The Crystal Structure of $Pd_{15}P_2$

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The crystal structure of $Pd_{15}P_2$ has been determined and refined from 2080 three-dimensional single-crystal X-ray diffractometer data to an $R(F^2)$ value of 0.092. The space group is $R\bar{3}$ (No. 148). The hexagonal unit cell, of dimensions $a = 7.1067(2)$ Å, $c = 17.0867(6)$ Å, contains three formula units. The structure is related geometrically to the α-boron structure.

In the $Pd-P$ system Gullman [1] found a very palladium-rich intermediate phase which forms peritectically at 799 °C and has the approximate composition Pd_6P. In the present paper the results from a crystal structure analysis of this phase are presented. The ideal crystallographic formula is $Pd_{15}P_2$.

EXPERIMENTAL

Preparation. Starting materials were palladium powder (Heraeus, Germany) with a claimed purity of 99.9 % and red phosphorus of purity greater than 99 %. Polycrystalline $Pd_{15}P_2$ samples were prepared in exactly the same manner as described by Gullman.[1] To obtain single crystals for X-ray investigations, pressed pellets of well-mixed palladium and phosphorus powder were heated in evacuated silica tubes at 830 °C for two days and 795 °C for five months. In spite of the long heat-treatment the sample contained Pd and Pd_6P in addition to $Pd_{15}P_2$. Out of the crushed sample good crystals could be obtained, even though they were all of an irregular needle shape.

X-Ray powder investigations. Powder diffraction patterns were obtained with focusing Hägg-Guinier-type cameras using $CrK\alpha_1$ or $CuK\alpha_1$ radiation and silicon $(a = 5.431065$ Å) [2] or germanium $(a = 5.65806$ Å) as calibration standards. Cell parameters were refined by the least-squares method using the local program CELNE.[3] Powder diffraction intensity data were obtained by measuring Hägg-Guinier photographs on an automatic drum densitom-

eter (SAAB model 2), using a method similar to that described by Malmros and Werner.[4]

Single crystal investigations. Single crystal diffraction intensity data were recorded on a Stoe four-circle diffractometer with a graphite monochromator using $MoK\alpha$ radiation. The intensity measurements were made using the ω-2θ step scan technique, to a maximum in 2θ of 100°. For symmetry control, symmetry-related reflexions were measured in the region $0 \leq 2\theta \leq 40°$ and their hexagonal indices were limited by $-3 \leq h \leq 5$, $-5 \leq k \leq 3$ and $-12 \leq l \leq 12$. For $2\theta > 40°$ the hexagonal indices ranged between $0 \leq h \leq 15$, $-13 \leq k \leq 0$ and $-36 \leq l \leq 36$. Instrumental stability and the crystal setting were checked regularly using three standard reflexions remeasured every 50 reflexions. The weakest of these three, $(0\bar{1}7)$, was found to vary somewhat erratically, while the other two remained within expected fluctuations.

Absorption corrections were applied to the single crystal data. The shape of the crystal was approximated to a triangular prism bounded by $\{\bar{1}\bar{1}\bar{1}\}$, $\{\bar{3}4\bar{6}\}$, $\{0\bar{1}7\}$, $\{116\}$ and $\{3\bar{2}9\}$ planes. The length of the crystal was 0.120 mm and the edges of the triangular cross-sections ranged from 0.033 to 0.057 mm. The minimum and maximum transmission factors were 0.157 and 0.789, using a calculated linear absorption coefficient of 259 cm^{-1}.

The calculations were performed on IBM 370/155 and IBM 1800 computers using crystallographic programs listed in Ref. 5.

STRUCTURE ANALYSIS

The powder diffraction data obtained for $Pd_{15}P_2$ were in very good agreement with Gullman's [1] Pd_6P results. The $Pd_{15}P_2$ powder data as obtained in this study are given in Table 1. Using the information from Weissenberg photographs the powder pattern could be indexed with a hexagonal cell of dimensions $a = 7.1067(2)$ Å and $c = 17.0867(6)$ Å at 25 °C (numbers in parentheses are the calculated standard devia-

Table 1. Powder diffraction data for Pd$_{15}$P$_2$. (Guinier-Hägg camera, CuKα_1 radiation, internal calibration standard silicon $a = 5.431065$ Å, intensities from film scanner.)

