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The Crystal Structure of Rh_3Si_4

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The crystal structure of Rh_3Si_4 has been determined and refined by single crystal X-ray methods. The orthorhombic unit cell has the following dimensions: $a=18.810$ Å, $b=3.614$ Å, and $c=5.813$ Å. There are four formula units in the unit cell and all the atoms are situated in the fourfold position 4(*c*) of the space-group *Pnma*. The structure of Rh_3Si_4 is related to the MnP (*B*31) type.

In the rhodium-silicon system there exist at least two silicon-rich intermediate phases.[1] This paper gives an account of the structure determination of one of these, Rh_3Si_4. A discussion of the structure will be given in a separate paper [2] in this journal by one of the authors (I.E.).

EXPERIMENTAL

Preparation. An alloy of the nominal composition $Rh_{38}Si_{62}$ 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 and 1040°C for another two periods of fourteen days before quenching.

Powder diffraction examination. Powder photographs were recorded in a Guinier-Hägg type focussing camera. Cu$K\alpha_1$-radiation was used with silicon as internal calibration standard ($a=5.43054$ Å). The powder photographs showed only the diffraction pattern of Rh_3Si_4. The unit cell dimensions of the compound were determined from the powder photographs.

Single crystal examination. Single crystal diffraction patterns were recorded in an equi-inclination Weissenberg camera using Zr-filtered MoK-radiation. The single crystal fragment was rotated about the *b* axis. The intensities were recorded for $k=0$, 1, 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. No absorption correction was made.

Calculations. The unit cell dimensions of Rh_3Si_4 were refined using the least-squares method. The atomic scattering and dispersion correction factors for rhodium and silicon were obtained from Ref. 3. The structure was refined by the method of least-squares employing a weighting scheme. The weights, w, were calculated according to an equation suggested by Cruickshank *et al.*[4] as follows: $w=1/(a+|F_o|+c|F_o|^2)$. The values used for a and c were 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 used together with their authors.

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.

DETERMINATION AND REFINEMENT OF THE Rh_3Si_4 CRYSTAL STRUCTURE

The orthorhombic symmetry of Rh_3Si_4 was confirmed from the oscillation and Weissenberg photographs. The unit cell dimensions were determined from powder diffraction data and are given in Table 3.

No systematic extinctions of *hkl* reflections were observed, thus indicating that the unit cell of Rh_3Si_4 is primitive. As *hk*0 reflections were observed for $h=2n$ only and 0*kl* reflections for $k+l=2n$ only two space-groups are possible for the structure *viz.* *Pnma* and $Pn2_1a$. A striking similarity between the *h*0*l* and *h*2*l* layers and the fact that the *b* axis is very short indicates that the atomic arrangement in the unit cell is confined to two planes perpendicular to the *b* axis, with a spacing of *b*/2. In view of the characteristics of the structure given above the most probable space-group is *Pnma*, with all atoms situated in the mirror planes.

Taking into account the usual loss of about 3 at.-% of silicon during the arc-melting, the composition of the homogeneous sample could probably lie between the limits of about $Rh_{40}Si_{60}$—$Rh_{43}Si_{57}$. From the extrapolation of the average atomic volumes of rhodium-silicon compounds already known to the actual range of composition an approximate unit cell content could be obtained. The number of atoms in the unit cell was estimated to be about 28. At this stage the composition of the compound could be assumed to be Rh_3Si_4 with four formula units in the unit cell and the atoms occupying the fourfold position 4(*c*).

The short *b* axis and the suggested space-group makes it possible to determine all the positional parameters from a projection along [010]. The analysis of the Patterson projection, $P(UW)$, was complicated on account of a considerable overlapping of the Harker peaks by other peaks. Great similarities in the Patterson projections of Rh_3Si_4 and Rh_4Si_5 [2] were seen, and since the structure of the latter compound had recently been determined, it was possible to use it as a starting point in the structure determination of Rh_3Si_4.

Table 2. Observed and calculated structure factors of Rh_3Si_4. Reflections not included in the last cycles of the refinement are indicated with an asterisk.

