

The Crystal Structure of Ru₂Si

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The crystal structure of Ru₂Si has been refined from single crystal data. The unit cell dimensions are $a = 5.27_8$ Å, $b = 4.00_5$ Å and $c = 7.41_8$ Å. The space-group is *Pnma* and the atoms are situated in 4(c) positions with the following atomic parameters: Ru_I: $x = 0.8319$, $z = 0.0650$; Ru_{II}: $x = 0.9820$, $z = 0.7119$; Si: $x = 0.2964$, $z = 0.1013$. Interatomic distances in the isomorphous phases Co₂P, Co₂Si, Ru₂P and Ru₂Si are discussed.

It was reported previously ¹ that a ruthenium silicide with the approximate composition Ru₂Si crystallizes in the *C23* (anti-PbCl₂) type structure. The structure of Ru₂Si has now been refined and the results are presented in this paper.

EXPERIMENTAL

Alloys were prepared by arc-melting or by sintering mixtures of ruthenium (claimed purity 99.9 % from Heraeus, Hanau, Germany) and silicon (claimed purity 99.9 % from Pechiney, Paris). Powder photographs were taken in Guinier cameras with CuK α -radiation. Diffraction patterns from single crystals of Ru₂Si rotated about the *b*-axis were obtained in a Weissenberg camera using MoK α -radiation. The multiple film technique was employed using thin iron foil between the films, and the intensities were estimated visually. The atomic parameters were refined from successive $\rho_o(xz)$ and $\rho_o(xz) - \rho_c(xz)$ electron density projections. Fourier summations and structure factor computations were made on the electronic digital computer BESK with programs available at BESK.

RESULTS

By examining the powder photographs of the arc-melted alloys which had been allowed to cool rapidly in the arc furnace, it was found that alloys with nominal compositions ranging from RuSi_{0.33} — RuSi_{0.50} contained ruthenium and Ru₂Si (Table 1), while alloys with compositions RuSi_{0.54} — RuSi_{0.56} contained Ru₂Si and an unknown phase (or phases) probably more silicon-rich than Ru₂Si. In the powder photograph of RuSi_{0.52} only the powder lines of Ru₂Si could be detected.

Table 1. Powder photograph of an arc-melted alloy with the nominal composition $\text{RuSi}_{0.50}$. (CuK α -radiation). (Only diffraction lines for which $\sin^2\Theta < 0.203$ are given).

hkl for Ru_2Si	$\sin^2\Theta_{\text{obs}}$	$\sin^2\Theta_{\text{calc}}$	I_{obs}	$p/F^2_{\text{calc}} \times 10^{-3} *$
101	—	0.0321	—	2.0
002	—	0.0432	—	0.6
011	0.0480	0.0478	m-	13.8
102	0.0646	0.0645	w+	14.1
111	0.0693	0.0692	st-	47.3
200	—	0.0853	—	1.7
201	—	0.0961	—	3.3
112	0.1015	0.1016	st-	75.4
(Ru)	0.1088		m	
103	0.1183	0.1185	m	47.0
210	0.1223	0.1223	st	99.2
202	0.1285	0.1285	st	105.0
(Ru)	0.1293		m	
211	0.1330	0.1331	vst	208.6
013	0.1337	0.1342	vst	239.7
(Ru)	0.1412		vst	
020	0.1481	0.1482	st	155.5
113	0.1555	0.1556	vw	24.6
212	0.1657	0.1656	vw	21.2
004	—	0.1728	—	2.1
121	—	0.1803	—	2.4
203	0.1825	0.1825	m	67.9
022	—	0.1914	—	0.7
104	0.1944	0.1941	vw	20.1
301	0.2027	0.2027	m-	47.9

* An isotropic temperature factor with $B = 0.50 \text{ \AA}^2$ has been applied.

The powder photographs of alloys prepared by sintering mixtures of the elements at 1100°C were complex and no phase with the $C23$ structure was present in these alloys.

Our observations show that an intermediate phase in the Ru-Si system has a composition closely corresponding to the formula Ru_2Si . This phase exists at elevated temperatures, where it is in equilibrium with the solid solution of silicon in ruthenium, and when cooled rapidly it may be retained down to room temperatures.