hk l	Qx10⁵ (Å⁻²) obs.	calc.	Intensity obs.	calc.
10 1		2982	-	0
00 3		3083	-	0
01 2		4010	-	1
11 0		7920	-	0
10 4		8120	-	0
02 1	10896	10902	2	1
1̄2 3			-	0
11 3	11004	11002	-	1
01 5	11196	11203	-	1
20 2	11917	11930	-	0
00 6		12331	-	0
02 4		16040	-	0
2̄3 1				3
21 1	18814	18822	74	73 / 27
20 5	19125	19123	45	64
10 7	19432	19423	32	35
1̄3 2			66	12 / 30
12 2	19849ᵃ	19850		
12 6			75	24 / 65
11 6	20249	20251		
30 0	23756	23760	20	23
2̄3 4				0
21 4	23953	23960	11	0 / 11
01 8		24561	-	0
03 3			5	5 / 0
30 3	26846	26842		
1̄3 5				28
12 5	27045	27043	24	4
02 7	27338	27343	5	5
00 9	27734	27744	-	0
22 0	31659	31680	2	1
2̄0 8	32482	32481	-	0
14 1			5	2
13 1	34665	34662		2 / 0
2̄4 3		34762	-	0
22 3				0
2̄3 7		35263	-	0
21 7				0
1̄2 9			-	2
11 9	35670	35664	5	1 / 6
3̄4 2		35690		0
31 2				0
03 6	36090	36090	1	1
30 6				0
1̄010	36892	36892	2	2
1̄4 4			7	4
13 4	39798	39800		4
1̄3 8			7	4
12 8	40396	40401		4
40 1		42582	-	0
3̄4 5				0
31 5		42882	-	0
04 2	43584	43610	4	4
2̄4 6				0
22 6	44062	44010	4	1
0111		44085		2
02̄10	44809	44812	3	3
40 4		47720	-	0
0012	49307	49323	6	6
3̄5 1			7	3 / 3
32 1	50482	50502		3
04 5	50828	50802	5	4
1̄4 7			18	11 / 5
13 7	51087	51103		
03 9		51504		3
30 9				0
2̄5 2	51511		6	1
23 2		51530		0
2011		52005	-	0
2̄310		52732	-	1
2110				0
14 0	55446	55439	28	6 / 16
41 0				5
35 4	55642	55640	17	9
32 4				3
34 8	56243	56241	10	3
3̄1 8				3
1̄212	57242	57243	22	14 / 3
1112				3
45 3				9
15 3	58524	58522	14	3 / 1
41 3				1
14 3				1
25 5	58713	58722	20	4 / 14
23 5				
40 7	59042	59023	23	22
24 9	59431	59424	5	1 / 2
22 9				
1̄311	59932	59925	23	6 / 10
1211				
1013		60526	-	0
04 8		64161	-	0
05 1		66342	-	0
35 7				0
32 7		66943	-	0
50 2	67380	67369	2	1
15 6				0
45 6	67778	67770	5	0
41 6				0
14 6				0
0213		68446	-	1
1̄410				0
1310	68578	68572	8	5
0114	69760	69774	5	4
33 0		71279	-	0
05 4		71480	-	0
25 8	72091	72081	14	9 / 6
23 8				0
3012		73082	-	0
0312				0
26 1		74262	-	0
24 1				1
3̄6 3	74264		4	0 / 1
33 3		74362		1
50 5		74562	-	1
46 2	75280	75289	20	12 / 9
42 2				
3411	75758	75764	8	0 / 5
3111				0
2̄313	76401	76366	32	9 / 11
2113				
4010		76491		8
0015		77067	-	0
2014	77700	77694	2	3
26 4				1
24 4		79400	-	3
2̄412				4
2212	81020	81002	8	3 / 5
56 1				5
51 1	82176	82182	4	1
46 5	82499	82482	2	1 / 1
42 5				2
05 7	82801	82783	2	3

ᵃ overlapped by Fd.

tions). No significant changes in the unit cell dimensions were observed for different samples.

Weissenberg photographs taken with the crystal rotating about the hexagonal a-axis showed that the rhombohedral condition $-h + k + l = 3n$ was obeyed for all reflexions. Since

only a three-fold symmetry was observed, most likely space groups were $R3$ and $R\bar{3}$. The cell volume and the approximate composition Pd$_8$P suggested a unit cell content of about 48 palladium and six phosphorus atoms.

