Least-squares Refinement of the Structure of RhSi (FeSi-type)

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In the course of a study of the Rh—Si system[1,2] single crystals of RhSi were obtained. The structure of RhSi (FeSi-type) has previously been determined by Geller and Wood.[3] However, it was decided to re-determine the structure employing more accurate refinement techniques. The results of this determination are reported below.

Powder diffraction examination. An alloy with 55 atomic % silicon was prepared by arc-melting rhodium metal powder (Heraeus, claimed purity 99.9 %) and silicon powder (Pechiney and C:ie, claimed purity 99.9 %). The arc-melted alloy was annealed in an evacuated and sealed silica tube at 1100°C for five days. The unit cell dimensions were determined from powder photographs recorded in a Guinier-Hägg focussing camera with Cu-$K\alpha_1$ radiation. Silicon (a = 5.4305 Å) was used as the internal calibration standard.

In addition to the reflections of RnSi (FeSi-type) the powder photographs showed reflections of a phase, the composition and structure of which is unknown at present.

Single crystal examination. A single crystal fragment which measured about 0.1 × 0.1 × 0.2 mm was used for the structure determination. The intensities of the $hk0$ reflections were recorded in an ordinary Weissenberg camera, with zirconium-filtered MoK radiation. The multiple film technique was used with thin iron foils placed between successive films, and the intensities were estimated visually.

Structure refinement. 102 independent $hk0$ reflections were observed. Twelve of these were omitted from the refinement because of extinction effects and are not included in the final R-value quoted below.

The atomic scattering factors for rhodium and silicon were obtained from Ref. 7 and the real part of the dispersion correction factors which were included in the structure factor calculations were taken from the same reference.

The refinement of the structure was carried out by the least-squares method. A weighting scheme according to Cruickshank *et al.*,[8] $w = 1/(a + |F_o| + c|F_o|^2)$, was used where the constants a and c were given the values 9.5 and 0.033, respectively.

The following is a summary of the methods used for the calculations:

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	Calculations of weighting factors	Ref. 6
IBM 7090	Least-squares refinement	Ref. 5 No. 360

Results. The unit cell dimension of RhSi (FeSi-type) is 4.674 ± 0.001 Å. This is in good agreement with that reported earlier.[3]

The space-group was assumed to be $P2_13$ and nothing was found during the refinement that contradicted the choice of this space-group.

During the least-squares refinement of the structure five parameters were varied. Apart from the two positional parameters two individual isotropic temperature factors and one scale factor were varied. After the final refinement the shifts of the parameters varied were less than 0.004 % of the standard deviations. The result of the refinement is given below.

RhSi

Space-group: $P2_13$ (T^4), Z = 4 (Structure type FeSi, B20). a = 4.674 ± 0.001 Å, U = 102.1 Å^3.

Atom	Position			Isotropic temp.factor	
		x	$\sigma(x)$	B	$\sigma(B)$
Rh	4(a)	0.1459	0.0002	0.29	0.03
Si	4(a)	0.8403	0.0010	0.33	0.07

Final R-value = 0.099.

The positional parameters are in good agreement with those given by Geller and Wood,[3] who obtained $x_{Rh} = 0.144 \pm 0.003$ and $x_{Si} = 0.840 \pm 0.007$. However, the accuracy of the parameters is higher than in the earlier investigation.

In Table 1 the interatomic distances in RhSi are listed. A comparison of the distances with those given in the earlier investigation shows no significant differences.

Table 1. Interatomic distances in RhSi (FeSi-type).

Rh	−6 Rh:	2.87_5
	−7 Si:	2.47, 2.45 (3), 2.57 (3)
Si	−7 Rh:	2.47, 2.45 (3), 2.57 (3)
	−6 Si:	2.90

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1. Engström, I. *Acta Chem. Scand.* **17** (1963) 775.
2. Engström, I. *Acta Chem. Scand.* **19** (1965). *In press.*
3. Geller, S. and Wood, E. A. *Acta Cryst.* **7** (1954) 441.
4. Lundberg, B. Program available at BESK.
5. *IUCr World List of Crystallographic Computer Programs*, 1st Ed., Sept. 1962.
6. Lindgren, J. Program available at IBM 1620.
7. *International Tables for X-ray Crystallography*, Vol. III, The Kynoch Press, Birmingham, England 1962.
8. Cruickshank, D. W. J., Philling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and The Phase Problem*, Oxford, Pergamon Press 1961, p. 32.

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The Crystal Structure of Tetramethylthiuram Disulphide

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Tetramethylthiuram disulphide, or bis(dimethylthiocarbamyl) disulphide, crystallizes in the space group $C2/c$ (No. 15) with four $[(CH_3)_2NC(S)]_2S_2$ molecules per unit cell, of dimensions, $a = 9.66$ Å, $b = 9.95$ Å, $c = 11.85$ Å, $\beta = 99\frac{1}{2}°$. With re-orientation of axes, these agree well with reported data.[1] The molecule possesses, by space group requirements, a twofold axis of symmetry.

The crystal structure has been solved, and refined by least squares analysis of 239 observed *h0l*, *hhl*, and *hk0* reflections, estimated visually from zero-layer Weissenberg photographs taken with Cu$K\alpha$ radiation. The reliability index, *R*, is 0.10 at the present stage. Anisotropic temperature factors were used for the sulphur atoms. The atomic coordinates, listed in Table 1, give 2.00 Å for the length of the S−S bond, with an e.s.d. of about 0.01 Å. The bond angle of the sulphur atoms of the disulphide group is 104°, and the dihedral angle is 88°. The dimethyldithiocarbamate groups, excluding the hydrogen atoms, are planar within the experimental error.

Table 1. Atomic coordinates, in fractions of monoclinic cell edges, for tetramethylthiuram disulphide. Origin at a centre of symmetry.

	x	*y*	*z*
S_1	−0.0283	0.3259	0.1651
S_2	0.1955	0.1086	0.2033
C_1	0.085	0.195	0.115
N	0.063	0.191	0.003
C_2	−0.045	0.271	−0.077
C_3	0.142	0.088	−0.056

Further refinement, based on more complete three-dimensional data, is in progress.

1. Yamada, T. and Mizuno, K. *J. Soc. Chem. Ind. Japan* **44** (1941) 708; *Chem. Abstr.* **42** (1948) 2155.

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