The Crystal Structure of the Iridium Silicide Ir_3Si_5

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The crystal structure of Ir_3Si_5 has been determined and refined from single-crystal X-ray diffractometer data. The compound crystallizes in the monoclinic space group $P2_1/c$. The unit cell dimensions are a = 6.4060(8), b = 14.162(2) and c = 11.553(1) Å, with β = 116.69(1)° and Z = 8. The atoms occupy 16 four-fold positions. The structure was refined from 2732 independent reflections to an R-value of 0.094. The structure type is new and the most characteristic feature of the structure is the almost regular empty cubes formed by silicon atoms.

Transition metal silicides have become a subject of great interest to the electronics industry. However, knowledge of the structures and properties of many of the silicides is still incomplete, so that their application in microelectronic devices is far from optimized.

The present paper deals with the structural characterization of one of the phases in the Ir–Si system, a phase which has been the subject of several investigations during recent years.[1–3]

Earlier investigations of the silicon-rich part of the Ir–Si system[4–6] have revealed the existence of several intermediate phases. The phase of interest in this study was first assigned the approximate composition $IrSi_{\sim 1.5}$ and was characterized by a monoclinic unit cell.[4] Later, X-ray diffraction analyses of Ir–Si thin films[3] showed that the same monoclinic phase was formed in the reaction between a silicon substrate and an iridium metal thin film. The composition of the phase was then estimated as $IrSi_{\sim 1.75}$. The composition now established in the present work for this phase is Ir_3Si_5.

The unit cell dimensions given in Ref. 4 for Ir_3Si_5 correspond to the non-standard space group $P2_1/n$. An appropriate unit cell transformation to the space group $P2_1/c$ gives the unit cell dimensions found in this study.*

*A misprint concerning the length of the a-axis for $IrSi_{\sim 1.5}$ gave the value 5.542 Å, instead of 6.642 Å, in Refs. 4 and 5.

Experimental

Preparation. Samples were prepared by arc-melting iridium powder (purity 99.99 %) and silicon powder (purity 99.9 %) by conventional techniques. For the phase analysis, arc-melted samples were heat-treated in evacuated sealed silica tubes.

X-Ray methods. Phase analyses were carried out in Guinier-Hägg type X-ray powder cameras with $CuK\alpha_1$ and $CrK\alpha_1$ radiation. Silicon (a = 5.431065 Å) was used as calibrant.

Phase analysis showed no significant variation in the unit cell dimensions with composition, indicating no deviation from the stoichiometry of Ir_3Si_5.

The single-crystal investigation was carried out on an automatic four-circle diffractometer (Enraf-Nonius Cad-4), using graphite-monochromated $MoK\alpha$ radiation. The single-crystal fragment used measured about 40×50×15 μm. An absorption correction was applied. The very irregular shape of the crystal, together with the high linear absorption coefficient (μ = 85 mm^{-1}), made the absorption correction only approximate, however.

In the single-crystal investigation, the refinement of the lattice spacings was based on 25 reflections in the θ-range 9.4 to 20.5°. The ω-2θ scan was applied, and the scan speed was allowed to vary between 0.22 and 2.5° min^{-1}, depending on the intensity of the reflection. During the data

collection, five standard reflections were measured after every 45 reflections. No significant variation in the intensities of these reflections was observed. The orientation of the crystal was checked after every 75 reflections.

A total of 3861 reflections were measured; 2732 independent reflections with intensities $I>3\sigma(I)$ were used in the subsequent calculations. The indexes were in the range $0\leqq h\leqq 8$, $0\leqq k\leqq 19$ and $-16\leqq l\leqq 10$. The maximum $\sin\theta/\lambda$-value was 0.703.

Structure determination. The monoclinic symmetry of the compound was assigned earlier on the basis of Weissenberg photographs.[4] The systematically absent reflections $h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$ in the single crystal diffractometer data uniquely determined the space-group for Ir_3Si_5 as $P2_1/c$.

