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X-Ray Studies of Silicon-rich Iridium Silicides

INGVAR ENGSTRÖM and FOLKE ZACKRISSON

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The silicon-rich part of the Ir-Si system has been investigated by X-ray powder and single crystal methods. Previously reported phases have been characterized and the following compounds were found: Ir_4Si_5 (Rh_4Si_5 type), Ir_3Si_4 (Rh_3Si_4 type), $IrSi_{\sim 1.5}$ (monoclinic). In addition the existence of $IrSi_3$ has been confirmed. The crystal structure of Ir_3Si_4 has been refined from single crystal X-ray data.

In earlier investigations of the iridium-silicon system three intermediate silicon-rich compounds were reported. Buddery and Welch[1] observed two silicon-rich phases, Ir_2Si_3 and $IrSi_3$. Besides these two phases, Bhan and Schubert[2] and Finnie[3] subsequently reported the existence of $IrSi_2$. The compositions of the compounds were not established and the formulas allotted to them must be considered as approximate only.

As a part of crystal-chemical investigations of platinum metal silicides at this institute a reinvestigation of the silicon-rich part of the iridium-silicon system was undertaken. Within the region 50 – 100 at.-% Si five intermediate phases were found besides IrSi (MnP type). The two phases, Ir_4Si_5 and Ir_3Si_4 are isomorphous with Rh_4Si_5[4] and Rh_3Si_4,[5] respectively. The structure of Ir_3Si_4 has been refined from single crystal X-ray data and the results are presented in this paper. At about 60 at.-% Si a monoclinic phase was found and the unit cell dimensions reported are based on both single crystal and powder data. Of the two remaining phases one is identical with $IrSi_3$, reported before, and the other is a new phase of about the same composition but which has not yet been characterized. In this paper it is shown that the structure type proposed for $IrSi_3$ by Finnie[3] is incorrect.

EXPERIMENTAL

Preparation. Iridium-silicon alloys were prepared using iridium metal powder (Johnson, Matthey & Co., Ltd., spectroscopically pure) and silicon powder (Pechiney, claimed purity 99.9 %) as starting materials. The mixtures were arc-melted and then annealed in evacuated and sealed silica tubes at different temperatures for about seven days and finally quenched.

Powder diffraction examination. Powder photographs were recorded in Guinier-Hägg type focussing cameras with Cu$K\alpha_1$ and Cr$K\alpha_1$ radiations ($\lambda = 1.54051$ and 2.28962 Å, respectively). Silicon was used as internal calibration standard ($a_{\rm Si} = 5.4305$ Å).

Single crystal examination. An equi-inclination Weissenberg camera with Zr filtered MoK-radiation was used. Single crystal diffraction patterns were recorded for $\rm IrSi_{\sim 1.5}$ in order to obtain starting parameters in indexing the powder diffraction pattern and for $\rm Ir_3Si_4$ in order to obtain single crystal data for a structure determination.

A single crystal fragment of $\rm Ir_3Si_4$ was rotated about the b-axis. It measured roughly 0.040×0.025 mm in the plane perpendicular to the rotation axis. The multiple film technique was employed with thin iron foils interleaved with the films and the intensities $I(hkl)$ were recorded for $k = 0$, 1, and 2. The intensities were estimated visually with a calibrated intensity scale. 593 non-equivalent reflections of $h0l$ and $h1l$ type were used in the determination of the structure. No absorption correction was made because of the irregular shape of the crystal fragment.

Calculations. The unit cell dimensions of the different compounds were refined from powder diffraction data using the least-squares method. The structure of $\rm Ir_3Si_4$ was refined using a full matrix least-squares program. The atomic scattering and dispersion correction factors for iridium and silicon were taken from Ref. 6. The reflections were weighted according to the formula: $w = 1/(a + |F_o| + c|F_o|^2)$ suggested by Cruickshank *et al.*[8] a and c were given the values 58 and 0.0058, respectively. The calculations were carried out on a CDC 3600 electronic computer and the programs used are listed in Table 1.

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-polarisation 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.

PHASE ANALYSIS OF THE SILICON-RICH PART OF THE Ir-Si SYSTEM

Table 2 gives crystallographic data for the different intermediate phases of the silicon-rich part of the Ir-Si system. The unit cell dimensions were determined in the two-phase regions on both sides of the homogeneity region of each phase. As the variations of the cell parameters of the different compounds were within $\pm 3\sigma$-limits, the homogeneity ranges are probably very narrow. Because of the very complicated powder diffraction patterns of $\rm Ir_4Si_5$, $\rm Ir_3Si_4$, and $\rm IrSi_{\sim 1.5}$ the unit cell dimensions of these compounds were determined using Cr$K\alpha_1$ radiation (*cf.* experimental section).

Table 2. Intermediate phases in the silicon-rich part of the Ir-Si system.

