

## The Crystal Structure of $Rh_4Si_5$ and its Relation to Other Members of the MnP Structure Family

INGVAR ENGSTRÖM

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

The crystal structure of  $Rh_4Si_5$  has been determined and refined from single crystal X-ray data. The monoclinic unit cell has the following dimensions:  $a=12.335$  Å,  $b=3.508$  Å,  $c=5.924$  Å, and  $\beta=100.181^\circ$ . There are two formula units in the unit cell and the space-group is  $P2_1/m$ . All the atoms are situated in the twofold position 2(c).

The crystal structure of  $Rh_3Si_4$  is described and discussed in relation to the structure of  $Rh_3Si_4$  and the MnP structure family.

In their investigation of the rhodium-silicon system Bhan and Schubert<sup>1</sup> state that there exist three silicon-rich intermediate phases. The compositions of the phases were not established and the X-ray powder patterns were not interpreted. In the course of the study of the crystal structures of the rhodium silicides at this institute<sup>2-4</sup> a reinvestigation of the silicon-rich part of the Rh—Si system has been undertaken and the crystal structures of two silicon-rich rhodium-silicides have been determined. This paper gives an account of the structure of  $Rh_4Si_5$ , that of  $Rh_3Si_4$  having been described in a separate paper<sup>5</sup> in this journal.

Earlier investigations of the platinum metal silicides and germanides show that the structure element present in the MnP structure type is also present in structures differing from the 1:1 composition. As examples the structures of  $Pt_6Si_5$ <sup>6</sup> and  $Pt_3Ge_2$ <sup>1</sup> may be mentioned. The structures of  $Rh_4Si_5$  and  $Rh_3Si_4$  presented in this paper are non-metal-rich representatives of the same structure family.

### EXPERIMENTAL

*Preparation.* An alloy of the composition  $Rh_{14}Si_{10}$  was prepared by arc-melting rhodium metal powder (Heraeus, claimed purity 99.9 %) and silicon powder (Pechiney, claimed purity 99.9 %). After melting the alloy was annealed in an evacuated silica tube at about 950°C for fourteen days and at 1020°C for another fourteen days followed by quenching.

*Powder diffraction examination.* Powder photographs were recorded in a Guinier-Hägg type focussing camera using  $CuK\alpha_1$ -radiation ( $\lambda=1.54051$  Å). In addition to the diffrac-

Table 1. Programs used in performing the crystallographic calculations on a CDC 3600 computer. (All programs are written in FORTRAN IV).

Program	Authors
Least-squares refinement of unit cell dimensions.	J. Tegenfeldt, Uppsala, Sweden
Lorentz-polarization corrections. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Least-squares refinements of positional parameters, scale and temperature factors.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Interatomic distances.	A. Zalkin, Berkeley, U.S.A.

tion pattern of  $\text{Rh}_4\text{Si}_5$ , the powder photographs showed very weak diffraction lines from  $\text{RhSi}$  (MnP type). The cell dimensions were determined from the powder photographs with silicon as an internal calibration standard ( $a = 5.43054 \text{ \AA}$ ).

*Single crystal examination.* Single crystal diffraction patterns were recorded in an equi-inclination Weissenberg camera using Zr-filtered  $\text{MoK}\alpha$ -radiation. The single crystal fragment was rotated about the  $b$  axis. The intensities,  $I(hkl)$ , were recorded for  $k = 0, 1, \text{ and } 2$  using the multiple film technique with thin iron foils interleaved with the films. A calibrated intensity scale was used for the visual estimation of the intensities. In addition to the rotation about the  $b$  axis the crystal was rotated about the  $c$  axis and the intensities,  $I(hk0)$ , were recorded. No absorption correction was made.

*Calculations.* The unit cell dimensions of  $\text{Rh}_4\text{Si}_5$  were refined using the least-squares method. The atomic scattering and dispersion correction factors for rhodium and silicon were obtained from Ref. 7. The structure was refined using a full matrix least-squares program employing a weighting scheme. The weights,  $w$ , were calculated according to an equation suggested by Cruickshank *et al.*<sup>8</sup> as follows:  $w = 1/(a + |F_o| + c|F_o|^2)$ .  $a$  and  $c$  were given the values 30 and 0.01, respectively. All the calculations were carried out on a CDC 3600 electronic computer. Table 1 gives a list of the programs together with authors.

