The Crystal Structure of Pd₃Si

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The crystal structure of Pd_3Si has been established from single crystal data. The space-group is *Pnma*, and there are four formula units in the elementary cell which has the dimensions $a = 5.735$ Å, $b = 7.555$ Å, and $c = 5.260$ Å. The twelve palladium atoms are situated in 8 (d) $(x = 0.1810, y = 0.0508, z = 0.3217)$ and 4 (c) $(x = 0.0053, z = 0.9036)$ positions, and the silicon atoms occupy a 4 (c) position $(x = 0.897_8, z = 0.469_4)$. Pd_3Si, thus, crystallizes in the cementite (DO_{11}) structure. The atomic arrangement in Pd_3Si is compared with those in isomorphous phases.

The crystal structures of some platinum metal silicides are being investigated at this Institute principally to elucidate the coordination around the silicon atom. In this paper we present the results of the structure determination of Pd_3Si and also comment on the Pd—Si system. The crystal structures of Ru_2Si and Rh_2Si have been reported in a preliminary note [1] and will be dealt with more comprehensively in a future paper.

EXPERIMENTAL

Palladium powder, (claimed purity 99.9 %, containing traces of Fe, Cu, and Ag), was obtained from Heraeus (Hanau, Germany), and silicon powder (claimed purity 99.9 %) from Pechiney (Paris). Because of the comparatively low melting points of Pd—Si alloys the samples were easily prepared by sintering (or melting) mixtures of the elements in evacuated and sealed silica tubes. No chemical analyses were made.

Powder photographs were taken in cameras of the Guinier type with CaF_2 ($a = 5.4630$ Å) as an internal standard. Two small single crystals ($\sim$0.3 × 0.04 × 0.04 mm) were picked out of an alloy which had the nominal composition $PdSi_{0.3}$ and had been annealed for two days at 900°C. (This temperature is slightly below the reported peritectic temperature [2,3] of 950°C.) Weissenberg photographs were taken around the *b*- and *c*-axes using $MoK\alpha$ radiation and the multiple film technique with thin iron foil between the films. Fourier projections were calculated with Beevers-Lipson strips and on the digital electronic computer BESK with a program (available at BESK) devised by M. Edstrand. The structure factors were also computed on BESK with a program devised by Åsbrink *et al.*[4] The following expression was used for the scattering factors:

$$f_i = A_i \cdot \exp(-\frac{a_i}{\lambda^2} \sin^2\Theta) + B_i \cdot \exp(-\frac{b_i}{\lambda^2} \sin^2\Theta) + C_i \cdot \exp(-\frac{c_i}{\lambda^2} \sin^2\Theta)$$

Table 1. Crystallographic constants of the well established silicides of palladium.

	Structure type	Lattice parameters (in Å)			References
Pd₃Si	DO_{11}	$a = 5.735,$	$b = 7.555,$	$c = 5.260$	(This work)
Pd₂Si	$C22$	$a = 6.497,$		$c = 3.432$ (silicon-poor) *	» »
	(revised)	$a = 6.528,$		$c = 3.437$ (silicon-rich) *	» »
PdSi	$B\ 31$	$a = 5.599,$	$b = 3.381,$	$c = 6.133$	10

* These values refer to alloys sintered at 800°C.

Appel [7] has calculated the following constants on the basis of the scattering factor tables by Tomas and Umeda [5] (palladium) and Tomiie and Stam [6] (silicon).

	A	B	C	a	b	c
Pd	15.865	17.354	12.288	0.233	2.565	19.828
Si	2.8315	6.8065	·4.3870	0.3235	2.2965	51.770

RESULTS

The Pd—Si system: We confirmed the existence of the earlier reported phases Pd₃Si[2,8], Pd₂Si[9,2,8], and PdSi [10,8]. In alloys containing more than 75 atom per cent palladium and annealed at 600—700°C, two additional intermediate phases were observed. The thermal effects observed by Lebeau and Jolibois [11] around 600°C in palladium alloys may have been caused by the formation of one of these phases, rather than by the supercooling of the peritectic formation of Pd₃Si as suggested in the handbook by Hansen [3]. The phase Pd₉Si₄ reported by Rao and Winterhager [8] could not be detected in our alloys.