Phase	Struct. type	Space-group	Cell dimensions (Å)		Volume (Å ^{3})	Annealing temp.°C
IrSi	MnP	*Pnma* No. 62	$a=5.5579$ $b=3.2213$ $c=6.2673$	$\sigma(a)=0.0029$ $\sigma(b)=0.0010$ $\sigma(c)=0.0012$	112.21	1250
Ir_4Si_5	Rh_4Si_5	$P2_1/m$ No. 11	$a=12.359$ $b=3.6181$ $c=5.8805$ $\beta=100.14°$	$\sigma(a)=0.0027$ $\sigma(b)=0.0014$ $\sigma(c)=0.0014$ $\sigma(\beta)=0.02°$	258.74	1250
Ir_3Si_4	Rh_3Si_4	*Pnma* No. 62	$a=18.8741$ $b=3.6979$ $c=5.7717$	$\sigma(a)=0.0029$ $\sigma(b)=0.0008$ $\sigma(c)=0.0010$	402.83	1020
$IrSi_{\sim 1.5}$	new	monoclinic	$a=5.542$ $b=14.166$ $c=12.426$ $\beta=120.61°$	$\sigma(a)=0.001$ $\sigma(b)=0.003$ $\sigma(c)=0.003$ $\sigma(\beta)=0.02°$	1006.5	1020
$IrSi_3$	new	hexagonal ?	$a=4.3538$ $c=6.6277$	$\sigma(a)=0.0009$ $\sigma(c)=0.0015$	108.8	1020

The unit cell dimensions of IrSi obtained in this investigation are in good agreement with earlier results.[11] The unit cell dimensions of $IrSi_3$, however, differ somewhat from those reported earlier.[2,3] The unit cell volumes of Ir_4Si_5 and Ir_3Si_4 are about 2.5 % larger than those of the corresponding rhodium silicides, thus reflecting the difference in radii for the two metal atoms.

Table 3.

Space-group: *Pnma*. No. 62. $Z=4$

$a=18.8701$ Å $\sigma(a)=0.0017$ Å
$b=3.6967$ Å $\sigma(b)=0.0003$ Å
$c=5.7742$ Å $\sigma(c)=0.0004$ Å $U=402.79$ Å^3

Atom	Position parameters and stand. deviations				Isotr. temp. fact.	
	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Ir(1)	0.03154	0.00010	0.19246	0.00038	0.21	0.02
Ir(2)	0.17630	0.00010	0.99915	0.00034	0.21	0.02
Ir(3)	0.32570	0.00010	0.10929	0.00033	0.18	0.02
Si(1)	0.14371	0.00093	0.38561	0.00330	0.35	0.22
Si(2)	0.77035	0.00098	0.78485	0.00349	0.45	0.23
Si(3)	0.40882	0.00100	0.41676	0.00380	0.51	0.23
Si(4)	0.95882	0.00090	0.52331	0.00306	0.21	0.18

