ACTA CHEMICA SCANDINAVICA 19 (1965) 1924–1932

The Crystal Structure of $Rh_{20}Si_{13}$

INGVAR ENGSTRÖM

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of $Rh_{20}Si_{13}$ has been determined and refined by X-ray single crystal methods. The crystals are hexagonal with unit cell dimensions $a = 11.851$ Å and $c = 3.623$ Å. There is one formula unit in the unit cell. The refinement of the structure is based on the space-group $P6_3/m$ with the atoms in the following positions: 18 rhodium atoms and 12 silicon atoms in five sets of 6(*h*), 2 rhodium atoms in 2(*c*) and one silicon atom in the half-filled position 2(*b*). As the sites (000) and (00½) in the last-mentioned position are separated by only 1.81 Å they are assumed to be randomly occupied by one silicon atom.

The structure of $Rh_{20}Si_{13}$ is described and the atomic arrangement is discussed in relation to the atomic arrangement in Th_7S_{12} and Fe_2P, which can be considered as members of the same series of homologous structures as $Rh_{20}Si_{13}$.

In a previous paper[1] dealing with rhodium silicides a new phase with the approximate composition $Rh_{\sim 1.5}Si$ was reported. The crystal structure of this phase has now been determined and its chemical composition established as $Rh_{20}Si_{13}$.

EXPERIMENTAL

Preparation. Alloys were prepared by arc-melting rhodium metal powder (Heraeus, claimed purity 99.9 %) and silicon powder (Pechiney, claimed purity 99.9 %). The arc-melted alloys were annealed in evacuated silica tubes at about 1100°C for fourteen days and then quenched.

Powder diffraction examination. Powder photographs of the sample used for the single crystal examination were recorded in a Guinier-Hägg focussing camera using Cu-$K\alpha$-radiation. Silicon was used as internal calibration standard ($a = 5.4305$ Å). In addition to the reflections of $Rh_{20}Si_{13}$ weak reflections were observed indicating the presence of small amounts of a second phase not yet identified. The cell dimensions were determined to an accuracy of about 0.1 %.

Single crystal examination. A single crystal fragment was selected from an alloy prepared as mentioned above. The cross section of the fragment measured roughly 0.04 × 0.07 mm perpendicular to the *c*-axis. Single crystal diffraction patterns were recorded in an equi-inclination Weissenberg camera with the *c*-axis as the rotation axis. Intensities for the layer lines $l = 0$ and $l = 1$ were recorded using Nb-filtered Mo-K radiation. The multiple film method was employed with thin iron foils interleaved between the films. The intensities were estimated by visual comparison with a calibrated intensity scale. A total of 188 independent $hk0$ and 108 independent $hk1$ reflections was measured.

Calculation. In the structure factor calculation the atomic scattering factors of silicon and rhodium were obtained from Ref. 2. The real part of the dispersion correction factors given in the same reference were included in these calculations. The structure was refined by the method of least squares employing a weighting scheme according to Cruickshank[3] *et al.*, $w = 1/(a + |F_o| + c|F_o|^2)$, where the weighting constants a and c were given the values 20.0 and 0.006, respectively. The electronic computers and programmes used for the various calculations are listed below.

Type of computer	Kind of calculation	Computer program
BESK and FACIT EDB	Lorentz and polarization factor corrections.	Ref. 4
	Structure factor calculations.	Ref. 5 No. 6015
	Summation of Fourier series.	Ref. 5 No. 6014
	Calculations of interatomic distances.	Ref. 5 No. 6016
IBM 1620	Calculation of weighting-factors.	Ref. 6
IBM 7090	Least squares refinement.	Ref. 5 No. 360

DETERMINATION OF THE CRYSTAL STRUCTURE

Single crystal intensity data for $Rh_{20}Si_{13}$ were recorded with the c-axis as the rotation axis. The crystals have the Laue symmetry $6/m$ and no systematic absences were observed for hkl reflections recorded in the Weissenberg camera. A possible systematic extinction was indicated by the powder photographs from which the 001 and 003 reflections were absent while 002 appeared strong; this effect is consistent with the operation of a 6_3 symmetry axis.

