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Some Notes on the Palladium-Silicon System

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The crystal structure of metal-rich Pd_2Si, (revised $C22$ type) has been refined by single-crystal X-ray methods. Silicon-rich Pd_2Si has a hexagonal superstructure with $a = 13.05_5$ Å and $c = 27.49_0$ Å. A powder diffraction film of a metal-rich phase, of probable composition $Pd_{4.5}Si$, has been indexed with an orthorhombic cell where $a = 7.418$ Å, $b = 9.396$ Å, and $c = 9.048$ Å.

The binary system palladium-silicon has been the subject of earlier investigations at this Institute.[1] Pd_2Si showed marked lattice parameter variations and has been the subject of further investigations.

EXPERIMENTAL

Preparation. The starting materials were palladium powder (Heraeus, Hanau, Germany, claimed purity 99.9 % and Johnson, Matthey & Co., Ltd., London, claimed purity 99.9 %) and semiconductor grade silicon powder. Samples of suitable compositions were sintered or melted in evacuated and sealed silica tubes. The heat-treatments were generally interrupted by dropping the silica tubes into cold water.

X-Ray work. X-Ray powder photographs were taken in Guinier-Hägg focusing cameras with Cu$K\alpha$ ($\lambda = 1.54178$ Å), Cu$K\alpha_1$ ($\lambda = 1.54051$ Å), and Cr$K\alpha_1$ ($\lambda = 2.28962$ Å) radiations. CaF_2 ($a = 5.4630$ Å) and Si ($a = 5.4305$ Å) were used as internal calibration standards.

A single-crystal fragment was picked from an alloy containing Pd_2Si and a small amount of Pd_3Si. The nominal composition was $PdSi_{0.48}$. The sample had been melted and was then sintered at 900°C for two days. The crystal form could be approximated to a right triangular prism of height 105 μ. The triangular edges were 25, 30, and 30 μ. Photographs were taken in an equi-inclination Weissenberg camera with Zr-filtered Mo$K\alpha$ radiation. Intensity data were obtained using the multiple-film technique with thin iron foils interleaved between the films. The crystal was rotated about the c-axis, approximately perpendicular to the triangular faces of the prism, and the layer lines $hk0$ and $hk1$ were recorded. The intensities were estimated visually by comparison with a calibrated intensity scale. A total of 59 independent $hk0$ and 53 independent $hk1$ reflexions were measured.

Calculations. All the calculations were performed on the digital electronic computers listed below. The cell dimensions were refined by the least squares method. Lorentz and polarisation factors were applied to intensity data. In the structure factor calculations the atomic scattering factors of palladium and silicon were obtained from *Int. Tab. for X-ray Cryst.*[2] The structure was refined by the method of least squares employing a weighting scheme according to Cruickshank *et al.*,[3] $w = 1/(a + |F_o| + c|F_o|^2)$, where the weighting constants a and c were put equal to $2|F_{o,min}|$ and $2/|F_{o,max}|$, respectively.

Type of computer	Kind of calculation	Programme Author
BESK and FACIT EDB	Lorentz and polarisation factor corrections.	Lundberg, B. University of Umeå.
	Structure factor calculations.	Liminga, R. and Olovsson, I. University of Uppsala.
	Summation of Fourier series.	Liminga, R. and Olovsson, I.
	Calculations of interatomic distances.	Liminga, R. and Olovsson, I.
IBM 1620	Least squares refinement of unit cell dimensions.	Tegenfeldt, J. University of Uppsala.
	Application of film factors on intensity data.	Lundgren, J.-O. University of Uppsala.
	Calculation of weighting-factors.	Lindgren, J. University of Uppsala.
IBM 7090	Least squares refinement.	Busing, W. R., Martin, K. O. and Levy, H. A. Oak Ridge National Laboratory, Tennessee, U.S.A.

THE PALLADIUM-SILICON SYSTEM

Two new metal-rich phases were reported in an earlier note.[1] Powder diffraction films of good quality have now been obtained where one of the phases, evidently the most metal-rich, appears together with palladium and the other phase appears together with Pd_3Si. Films were also obtained where both of the phases appear together. Diffraction patterns of the less metal-rich phase can be indexed on the basis of an orthorhombic cell with $a = 7.418$ Å, $b = 9.396$ Å, and $c = 9.048$ Å with standard deviations of 0.0009, 0.0006, and 0.0005 Å, respectively. The cell volume is 630.7 Å^3, and from density considerations a possible cell content could be 36 palladium atoms and 8 silicon atoms. The recently investigated palladium phosphide $Pd_{4.8}P$ [4] has 18 palladium atoms in a cell volume of 318.8 Å^3, which is approximately one half of the cell volume for the silicide. It is very difficult to obtain a single crystal for X-ray examination as the metal-rich palladium-silicon preparations are malleable. Interesting phenomena are observed in samples containing 15—23 at.% silicon.[5]

Table 1. Lattice parameters (in Å) of Pd_2Si in alloys quenched from various temperatures. Standard deviations 0.001 Å or smaller.