Final R value $=0.127$

Table 4. Observed and calculated structure factors. Reflexions not included in the last cycles of the refinement are indicated with an asterisk.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	
8	0	0	220.3	402.1	*
10	0	0	94.1	130.6	
14	0	0	350.3	553.4	*
12	0	0	127.9	180.1	
20	0	0	400.0	405.8	*
16	0	0	110.5	104.8	
22	0	0	193.4	201.7	
26	0	0	201.3	182.0	
28	0	0	300.5	277.9	
30	0	0	108.2	86.7	
32	0	0	79.7	75.9	
34	0	0	339.4	289.7	
38	0	0	91.2	76.6	
40	0	0	179.1	159.3	
42	0	0	164.9	119.0	
44	0	0	84.6	75.2	
46	0	0	62.4	54.2	
48	0	0	173.4	161.4	
50	0	0	58.4	49.3	
8	0	1	121.0	142.9	
10	0	1	267.5	392.9	*
11	0	1	64.9	85.2	
13	0	1	60.1	74.9	
15	0	1	76.2	97.5	
16	0	1	74.7	96.8	
18	0	1	117.8	135.9	
19	0	1	123.4	117.6	
24	0	1	218.5	215.8	
26	0	1	114.6	108.6	
30	0	1	120.1	101.6	
33	0	1	93.9	93.6	
38	0	1	127.4	109.4	
40	0	1	102.0	87.0	
44	0	1	101.6	90.4	
48	0	1	62.9	37.5	
4	0	2	269.4	206.1	*
6	0	2	200.7	206.4	
8	0	2	221.2	266.1	
9	0	2	49.7	49.0	
10	0	2	71.9	68.3	
11	0	2	30.5	25.3	
12	0	2	259.3	279.5	
13	0	2	210.0	263.3	
14	0	2	100.7	106.5	
15	0	2	113.4	124.2	
16	0	2	195.1	216.7	
17	0	2	53.7	65.7	
18	0	2	179.6	202.4	
19	0	2	119.5	134.1	
20	0	2	54.1	64.2	
21	0	2	193.4	210.5	
22	0	2	164.1	170.8	
23	0	2	103.8	105.1	
26	0	2	201.1	191.2	
27	0	2	185.6	174.4	
28	0	2	67.8	61.6	
30	0	2	134.6	122.6	
32	0	2	180.4	165.3	
33	0	2	81.9	74.9	
35	0	2	90.4	88.6	
36	0	2	120.8	102.7	
37	0	2	84.4	70.0	
38	0	2	76.9	60.4	
40	0	2	112.2	98.2	
41	0	2	138.7	121.7	
46	0	2	114.1	116.9	
1	0	3	75.6	68.6	
2	0	3	219.4	213.9	
3	0	3	456.2	535.0	*
4	0	3	117.5	107.1	
5	0	3	114.8	111.5	
6	0	3	125.2	167.4	
7	0	3	54.8	51.5	
8	0	3	148.0	135.3	
9	0	3	265.1	222.0	
10	0	3	99.0	99.7	
11	0	3	367.4	388.9	
12	0	3	170.6	175.8	
13	0	3	89.0	93.5	
14	0	3	145.9	139.9	
16	0	3	167.5	169.2	
17	0	3	315.4	351.3	
18	0	3	73.9	92.6	
20	0	3	50.4	49.9	
22	0	3	157.7	180.2	
23	0	3	190.5	195.6	
25	0	3	171.6	184.3	
26	0	3	61.6	62.2	
27	0	3	65.5	65.8	
28	0	3	113.2	114.4	
29	0	3	68.4	65.5	
30	0	3	61.8	55.0	
31	0	3	229.2	235.4	
36	0	3	127.4	122.9	
37	0	3	165.2	160.3	
41	0	3	60.0	50.1	
42	0	3	84.9	83.9	
43	0	3	56.9	64.6	
45	0	3	126.6	124.8	
3	0	4	154.3	144.7	
4	0	4	88.6	82.7	
7	0	4	112.4	102.8	
8	0	4	49.5	43.8	
9	0	4	251.5	211.4	
11	0	4	170.2	171.3	
12	0	4	46.6	46.0	
13	0	4	44.2	31.5	
14	0	4	70.6	66.1	
15	0	4	78.4	77.5	
16	0	4	49.8	23.2	
17	0	4	54.9	43.7	
19	0	4	150.6	150.0	
21	0	4	76.9	91.6	
23	0	4	88.8	101.8	
25	0	4	138.2	146.3	
29	0	4	77.2	73.0	
39	0	4	117.7	98.1	
45	0	4	67.7	59.1	
1	0	5	344.2	318.6	
3	0	5	255.9	245.1	
4	0	5	72.2	68.7	
5	0	5	403.0	378.0	*
7	0	5	117.0	107.4	
9	0	5	350.0	304.0	*
10	0	5	68.1	65.0	
11	0	5	186.5	160.0	
13	0	5	167.4	148.4	
15	0	5	350.0	335.3	
16	0	5	71.1	67.5	
17	0	5	148.5	149.2	
19	0	5	237.7	255.8	
21	0	5	162.3	172.8	
23	0	5	177.1	189.3	
25	0	5	129.7	152.0	
27	0	5	64.6	60.9	
29	0	5	249.7	267.8	
31	0	5	70.8	77.7	
33	0	5	119.2	117.9	
35	0	5	211.1	188.7	