The structures and unit cells of Pd₃Si, Pd₂Si and PdSi are given in Table 1. Schubert and Pfisterer [10] found the structure of PdSi to be of the $B\ 31$ type. Schubert and Anderko [2] found that Pd₂Si and Fe₂P were isomorphous and, as pointed out by Rundqvist and Jellinek [12], it is very probable that Pd₂Si, similarly to Fe₂P crystallizes in the revised $C\ 22$ structure. The lattice parameters (1. p.) of Pd₃Si, (the existence of this phase was first established by Schubert and Anderko[2]), were determined by the present authors. A typical powder photograph of an alloy with the nominal composition PdSi₀.₃ is given in Table 2. We could not detect any significant (*i.e.* > 0.05 %) l.p. variations for Pd₃Si. The l.p's of Pd₂Si, however, were considerably larger in silicon-rich alloys than in silicon-poor — indicating that Pd₂Si has an appreciable range of homogeneity.

The structure of Pd₃Si: The single crystal photographs showed that Pd₃Si is orthorhombic. Since $0kl$ reflexions were only observed for $k + l = 2n$ and $hk0$ reflexions only for $h = 2n$, the possible space-groups are *Pnma* and *Pn2₁a*. From the unit cell dimensions of Pd₃Si it was thought likely that it had the cementite structure [13-15] (space group *Pnma*). With this assumption the

Table 2. Powder photograph with Cr$K\alpha$ radiation of an alloy with the nominal composition PdSi$_{0.3}$. (The alloy was sintered at 780°C for five days.)

$h\,k\,l$	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$ for Pd₃Si	I_{obs}
101	0.0872	0.0873	w
020	∼0.0918	0.0919	vw
200	∼0.1592	0.1596	vw
121	0.1792	0.1793	st
002	0.1899	0.1897	w −
?	0.2037		vw
201	0.2069	02070	m
102	0.2298	⎰0.2296	st +
211		⎱0.2300	
?	0.2253		m −
220	0.2515	0.2515	st
112	0.2526	0.2526	st
031	0.2544	0.2543	st
?	0.2778		w
022	0.2816	0.2816	m
131	0.2940	0.2942	m −
221	0.2989	0.2989	st −
122	0.3216	0.3215	m
202	∼0.3495	0.3495	vw
230	0.3666	0.3664	w +
040	0.3676	0.3678	w +
301	∼0.407	0.4065	w
231	∼0.413	0.4139	vw

$\varrho(xz)$ and $\varrho(xy)$ projections were found to contain the expected number of maxima on an even background. We concluded that Pd₃Si was isomorphous with cementite (DO_{11}-type).

The atomic parameters were refined from successive difference syntheses until the backshift corrections were less than half the estimated standard deviations.

In both projections the observed intensities of the strongest reflexions were weaker than the calculated values, probably mainly due to secondary extinction. In the last stages of refinement the F_o-values of these reflexions, (which are marked with an asterisk in Table 3), were replaced by the corresponding F_c-values. Empirical isotropic temperature factors with $B = 0.55_9$ Å^2 ($h0l$-zone), and $B = 0.44_7$ Å^2 ($hk0$-zone) were applied. No corrections were made for absorption or dispersion.