#### DETERMINATION OF THE CRYSTAL STRUCTURE OF $\text{Rh}_4\text{Si}_5$

The monoclinic symmetry of  $\text{Rh}_4\text{Si}_5$  was evident from the rotation and Weissenberg photographs obtained by rotating the crystal about both the  $b$  and  $c$  axes. The unit cell dimensions were determined from powder diffraction data. Systematic extinctions of  $0k0$ -reflections for  $k = 2n + 1$  confines the number of possible space-groups to two, *viz.*  $P2_1$  and  $P2_1/m$ . The fact that the  $b$  axis is very short and the intensities of the  $h0l$  layer reflections are distributed in the same way as those of the  $h2l$  layer favours the choice of  $P2_1/m$  as the most suitable space-group. This requires the atoms to be situated in the mirror planes.

The nominal composition of the sample was  $\text{Rh}_{42}\text{Si}_{58}$ . Usually there is a loss of about 3 at.-% Si during the arc-melting so the composition which was expected after the melting and heat-treatment was about  $\text{Rh}_{45}\text{Si}_{55}$ . As

Table 2. Observed and calculated structure factors of Rh<sub>4</sub>Si<sub>5</sub>. Reflections not included in the last cycles of the refinement are indicated with an asterisk.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
3	4	7	11	18.7	5	7	9	39.5	37.8					
4	7	9	31.1	29.5	6	7	9	32.4	34.1					
5	7	9	32.9	28.5	7	7	9	44.7	44.7					
6	7	9	20.1	20.1	8	7	9	70.7	70.7					
7	7	9	20.1	20.1	9	7	9	45.9	45.9					
8	7	9	16.6	16.6	10	7	9	42.1	42.1					
9	7	9	91.5	91.5	11	7	9	50.2	50.2					
10	7	9	16.4	16.4	12	7	9	44.6	44.6					
11	7	9	17.5	17.5	13	7	9	29.1	29.1					
12	7	9	16.4	16.4	14	7	9	17.3	17.3					
13	7	9	30.4	30.4	15	7	9	23.6	23.6					
14	7	9	33.5	33.5	16	7	9	43.5	43.5					
15	7	9	27.5	27.5	17	7	9	22.0	22.0					
16	7	9	27.5	27.5	18	7	9	26.8	26.8					
17	7	9	38.6	38.6	19	7	9	43.5	43.5					
18	7	9	37.1	37.1	20	7	9	29.0	29.0					
19	7	9	27.1	27.1	21	7	9	42.3	42.3					
20	7	9	37.1	37.1	22	7	9	67.0	67.0					
21	7	9	44.9	44.9	23	7	9	83.7	83.7					
22	7	9	54.9	54.9	24	7	9	71.6	71.6					
23	7	9	54.9	54.9	25	7	9	83.7	83.7					
24	7	9	76.3	76.3	26	7	9	61.3	61.3					
25	7	9	44.2	44.2	27	7	9	35.8	35.8					
26	7	9	10.1	10.1	28	7	9	21.5	21.5					
27	7	9	44.2	44.2	29	7	9	38.2	38.2					
28	7	9	85.0	85.0	30	7	9	61.3	61.3					
29	7	9	44.2	44.2	31	7	9	21.5	21.5					
30	7	9	58.8	58.8	32	7	9	38.2	38.2					
31	7	9	15.1	15.1	33	7	9	61.3	61.3					
32	7	9	15.1	15.1	34	7	9	41.0	41.0					
33	7	9	15.1	15.1	35	7	9	30.6	30.6					
34	7	9	15.1	15.1	36	7	9	47.8	47.8					
35	7	9	15.1	15.1	37	7	9	55.0	55.0					
36	7	9	15.1	15.1	38	7	9	33.3	33.3					
37	7	9	15.1	15.1	39	7	9	43.5	43.5					
38	7	9	15.1	15.1	40	7	9	23.2	23.2					
39	7	9	15.1	15.1	41	7	9	35.8	35.8					
40	7	9	15.1	15.1	42	7	9	43.5	43.5					
41	7	9	15.1	15.1	43	7	9	41.1	41.1					
42	7	9	15.1	15.1	44	7	9	35.8	35.8					
43	7	9	15.1	15.1	45	7	9	20.6	20.6					
44	7	9	15.1	15.1	46	7	9	35.8	35.8					
45	7	9	15.1	15.1	47	7	9	37.1	37.1					
46	7	9	15.1	15.1	48	7	9	23.6	23.6					
47	7	9	15.1	15.1	49	7	9	23.6	23.6					
48	7	9	15.1	15.1	50	7	9	23.6	23.6					
49	7	9	15.1	15.1	51	7	9	23.6	23.6					
50	7	9	15.1	15.1	52	7	9	23.6	23.6					
51	7	9	15.1	15.1	53	7	9	23.6	23.6					
52	7	9	15.1	15.1	54	7	9	23.6	23.6					
53	7	9	15.1	15.1	55	7	9	23.6	23.6					
54	7	9	15.1	15.1	56	7	9	23.6	23.6					
55	7	9	15.1	15.1	57	7	9	23.6	23.6					
56	7	9	15.1	15.1	58	7	9	23.6	23.6					
57	7	9	15.1	15.1	59	7	9	23.6	23.6					
58	7	9	15.1	15.1	60	7	9	23.6	23.6					
59	7	9	15.1	15.1	61	7	9	23.6	23.6					
60	7	9	15.1	15.1	62	7	9	23.6	23.6					
61	7	9	15.1	15.1	63	7	9	23.6	23.6					
62	7	9	15.1	15.1	64	7	9	23.6	23.6					
63	7	9	15.1	15.1	65	7	9	23.6	23.6					
64	7	9	15.1	15.1	66	7	9	23.6	23.6					
65	7	9	15.1	15.1	67	7	9	23.6	23.6					
66	7	9	15.1	15.1	68	7	9	23.6	23.6					
67	7	9	15.1	15.1	69	7	9	23.6	23.6					
70	7	9	15.1	15.1	70	7	9	23.6	23.6					