37	0	5	123.7	120.7	
39	0	5	88.7	86.5	
43	0	5	164.1	167.5	
1	0	6	80.0	68.1	
2	0	6	62.7	50.8	
3	0	6	75.9	71.1	
4	0	6	78.8	70.7	
5	0	6	220.3	190.5	
6	0	6	140.7	110.8	
8	0	6	88.8	78.1	
9	0	6	228.1	197.6	
10	0	6	50.0	38.1	
11	0	6	181.8	153.8	
12	0	6	47.1	44.4	
13	0	6	74.2	64.9	
14	0	6	145.3	148.3	
15	0	6	120.4	130.1	
18	0	6	57.4	36.1	
19	0	6	155.6	157.2	
20	0	6	98.8	96.0	
23	0	6	76.9	82.7	
25	0	6	164.3	183.4	
28	0	6	77.8	94.6	
33	0	6	86.6	86.4	
34	0	6	68.6	70.5	
39	0	6	109.4	119.8	
42	0	6	56.7	53.8	
45	0	6	75.5	69.2	
1	0	7	59.4	51.8	
2	0	7	183.5	160.9	
3	0	7	232.3	189.8	
5	0	7	65.8	55.0	
6	0	7	197.6	172.6	
8	0	7	230.0	187.7	
9	0	7	129.9	100.2	
10	0	7	54.8	38.1	
11	0	7	180.4	172.5	
12	0	7	176.1	157.4	
14	0	7	74.5	77.2	
16	0	7	150.5	142.9	
17	0	7	171.5	177.3	
22	0	7	155.4	180.8	
23	0	7	80.4	89.1	
25	0	7	79.9	89.4	
28	0	7	95.0	109.1	
31	0	7	120.9	126.1	
36	0	7	114.1	111.1	
42	0	7	97.7	100.1	
45	0	7	72.5	76.5	
1	0	8	138.9	100.8	
2	0	8	284.9	246.2	
4	0	8	181.5	160.3	
6	0	8	209.5	176.0	
7	0	8	152.9	138.4	
8	0	8	215.2	171.8	
12	0	8	257.7	231.7	
13	0	8	106.3	90.7	
14	0	8	87.7	77.5	
15	0	8	70.1	73.8	
16	0	8	169.8	178.5	
18	0	8	181.4	191.2	
19	0	8	78.0	73.9	
20	0	8	85.4	98.4	
21	0	8	77.1	93.3	
22	0	8	129.0	143.7	
26	0	8	151.4	178.7	
32	0	8	190.0	183.5	
40	0	8	105.8	111.8	
4	0	9	80.2	65.4	
6	0	9	103.7	98.8	
8	0	9	111.0	103.2	
10	0	9	112.3	112.9	
12	0	9	74.9	68.1	
24	0	9	89.0	103.6	
26	0	9	83.9	86.5	
5	0	10	85.7	72.3	
6	0	10	236.0	208.8	
8	0	10	161.6	149.5	
9	0	10	82.2	81.5	
11	0	10	80.5	58.3	
12	0	10	96.0	81.6	
14	0	10	243.3	241.0	
20	0	10	192.8	208.6	
22	0	10	83.9	80.7	
26	0	10	83.4	101.2	
28	0	10	136.3	161.1	
34	0	10	178.0	168.8	
1	0	11	102.8	101.6	
4	0	11	163.4	140.4	
5	0	11	86.4	76.3	
10	0	11	157.9	155.5	
13	0	11	84.4	76.1	
15	0	11	84.1	93.1	
30	0	11	78.2	78.6	
1	0	12	79.1	71.9	
7	0	12	149.9	141.1	
13	0	12	114.1	116.8	
21	0	12	97.0	106.1	
27	0	12	74.7	106.8	
9	0	13	110.0	107.3	
11	0	13	140.0	159.0	
17	0	13	156.7	185.5	
23	0	13	102.9	126.1	
25	0	13	82.2	101.6	
1	0	15	74.2	93.3	
3	0	15	61.2	60.3	
4	0	15	56.1	66.8	
5	0	15	81.0	96.3	
10	0	15	52.0	72.5	
0	0	4	56.5	41.8	
0	0	6	178.7	142.8	
0	0	8	121.3	107.2	
0	0	10	324.2	303.7	
9	0	15	81.2	97.4	
6	1	0	79.2	169.2	
8	1	0	140.7	284.6	
10	1	0	153.0	198.1	
12	1	0	115.2	164.0	
16	1	0	44.1	74.5	
18	1	0	40.0	41.5	
20	1	0	140.6	133.3	
22	1	0	117.3	106.8	
24	1	0	142.1	149.8	
26	1	0	188.3	194.4	
34	1	0	68.2	88.3	
36	1	0	64.3	52.8	
38	1	0	69.7	77.5	
40	1	0	126.2	117.9	
46	1	0	47.1	44.0	
48	1	0	51.4	50.5	
5	1	1	221.0	185.1	
6	1	1	266.2	259.5	
7	1	1	466.5	561.4	
8	1	1	109.9	121.0	
9	1	1	87.9	98.6	
10	1	1	60.6	80.6	
11	1	1	73.2	90.7	
13	1	1	253.2	357.5	
14	1	1	190.8	267.6	
15	1	1	213.4	290.6	
16	1	1	109.8	146.2	
17	1	1	57.6	68.5	
18	1	1	97.2	110.2	
19	1	1	221.0	232.1	
20	1	1	147.6	171.1	
21	1	1	256.0	281.4	
24	1	1	46.2	47.8	
25	1	1	117.8	120.8	
26	1	1	53.6	49.1	
27	1	1	224.6	235.5	
28	1	1	146.9	154.1	
