	2.61
$\text{Rh}_5\text{Ge}_3$	$\text{Ge}_\text{I}$ — 8 Rh: 2.41(2), 2.45(4), 2.71(2)	2.51
	$\text{Ge}_\text{II}$ — 10 Rh: 2.44, 2.46(2), 2.51, 2.60(2), 2.78(2), 2.92, 3.06	2.66

Fig. 1. The environment of the Si atom in  $\text{Ru}_2\text{Si}$  (a) and  $\text{Rh}_2\text{Si}$  (b).



and silicon. (It should be pointed out that the value of 2.44 Å given by Geller for one of the Rh—Ge distances in  $\text{Rh}_5\text{Si}_3$  is incorrect. The correct value is 3.06 Å).

The interatomic distances in  $\text{Rh}_2\text{Si}$  are similar to those found in other phases with the C23 structure type. There are some differences in detail, however. In  $\text{Ru}_9\text{Si}$  the silicon atoms are surrounded by ten ruthenium atoms at distances between 2.45–2.84 Å, (see Fig. 1a), while in  $\text{Rh}_2\text{Si}$  the silicon atoms have nine metal atoms at distances between 2.41–2.80 Å and the tenth at a distance of 3.03 Å (Fig. 1b). A similar tendency for a reduction in the number of close metal neighbours about silicon is also found on passing from  $\text{Co}_2\text{Si}$ <sup>11</sup> to  $\text{Ni}_2\text{Si}$  (C23-type)<sup>12</sup>.

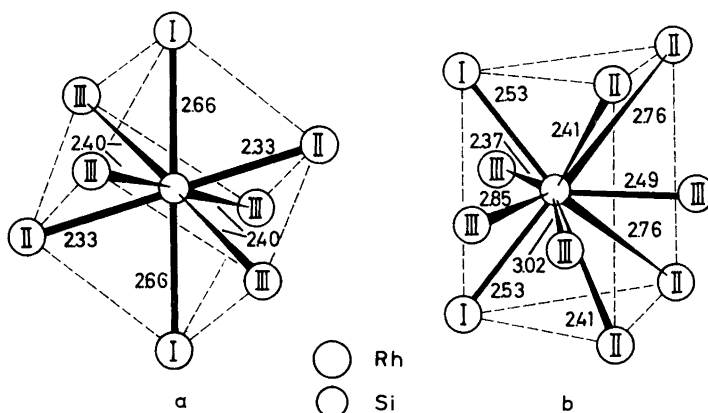


Fig. 2. The environment of the  $\text{Si}_I$  atom in  $\text{Rh}_5\text{Si}_3$  (a) and the environment of the  $\text{Si}_{II}$  atom in  $\text{Rh}_5\text{Si}_3$  (b). (The Roman numerals refer to the notations for the different crystallographic positions of the metal atoms).

The present work has shown that the interatomic distances in  $\text{Rh}_2\text{Si}$  and the alleged  $\text{Rh}_2\text{B}$ -phase are identical within the limits of experimental error. This supports the suggestion made by Aronsson *et al.*<sup>3</sup> that the  $\text{Rh}_2\text{B}$  crystals studied by Mooney and Welch<sup>13</sup> were in fact crystals of  $\text{Rh}_2\text{Si}$ .

With regard to the form of the coordination polyhedron and the Rh—Si interatomic distances, the environment of the  $\text{Si}_{II}$  atoms in  $\text{Rh}_5\text{Si}_3$  (Fig. 2b) is similar to that of the Si atoms in  $\text{Rh}_2\text{Si}$ . The  $\text{Si}_I$  atoms in  $\text{Rh}_5\text{Si}_3$  (Fig. 2a) have a slightly distorted cubic environment of metal atoms.

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