there were weak diffraction lines present from the MnP (*B31*) type of RhSi the composition of the new phase ought to be between Rh<sub>43</sub>Si<sub>57</sub> and Rh<sub>45</sub>Si<sub>55</sub>. Extrapolating the specific atomic volumes from rhodium silicides already known to the actual range of composition gave a unit cell content of about eighteen atoms. Thus the structure determination was initiated on the assumption that the atoms were situated in nine twofold positions, four of them occupied by rhodium and five by silicon atoms.

Using the  $F_o$ -values of the  $h0l$ -reflections the Patterson projection,  $P(UW)$ , was evaluated. In the analysis of the Patterson projection a set of atomic positions was found which explained all the maxima. The result was in good agreement with the initial assumptions made earlier.

From comparisons of the electron density projections  $\rho_{\text{obs}}(xz)$  and  $\rho_{\text{calc}}(xz)$  the atomic positions were improved by the back-shift method. The least-squares refinement of the structure parameters was based on 375 non-equivalent  $h0l$ -reflections and giving a reliability index of 0.123. In order to reduce extinction effects the 32 reflections with the strongest estimated intensities were omitted and the  $R$  value was reduced to 0.102. In the same time the standard deviations were reduced by about 10 %. In both cases the parameter shifts after the last cycle of the refinement were less than 0.1 % of the calculated standard deviations. In addition to the eighteen positional parameters, nine temperature factors and one scale factor were varied during the refinement. A final difference synthesis confirmed the correctness of the structure determination. The  $F_o$ - and  $F_c$ -values of the  $h0l$ -reflections are listed in Table 2. Table 3 gives final structural data of Rh<sub>4</sub>Si<sub>5</sub>.

Table 3.