29	1	1	84.0	97.3	
30	1	1	93.5	98.0	
31	1	1	72.5	73.7	
32	1	1	50.2	43.7	
33	1	1	158.5	159.2	
34	1	1	128.3	144.9	
35	1	1	145.3	132.2	
36	1	1	52.5	50.3	
39	1	1	100.2	94.3	
41	1	1	170.5	156.9	
44	1	1	120.2	76.2	
45	1	1	45.4	61.1	
47	1	1	127.8	119.4	
48	1	1	102.7	86.4	
49	1	1	82.6	61.0	
50	1	1	55.6	52.2	
51	1	1	45.3	41.4	
1	1	2	78.8	60.2	
2	1	2	78.6	62.5	
3	1	2	482.6	413.3	*
4	1	2	465.9	375.3	
5	1	2	119.0	106.0	
6	1	2	113.8	100.8	
7	1	2	68.8	59.0	
8	1	2	91.9	101.4	
9	1	2	154.1	163.2	
11	1	2	185.8	198.0	
13	1	2	105.1	113.7	
16	1	2	102.8	114.7	
17	1	2	247.8	274.3	
18	1	2	197.2	209.4	
23	1	2	121.1	129.4	
24	1	2	178.7	189.3	
27	1	2	45.6	57.7	
29	1	2	47.8	55.4	
30	1	2	118.7	106.2	
31	1	2	157.3	166.2	
32	1	2	56.6	65.9	
33	1	2	57.4	70.2	
37	1	2	133.5	115.6	
38	1	2	146.3	126.9	
41	1	2	56.6	62.1	
44	1	2	110.8	90.2	
45	1	2	82.6	67.9	
47	1	2	69.8	64.7	
51	1	2	80.1	72.9	
0	1	3	205.5	161.0	
1	1	3	144.1	109.9	
2	1	3	314.1	236.4	
3	1	3	160.6	122.2	
4	1	3	196.8	161.2	
5	1	3	242.1	205.7	
6	1	3	143.7	112.9	
7	1	3	63.6	56.4	
8	1	3	126.9	106.0	
9	1	3	220.6	201.0	
10	1	3	39.0	35.8	
11	1	3	173.4	176.0	
12	1	3	207.1	226.2	
14	1	3	39.9	39.4	
15	1	3	124.4	111.7	
16	1	3	86.5	76.5	
17	1	3	35.6	24.2	
18	1	3	132.4	133.0	
19	1	3	135.9	120.3	
20	1	3	75.3	82.2	
22	1	3	102.9	111.1	
23	1	3	167.8	183.4	
25	1	3	115.7	129.2	
26	1	3	118.5	129.7	
29	1	3	106.2	112.2	
32	1	3	132.2	124.5	
33	1	3	89.8	74.3	
34	1	3	52.3	53.0	
37	1	3	101.9	94.6	
38	1	3	90.6	78.9	
39	1	3	108.8	98.4	
40	1	3	76.5	67.5	
43	1	3	94.4	82.2	
46	1	3	80.0	80.2	
51	1	3	38.5	46.7	
1	1	4	255.4	199.8	
3	1	4	90.5	77.4	
4	1	4	467.4	337.0	*
5	1	4	203.4	167.6	
6	1	4	150.1	122.1	
7	1	4	119.1	93.0	
8	1	4	260.6	193.4	
9	1	4	140.3	121.3	
10	1	4	418.3	357.6	
11	1	4	29.7	31.0	
12	1	4	310.4	266.4	
13	1	4	198.6	157.6	
14	1	4	110.9	106.5	
15	1	4	171.6	170.2	
16	1	4	270.7	267.0	
17	1	4	98.4	90.2	
18	1	4	253.5	233.5	
19	1	4	150.6	135.8	
21	1	4	122.3	120.6	
22	1	4	190.7	229.9	
24	1	4	170.2	205.8	
26	1	4	66.6	86.7	
27	1	4	69.4	64.6	
28	1	4	121.7	137.6	
29	1	4	138.8	146.5	
30	1	4	140.3	177.2	
31	1	4	66.3	98.2	
32	1	4	109.1	118.2	
33	1	4	82.7	94.8	
35	1	4	83.3	95.7	
36	1	4	156.3	157.5	
38	1	4	108.8	111.2	
42	1	4	108.5	108.9	
43	1	4	96.0	78.7	
44	1	4	136.8	124.6	
47	1	4	54.0	51.2	
48	1	4	65.3	53.8	
49	1	4	82.9	71.4	
50	1	4	111.8	112.4	
0	1	5	190.3	126.0	
1	1	5	83.8	54.0	
3	1	5	179.5	153.8	
4	1	5	29.4	25.4	
5	1	5	171.0	130.9	
6	1	5	97.0	74.1	
7	1	5	269.2	185.3	
8	1	5	78.9	41.5	
9	1	5	194.0	140.8	
10	1	5	81.6	52.8	
11	1	5	147.0	136.4	
13	1	5	87.2	73.4	
14	1	5	87.0	72.7	
19	1	5	128.3	132.8	
20	1	5	48.4	55.5	
21	1	5	117.0	115.2	
23	1	5	56.5	68.9	
25	1	5	95.9	108.2	
27	1	5	99.3	93.7	
35	1	5	75.8	74.2	
39	1	5	93.1	82.3	
41	1	5	74.5	68.5	
45	1	5	62.0	58.3	
49	1	5	43.7	40.6	
1	1	6	303.8	214.8	
2	1	6	316.6	239.3	
4	1	6	271.1	169.2	
5	1	6	190.1	143.9	
6	1	6	217.9	151.6	
7	1	6	91.0	72.2	
8	1	6	230.1	180.5	
9	1	6	218.7	171.5	