The positions of the irridium atoms were deduced from plots of the Patterson function, and the silicon atom positions were obtained by subsequent least-squares iterations and difference electron density calculations. The refinement of the 48 positional parametes and 16 isotropic thermal parameters resulted in a conventional R-value of 0.094. An anisotropic refinement resulted in an R-value of 0.087. The refinement was based on F_o^2-data and the weighting made according to a weighting factor $w=\sigma_m^{-2}$. The σ-values were modified using the expression $\sigma_m^2=(C_1\cdot\sigma_i)^2+(C_2\cdot F_o^2)^2$. Here, σ_i is the value read from the reflection data file and the constants C_1 and C_2 were given the values 1.10 and 0.110, respectively. A difference synthesis calculated after the final cycle of the refinement showed a maximum peak height of 1.6 % of the iridium peak of the F_o-synthesis.

The atomic scattering factors and the factors correcting for anomalous dispersion were taken from Ref. 7. The calculations were performed on a VAX11/780 computer using crystallographic programmes described in Ref. 8. A list of observed and calculated structure factors is available from the authors on request.

The results of the structure determination of Ir_3Si_5 are summarized in Table 1.

Results and discussion

The atoms in the unit cell of Ir_3Si_5 all occupy the general 4(*e*) positions and are denoted Ir(1)–Ir(6) and Si(1)–Si(10) in Tables 1 and 2 and in Fig. 1. Fig. 1 shows the structure in two projections, one in the [100] and the other in the [001] direction. The environments of the atoms are evident from

Table 1. Structure data for Ir_3Si_5. Space group: $P2_1/c$ (No. 14), $Z=8$, $a=6.4060(8)$, $b=14.162(2)$, $c=11.553(1)$ Å, $\beta=116.69(1)°$, $V=936.4$ Å^3, $D_x=10.17$ g·cm^{-3}. All atoms in general 4(*e*) positions. Standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	*B*/Å^2
Ir(1)	0.42750(14)	0.40242(6)	0.11091(8)	0.038(16)
Ir(2)	0.56548(14)	0.59420(6)	0.39615(8)	0.039(15)
Ir(3)	0.95284(14)	0.75207(6)	0.24404(7)	0.021(15)
Ir(4)	0.08273(14)	0.95573(6)	0.27298(7)	0.043(15)
Ir(5)	0.23674(14)	0.66758(6)	0.13398(8)	0.063(16)
Ir(6)	0.23328(14)	0.83505(6)	0.99249(8)	0.060(16)
Si(1)	0.9263(10)	0.8400(4)	0.0669(6)	0.23(8)
Si(2)	0.7450(10)	0.4903(4)	0.5760(6)	0.11(8)
Si(3)	0.8636(11)	0.6099(4)	0.3272(6)	0.22(8)
Si(4)	0.3304(11)	0.9427(4)	0.1645(6)	0.38(9)
Si(5)	0.8596(10)	0.6127(4)	0.1081(6)	0.20(8)
Si(6)	0.3547(11)	0.9354(4)	0.5102(6)	0.47(9)
Si(7)	0.9515(11)	0.6508(4)	0.9084(6)	0.18(8)
Si(8)	0.2565(10)	0.9875(4)	0.7037(6)	0.18(8)
Si(9)	0.3849(10)	0.7498(4)	0.8572(6)	0.12(8)
Si(10)	0.5549(11)	0.7797(4)	0.1892(6)	0.36(9)

Table 2. Interatomic distances (Å) in Ir_3Si_5. Standard deviations are for Ir–Ir, Ir–Si and Si–Si type distances less than 0.001, 0.006 and 0.013 Å, respectively. Distances less than 3.1 Å are listed.