The final parameters and standard deviations estimated using Cruickshank's formula [16] are as follows (space-group $Pnma$):

8 Pd$_I$ in 8 (d) : $x = 0.1810 \pm 0.0002$, $y = 0.0508 \pm 0.0003$,
$$z = 0.3217 \pm 0.0002$$
4 Pd$_{II}$ in 4 (c) : $x = 0.0053 \pm 0.0005$, $z = 0.9036 \pm 0.0005$
4 Si   in 4 (c) : $x = 0.897_6 \pm 0.002_0$, $z = 0.469_6 \pm 0.002_0$

Observed and calculated structure factors are given in Table 3. The final R values are 6.1 % for the 94 observed $h0l$ reflexions, and 8.2 % for the 66

Table 3. Observed and calculated structure factors for Pd₃Si.

hkl			F_c	$|F_o|$		hkl			F_c	$|F_o|$
0	0	2	−95.6	82.9 *		4	0	4	−68.1	69.1
0	0	4	−104.9	96.2 *		4	0	5	−80.0	78.4
0	0	6	76.9	75.7		4	0	6	−77.4	71.9
0	0	8	−84.9	87.7		4	0	7	103.8	95.0
0	0	10	46.0	43.3		4	0	8	18.4	—
0	0	12	40.8	42.8		4	0	9	−44.3	43.1
0	0	14	−43.6	37.0		4	0	10	29.6	—
						4	0	11	8.8	—
1	0	1	39.6	—		4	0	12	9.3	—
1	0	2	198.3	162.2 *		4	0	13	34.9	33.2
1	0	3	47.7	47.4		4	0	14	−2.0	—
1	0	4	−188.7	150.2 *						
1	0	5	−153.3	144.6 *		5	0	1	32.8	29.3
1	0	6	45.0	50.2		5	0	2	−63.1	56.6
1	0	7	−31.4	35.1		5	0	3	129.4	108.0 *
1	0	8	32.5	38.7		5	0	4	89.0	80.7
1	0	9	57.6	62.0		5	0	5	−136.9	120.3 *
1	0	10	−66.5	72.5		5	0	6	−30.2	28.9
1	0	11	5.5	—		5	0	7	−20.0	—
1	0	12	31.8	35.7		5	0	8	−26.5	24.4
1	0	13	8.4	—		5	0	9	66.9	66.3
1	0	14	0.4	—		5	0	10	31.2	35.4
						5	0	11	−18.9	—
2	0	0	−33.8	32.8		5	0	12	−14.4	—
2	0	1	−186.6	136.6 *		5	0	13	4.5	—
2	0	2	158.0	130.9 *		5	0	14	1.5	—
2	0	3	60.1	56.8						
2	0	4	−38.7	37.8		6	0	0	201.7	161.0 *
2	0	5	97.9	94.6		6	0	1	−67.3	66.4
2	0	6	−143.0	127.6 *		6	0	2	−68.7	67.8
2	0	7	−80.6	79.9		6	0	3	23.0	24.0
2	0	8	64.1	67.8		6	0	4	−81.5	81.2
2	0	9	44.7	48.4		6	0	5	31.0	31.0
2	0	10	23.4	—		6	0	6	31.0	34.4
2	0	11	15.4	—		6	0	7	−58.4	63.0
2	0	12	−7.2	—		6	0	8	−52.5	55.4
2	0	13	−23.3	21.5		6	0	9	11.2	—
2	0	14	10.3	—		6	0	10	36.2	37.6
						6	0	11	5.0	—
3	0	1	217.3	153.8 *		6	0	12	32.2	34.0
3	0	2	−47.8	47.6		6	0	13	−12.5	—
3	0	3	−208.8	156.1 *						
3	0	4	37.0	37.3		7	0	1	64.2	59.2
3	0	5	43.8	48.1		7	0	2	121.9	107.5
3	0	6	−32.7	36.8		7	0	3	−24.6	—
3	0	7	−23.1	21.3		7	0	4	−90.7	84.9
3	0	8	−25.9	23.0		7	0	5	−38.8	43.1
3	0	9	−34.1	44.8		7	0	6	41.4	40.9
3	0	10	10.6	—		7	0	7	−16.6	—
3	0	11	74.9	79.3		7	0	8	28.6	30.9
3	0	12	−10.1	—		7	0	9	13.8	—
3	0	13	−15.9	—		7	0	10	−44.7	43.3
3	0	14	0.0	—		7	0	11	22.5	—
						7	0	12	31.7	30.8
4	0	0	47.9	46.1		7	0	13	− 1.9	—
4	0	1	200.8	146.6 *						
4	0	2	34.0	31.8		8	0	0	−48.3	52.5
4	0	3	−20.3	—		8	0	1	−27.1	25.7