Inspection of the zero and second layer lines showed that the intensity distribution for the $hk0$ and $hk2$ reflections were the same. This indicates strongly that the atomic positions are confined to two planes perpendicular to c and spaced $c/2$ apart. Using only $F_0{}^2$-values for $hk0$ and $hk1$, the two Patterson sections $P(UV0)$ and $P(UV\frac{1}{2})$ were evaluated.

In the analysis of the Patterson sections the following preliminary consideration was made. For determining the positions of those atoms which are not situated on the sixfold or threefold symmetry axes, the most profitable attack appears to be an analysis of the Patterson function in the terms of the threefold positions in the space group $P\bar{6}$. This line of attack should cover all alternatives presented in the remaining possible space-groups $P6$, $P6/m$, $P6_3$ and $P6_3/m$.

Eventually, a set of atomic positions was found, which was capable of accounting for the positions and heights of all maxima observed in the two Patterson sections. This structure proposal involved 9 Rh atoms in three sets of $3(j)$ position, 9 Rh atoms in three $3(k)$ positions, 6 Si in two $3(j)$ positions and 6 Si in two $3(k)$ positions. Furthermore, Rh atoms also occupied the positions $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$ and $(\frac{1}{3},\frac{2}{3},0)$. The atomic arrangement was found to correspond very closely to the higher symmetry of the space-group $P6_3/m$ (or $P6_3$), while the space-groups $P6$ and $P6/m$ were definitely excluded.

On the basis of the proposed structure an electron density projection on (001) was calculated. This projection contained maxima with the expected positions and heights, but in addition a peak appeared at the origin with a height of the same magnitude as the silicon maxima in the projection.

For spatial reasons occupancy of the positions on the hexagonal axis in the same plane as the surrounding rhodium atoms is not possible. Furthermore, the absence of corresponding peaks in the two Patterson sections excludes this possibility. The remaining possibility is the occupation of the two octahedral holes on the hexagonal axis formed by the rhodium atoms closest to the axis. The occupation of these two positions presents a considerable packing problem since, owing to the short c dimension of the unit cell the positions $(0,0,\frac{1}{4})$ and $(0,0,\frac{3}{4})$ have a separation of only 1.81 Å. Simultaneous occupation of both positions by silicon atoms is accordingly impossible since the separation is less than the atomic diameter.

At this stage of the determination of the structure the following can be stated:

1. Nothing in the diffraction pattern argues for a larger unit cell.
2. No evidence could be found for a lower Laue symmetry than $6/m$.
3. An ordered occupation of the positions on the hexagonal axis does not agree with theoretical space-group considerations.

The three observations can be accounted for in the following way. For spatial reasons, a completely random occupation of a fraction of the octahedral holes along the hexagonal axis is impossible, since this would imply at least some Si—Si distances as short as 1.81 Å. Such short contacts can be avoided, however, if the two octahedral holes adjacent to each silicon atom are empty. This means that one half of the octahedral holes can be occupied by silicon atoms by assuming that the silicon atoms are located to either $(0,0,\frac{1}{4})$ or $(0,0,\frac{3}{4})$ exclusively along one and the same hexagonal axis. Since it appears equally probable that silicon atoms are located in $(0,0,\frac{1}{4})$ as in $(0,0,\frac{3}{4},)$ the occupation of these positions on different hexagonal axes should be completely random.

After a least-squares refinement of the positional parameters of the atoms arranged according to the symmetry of the space-group $P\bar{6}$ the R-value obtained was 0.106. The atomic parameters corresponded so closely to the operation of a 6_3 axis that the higher symmetry, $P6_3/m$, was obvious.

Arranging the atoms of $Rh_{20}Si_{13}$ on the basis of the space-group $P6_3/m$, 18 Rh and 12 Si atoms occupy five sets of the sixfold position $6(h)$. Two Rh atoms occupy the twofold position $2(c)$ and one Si atom is in the half-filled position $2(b)$. The two sites of the position $2(b)$, though occupied to an undetermined extent by silicon atoms, have been assumed to be occupied by half a silicon atom each.

The structure, based on the space-group $P6_3/m$, was refined using the least squares method for crystal structure refinements. Six of the 296 independent reflections were omitted from the refinement because of extinction effects, and are not included in the final R-value quoted below. After the final refinement the shifts of the 13 parameters varied were less than 2 % of the standard deviation. In addition to the positional parameters, two scale factors and one temperature factor were refined. The result of the structure determination is given in Table 1.