Phases in the sample	Temp.	a	c
Pd_3Si and Pd_2Si	900°C	6.496	3.433
Pd_3Si and Pd_2Si	1050°C	6.492	3.434
Pd_3Si and Pd_2Si	1100°C	6.503	3.432
Pd_2Si and PdSi	850°C	6.531	3.437
Pd_2Si and PdSi	900°C	6.528	3.436
Pd_2Si and PdSi	1000°C	6.529	3.435
Pd_2Si and PdSi	1150°C	6.527	3.435

Attempts have been made to determine the lattice parameter variations in Pd_2Si but it is extremely difficult to achieve thermodynamical equilibrium in the samples. Some results are presented in Table 1. When a diffraction pattern of silicon-rich Pd_2Si has been indexed hexagonally with $a = 6.53$ Å and $c = 3.44$ Å some weak diffraction lines, which do not belong to PdSi, generally remain. They fit into the pattern, as revealed in Table 2, if a hexagonal cell with $2a$ and $8c$ is used. This indicates a superstructure which has been confirmed by a single crystal oscillation photograph where the crystal was rotated about the c-axis.

During the investigations of the palladium-silicon system there were indications that PdSi does not exist below approximately 600°C.

Table 2. Powder diffraction data for silicon-rich Pd_2Si with superstructure, sintered at 900°C. Cu$K\alpha$ radiation, $\lambda = 1.54178$ Å. $a = 13.05_5$ Å, $c = 27.49_0$ Å.

$h\ k\ l$	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	I_{obs}
2 0 0	0186.1	0186.0	w−
1 1 4	0263.7	0265.3	w
2 0 4	0314.1	0311.8	w
3 0 0	0417.5	0418.4	w−
0 0 8	~0499	0503.3	w− −
2 2 0	0557.6	0557.9	m
2 0 8	0689.9	0689.3	m−
4 0 0*	0752.2	0743.9	w+
2 2 8	1061.5	1061.2	st+
2 0 11	1137.1	1137.5	w
1 0 12	1184.2	1178.9	w−
5 0 2		1193.7	
4 0 8	1248.1	1247.1	st
2 4 0	1302.0	1301.8	st
3 0 11	1371.4	1369.9	w
2 4 3		1372.5	
1 0 13		1375.5	
6 0 0	1673.7	1673.7	st−
2 4 8	1805.2	1805.0	m
0 0 16	2014.0	2013.1	m+
6 2 0	2416.6	2417.5	m
2 2 16	2569.5	2571.0	m−
4 4 8	2734.1	2734.9	m−
2 6 7	2804.9	2802.9	w
6 0 12		2806.1	
4 5 0	2838.2	2836.0	w
0 0 19		2838.9	
2 4 14		2843.1	
4 5 1		2843.8	
6 2 8	2919.4	2920.8	m+
8 0 0	2972.1	2975.4	w+
1 7 7	3041.2	3035.3	w−
0 8 3		3046.2	
2 4 15	~3090	3071.1	diffuse
0 8 4		3101.3	
2 2 18		3105.8	
2 4 16	3315.0	3314.9	m+
8 0 8	3478.7	3478.7	m

Table 2. Continued.

h k l	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	I_{obs}
6 4 0	3531.8	3533.3	m−
6 0 16*	3688.4	3686.8	m+
8 2 0	~3913	3905.3	diffuse
6 4 8	4038.1	4036.6	st
0 0 23	4162.2	4160.0	w+
4 5 13		4164.9	
4 4 16	4244.4	4244.7	w−
2 8 7	4294.3	4290.6	w−
0 7 16		4291.2	
3 5 16		4291.2	
1 1 23		4299.5	
1 9 3		4301.5	
6 2 16	4430.0	4430.7	m
1 9 6	4523.8	4513.8	w
5 6 6		4513.8	
0 8 14		4516.7	
3 8 1		4517.5	
7 4 5		4520.3	
1 8 12		4526.2	
0 0 24		4529.6	
10 0 0	4647.4	4649.1	w+
8 0 16	4990.6	4988.6	w

* overlapped by a line belonging to PdSi.