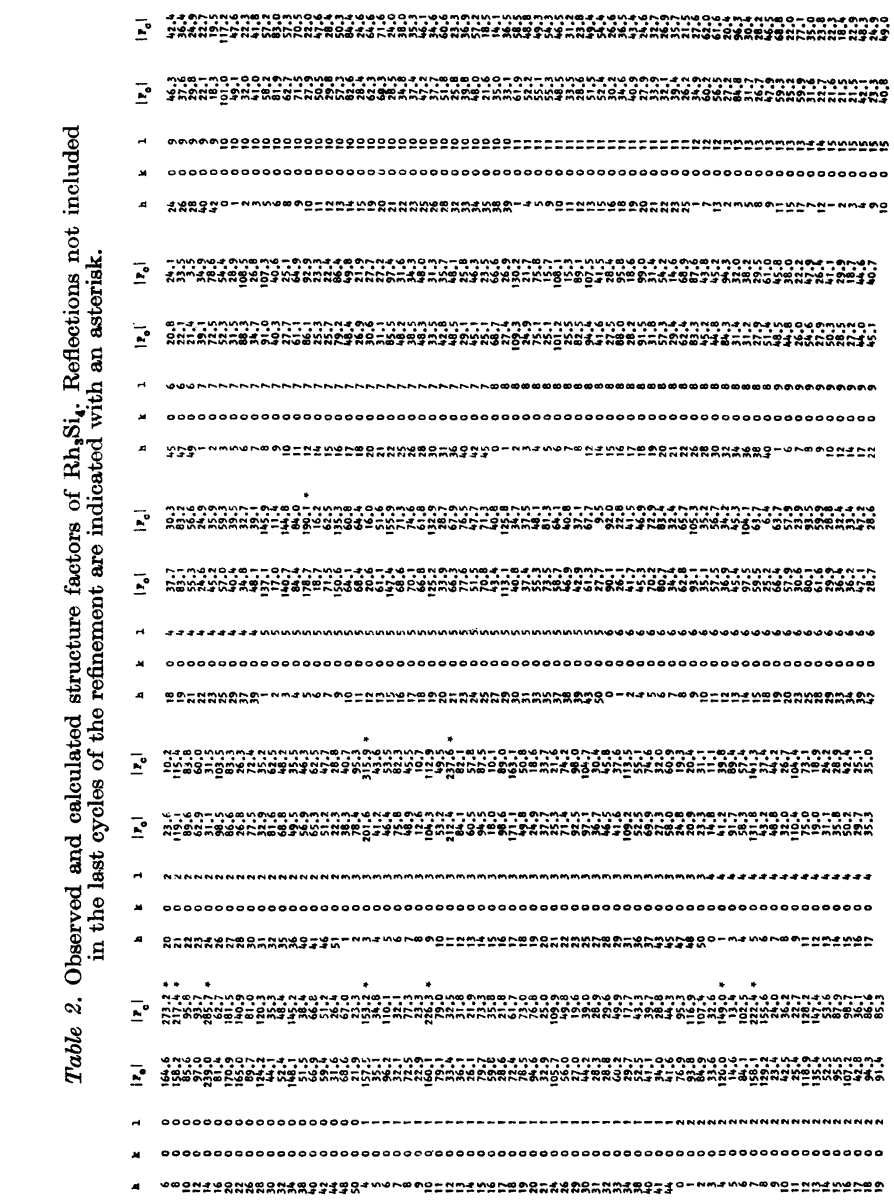

Table 3.

Rh_3Si_4

Space-group: *Pnma* (D_{2h}^{16}), $Z = 4$.
$a = 18.810$ Å, $\sigma(a) = 0.002$ Å, $b = 3.614$ Å, $\sigma(b) = 0.001$ Å,
$c = 5.813$ Å, $\sigma(c) = 0.001$ Å, $U = 395.17$ Å^3.