Table 1.

$Rh_{20}Si_{13}$

Space-group: $P6_3/m$ (C_{6h}^2), $Z = 1$. $a = 11.851$ Å, $c = 3.623$ Å, $U = 440.7$ Å^3.

Atom	Position	Position parameters and standard deviations			
		x	$\sigma(x)$	y	$\sigma(y)$
$\mathrm{Rh_{I}}$	6 (h)	0.8124	0.0003	0.8157	0.0003
$\mathrm{Rh_{II}}$	6 (h)	0.5992	0.0003	0.8717	0.0003
$\mathrm{Rh_{III}}$	6 (h)	0.3900	0.0003	0.9287	0.0003
$\mathrm{Rh_{IV}}$	2 (c)				
$\mathrm{Si_{I}}$	6 (h)	0.7667	0.0011	0.1058	0.0011
$\mathrm{Si_{II}}$	6 (h)	0.5497	0.0011	0.1678	0.0011
$\mathrm{Si_{III}}$	2 (b) *				

* (Half-filled position, see the text). Overall temperature factor $B = 0.18$. $\sigma(B) = 0.02$. Final R-value $= 0.105$.

DESCRIPTION OF THE STRUCTURE

The structure of $\mathrm{Rh_{20}Si_{13}}$ is described with reference to Fig. 1, which illustrates the projection of the structure along the unique axis.

The unit cell of the structure, seen in a rough outline, is built up of two kinds of composite triangular prisms, mutually displaced $c/2$ in the [001] direction. Each composite prism contains ten metal atoms arranged so as to subdivide the prism into nine simple triangular prisms. Within each com-

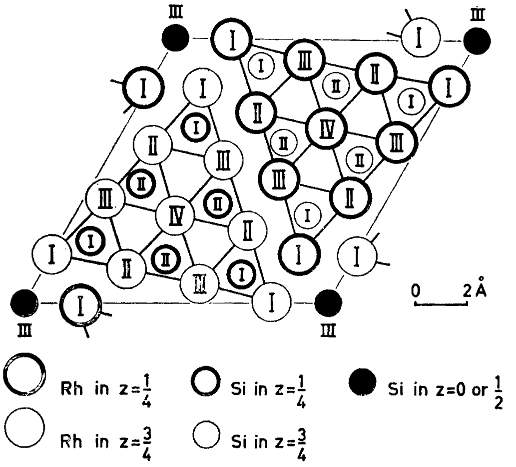

Fig. 1. Projection of the structure of $\mathrm{Rh_{20}Si_{13}}$ along [001]. (The Roman numerals refer to the notations for the different crystallographic positions used in the text).

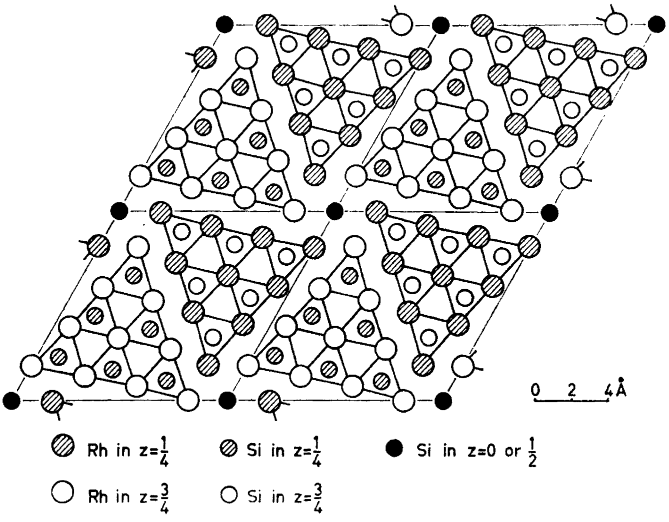

Fig. 2. Four unit cells of $Rh_{20}Si_{13}$ viewed along the sixfold axis.

posite prism the centres of six of the nine simple prisms are occupied by silicon atoms. Accordingly twelve of the thirteen silicon atoms in the unit cell have a triangular prismatic environment. The thirteenth silicon atom is situated on the unique axis, where it "links" together the six surrounding prismatic units (Fig. 2). The locations of the atom have already been discussed in detail in the preceding section.