Rh<sub>4</sub>Si<sub>5</sub>Space-group:  $P2_1/m$  ( $C_{2h}^2$ ),  $Z=2$ . $a = 12.335 \text{ \AA}$ ,  $\sigma(a) = 0.005 \text{ \AA}$ ,  $b = 3.508 \text{ \AA}$ ,  $\sigma(b) = 0.001 \text{ \AA}$ , $c = 5.924 \text{ \AA}$ ,  $\sigma(c) = 0.002 \text{ \AA}$ ,  $\beta = 100.181^\circ$   $\sigma(\beta) = 0.030^\circ$  $U = 252.23 \text{ \AA}^3$ .

Atom	Position	Position parameters and standard deviations				Isotr. temp. fact.	
		$x$	$\sigma(x)$	$z$	$\sigma(z)$	$B$	$\sigma(B)$
Rh <sub>I</sub>	2(c)	0.05022	0.00023	0.20598	0.00052	0.18	0.04
Rh <sub>II</sub>	»	0.27354	0.00022	0.10782	0.00051	0.21	0.04
Rh <sub>III</sub>	»	0.50051	0.00022	0.30142	0.00053	0.17	0.03
Rh <sub>IV</sub>	»	0.72970	0.00023	0.28419	0.00053	0.23	0.04
Si <sub>I</sub>	»	0.63625	0.00101	0.63951	0.00219	0.44	0.16
Si <sub>II</sub>	»	0.42151	0.00106	0.89332	0.00229	0.55	0.17
Si <sub>III</sub>	»	0.22434	0.00111	0.46715	0.00235	0.58	0.18
Si <sub>IV</sub>	»	0.14178	0.00102	0.98125	0.00222	0.43	0.16
Si <sub>V</sub>	»	0.92243	0.00094	0.48526	0.00210	0.32	0.14

Final  $R$  value = 0.102

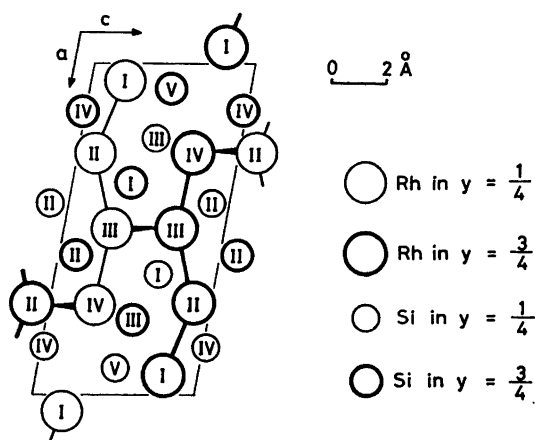


Fig. 1. The structure of  $\text{Rh}_4\text{Si}_5$  projected on the  $ac$  plane.

#### DESCRIPTION OF THE CRYSTAL STRUCTURE OF $\text{Rh}_4\text{Si}_5$

A projection along the monoclinic axis of the crystal structure of  $\text{Rh}_4\text{Si}_5$  is shown in Fig. 1. The notations used in the figure for different crystallographic positions correspond to those used in the Tables 3 and 5.

The atomic arrangement in the asymmetric unit of the unit cell is characterized by four rhodium atoms,  $\text{Rh}_I$ – $\text{Rh}_{IV}$ , arranged in a zigzag pattern perpendicular to the  $bc$  plane. The distances between these atoms varies between 2.83 and 2.91 Å. At a distance of  $b/2$  Å from the zigzag row of metal atoms in the direction of the  $b$  axis there are four silicon atoms,  $\text{Si}_I$ – $\text{Si}_{IV}$ , also in a zigzag arrangement. However, these silicon atoms are considerably more distant from each other than the metal atoms are. The distances between the silicon atoms are about 3.2 Å. The fifth silicon atom,  $\text{Si}_V$ , is situated along the extension of the zigzag row of metal atoms.

All rhodium atoms of  $\text{Rh}_4\text{Si}_5$  are surrounded by ten nearest neighbours. Six of them are always silicon atoms which occupy corners of deformed octahedra, whereas the remaining four atoms vary as regards the atomic species. Thus, the  $\text{Rh}_I$  and  $\text{Rh}_{IV}$  atoms have, besides the deformed silicon octahedron, three rhodium neighbours and one silicon neighbour. The  $\text{Rh}_{II}$  and  $\text{Rh}_{III}$  atoms both have four rhodium atoms as additional neighbours.