Atom	Position	Position parameters and standard deviations				Isotr. temp. factor	
		x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Rh_I	4(*c*)	0.03206	0.00011	0.18556	0.00037	0.27	0.03
Rh_{II}	4(*c*)	0.17634	0.00011	0.00325	0.00033	0.22	0.03
Rh_{III}	4(*c*)	0.32534	0.00011	0.11571	0.00033	0.19	0.02
Si_I	4(*c*)	0.14372	0.00049	0.38705	0.00149	0.39	0.11
Si_{II}	4(*c*)	0.23145	0.00041	0.21954	0.00127	0.20	0.09
Si_{III}	4(*c*)	0.40930	0.00048	0.42956	0.00147	0.33	0.10
Si_{IV}	4(*c*)	0.04870	0.00048	0.48056	0.00147	0.23	0.10

Final R value = 0.100

The electron density projection, $\varrho(xz)$, was calculated with the approximate positional parameters of the atoms obtained from the analysis of the Patterson projection. The maxima had the expected heights and positions, thus indicating that the structure proposal was correct. Back-shift corrections were applied to the atomic coordinates and the structure was subsequently refined using the least-squares method and full matrix program. Before the last stages of the refinement ten reflections with the strongest observed intensities were omitted in order to decrease the influence of extinction effects. The number of non-equivalent *h0l*-reflections was then reduced to 332. The omission reduced the R value from 0.116 to 0.100 (the R value is based on observed reflections only) at the same time as the calculated standard deviations were reduced by about 15 %. A final difference synthesis was made and the correctness of the structure determination was ascertained.

During the refinement the following parameters were allowed by vary: 1 scale factor, 14 positional parameters, and 7 temperature factors. The final parameter shifts were less than 0.2 % of the calculated standard deviations. The observed and calculated structure factors are given in Table 2 and the result of the structure determination is given in Table 3.

DESCRIPTION OF THE CRYSTAL STRUCTURE OF Rh_3Si_4

Rh_3Si_4 crystallizes in a new structure type. Fig. 1 shows the structure projected on the *ac* plane. The Roman numerals used in the figure correspond to the notations used for the different crystallographic positions in Table 3.

Rh_3Si_4 crystallizes in the same space-group as the MnP structure type and can also be described on the basis of the latter. Two of the axes of the unit cell of Rh_3Si_4, *viz.* *b* and *c*, correspond to those of the MnP type, whereas the *a* axis is not related to the *a* axis of the MnP structure type. (The choice of axes is described in Ref. 2, Fig. 2).

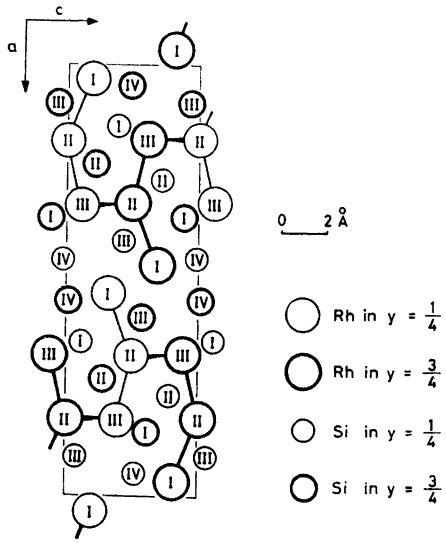

Fig. 1. The structure of Rh_3Si_4 projected on the *ac* plane.

The atomic arrangement of Rh_3Si_4 is in part very similar to that in the MnP structure. In general outline the structure of Rh_3Si_4 can be described as built up of alternating layers of MnP type and more silicon-rich units in the direction of the *a* axis. The thickness of the MnP type layers is half the length of the *a* axis of the MnP type structure. In Rh_3Si_4 these layers are formed by the atoms designated Rh_{II}, Rh_{III}, and Si_{II}. Interleaved with the MnP type layers there are more silicon-rich layers formed by the atoms designated Rh_I, Si_I, Si_{III}, and Si_{IV} in Fig. 1.

The number of atoms coordinating the metal atoms in Rh_3Si_4 is ten. The Rh_I and Rh_{III} atoms have three metal atoms and seven non-metal atoms as nearest neighbours, while the Rh_{II} atoms are surrounded by four metal atoms and six non-metal atoms. The distances to atoms outside the first coordination sphere are considerably longer.