The Rh_{IV} atoms of the structure are surrounded by six rhodium atoms in the same z-plane. These atoms form an almost regular hexagon. There are in addition six silicion atoms which form an equilateral triangular prism with the Rh_{IV} atom in the centre.

The Rh_{II} and Rh_{III} atoms have coordination polyhedra which are very similar. The atomic environment of these atoms consists of four rhodium atoms and one silicon atom in the same layer and in addition four rhodium and four silicon atoms from the adjacent layers above and below.

The fourth non-equivalent rhodium atom, Rh_{I} coordinates two rhodium atoms and one silicon atom from the same layer and six rhodium and three silicon atoms from the adjacent layers. One of these silicon atoms, Si_{III}, corresponds to the defect and disordered position 2(*b*).

Each of the three non-equivalent silicon atoms of the structure has a different type of coordination polyhedron. The Si_{II} atoms have a triangular prismatic environment of rhodium atoms and a further rhodium atom is situated outside the centre of one of the rectangular faces of the triangular prism. The Si_{I} atoms also have the prismatic coordination, but in this instance there are metal atoms outside the centre of two of the rectangular faces of the prism. The third non-equivalent silicon atom, Si_{III}, is situated at the centre of the triangular anti-prism formed by the Rh_{I} atoms. As has already been mentioned the two adjacent antiprismatic holes cannot be occupied simultaneously by silicon atoms; of the two antiprismatic holes in each unit cell only one of them is occupied on average. The formula $Rh_{20}Si_{13}$ corresponds to a situation in which exactly half the number of the antiprismatic holes are occupied by silicon atoms in a random way. Whether there is a tendency towards the formation of an extended homogeneity range depending on the variation of the silicon content has not yet been investigated.

Table 2. Interatomic distances in $Rh_{20}Si_{13}$. (Distance shorter than 3.5 Å are listed).

Rh_I	$-$ 4 Rh_I	: 2.85_6
	$-$ 3 Rh_{II}	: $2.88_4(2)$, 2.91_4
	$-$ 1 Rh_{III}	: 2.92_4
	$-$ 3 Si_I	: 2.39, 2.41(2)
	$-$ 1 Si_{III}	: 2.38
Rh_{II}	$-$ 3 Rh_I	: $2.88_4(2)$, 2.91_4
	$-$ 4 Rh_{III}	: 2.80_9, 2.87_9, $2.93_6(2)$
	$-$ 1 Rh_{IV}	: 2.85_9
	$-$ 3 Si_I	: 2.48, 2.51(2)
	$-$ 2 Si_{II}	: 2.41
Rh_{III}	$-$ 1 Rh_I	: 2.92_4
	$-$ 4 Rh_{II}	: 2.80_9, 2.87_9, $2.93_6(2)$
	$-$ 2 Rh_{III}	: 2.92_6
	$-$ 1 Rh_{IV}	: 2.82_9
	$-$ 2 Si_I	: 2.48
	$-$ 3 Si_{II}	: 2.44(2), 2.50
Rh_{IV}	$-$ 3 Rh_{II}	: 2.85_9
	$-$ 3 Rh_{III}	: 2.82_9
	$-$ 6 Si_{II}	: 2.52
Si_I	$-$ 3 Rh_I	: 2.39, 2.41(2)
	$-$ 3 Rh_{II}	: 2.48, 2.51(2)
	$-$ 2 Rh_{III}	: 2.48
	$-$ 2 Si_{II}	: 2.96, 3.01
Si_{II}	$-$ 2 Rh_{II}	: 2.41
	$-$ 3 Rh_{III}	: 2.44(2), 2.50
	$-$ 2 Rh_{IV}	: 2.52
	$-$ 2 Si_I	: 2.96, 3.01
	$-$ 2 Si_{II}	: 3.03
Si_{III}	$-$ 6 Rh_I	: 2.38

Table 2 gives the interatomic distances shorter than 3.5 Å. The Roman numerals used in the table correspond to the different crystallographic species according to the designation used earlier in the text and in Fig. 1.