In the preliminary structure analysis, the Harker section $P(u,v,0)$ of the Patterson function indicated $R\bar{3}$ space group symmetry with palladium atoms in two general positions. Space considerations and the Harker section $P(u,0,w)$ indicated two further palladium sites, in 6c and 3b, and one phosphorus site in 6c. The ideal crystallographic composition should accordingly be Pd$_{15}$P$_2$. Since the structure model thus derived appeared quite reasonable from the crystal chemical point of view, least-squares refinements of the parameters were immediately started. The positional parameters, a scale factor and individual isotropic temperature factors were refined using a full-matrix least-squares program.[5] The atomic scattering factors and the dispersion correction factors were taken from Ref. 6. After three cycles a conventional R-value of 0.106 was obtained based on the 1495 strongest reflexions. Since the structure proposal seemed to be correct, a linear absorption coefficient was calculated, and an absorption correction applied to the observed intensities. In order to correct for extinction effects only reflexions having identical indices were averaged.

A series of least-squares refinements on both F and F^2 were performed. The function minimized was $w(|F_o{}^n| - |F_c{}^n|)^2$ with $n = 1$ or 2, respectively. Weights were assigned to the reflexions according to the formula $w^{-1} = \sigma^2(F_o{}^n) + (p_n F_o{}^n)^2$, where $\sigma^2(F_o{}^n)$ is based on counting statistics and the empirical factor p_n was set to $p_1 = 0.02$ and $p_2 = 0.03$. An isotropic extinction parameter, according to the expression by Coppens and Hamilton[7] based on approximations introduced by Zachariasen, and anisotropic temperature factors for the palladium atoms was introduced. 32 strong reflexions were assigned zero weight in the refinements because their extinction correction factors did not satisfy the condition for Zachariasen's approximations. The value for the extinction parameter g[7] finally obtained was 0.50(5). For the 2080 reflexions refined the following agreement factors were obtained,

Table 2. Structure data for $Pd_{15}P_2$, including anisotropic thermal parameters $\beta_{ij}(\times 10^5)$ for the palladium atoms. The form of the temperature factor is exp $(-\beta_{11}h^2 - \beta_{22}k^2 \cdots - 2\beta_{12}hk\cdots)$.

Atom	Position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	18 f	0.40049(7)	0.28437(7)	0.96339(2)	556(8)	487(8)	61(1)	232(6)	−6(2)	−14(2)
Pd(2)	18 f	0.25807(7)	0.23813(7)	0.79537(2)	488(8)	589(8)	59(1)	274(6)	13(2)	−7(2)
Pd(3)	6 c	0	0	0.07941(4)	542(8)	542(8)	56(2)	271(4)	0	0
Pd(4)	3 b	0	0	1/2	440(10)	440(10)	56(2)	220(5)	0	0
P	6 c	0	0	0.28552(16)	a					

a Isotropic temperature factor 0.96(3) (Å^2).

$R(F^2) = 0.092$, $R(F) = 0.066$ and $R_w(F^2) = 0.144$, where

$R(F^n) = \sum||F_o{}^n| - |F_c{}^n||/\sum|F_o{}^n|$ and

$R_w(F^n) = [\sum w(|F_o{}^n| - |F_c{}^n|)^2/\sum w|F_o{}^n|^2]^{\frac{1}{2}}$

In subsequent refinements the occupancy factors were varied but the refinements invariably terminated with insignificant deviations from full occupancy. Experimental errors in the geometrical description of the crystal, together with the very strong absorption, are probably responsible for the comparatively high final values obtained for the agreement factors.

The final structure data obtained are presented in Table 2. A table of observed and calculated structure factors can be obtained from the author on request.

DESCRIPTION AND DISCUSSION OF THE $Pd_{15}P_2$ STRUCTURE

Calculated interatomic distances are given in Table 3. Each palladium atom coordinates $12-15$ palladium and phosphorus neighbours, and the phosphorus atoms have nine palladium neighbours. The structure can be described in terms of slightly distorted icosahedral building elements with six Pd(1) and six Pd(2) atoms at the corners and one Pd(4) atom at the centre. The icosahedra are arranged in nearly the same way as spheres in cubic close-packing.

In the "cubic close-packing" of palladium icosahedra in $Pd_{15}P_2$, the "octahedral holes" are filled with pairs of Pd(3) atoms and the "tetrahedral holes" with phosphorus atoms.

The "octahedral hole" is illustrated stereoscopically in Fig. 1. It is actually a polyhedron with 18 palladium atoms at the vertices: each

of the surrounding six palladium icosahedra contributing three corner atoms to this polyhedron.

The "tetrahedral hole" is illustrated stereoscopically in Fig. 2. The central phosphorus atom is surrounded by nine palladium neighbours, six of them situated at the corners of a distorted triangular prism, and the remaining three more remotely outside the quadrilateral faces of the prism. This kind of environment

Table 3. Interatomic distances in $Pd_{15}P_2$ (Å). The maximum standard deviation obtained was 0.0008 Å for Pd−Pd distances and 0.0018 Å for P−Pd distances. Distances shorter than 3.5 Å are listed.