The number of nearest neighbours around the silicon atoms varies between seven and nine. The  $\text{Si}_I$  and  $\text{Si}_{II}$  atoms both are surrounded by six rhodium atoms at the corners of irregular prisms and two silicon atoms outside the plane through one of the triangular faces of the prism. The coordination polyhedron about the  $\text{Si}_{III}$  atom is of about the same shape as the one just mentioned, but two of the metal atoms at the corners of the prism are replaced by silicon atoms. The  $\text{Si}_{IV}$  atom is surrounded by five rhodium and one silicon atom in a triangular prismatic arrangement, with an additional rhodium atom outside one of the triangular faces. The highest coordination number

Table 4. Interatomic distances with standard deviations in Rh<sub>4</sub>Si<sub>5</sub>. (In Ångström units. Only distances shorter than 3.7 Å are listed).

	Atoms	Dist.	St.dev.		Atoms	Dist.	St.dev.	
Rh <sub>I</sub>	— Rh <sub>II</sub>	2.914	0.004	Si <sub>II</sub>	— Si <sub>II</sub>	3.269	0.018	
	— 2 Rh <sub>I</sub>	3.082	0.005		— 2 Si <sub>II</sub>	3.455	0.016	
	— 2 Rh <sub>I</sub>	3.508	0.001		— 2 Si <sub>I</sub>	3.508	0.001	
	— Si <sub>III</sub>	2.415	0.014		— 2 Si <sub>II</sub>	3.571	0.016	
	— Si <sub>IV</sub>	2.431	0.013		— 2 Rh <sub>III</sub>	2.393	0.009	
	— Si <sub>V</sub>	2.479	0.012		— Rh <sub>II</sub>	2.401	0.013	
	— 2 Si <sub>V</sub>	2.513	0.009		— Rh <sub>III</sub>	2.442	0.014	
	— 2 Si <sub>IV</sub>	2.580	0.010		— 2 Rh <sub>IV</sub>	2.640	0.010	
	Rh <sub>II</sub>	— Rh <sub>III</sub>	2.832		0.004	— 2 Si <sub>II</sub>	2.749	0.020
		— 2 Rh <sub>IV</sub>	2.905		0.003	— Si <sub>III</sub>	3.181	0.019
— Rh <sub>I</sub>		2.914	0.004	— Si <sub>I</sub>	3.269	0.018		
— 2 Rh <sub>II</sub>		3.508	0.001	— 2 Si <sub>I</sub>	3.455	0.016		
— Si <sub>III</sub>		2.314	0.014	— 2 Si <sub>II</sub>	3.508	0.001		
— Si <sub>II</sub>		2.401	0.013	— 2 Si <sub>I</sub>	3.571	0.016		
— 2 Si <sub>IV</sub>		2.418	0.009	Si <sub>III</sub>	— 2 Rh <sub>IV</sub>	2.296	0.009	
— 2 Si <sub>I</sub>		2.442	0.009	— Rh <sub>II</sub>	2.314	0.014		
Rh <sub>III</sub>		— Rh <sub>II</sub>	2.832	0.004	— Rh <sub>I</sub>	2.415	0.014	
		— Rh <sub>IV</sub>	2.847	0.004	— 2 Si <sub>V</sub>	2.572	0.013	
	— 2 Rh <sub>III</sub>	2.936	0.005	— 2 Si <sub>I</sub>	2.611	0.014		
	— 2 Rh <sub>III</sub>	3.508	0.001	— Si <sub>II</sub>	3.181	0.019		
	— Si <sub>I</sub>	2.373	0.013	— 2 Si <sub>IV</sub>	3.371	0.016		
	— 2 Si <sub>II</sub>	2.393	0.009	— 2 Si <sub>III</sub>	3.508	0.001		
	— Si <sub>II</sub>	2.442	0.014	Si <sub>IV</sub>	— 2 Rh <sub>II</sub>	2.418	0.009	
	— 2 Si <sub>I</sub>	2.501	0.009	— Rh <sub>IV</sub>	2.422	0.013		
	Rh <sub>IV</sub>	— Rh <sub>III</sub>	2.847	0.004	— Rh <sub>I</sub>	2.431	0.013	
		— 2 Rh <sub>II</sub>	2.905	0.003	— 2 Rh <sub>I</sub>	2.580	0.010	
— 2 Rh <sub>IV</sub>		3.508	0.001	— Si <sub>V</sub>	2.737	0.018		
— 2 Si <sub>III</sub>		2.296	0.009	— Si <sub>I</sub>	3.220	0.018		
— Si <sub>IV</sub>		2.422	0.013	— 2 Si <sub>III</sub>	3.371	0.016		
— Si <sub>V</sub>		2.464	0.012	— Si <sub>V</sub>	3.391	0.018		
— Si <sub>I</sub>		2.572	0.013	— 2 Si <sub>IV</sub>	3.508	0.001		
— 2 Si <sub>II</sub>		2.640	0.010	Si <sub>V</sub>	— Rh <sub>IV</sub>	2.464	0.012	
Si <sub>I</sub>		— Rh <sub>III</sub>	2.573	0.013	— Rh <sub>I</sub>	2.479	0.012	
		— 2 Rh <sub>II</sub>	2.442	0.009	— 2 Rh <sub>I</sub>	2.513	0.009	
	— 2 Rh <sub>III</sub>	2.501	0.009	— 2 Si <sub>III</sub>	2.572	0.013		
	— Rh <sub>IV</sub>	2.572	0.013	— 2 Si <sub>V</sub>	2.579	0.017		
	— 2 Si <sub>III</sub>	2.611	0.014	— Si <sub>IV</sub>	2.737	0.018		
	— Si <sub>IV</sub>	3.220	0.018	— Si <sub>IV</sub>	3.391	0.018		
				— 2 Si <sub>V</sub>	3.508	0.001		