Table 3. Cont.

h k l	F_c	$|F_o|$
8 0 2	89.3	85.5
8 0 3	14.6	—
8 0 4	−10.7	—
8 0 5	11.8	—
8 0 6	−98.2	97.4
8 0 7	−36.3	34.1
8 0 8	54.4	59.8
8 0 9	0.9	—
8 0 10	11.6	—
8 0 11	2.3	—
8 0 12	−11.4	—
9 0 1	57.7	54.3
9 0 2	−38.5	42.2
9 0 3	−77.4	77.2
9 0 4	69.1	68.3
9 0 5	0.5	—
9 0 6	−22.5	—
9 0 7	−13.7	—
9 0 8	−22.4	—
9 0 9	−9.7	—
9 0 10	28.0	31.4
9 0 11	38.4	38.2
9 0 12	−11.4	—
10 0 0	78.1	75.3
10 0 1	76.1	81.8
10 0 2	2.8	—
10 0 3	−2.6	—
10 0 4	−25.1	—
10 0 5	−35.8	41.2
10 0 6	−2.6	—
10 0 7	41.6	42.2
10 0 8	−12.1	—
10 0 9	−27.2	27.1
10 0 10	17.7	—
10 0 11	−4.5	—
11 0 1	−8.4	—
11 0 2	6.4	—
11 0 3	51.0	58.2
11 0 4	7.5	—
11 0 5	−70.4	72.9
11 0 6	−8.4	—
11 0 7	−10.8	—
11 0 8	−10.5	—
11 0 9	39.1	39.2
11 0 10	−1.2	—
12 0 0	54.6	61.3
12 0 1	−38.2	36.8
12 0 2	−6.6	—
12 0 3	23.0	—
12 0 4	−22.5	—
12 0 5	30.4	28.5
12 0 6	1.1	—
12 0 7	−37.7	40.5
12 0 8	−12.4	—

h k l	F_c	$|F_o|$
12 0 9	14.4	—
13 0 1	32.6	33.4
13 0 2	37.1	41.5
13 0 3	−29.8	29.2
13 0 4	−29.4	29.7
13 0 5	1.6	—
13 0 6	6.3	—
13 0 7	−5.9	—
13 0 8	2.3	—
14 0 0	−24.5	25.6
14 0 1	13.0	—
14 0 2	27.1	25.0
14 0 3	7.1	—
14 0 4	−5.9	—
14 0 5	−0.7	—
14 0 6	−40.1	34.7
14 0 7	1.2	—
15 0 1	22.5	—
15 0 2	−17.2	16.1
15 0 3	−7.9	—
15 0 4	33.2	27.9
15 0 5	−6.2	—
0 2 0	54.7	50.6
0 4 0	236.8	157.1 *
0 6 0	−198.9	145.3 *
0 8 0	−33.0	—
0 10 0	213.1	176.8 *
0 12 0	−16.3	—
0 14 0	−79.7	85.5
0 16 0	62.6	79.7
0 18 0	13.7	—
0 20 0	62.9	—
2 0 0	−33.9	35.7
2 1 0	−44.0	49.0
2 2 0	−295.6	189.5 *
2 3 0	−184.2	145.2 *
2 4 0	81.6	79.5
2 5 0	−141.3	121.8 *
2 6 0	−61.3	56.6
2 7 0	−121.3	106.1
2 8 0	169.0	145.4 *
2 9 0	−16.1	—
2 10 0	14.3	—
2 11 0	22.0	—
2 12 0	102.9	106.5
2 13 0	63.4	68.8
2 14 0	−29.9	—
2 15 0	49.0	55.0
2 16 0	17.2	—
2 17 0	34.8	39.0
2 18 0	−53.0	58.0
2 19 0	5.2	—
2 20 0	−4.6	—