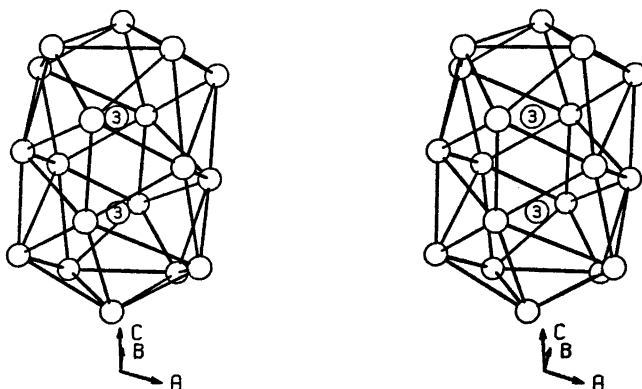|					
Pd(1)−P	2.263		Pd(3)−3Pd(1)	2.640
	Pd(3)	2.640		Pd(3)	2.714
	Pd(2)	2.730		3Pd(2)	2.775
	Pd(4)	2.825		3Pd(2)	2.940
	2Pd(1)	2.828		3Pd(1)	3.219
	Pd(2)	2.857			
	Pd(2)	2.875		Pd(4)−6Pd(2)	2.710
	Pd(1)	2.937		6Pd(1)	2.825
	P	2.990			
	Pd(2)	3.007		P−3Pd(2)	2.244
	2Pd(1)	3.021		3Pd(1)	2.263
	Pd(3)	3.219		3Pd(1)	2.990
	Pd(2)	3.352			
Pd(2)−P	2.244			
	Pd(2)	2.638			
	Pd(4)	2.710			
	Pd(1)	2.730			
	Pd(3)	2.775			
	Pd(1)	2.857			
	Pd(1)	2.875			
	2Pd(2)	2.934			
	Pd(3)	2.940			
	Pd(1)	3.007			
	2Pd(2)	3.061			
	Pd(1)	3.352			

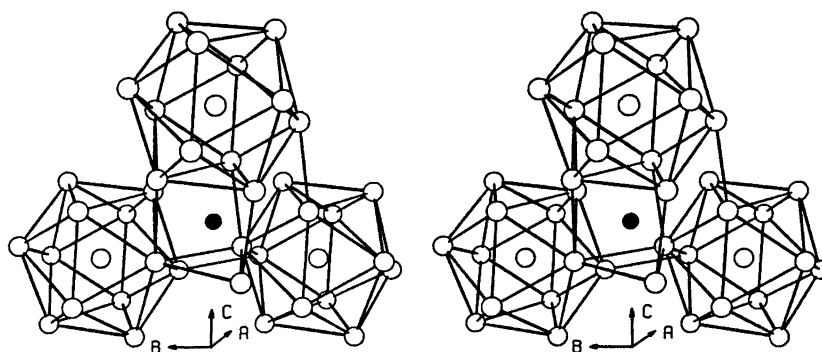*Fig. 1.* The "octahedral hole" enclosing the two Pd(3) atoms.

Fig. 2. The "tetrahedral hole" and the environment of the phosphorus atom. For clarity, only one atom of the fourth icosahedron is represented.

of the phosphorus atom is very common in metal-rich transition metal phosphide structures and has been discussed in detail earlier.[8,9] In particular it occurs [10–12] in the three palladium phosphides $Pd_{4.8}P$, Pd_3P and Pd_6P.

The palladium polyhedron enclosing the central phosphorus atom is built up of the four surrounding palladium icosahedra in the following way. One triangular face of the triangular prism is identical with a triangular face of one of the icosahedra. The second triangular face of the prism is formed by one corner atom from each of the three remaining icosahedra, which also each contribute one of the palladium atoms outside the quadrilateral faces of the prism.

Geometrically, the $Pd_{15}P_2$ structure is closely related to the rhombohedral α-boron [13] struc-

ture, where boron icosahedra are packed in a slightly deformed cubic close-packing. Matkovich *et al.*[14] have discussed this kind of packing model in detail. α-Boron crystallizes in space group $R\bar{3}m$ with the hexagonal unit-cell axes $a = 4.908$ Å and $c = 12.567$ Å.

In interstitial compounds derived from α-boron,[15,16] for instance $B_{12}C_2$ and $B_{13}C_2$, the "octahedral holes" enclose two to three interstitial atoms, while the "tetrahedral holes" are empty.

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