displayed by a silicon atom, *i.e.* nine, is exhibited by the Si<sub>V</sub> atoms. Here the corners of the triangular prism are occupied by three rhodium atoms and three silicon atoms whereas the remaining three atoms, all of which are silicon, are situated outside the triangular faces of the prism. Two of them are situated outside one of the triangular faces and one outside the other triangular face.

The following can be noticed with respect to the interatomic distances in  $\text{Rh}_4\text{Si}_5$ . The average of fourteen short Rh—Rh distances is about 2.94 Å or about the same as in  $\text{Rh}_3\text{Si}_4$  and 10 % more than the Rh—Rh distance in rhodium metal. The average Rh—Si distance is also about the same as in  $\text{Rh}_3\text{Si}_4$ , *i.e.* 2.47 Å. The shortest Rh—Si and Si—Si distances are 2.30 and 2.57 Å, respectively. The latter two distances are the shortest found in any of the rhodium silicides at present known.

The interatomic distances in  $\text{Rh}_4\text{Si}_5$  together with their standard deviations are given in Table 4.

#### A STRUCTURAL COMPARISON BETWEEN $\text{RhSi}$ (MnP-TYPE), $\text{Rh}_4\text{Si}_5$ AND $\text{Rh}_3\text{Si}_4$

The two new rhodium silicides,  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$ , are composed of structure elements which are very similar. Structurally the compounds can be classified among those of the MnP (*B31*) structure family. In order to facilitate the comparison between the structures of  $\text{RhSi}$  (MnP type),  $\text{Rh}_4\text{Si}_5$ , and  $\text{Rh}_3\text{Si}_4$  a schematic representation is presented in Fig. 2. In the following text the same choice of crystallographic axes is made as in the figure. The lines joining metal atoms in the figure are only for the purpose of emphasizing special features of the three structures.