The environment of the Si_{II} atoms in Rh_3Si_4 is similar to that of the non-metal atoms in the MnP structure type. The Si_I and Si_{IV} atoms have both four rhodium and five silicon atoms as their nearest neighbours while the Si_{III} atoms have six rhodium and only one silicon neighbour.

The average of ten Rh—Rh distances in Rh_3Si_4 is 2.93 Å, or about 10 % longer than in pure rhodium. Twenty Rh—Si distances give an average of 2.46 Å. The shortest Si—Si distance is 2.58 Å, or less than 10 % more than the Si—Si distance in silicon.

The interatomic distances and standard deviations in Rh_3Si_4 are listed in Table 4.

Table 4. Interatomic distances with standard deviations in Rh_3Si_4. (In Ångström units. Only distances shorter than 3.7 Å are listed).

Atoms			Dist.	St.dev.
Rh_I	—	Rh_{II}	2.914	0.003
	−2	Rh_I	3.062	0.003
	−2	Rh_I	3.614	0.000
	—	Si_{III}	2.404	0.009
	—	Si_I	2.405	0.009
	—	Si_{IV}	2.465	0.009
	−2	Si_{IV}	2.511	0.006
	−2	Si_{III}	2.588	0.006
Rh_{II}	—	Rh_{III}	2.878	0.003
	−2	Rh_{III}	2.888	0.002
	—	Rh_I	2.914	0.003
	−2	Rh_{II}	3.614	0.000
	—	Si_I	2.314	0.009
	—	Si_{II}	2.393	0.008
	−2	Si_{II}	2.433	0.005
	−2	Si_{III}	2.458	0.006
	—	Si_I	3.634	0.009
Rh_{III}	—	Rh_{II}	2.878	0.003
	−2	Rh_{II}	2.888	0.002
	−2	Rh_{III}	3.614	0.000
	−2	Si_I	2.318	0.006
	—	Si_{III}	2.413	0.009
	—	Si_{IV}	2.496	0.009
	—	Si_{II}	2.539	0.008
	−2	Si_{II}	2.598	0.006
	—	Si_{II}	3.669	0.008
Si_I	—	Rh_{II}	2.314	0.009
	−2	Rh_{III}	2.318	0.006
	—	Rh_I	2.405	0.009
	—	Rh_{II}	3.634	0.009
	−2	Si_{IV}	2.599	0.009
	−2	Si_{II}	2.634	0.009
	—	Si_{II}	3.041	0.012
	−2	Si_{III}	3.366	0.010
	−2	Si_I	3.614	0.000
Si_{II}	—	Rh_{II}	2.393	0.008
	−2	Rh_{II}	2.433	0.005
	—	Rh_{III}	2.539	0.008
	−2	Rh_{III}	2.598	0.006
	—	Rh_{III}	3.669	0.008
	−2	Si_I	2.634	0.009
	—	Si_I	3.041	0.012
	—	Si_{III}	3.139	0.012
	−4	Si_{II}	3.493	0.003
	−2	Si_{II}	3.614	0.000
Si_{III}	—	Rh_I	2.404	0.009
	—	Rh_{III}	2.413	0.009
	−2	Rh_{II}	2.458	0.006
	−2	Rh_I	2.588	0.006
	—	Si_{IV}	2.727	0.012
	—	Si_{II}	3.139	0.012
	—	Si_{IV}	3.299	0.012
	−2	Si_I	3.366	0.010
	−2	Si_{III}	3.614	0.000
Si_{IV}	—	Rh_I	2.465	0.009
	—	Rh_{III}	2.496	0.009
	−2	Rh_I	2.511	0.006
	−2	Si_{IV}	2.583	0.013
	−2	Si_I	2.599	0.009
	—	Si_{III}	2.727	0.012
	—	Si_{III}	3.299	0.012
	−2	Si_{IV}	3.614	0.000

The crystal structure of Rh_3Si_4 is further discussed in relation to other structure types in Ref. 2.

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