Table 3. Cont.

h k l	F_c	$|F_o|$		h k l	F_c	$|F_o|$
4 0 0	48.6	53.0		8 11 0	23.6	—
4 1 0	69.2	75.5		8 12 0	80.4	86.5
4 2 0	−108.9	104.7		8 13 0	3.3	—
4 3 0	162.5	137.8 *		8 14 0	−15.5	—
4 4 0	64.0	59.9		8 15 0	25.5	—
4 5 0	177.1	148.3 *		8 16 0	6.7	—
4 6 0	−54.4	52.0		8 17 0	0.5	—
4 7 0	117.3	102.1		8 18 0	−46.7	—
4 8 0	72.4	67.4				
4 9 0	32.6	31.0		10 0 0	85.0	88.3
4 10 0	−26.3	31.0		10 1 0	12.9	—
4 11 0	−35.4	36.6		10 2 0	−24.9	—
4 12 0	47.9	49.8		10 3 0	78.2	79.5
4 13 0	−63.4	73.6		10 4 0	57.0	55.3
4 14 0	−27.0	—		10 5 0	63.7	61.0
4 15 0	−62.7	73.6		10 6 0	−54.0	53.3
4 16 0	20.6	—		10 7 0	−64.1	65.4
4 17 0	−39.4	46.2		10 8 0	18.0	—
4 18 0	−25.9	—		10 9 0	− 6.3	—
4 19 0	− 7.8	—		10 10 0	−55.8	54.6
4 20 0	9.6	—		10 11 0	−10.3	—
				10 12 0	14.1	
6 0 0	208.0	177.6 *		10 13 0	−44.3	45.3
6 1 0	−57.5	61.5		10 14 0	−27.8	26.5
6 2 0	48.2	49.8		10 15 0	−30.8	29.2
6 3 0	−37.0	37.7		10 16 0	24.7	—
6 4 0	96.2	94.0				
6 5 0	−98.7	100.9		12 0 0	61.7	57.4
6 6 0	−90.9	83.5		12 1 0	−24.6	—
6 7 0	−27.8	25.6		12 2 0	− 6.1	—
6 8 0	−35.3	36.2		12 3 0	−39.2	—
6 9 0	−32.2	36.2		12 4 0	37.5	37.0
6 10 0	−119.4	115.0		12 5 0	−58.8	54.5
6 11 0	30.4	—		12 6 0	−36.2	—
6 12 0	−20.1	—		12 7 0	−32.2	—
6 13 0	19.1	—		12 8 0	4.2	—
6 14 0	−39.7	46.5		12 9 0	−16.9	—
6 15 0	38.3	50.6		12 10 0	−43.4	40.6
6 16 0	38.6	45.9		12 11 0	18.6	—
6 17 0	10.7	—		12 12 0	4.9	—
6 18 0	12.6	—		12 13 0	23.3	—
6 19 0	9.6	24.4		12 14 0	−19.9	—
8 0 0	−51.0	60.8		14 0 0	−29.0	27.8
8 1 0	−41.9	48.0		14 1 0	− 5.9	—
8 2 0	−155.9	150.2		14 2 0	−54.2	45.3
8 3 0	− 2.7	—		14 3 0	16.8	—
8 4 0	29.1	29.1		14 4 0	3.9	—
8 5 0	−60.0	61.5		14 5 0	0.9	—
8 6 0	−21.4	—		14 6 0	− 1.8	—
8 7 0	− 2.0	—		14 7 0	14.6	—
8 8 0	117.2	109.3		14 8 0	45.6	34.0
8 9 0	−25.7	—		14 9 0	− 5.0	—
8 10 0	31.9	39.7		14 10 0	20.8	—

* F_o values with an asterisk have been omitted in the last stages of refinement and are not included in the final R-values.

Table 4. Interatomic distances (< 3.6 Å) in Pd$_3$Si (in Å units).