The characteristic building unit of the MnP structure type is the strongly deformed triangular prismatic arrangement of metal atoms about the non-metal atoms. Following the notation used in Fig. 2a the structure of  $\text{RhSi}$  (MnP type) can be symbolically described by  $nA$ , which reflects the infinite repetition of the characteristic structure element in the direction perpendicular to the *bc* plane. In  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$  the same basic arrangement is to

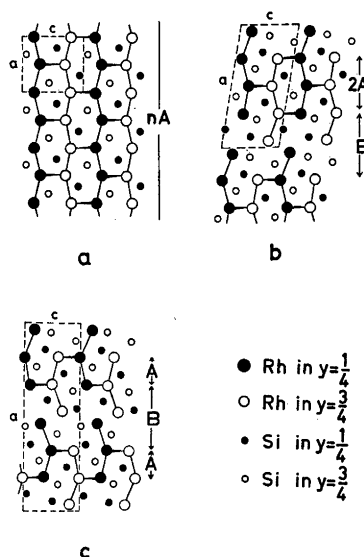


Fig. 2. Schematic representations of the structures of (a)  $\text{RhSi}$  (MnP type), (b)  $\text{Rh}_4\text{Si}_5$  and (c)  $\text{Rh}_3\text{Si}_4$  projected on their *ac* planes. The notations used in the figures are explained in the text.

be found, but here the extension of the  $A$  elements is finite. Instead there is in  $\text{Rh}_4\text{Si}_5$  a different structure element, denoted  $B$ , between every double layer of the structure element  $A$  (Fig. 2b). In  $\text{Rh}_3\text{Si}_4$  the structure can be described as composed of alternating structure elements  $A$  and  $B$  in the direction perpendicular to the  $bc$  plane (Fig. 2c). The structures of  $\text{RhSi}$  (MnP type),  $\text{Rh}_4\text{Si}_5$ , and  $\text{Rh}_3\text{Si}_4$  can then be described as  $AAAAA\dots$ ,  $2A B 2A B 2A B\dots$ , and  $A B A B' A B A B' A\dots$ , respectively. The notation  $B'$  symbolizes an atomic arrangement of the same kind as  $B$  but with an orientation which is the mirror image of  $B$ .

It is obvious that a whole series of structure types can be formed by varying the number of  $A$  elements between two subsequent  $B$  elements. The general formula of such a series will be  $\text{Me}_n\text{X}_{n+1}$ . The structures of  $\text{Rh}_3\text{Si}_4$  and  $\text{Rh}_4\text{Si}_5$  represent the members of the series where  $n=3$  and  $4$ , respectively, and  $\text{RhSi}$  (MnP type) the limiting case when  $n=\infty$ . The hypothetical series of homologous structures can be divided into two sub-groups depending on the number  $n$  in the general formula. When  $n$  is an even number the corresponding members of the series, composed of  $A$  and  $B$  elements, have monoclinic symmetry and the same space-group as  $\text{Rh}_4\text{Si}_5$ . For odd numbers of  $n$  the corresponding members of the series, composed of  $A$ ,  $B$ , and  $B'$  elements, can be described with the same orthorhombic space-group as  $\text{Rh}_3\text{Si}_4$ . For  $n=2$  the typical MnP element  $A$  will disappear and the structure loses the characteristic feature of the series, implying a structure type composed of  $B$  elements only. Until now there is only one representative found, *viz.*  $\text{Pt}_2\text{Ge}_3$ ,<sup>1</sup> which has structural features somewhat reminiscent of the structure type expected for the member  $\text{Me}_2\text{X}_3$  of the series. Unfortunately, the structure of  $\text{Pt}_2\text{Ge}_3$  has only been determined in outline, and a new structure determination has been undertaken at this institute in order to elucidate the atomic arrangement in detail. The result of the structure determination will be the subject of a future paper in this journal.