10	1	6	228.9	164.3	
12	1	6	280.1	211.0	
13	1	6	135.3	124.4	
14	1	6	133.4	112.4	
15	1	6	191.7	172.9	
16	1	6	209.1	188.5	
18	1	6	145.1	140.3	
19	1	6	104.9	103.3	
20	1	6	72.6	69.1	
21	1	6	83.1	84.9	
22	1	6	198.9	200.5	
23	1	6	76.4	84.1	
24	1	6	98.2	105.8	
26	1	6	94.5	113.2	
28	1	6	103.4	121.5	
29	1	6	132.9	144.7	
30	1	6	122.1	110.4	
32	1	6	102.0	88.6	
33	1	6	58.8	66.7	
35	1	6	106.8	103.7	
36	1	6	156.9	150.5	
42	1	6	107.1	99.6	
43	1	6	86.4	82.0	
44	1	6	85.9	72.8	
46	1	6	51.9	51.0	
0	1	7	92.4	74.0	
1	1	7	198.6	147.7	
2	1	7	213.4	180.7	
3	1	7	99.2	69.5	
4	1	7	178.3	144.2	
5	1	7	184.6	139.7	
6	1	7	148.0	97.4	
7	1	7	74.8	59.6	
8	1	7	140.8	114.2	
9	1	7	177.3	157.5	
11	1	7	148.7	117.7	
12	1	7	192.5	180.5	
13	1	7	109.0	103.9	
15	1	7	127.7	114.9	
16	1	7	133.5	120.7	
18	1	7	161.1	157.3	
19	1	7	133.2	138.7	
21	1	7	69.6	74.5	
22	1	7	92.1	107.6	
23	1	7	100.9	108.4	
25	1	7	103.0	121.6	
26	1	7	116.2	135.8	
32	1	7	142.3	153.7	
33	1	7	81.9	94.3	
37	1	7	84.5	45.9	
38	1	7	86.4	75.9	
39	1	7	74.9	96.3	
43	1	7	63.9	60.8	
3	1	8	162.9	112.7	
4	1	8	159.9	130.9	
5	1	8	76.7	61.3	
6	1	8	137.2	109.1	
8	1	8	122.9	110.4	
9	1	8	87.1	76.2	
10	1	8	181.7	138.1	
11	1	8	46.3	44.9	
9	1	9	142.6	129.0	
12	1	8	52.3	54.1	
17	1	8	124.9	112.9	
18	1	8	61.0	74.8	
22	1	8	76.1	88.8	
23	1	8	52.0	68.9	
24	1	8	114.1	124.6	
38	1	8	86.6	85.5	
42	1	8	54.7	57.4	
44	1	8	59.3	51.1	
0	1	9	157.6	149.0	
1	1	9	201.6	184.0	
2	1	9	133.9	114.9	
3	1	9	47.7	36.9	
4	1	9	73.0	69.3	
5	1	9	199.2	163.4	
6	1	9	48.2	46.6	
7	1	9	237.8	218.9	
11	1	9	113.5	97.3	
12	1	9	61.1	65.2	
13	1	9	212.5	207.4	
14	1	9	112.1	120.7	
15	1	9	177.6	164.2	
16	1	9	111.7	100.5	
18	1	9	67.0	78.6	
19	1	9	176.8	174.7	
20	1	9	52.4	63.5	
21	1	9	153.2	152.9	
25	1	9	138.1	135.0	
27	1	9	146.9	152.2	
28	1	9	51.4	60.1	
29	1	9	56.8	81.8	
30	1	9	50.1	62.8	
31	1	9	49.2	56.0	
32	1	9	48.2	61.2	
33	1	9	128.6	131.6	
34	1	9	55.9	67.6	
35	1	9	92.8	91.9	
39	1	9	106.3	106.3	
41	1	9	104.1	97.9	
1	1	10	70.1	76.6	
2	1	10	50.7	45.7	
3	1	10	50.8	42.5	
4	1	10	50.8	44.4	
5	1	10	51.0	63.4	
6	1	10	70.7	86.2	
8	1	10	101.7	101.7	
12	1	10	79.5	75.1	
15	1	10	97.0	87.5	
19	1	10	79.0	65.3	
20	1	10	83.2	73.6	
22	1	10	58.4	61.7	
0	1	11	159.7	136.2	
6	1	11	143.3	117.8	
7	1	11	191.0	183.1	
1	1	11	155.3	122.6	
20	1	11	158.5	107.5	
13	1	11	159.3	136.6	
14	1	11	150.1	114.0	
15	1	11	96.8	73.9	
19	1	11	68.0	59.7	
20	1	11	107.1	107.5	
21	1	11	61.8	141.5	
27	1	11	141.8	127.1	
28	1	11	111.0	90.4	
30	1	11	41.7	50.7	
33	1	11	71.6	63.4	
34	1	11	110.0	89.6	
35	1	11	86.6	84.7	
2	1	12	78.4	72.4	
3	1	12	158.9	155.0	
4	1	12	145.3	133.7	
9	1	12	63.3	55.5	
10	1	12	135.5	129.8	
11	1	12	111.9	118.1	
16	1	12	96.1	105.1	
31	1	12	103.7	101.7	
30	1	12	93.2	86.2	
2	1	14	92.2	94.6	
3	1	14	43.8	58.8	
4	1	14	141.3	138.5	
8	1	14	47.5	57.7	
10	1	14	138.0	153.3	
12	1	14	64.0	67.8	
16	1	14	87.1	117.8	
18	1	14	96.4	105.6	
24	1	14	106.0	123.6	
22	1	14	71.5	74.2	
6	1	15	52.0	66.4	
7	1	15	45.3	60.1	