Ir(1)	–Ir(4)	2.905
	–Si(4)	2.419
	–Si(5)	2.377
	–Si(6)	2.425
	–Si(6)	2.522
	–Si(7)	2.456
	–Si(8)	2.416
	–Si(9)	2.415
	–Si(10)	2.852
Ir(2)	–Ir(5)	2.994
	–Ir(6)	2.984
	–Si(1)	2.452
	–Si(2)	2.379
	–Si(2)	2.463
	–Si(3)	2.388
	–Si(4)	2.441
	–Si(8)	2.500
	–Si(9)	2.441
Ir(3)	–Ir(4)	2.979
	–Ir(5)	2.905
	–Ir(6)	2.891
	–Si(1)	2.335
	–Si(3)	2.408
	–Si(5)	2.424
	–Si(7)	2.348
	–Si(9)	2.475
	–Si(10)	2.369
Ir(4)	–Ir(1)	2.905
	–Ir(3)	2.979
	–Si(1)	2.686
	–Si(2)	2.455
	–Si(3)	2.565
	–Si(4)	2.431
	–Si(5)	2.552
	–Si(6)	2.519
	–Si(7)	2.572
	–Si(8)	2.444
Ir(5)	–Ir(2)	2.994
	–Ir(3)	2.905
	–Ir(6)	2.875
	–Si(1)	3.022
	–Si(5)	2.426
	–Si(6)	2.390
	–Si(7)	2.431
	–Si(8)	2.323
	–Si(9)	2.593
	–Si(10)	2.432
Ir(6)	–Ir(2)	2.984
	–Ir(3)	2.891
	–Ir(5)	2.873
	–Si(1)	2.477
	–Si(2)	2.362
	–Si(3)	2.410
	–Si(4)	2.356
	–Si(7)	3.072
	–Si(9)	2.492
	–Si(10)	2.413
Si(1)	–Ir(2)	2.452
	–Ir(3)	2.355
	–Ir(4)	2.686
	–Ir(5)	3.022
	–Ir(6)	2.477
	–Si(2)	2.693
	–Si(3)	2.709
	–Si(4)	2.734
Si(2)	–Ir(2)	2.379
	–Ir(4)	2.455
	–Ir(6)	2.362
	–Si(1)	2.693
	–Si(2)	2.841
	–Si(3)	2.653
	–Si(4)	2.683
	–Si(8)	2.550
Si(3)	–Ir(2)	2.388
	–Ir(3)	2.408
	–Ir(4)	2.565
	–Ir(6)	2.410
	–Si(1)	2.709
	–Si(2)	2.653
	–Si(4)	2.696
	–Si(5)	2.520
	–Si(10)	3.067
Si(4)	–Ir(1)	2.419
	–Ir(2)	2.441
	–Ir(4)	2.431
	–Ir(6)	2.356
	–Si(1)	2.734
	–Si(2)	2.683
	–Si(3)	2.696
	–Si(8)	2.586
	–Si(10)	2.667
Si(5)	–Ir(1)	2.377
	–Ir(3)	2.424
	–Ir(4)	2.552
	–Ir(5)	2.426
	–Si(3)	2.520
	–Si(6)	2.899
	–Si(6)	2.989
	–Si(7)	2.679
	–Si(8)	2.679
Si(6)	–Ir(1)	2.425
	–Ir(1)	2.522
	–Ir(4)	2.519
	–Ir(5)	2.390
	–Si(5)	2.894
	–Si(5)	2.989
	–Si(6)	2.696
	–Si(7)	2.612
	–Si(8)	2.683
Si(7)	–Ir(1)	2.456
	–Ir(3)	2.348
	–Ir(4)	2.572
	–Ir(5)	2.431
	–Ir(6)	3.072
	–Si(5)	2.679
	–Si(6)	2.612
	–Si(8)	2.694
	–Si(10)	2.840
Si(8)	–Ir(1)	2.416
	–Ir(2)	2.500
	–Ir(4)	2.444
	–Ir(5)	2.323
	–Si(2)	2.550
	–Si(4)	2.586
	–Si(5)	2.679
	–Si(6)	2.683
	–Si(7)	2.694
Si(9)	–Ir(1)	2.415
	–Ir(2)	2.441
	–Ir(3)	2.475
	–Ir(5)	2.593
	–Ir(6)	2.492
	–Si(10)	2.650
Si(10)	–Ir(1)	2.852
	–Ir(3)	2.369
	–Ir(5)	2.432
	–Ir(6)	2.413
	–Si(3)	3.067
	–Si(4)	2.667
	–Si(7)	2.840
	–Si(9)	2.650