The powder lines of Ru_2Si were not very sharp and the l.p. (lattice parameter) reported below are only accurate to about $\pm 0.1\%$. No l.p. variations of Ru_2Si were observed, which indicates that the homogeneity range of this phase is narrow. In the two phase alloys $\text{Ru} + \text{Ru}_2\text{Si}$ the cell dimensions of ruthenium were found to be $a = 2.699 \text{ \AA}$ and $c = 4.286 \text{ \AA}$. These values are slightly different from those quoted by Pearson² for pure ruthenium, $a = 2.706 \text{ \AA}$, $c = 4.282 \text{ \AA}$, indicating that there may be a small solid solubility of silicon in ruthenium. Since the determinations of cell dimensions are not very accurate, it is not possible to draw a definite conclusion on this point.

The crystal structure of Ru_2Si was refined from single crystal data until the difference synthesis did not display any gradients at the atomic positions.

Table 2. Interatomic distances in Ru₂Si (in Å). (Distances shorter than 3.75 Å are listed).

Ru _I	— 2 Ru _I	: 2.84 ₄ (2)
	— 6 Ru _{II}	: 2.73 ₇ , 2.76 ₃ , 2.77 ₇ (2), 2.81 ₈ (2)
	— 5 Si	: 2.45(2), 2.47, 2.48, 2.84
Ru _{II}	— 6 Ru _I	: 2.73 ₇ , 2.76 ₃ , 2.77 ₇ (2), 2.81 ₈ (2)
	— 4 Ru _{II}	: 2.69 ₄ (2), 3.73 ₃ (2)
	— 6 Si	: 2.46(2), 2.52, 2.84(2), 3.33
Si	— 5 Ru _I	: 2.45(2), 2.47, 2.48, 2.84
	— 6 Ru _{II}	: 2.46(2), 2.52, 2.84(2), 3.33
	— 4 Si	: 3.30(2), 3.44(2)

There was no indication that the scattering parameters should not be proportional to 44, 44 and 14, respectively. The final *R*-value for the 86 observed non-equivalent *h*0*l* reflexions was 6.7 %. An empirical isotropic temperature factor with $B = 0.50_0 \text{ \AA}^2$ was employed *. The structural data for Ru₂Si are summarized below:

Space-group: $Pnma$ (D_{2h}^{16}) $Z = 4$ (Structure type $C23$)			
$a = 5.27_9 \text{ \AA}$	$b = 4.00_5 \text{ \AA}$,	$c = 7.41_8 \text{ \AA}$,	$U = 156.8 \text{ \AA}^3$.
	x	z	
4 Ru _I in 4(<i>c</i>)	0.8319 ± 0.0003	0.0650 ± 0.0002	
4 Ru _{II} in 4(<i>c</i>)	0.9820 ± 0.0003	0.7119 ± 0.0002	
4 Si in 4(<i>c</i>)	0.2964 ± 0.0013	0.1013 ± 0.0011	

The standard deviations given above have been estimated using Cruickshank's formula ³.

The interatomic distances are collected in Table 2. In view of the low accuracy of the l.p. the standard deviation of Ru—Ru distances is estimated to be about 0.005 Å and that of Ru—Si distances to be about 0.015 Å.

DISCUSSION

Interatomic distances in Co₂P, Co₂Si and other phases with the *C23* structure were recently discussed by Rundqvist ⁴. The results of our study show that the relationship between Ru₂P and Ru₂Si is quite analogous to that between Co₂P and Co₂Si. The *a*-axis of the Me₂Si phase (Me = Co or Ru) is 12–15 % shorter than that of the corresponding Me₂P phase, while the *b*- and *c*-axes are somewhat longer (4–7 %). The unit cell volume of the silicide is slightly smaller than that of the phosphide. This is noteworthy, since the radius of the silicon atom is usually considered to be greater than that of the phosphorus atoms in metallic phases.

The immediate environments of the atoms in Co₂P and Ru₂P are very similar, but they differ considerably from those in the Me₂Si phases. This is parti-

* A list of calculated and observed structure factors may be obtained from this Institute on request.

cularly striking when the $\text{Me}_I\text{-X}$ distances ($\text{X} = \text{P, Si}$) are considered. In the phosphides, each Me_I atom has four close phosphorus neighbours (*e.g.* in Ru_2P at 2.26, 2.30, and 2.40(2) Å, respectively). In the silicides the corresponding distances are much longer (*e.g.* in Ru_2Si 2.47, 2.48, and 2.45(2) Å, respectively) while a fifth silicon atom has also been brought rather close (2.84 Å in Ru_2Si) to the Me_I atoms.

Thus, in the four isomorphous phases Co_2P , Co_2Si , Ru_2P , Ru_2S , the detailed atomic arrangement seems to be largely determined by the "character" of the non-metal atom.

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