At a nominal composition of 25 – 30 at.-% Ir and temperatures above 1050°C the diffraction pattern of another phase (or phases) was observed. The diffraction lines of this unknown phase are observed at about the same angles as for the $IrSi_3$ phases. A similar effect has been observed in the Ir-Al system.[10]

Table 5. Interatomic distances with standard deviations in Ir_3Si_4 (in Ångström units). Only distances shorter than 4.0 Å are listed.

Atoms	Dist.	St.dev.
Ir(1)— Ir(2)	2.953	0.004
—2Ir(1)	3.131	0.004
—2Ir(1)	3.712	0.006
— Si(1)	2.934	0.018
— Si(3)	2.402	0.020
— Si(4)	2.420	0.018
—2Si(4)	2.495	0.012
—2Si(3)	2.692	0.016
Ir(2)— Ir(3)	2.893	0.004
—2Ir(3)	2.917	0.004
— Ir(1)	2.953	0.004
—2Ir(2)	3.712	0.006
—2Ir(3)	3.981	0.005
— Si(1)	2.314	0.019
— Si(2)	2.417	0.020
—2Si(2)	2.453	0.013
—2Si(3)	2.501	0.013
— Si(1)	3.594	0.020
—2Si(1)	3.929	0.016
Ir(3)— Ir(2)	2.893	0.004
—2Ir(2)	2.917	0.004
—2Ir(3)	3.712	0.006
—2Ir(2)	3.981	0.005
—2Si(1)	2.334	0.012
— Si(3)	2.369	0.021
— Si(2)	2.503	0.020
— Si(4)	2.520	0.018
—2Si(2)	2.666	0.014
— Si(2)	3.694	0.021
— Si(1)	3.790	0.018
Si(1)— Ir(2)	2.314	0.019
—2Ir(3)	2.334	0.012
— Ir(1)	2.394	0.018
— Ir(2)	3.594	0.020
— Ir(3)	3.790	0.018
—2Ir(2)	3.929	0.016
—2Si(4)	2.655	0.018
—2Si(2)	2.655	0.019
Si(1)— Si(2)	3.056	0.026
—2Si(3)	3.428	0.024
— Si(4)	3.692	0.025
—2Si(1)	3.712	0.006
—2Si(3)	3.718	0.025
Si(2)— Ir(2)	2.417	0.020
—2Ir(2)	2.435	0.013
— Ir(3)	2.505	0.020
—2Ir(3)	2.666	0.014
— Ir(3)	3.694	0.021
—2Si(1)	2.655	0.019
— Si(1)	3.056	0.026
— Si(3)	3.132	0.028
—4Si(2)	3.519	0.009
—2Si(2)	3.712	0.006
— Si(4)	3.763	0.026
Si(3)— Ir(3)	2.369	0.021
— Ir(1)	2.402	0.020
—2Ir(2)	2.501	0.013
—2Ir(1)	2.692	0.016
— Si(4)	2.672	0.028
— Si(2)	3.132	0.028
— Si(4)	3.337	0.028
—2Si(1)	3.428	0.024
—2Si(3)	3.712	0.006
—2Si(1)	3.718	0.025
—2Si(4)	3.928	0.024
Si(4)— Ir(1)	2.420	0.018
—2Ir(1)	2.495	0.012
— Ir(3)	2.520	0.018
—2Si(4)	2.587	0.024
—2Si(1)	2.655	0.018
— Si(3)	2.672	0.028
— Si(3)	3.337	0.028
— Si(1)	3.692	0.025
—2Si(4)	3.712	0.006
— Si(2)	3.763	0.026
—2Si(3)	3.928	0.024

THE CRYSTAL STRUCTURE OF Ir_3Si_4

The unit cell dimensions of Ir_3Si_4 indicated that the structure might be isotypic with that of Rh_3Si_4.[5] A comparison of the Weissenberg films from the two compounds showed a close similarity, thus confirming the isotypism.