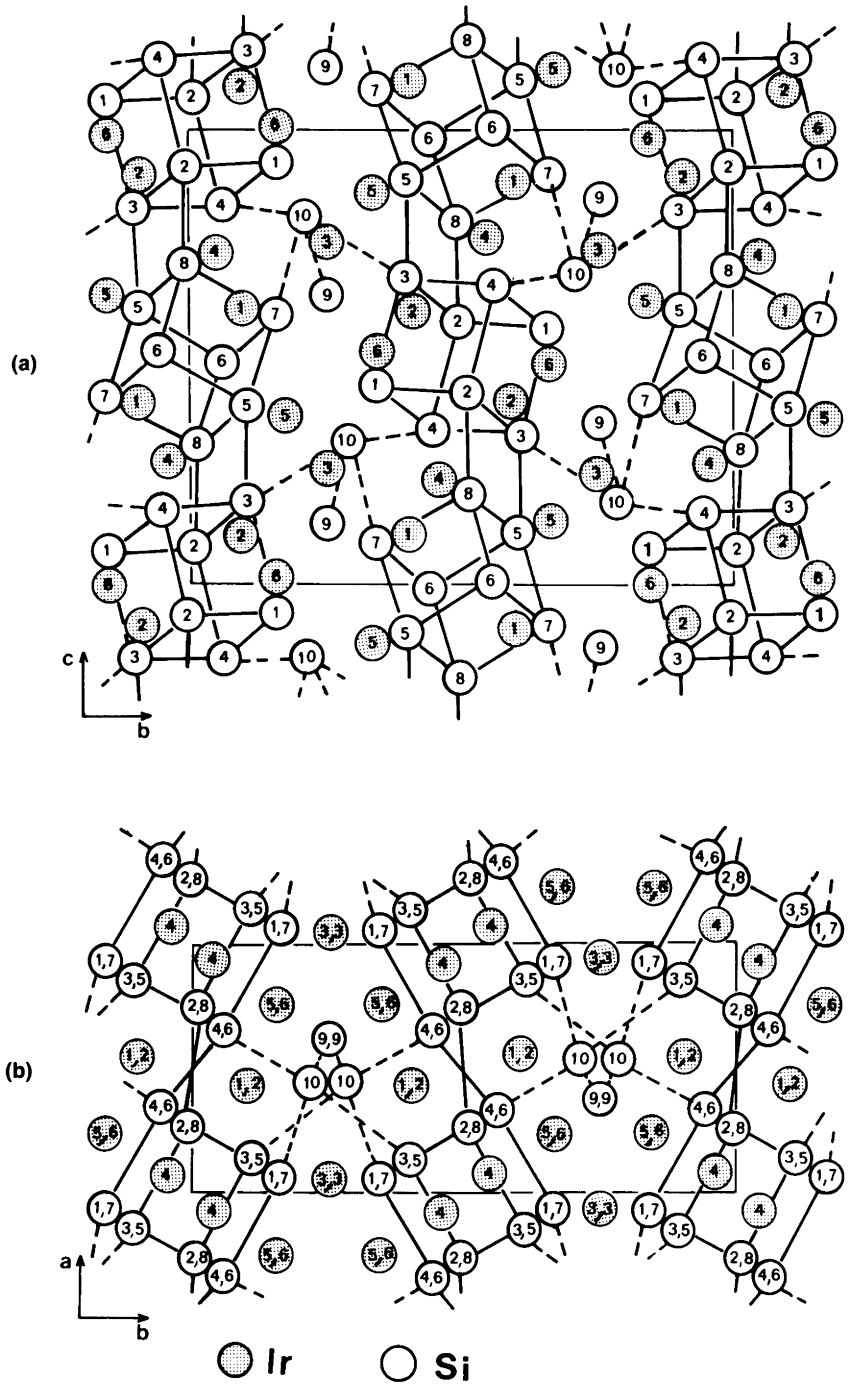

Fig. 1. Projections of the structure of Ir_3Si_5 (a) in the [$\bar{1}$00] direction, and (b) in the [001] direction. The figures correspond to notations used in Tables 1 and 2.

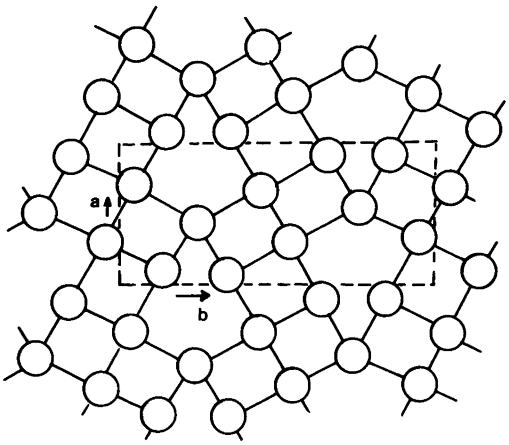

Fig. 2. Idealized net of silicon atoms in Ir_3Si_5. For the Ir-positions see Fig. 1b.