STRUCTURE REFINEMENT

From the observed intensity data for Pd_2Si it was evident that the structure-type proposed earlier was correct.[6] The positional parameters of Fe_2P were used for the calculation of electron density maps $\varrho(x,y,0)$ and $\varrho(x,y,\frac{1}{2})$, where the maxima of all the expected atoms were well resolved and no additional maxima appeared. Refinement with least squares methods was performed, and the atomic positional parameters, individual isotropic temperature factors and two scale factors were allowed to vary. The data were weighted according to the formula of Cruickshank *et al.* No absorption or dispersion corrections were included. The strong low-angle reflexion (111) was probably affected by extinction. After the last cycle of refinement the shifts were less than one tenth of the standard deviations. The *R*-value was 0.092. The temperature factors are greater than would be expected. The metal atoms in position II have a temperature factor significantly higher than the metal atoms in position I. This phenomenon has been observed earlier in the revised *C*22 structure.[7] Final structure data for Pd_2Si are given in Table 3. Interatomic distances are listed in Table 4.

DISCUSSION OF THE STRUCTURE

Schubert and Anderko [6] found that Pd_2Si and Fe_2P were isomorphous. It was pointed out by Rundqvist and Jellinek,[8] who determined the revised *C*22 structure, that Pd_2Si in common with Fe_2P, very probably also crystallizes with this structure type. This has now been confirmed in the present single crystal examination.

Table 3. Structure data for palladium-rich Pd_2Si. Space-group $P\bar{6}2m$ (D_{3h}^3); $z = 3$; $a = 6.496$ Å, $\sigma(a) = 0.0005$ Å, $c = 3.433$ Å, $\sigma(c) = 0.0004$ Å; $U = 125.5$ Å^3.

	x	$\sigma(x)$	B	$\sigma(B)$
3 Pd_I 3(*f*)	0.2636	0.0006	0.43	0.04
3 Pd_{II} 3(*g*)	0.6062	0.0008	0.85	0.07
2 Si_I 2(*c*)			0.66	0.29
1 Si_{II} 1(*b*)			1.28	0.65

Table 4. Interatomic distances (in Å) in Pd_2Si. Distances shorter than 3.6 Å are listed. The figure in brackets denotes the number of equivalent distances.

	Pd_I	Pd_{II}	Si_I	Si_{II}
Pd_I	2.97 (2)	2.81 (2)	2.42 (2)	2.42 (2)
	3.43 (2)	2.84 (4)		
Pd_{II}	2.81 (2)	3.43 (2)	2.63 (4)	2.56
	2.84 (4)	3.46 (4)		
Si_I	2.42 (3)	2.63 (6)	3.43 (2)	
Si_{II}	2.42 (6)	2.56 (3)		3.43 (2)

In a recent survey of transition metal phosphides [9] the individual differences in metal—non-metal distances of a *C*22 structure were explained on a geometrical basis for phosphides belonging to this group. The same kind of distance differences in this silicide (see Table 4) are comparable with those in the phosphides. Thus the same approach could be applied to this phase. From Table 4 it is also evident that the sum of the Goldschmidt CN12 palladium radius 1.37 Å and the covalent tetrahedral silicon radius 1.17 Å is considerably greater than the shortest Pd—Si distances in Pd_2Si. This is in accordance with the established fact that many borides, silicides and phosphides of the eighth group elements have remarkably short distances between unlike atoms.[10] However, this tendency seems to be less pronounced in Pd_2Si than it is in Pd_3Si.[1]

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REFERENCES

1. Aronson, B. and Nylund, A. *Acta Chem. Scand.* **14** (1960) 1011.
2. *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, England 1962.
3. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Pergamon, Oxford 1961, p. 32.

4. Sellberg, B. *Acta Chem. Scand. In print.*
5. Duwez, P., Willens, R. H. and Crewdson, R. C. *AEC Research and Development Report No. 29*, under Contract No. AT(04-3)-221, (1964).
6. Anderko, K. and Schubert, K. *Z. Metallk.* **44** (1953) 307.
7. Rundquist, S. *Acta Chem. Scand.* **16** (1962) 992.
8. Rundquist, S. and Jellinek, F. *Acta Chem. Scand.* **13** (1959) 425.
9. Rundquist, S. *Arkiv Kemi* **20** (1962) 67.
10. Aronsson, B., Lundström, T. and Rundquist, S. *Borides, Silicides and Phosphides*, Methuen, London 1965.

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