The atoms in the Ir_3Si_4 unit cell were thus assumed to be situated in the fourfold positions 4(*c*) of the space-group *Pnma*. The atomic parameters obtained for Rh_3Si_4 were used as starting parameters in the first electron density calculation. The preliminary atomic parameters were improved by successive electron density calculations, and the final refinement was made with the least-squares method. The following parameters were varied during the refinement: two scale factors, fourteen positional parameters and seven isotropic temperature factors. Reflections with intensities too weak to be observed were not included in the refinement and the eleven strongest reflections were omitted in order to reduce extinction effects. The final R value, based on 582 $h0l$ and hll reflections, was 0.127. The final shifts of all the parameters were less than 0.01 % of the calculated standard deviations. The result of the refinement of Ir_3Si_4 is given in Table 3, and the $|F_o|$ and $|F_c|$ values are listed in Table 4. Interatomic distances less than 4 Å are given in Table 5.

The structure was also refined with the atoms situated in the position 4(a) of the space-group $Pn2_1a$. Consequently another six parameters were added to those refined according to the space-group $Pnma$, namely the y-parameters. In the refinement one y-parameter was fixed in order to define the origin. The other y-parameters were given small displacements from the planes $y=1/4$ and $y=3/4$ before the refinement was started. After this refinement the y-parameters differed from the values 1/4 and 3/4 by less than 1/3 of the calculated standard deviation for the metal atoms and less than 1/2 of the calculated standard deviation for the non-metal atoms of the 4 (c) position in the space-group $Pnma$. The difference in reliability index between the two refinements was 0.001 which indicates that the most suitable space-group is $Pnma$.

Table 6. Average distances and differences for the compounds Ir_3Si_4 and Rh_3Si_4 expressed in Å.

M = Ir or Rh[a]

Distance type	Number of distances	Ir_3Si_4	Rh_3Si_4	Δ
M(1)–M	3	3.072	3.013	0.059
M(2)–M	4	2.920	2.892	0.028
M(3)–M	3	2.962	2.885	0.077
M(1)–Si	7	2.518	2.496	0.014
M(2)–Si	6	2.434	2.451	0.019
M(3)–Si	7	2.481	2.469	0.012
Si(1)–M	4	2.344	2.339	0.005
Si(2)–M	6	2.526	2.499	0.027
Si(3)–M	6	2.526	2.485	0.041
Si(4)–M	4	2.484	2.496	−0.013
Si(1)–Si	4	2.655	2.618	0.037
Si(2)–Si	2	2.655	2.634	0.021
Si(3)–Si	1	2.672	2.485	−0.055
Si(4)–Si	5	2.631	2.618	0.013

[a] The notations within brackets refer to the crystallographic positions in Table 3 and Ref. 5.

DISCUSSION OF THE STRUCTURE

The Rh_3Si_4 structure type represented by Ir_3Si_4, was described in detail in Ref. 5. This discussion will therefore be confined to a comparison between Rh_3Si_4 and Ir_3Si_4. Corresponding average interatomic distances in the two compounds are listed in Table 6. On examination of the different distances it can be noted that the average Ir – Ir distance in Ir_3Si_4 is about 0.05 Å longer than the corresponding distance in Rh_3Si_4 The metal-silicon and silicon-silicon distances in Ir_3Si_4 are somewhat longer than those in Rh_3Si_4 although not to a significant extent.

A COMMENT ON THE CRYSTAL STRUCTURE OF $IrSi_3$

According to an investigation made by Finnie[3] the $IrSi_3$ structure is of Na_3As type. An attempt to refine the only free parameter of the structure, *viz.*, the z-parameter of one of the silicon atoms, was not successful. A closer inspection of the atomic positions and the interatomic distances shows that the structure of $IrSi_3$, as suggested by Finnie, has one iridium atom and two silicon atoms on the line 1/3, 2/3, z within a distance of 6.6277 Å. A comparison of the unit cell dimensions of $IrSi_3$ with those of $IrAl_3$[8] (Na_3As type), $a = 4.246$ Å, $c = 7.756$ Å, shows that the c-axes differ by 1.13 Å. The length of the c-axis of $IrAl_3$ can be explained as the sum $2r_{Ir} + 4r_{Al}$ giving the approximate values 1.35 and 1.27 Å to the radii of Ir and Al, respectively. The radius of Ir is the one for 12 coordination while the radius of Al was obtained as an average from Table 7, Ref. 12. A calculation of the c-axis for the corresponding silicide of iridium gives a value of about 7.4 Å if the tetrahedral radius, 1.17 Å, is used for silicon. A c-axis of 6.63 Å thus reflects a silicon radius of ~1.0 Å, which is far too short. Further investigation [9] indicate that the silicon atoms do not occupy the positions proposed by Finnie, while the position of the iridium atom seems to be correct.

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