			Average
Pd$_I$ in 8 (d) —	6 Pd$_I$:	2.85 (2), 2.90, 2.97 (2), 3.01	2.95
	5 Pd$_{II}$:	2.78, 2.80, 2.85, 2.93, 3.56	
	3 Si :	2.35, 2.48, 2:56	
Pd$_{II}$ in 4 (c) —	10 Pd$_I$:	2.78 (2), 2.80 (2), 2.85 (2), 2.93 (2), 3.56 (2)	3.03
	2 Pd$_{II}$:	3.29 (2)	
	3 Si :	2.35, 2.37, 3.04	
Si in 4 (c) —	6 Pd$_I$:	2.35 (2), 2.48 (2), 2.56 (2)	2.44
	3 Pd$_{II}$:	2.35, 2.37, 3.04	(8 closest)

observed $hk0$ reflexions (excluding the reflexions marked with an asterisk in Table 3).

Interatomic distances are given in Table 4. The standard deviations of Pd—Pd distances are less than 0.01 Å, whereas the standard deviations of Pd—Si distances vary between 0.00$_8$ Å and 0.01$_4$ Å.

COMPARISON WITH ISOMORPHOUS PHASES

The cementite structure, that has been comprehensively described in earlier papers [14,15,17–19], consists of a rather densely packed framework of the larger atoms, (A atoms in the following), which each coordinate 11 or 12 similar atoms. The smaller atoms (X atoms) are situated in holes in the A atom skeleton; the X atoms have nine A neighbours, but no contact with atoms of their own kind. As seen from Table 5, the environment of the X atom is somewhat different in the four cementite-type phases which have been studied in detail, namely Fe$_3$C [15], Ni$_3$B [19], Pd$_3$Si and NiAl$_3$ [17]. In Fe$_3$C and Ni$_3$B, six A neighbours of the X atom are much closer than the other three, and form a triangular prism around the X atom. In Pd$_3$Si two of the A neighbours outside the 'prism' are brought nearer to the X atom whereas the ninth neighbour is still so remote

Table 5. Interatomic distances between unlike atoms in cementite phases (A$_3$X).

	Distances between the X atom and A atoms at the corners of the prism			Distances between the X atom and A atoms outside the prism		Ref.
	A atoms in 4 (c)	A atoms in 8 (d)	Average	A atoms in 8 (d)	A atom in 4 (c)	
Fe$_3$C	1.85, 1.89	2.06 (2), 2.15 (2)	2.03	2.31 (2)	3.02	15
Ni$_3$B	2.02, 2.09	1.99 (2), 2.07 (2)	2.04	2.30 (2)	2.59	19
Pd$_3$Si	2.35, 2.37	2.35 (2), 2.48 (2)	2.39	2.56 (2)	3.05	this work
NiAl$_3$	2.44, 2.46	2.42 (2), 2.44 (2)	2.44	2.52 (2)	2.72	17

that it probably need not be taken into consideration when discussing the environment of the X atom. The eight shortest Pd—Si distances in Pd_3Si are not very different and the polyhedron of palladium atoms around the silicon atom seems to be best described as distorted archimedian antiprism. Finally, in $NiAl_3$, the nine Ni—Al distances do not differ by more than 12 % and probably all represent bonding contacts.

It is also evident from Table 5 that a contraction of the $A-X$ distances takes place in the series Fe_3C, Ni_3B, Pd_3Si and $NiAl_3$. The difference (in Å) between the average of the six shortest $A-X$ distances and the A radii for coordination number 12, ($r_{Fe} = 1.27$, $r_{Ni} = 1.24$, $r_{Pd} = 1.37$ and $r_{Al} = 1.43$) are 0.76, 0.80, 1.02, and 1.01 in Fe_3C, Ni_3B, Pd_3Si, and $NiAl_3$, respectively. Thus, whereas the figures for Fe_3C and Ni_3B agree well with those found in other carbides and borides, the figure for Pd_3Si is considerably smaller than in previously studied silicides. In $NiAl_3$, as in a number of phases between aluminium and transition metals [18], the distances between unlike atoms are very short.

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