Table 2, which gives the interatomic distances less than 3.1 Å. The most striking feature of the structure is the occurrence of empty, almost regular cubes formed by silicon atoms. One kind of cube is formed by the atoms Si(1)–Si(4) and the other by the atoms Si(5)–Si(8). The cubes are connected in both the *a* and *c* directions. In Fig. 1, these atoms are connected by full lines.

The centres of the cubes mentioned above coincide with the centres of symmetry of the structure, and the distances from these centres to the corners occupied by silicon atoms vary between 2.180 and 2.507 Å for the Si(1)–Si(4) cube and between 2.190 and 2.434 Å for the Si(5)–Si(8) cube. The additional silicon atoms Si(9) and Si(10) complete the three-dimensional silicon network by bridging atoms in the direction of the *b*-axis. The bridging is shown by dashed lines in Fig. 1.

An attempt to idealize the structure has been made on the basis of the projection shown in Fig. 1b. The results is four identical nets of silicon atoms parallel to the *ab*-plane. One of these nets is shown in Fig. 2, where the metal atoms have been omitted. The structure, in an idealized form, exhibits fragments of atomic arrangements reminiscent of the CaF_2-type structure with filled and empty cubes. The iridium atoms Ir(1), Ir(2) and Ir(4) are located in these cubes. The other iridium atoms are located in regions between the CaF_2-type fragments.

A similar arrangement of empty interconnected silicon cubes is also found in the structure of $OsSi_2$.[9] Fig. 3 shows the double layer of silicon atoms in $OsSi_2$ projected onto the *bc*-plane with the osmium atoms located between the layers. As for the Ir(4) atoms in Ir_3Si_5, the osmium atoms in $OsSi_2$ are each surrounded by two empty cubes of silicon (Fig. 3). In $OsSi_2$, the silicon atoms forming the cubes are interconnected in the directions of the diagonals of the *bc*-plane.

The distances from the centres of the silicon cubes to the eight corners are, on average, 2.33 and 2.34 Å for the two types of cube in Ir_3Si_5. The corresponding value for $OsSi_2$ is 2.29 Å. These values should be compared with those for the ideal cubic arrangement in $CoSi_2$(CaF_2-type), where the distance from the centre of the silicon cube to the corner is 2.36 Å.

The average distance between the silicon atoms forming the cubes is 2.69 Å for the two types of cube Si(1)–Si(4) and Si(5)–Si(8). The shortest Si–Si distances in the structure are found, however, between the silicon atoms connecting the cubes. The distances here are 2.52 and 2.55 Å, and are thus significantly shorter than the distances within the cubes. These bridges exceed the single-bond distance in silicon by less than 10 %.

The list of interatomic distances in Ir_3Si_5 given in Table 2 shows that the number of close metal atom neighbours is 9 or 10. The number of close silicon neighbours varies between 6 and 9. A comparison of the average interatomic distances in Ir_3Si_5 with distances found in other iridium

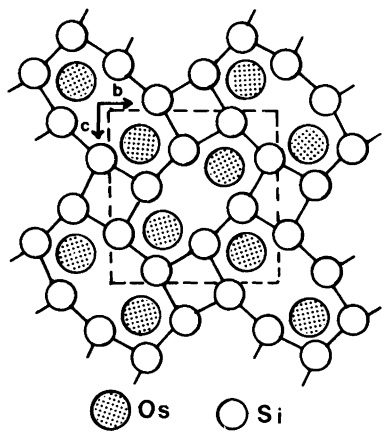

Fig. 3. Projection of a double layer of silicon atoms in $OsSi_2$; the Os atoms are localized between the layers.

silicides[5] suggests that the Ir–Si interaction increases with increasing silicon content. The average Ir–Si distances are 2.67, 2.46, 2.48 and 2.45 Å for Ir_3Si, IrSi, Ir_3Si_4 and Ir_3Si_5, respectively. A considerable interaction between the silicon atoms in Ir_3Si_5 cannot be disregarded, however. The average of short Si–Si distances is 2.70 Å, thus exceeding the single-bond distance for silicon by only 15 %.

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