STRUCTURAL RELATIONSHIPS BETWEEN THE Rh-Si PHASES

Until now, four intermediate phases of the Rh-Si-system have been investigated by single crystal X-ray methods. These are Rh_2Si,[1] Rh_5Si_3,[1] $Rh_{20}Si_{13}$ and RhSi (FeSi-type).[7] There are some similarities in the atomic arrangement in the different structure types and in addition there is a trend in the variation of the interatomic distances with chemical composition which is noteworthy.

In Rh_2Si the rhodium atoms coordinating silicon assume only one form of coordination polyhedron, namely triangular prismatic. Six rhodium atoms occupy the corners of the prism and another four rhodium atoms are located outside the rectangular faces. In Rh_5Si_3 two different types of silicon positions occur. The coordination polyhedron of one has roughly the same form as the triangular prismatic unit of Rh_2Si. The second silicon species has a distorted cubic environment of metal atoms.

In $Rh_{20}Si_{13}$ which demonstrates three non-equivalent silicon positions the rhodium atoms surrounding two of them exhibit the triangular prismatic coordination polyhedron. These two differ, however, in the number of metal atoms which are located outside the rectangular faces of the prism. The third non-equivalent silicon atom has an octahedral environment of metal atoms.

In the structure of RhSi(FeSi-type) the coordination polyhedra about both rhodium and silicon atoms can also be considered as triangular prismatic. The silicon atoms are surrounded by seven rhodium atoms, six of them occupy the corners of a triangular prism while the seventh lies outside the larger of the two triangular faces. The rhodium atoms are surrounded by silicon atoms in the same way as the silicon atoms are surrounded by rhodium atoms.

Different types of interatomic distances in Rh-Si phases are tabulated below (Table 3). Average distances have been obtained by taking mean-values of nearest neighbour distances. The numbers in parenthesis indicate the number of interatomic distances upon which the mean-values are based.

Table 3. Interatomic distances in Rh-Si phases.

	Rh_2Si	Rh_5Si_3	$Rh_{20}Si_{13}$	RhSi
Rh – Rh distances	2.80(16)	2.85(23)	2.88(20)	2.87(6)
Rh – Si »	2.58(10)	2.54(18)	2.44(21)	2.50(7)
Shortest Rh – Rh distance	2.76	2.75	2.81	2.87
» Rh – Si »	2.41	2.33	2.38	2.44
» Si – Si »	3.44	3.25	2.96	2.90

RELATIONSHIPS WITH OTHER STRUCTURE TYPES

An interesting feature of the structural architecture of $Rh_{20}Si_{13}$ is the highly regular WC-type stacking of Rh_6Si triangular prims into larger aggregates. It is possible to visualize a whole series of structures based on this theme with a varying number of subunits in the composite prisms. The general chemical formula of the members in this series can be written as $A_{n^2+n}B_{n^2-n+1}$. Thus the structure of $Rh_{20}Si_{13}$ is the member corresponding to $n = 4$ (see Fig. 2). For $n = 3$ the composition $A_{12}B_7$ is obtained and the representative structure type is that exhibited by Th_7S_{12}[8] (see Fig. 3). A comparison of the two structure types shows a striking similarity in the atomic arrangement. In Th_7S_{12} the ThS_6 triangular prisms correspond to the Rh_6Si triangular prisms of $Rh_{20}Si_{13}$. The disordered character of $Rh_{20}Si_{13}$ is also to be found in Th_7S_{12}. While in the silicide the antiprismatic octahedral holes are occupied by silicon atoms in a disordered way, the corresponding position in the sulphide is empty. Instead the disordered thorium atoms in the sulphide occupy the spaces between the octahedral holes. Thus in Th_7S_{12} the disordered atoms prefer, for some reason, the smaller triangular spaces between the octahedral holes. The structures of $Rh_{20}Si_{13}$ and Th_7S_{12} can be described on the basis of the same space group $P6_3/m$.