The structural properties of the MnP type ( $B31$ ) phases have been dealt with in detail by Schubert.<sup>9</sup> According to this description, the MnP structure family is divided into two groups depending on whether the axial ratio  $c/b$  is larger or smaller than  $\sqrt{3}$ . (The deviation from  $\sqrt{3}$  indicates the distortion of the MnP structure type from the ideal NiAs type). According to Schubert the structures with  $c/b > \sqrt{3}$  have lower electron concentrations than those with  $c/b < \sqrt{3}$ . In the structures of  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$  the  $b$  and  $c$  axes are to some extent comparable with the  $b$  and  $c$  axes of  $\text{RhSi}$  (MnP type). If the  $c/(b\sqrt{3})$  is calculated for the compounds  $\text{RhSi}$ ,  $\text{Rh}_4\text{Si}_5$ , and  $\text{Rh}_3\text{Si}_4$  the values obtained are: 1.20, 0.98, and 0.93, respectively. The value for  $\text{RhSi}$  is characteristic for compounds with low electron concentrations whereas the values for the other two compounds are characteristic for compounds with high electron concentrations. Considering only the distortions of the triangular prisms of the three structures, *i.e.* the  $A$  elements in Fig. 2a–2c, it is evident that the distortions of  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$  on the one hand and  $\text{RhSi}$  on the other have occurred in different directions in relation to the ideal arrangement represented by the NiAs structure type.



If the variation of the axial ratio  $c/b$  is applicable to the whole series of hypothetical structures mentioned above and only members with large  $n$ 's are taken into consideration the effects described below would be observed in X-ray powder patterns. Changes of the  $b$  and  $c$  axes from one member to another give deviations of the positions of the  $Ok\ell$  reflections. Taking this together with the fact that the diffraction lines belonging to the super-cell only will be very weak, if the number  $n$  in the general formula of the series,  $\text{Me}_n\text{X}_{n+1}$ , is very large, the effect may be misinterpreted as an extended homogeneity region of the MnP structure type.

Until now the discussion of the structures of  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$  has dealt with the similarities between them and the MnP structure type. There are, however, important differences to be considered. The arrangement of the non-metal atoms in a zigzag row in the MnP structure type is also found in the new rhodium silicides, but in addition there is another kind of arrangement for the silicon atoms which is novel. From Figs. 2b and 2c it is evident that there exist planes of silicon atoms in the structures. The planes are parallel to the  $b$  axis and they have an infinite extension in this direction. In the projection plane  $ac$  there are six silicon atoms in an almost straight line. Within the planes with the square-shaped arrangement of silicon atoms the interatomic distances are almost constant at about 2.60 Å. This distance exceeds the "single bond" distance in silicon by about 10 %. A certain interaction cannot be disregarded but the conditions are not very different from those in the MnP structure type where an interaction is also considered to be present.

Finally the differences in coordination numbers of the silicon atoms in  $\text{Rh}_4\text{Si}_5$  and  $\text{Rh}_3\text{Si}_4$  can be commented. As was pointed out by Aronsson *et al.*<sup>10</sup> the silicon atom is capable of "metallic behaviour" in many transition metal silicides. In the two new silicides of rhodium the coordination number of silicon varies between seven and nine, whereas the number of atoms surrounding the metal atoms is always ten. The highest coordination number of all silicon atoms in the two structures is exhibited by the silicon atoms which form a supposed extension of the zigzag row of metal atoms. These silicon atoms occupy positions having "metallic character" in the sense discussed by the above authors.

*Acknowledgements.* I wish to express my gratitude to Professor G. Hägg for all the facilities placed at my disposal. I also want to thank Dr. S. Rundqvist for stimulating interest and valuable advice. The work has been supported financially by the *Swedish Natural Science Research Council*.

#### REFERENCES

1. Bhan, S. and Schubert, K. *Z. Metallk.* **51** (1960) 327.
2. Engström, I. *Acta Chem. Scand.* **17** (1963) 775.
3. Engström, I. *Acta Chem. Scand.* **19** (1965) 1924.
4. Engström, I. and Johnsson, T. *Acta Chem. Scand.* **19** (1965) 1508.
5. Engström, I. and Persson, E. *Acta Chem. Scand.* **22** (1968) 3120.
6. Gohle, R. and Schubert, K. *Z. Metallk.* **55** (1964) 503.

7. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
8. Cruickshank, D. W., Philling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Oxford, Pergamon 1961, p. 32.
9. Schubert, K. *Kristallstrukturen zweikomponentiger Phasen*, Springer, Berlin, Göttingen, Heidelberg 1964.
10. Aronsson, B., Lundström, T. and Rundqvist, S. *Borides, Silicides and Phosphides*, Methuen, London, and Wiley, New York 1965.

Received May 4, 1968.