A further member of the series of structures is obtained when n is given the value 2. The chemical formula is then A_6B_3 or A_2B. The structure type corresponding to this member of the series is that of Fe_2P.[9] The unit cell of

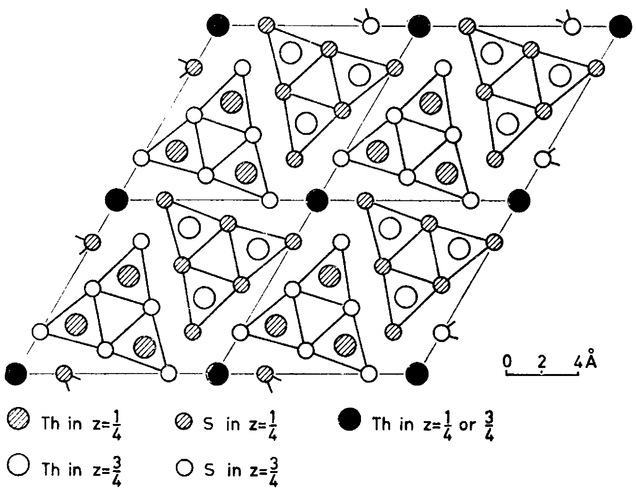

Fig. 3. Four unit cells of Th_7S_{12} viewed along the sixfold axis.

the Fe_2P type contains three formula units and may therefore be written as Fe_6P_3. This structure type differs from that of Th_7S_{12} as regards the size of the composite triangular prisms in the same way as Th_7S_{12} differs from $Rh_{20}Si_{13}$ (see Fig. 4). In this structure type the iron atoms form the triangular prisms and the phosphorus atoms occupy the prismatic holes. The atoms closest to the unique axis do not form antiprisms as in the two structure types already described. Instead, there is a triangular prismatic environment about the phosphorus atoms on the unique axis with a further three metal atoms lying outside the rectangular faces of the prism. (This triangular prism is indicated in Fig. 4). Disorder in Fe_2P of the same kind as that found in $Rh_{20}Si_{13}$ and Th_7S_{12} would probably lead to a structure with too high a degree of disorder. The structure of Fe_2P has a higher space-group symmetry than the other representatives of the series.

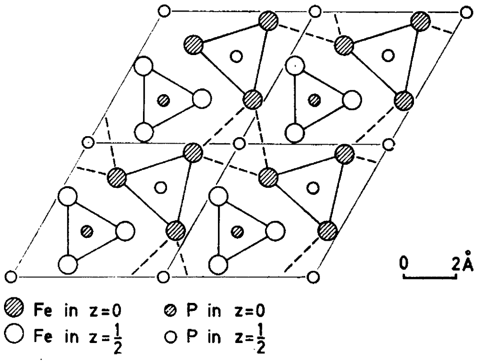

Fig. 4. Four unit cells of Fe_2P viewed along the sixfold axis.

From the general formula of the series of structures it is evident that when n increases the composition of the compound progressively approaches AB. The limiting composition to which the series converges exhibits the structure of the composite prisms which is that of WC.

Acknowledgement. I wish to thank Professor G. Hägg for his kind interest and for all facilities put at my disposal.

I also want to thank Dr. S. Rundqvist for valuable advice and stimulating discussions.

The work has been supported by the *Swedish Natural Science Research Council.* Facilities for use of the electronic computers BESK, FACIT and IBM 7090 were granted by the Computer Division of the *National Swedish Office for Administrative Rationalization and Economy.*

REFERENCES

1. Engström, I. *Acta Chem. Scand.* **17** (1963) 775.
2. *International Tables for X-ray Crystallography,* Vol. III. The Kynoch Press, Birmingham, England 1962.
3. Cruickshank, D.W.J., Philling, D.E., Bujosa, A., Lovell, F.M. and Truter, M.R. *Computing Methods and The Phase Problem,* Pergamon Press, Oxford 1961, p. 32.
4. Lundberg, B. The program "FLOYD". Available at BESK.
5. *IUCr World List of Crystallographic Computer Programs,* 1st Ed., Sept. 1962.
6. Lindgren, J. The program "VIKTOR". Available at IBM 1620.
7. Geller, S. and Wood, E.A. *Acta Cryst.* **7** (1954) 441.
8. Zachariasen, W.H. *Acta Cryst.* **2** (1949) 288.
9. Rundqvist, S. and Jellinek, F. *Acta Chem. Scand.* **13** (1959) 425.

Received July 6, 1965.