

The Crystal Structure of Pd_{4.8}P

BERTIL SELLBERG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Pd_{4.8}P has been determined and refined by X-ray single-crystal methods. The space group is $P2_1$ and the unit cell dimensions are $a = 5.004 \text{ \AA}$, $b = 7.606 \text{ \AA}$, $c = 8.416 \text{ \AA}$, and $\beta = 95.63^\circ$. The eighteen palladium atoms are situated in $2(a)$ positions. The phosphorus atoms occupy three sets of $2(a)$ positions, two of which seem to be half-filled, and the third filled to about 90 %. The unit cell dimensions are variable, indicating an extended homogeneity range, which nevertheless seems to be small. The structure of Pd_{4.8}P is described, and the atomic arrangement is discussed in relation to the Fe₃C structure.

Wiehage *et al.*¹ reported the occurrence of a phase Pd₅P with an extended homogeneity range. In a recent investigation of the palladium-phosphorus system, Gullman² found that the composition of this phase could be described as Pd_{4.8}P. The crystal structure has now been examined and its composition according to single-crystal data support the formula Pd_{4.8}P.

EXPERIMENTAL

Preparation. Phosphide samples were prepared from palladium powder (Johnson, Matthey & Co. Ltd., claimed purity 99.9 %) and red phosphorus (purity higher than 99 %). Mixtures of these elements were pressed to pellets, sealed off in evacuated silica tubes and heated at 750°C for several days. Because of the slow reaction rate, the material was crushed, pressed to pellets and reheated at the same temperature for another 4 days. The alloys were then quenched in water.

Powder diffraction examination. Powder photographs were recorded using Guinier-Hägg focussing cameras with Cu- $K\alpha_1$ and Cr- $K\alpha_1$ radiation. Silicon with $a = 5.4305 \text{ \AA}$ was used as internal calibration standard. In order to get sharp diffraction lines, the crushed and ground powder was annealed at 750°C for one hour and quenched in water. Gullman reported in his examinations of the Pd-P system that for phosphide samples with about 17 at-% phosphorus, there is a phosphorus loss of about 0.4 at-% during the preparation of phosphide alloys by the method described. Alloys with different nominal compositions were examined by the powder diffraction method in order to determine, whether the phase has an extended homogeneity range. Powder photographs of three samples with the nominal compositions Pd_{4.75}P, Pd_{4.65}P, and Pd_{4.5}P were indexed, and the results, given in Table 1, show a variation in the unit cell dimensions, which probably indicates a range of homogeneity. The limits were not established. The sample with the nominal composition Pd_{4.65}P was shown to consist of a pure single-phase.

Table 1.

Nominal composition	<i>a</i>	<i>b</i>	<i>c</i>	β	Phases
Pd _{4.75} P	5.006	7.608	8.420	95.64	Pd _{4.8} P + traces of Pd ₆ P
Pd _{4.65} P	5.004	7.606	8.416	95.63	Pd _{4.8} P
Pd _{4.5} P	5.011	7.616	8.430	95.64	Pd _{4.8} P + traces of Pd ₃ P

It seemed likely that there is a phosphorus loss in the preparation of the sample, and following Gullman's calculations, the composition of the phase would be Pd_{4.8}P.

Single-crystal examination. In spite of many efforts it was not possible to obtain well-shaped single-crystals. However, single-crystal fragments of irregular shape could be picked from crushed alloys. For the structure determination a single-crystal fragment was picked from an alloy of the nominal composition Pd_{4.65}P. Single-crystal diffraction patterns were recorded in an equi-inclination Weissenberg camera. Preliminary single-crystal studies indicated a monoclinic symmetry. The crystal was rotated about both the *b*-axis and the *a*-axis. A zirconium filter was used to reduce the β -radiation from the molybdenum target. The multiple-film technique was used with three thin iron foils interleaved between successive films. The intensities of the layer lines $0 \leq k \leq 7$ were estimated visually by comparing the reflexions with a calibrated scale. The total number of reflexions observed was 1087.

The shape of the single-crystal fragment was very irregular, and therefore it was difficult to correct the data for absorption. As the single-crystal was very small, the correction due to absorption was considered to be small enough to be neglected.

Fourier series summations,³ structure factor calculations,³ and correction for Lorentz and polarisation factors⁴ were carried out on a Facit EDB computer. The least-squares refinements⁵ and the calculation of interatomic distances⁶ were made on a CDC 3600 computer. In the structure factor calculations the atomic scattering factors for palladium and phosphorus, including the real part of anomalous dispersion corrections, were obtained from *Intern. Tables*.⁷

DETERMINATION OF THE CRYSTAL STRUCTURE

The single-crystal examination gave preliminary information of the symmetry, the lengths of the axes and the monoclinic angle of the unit cell. As a consequence of the low symmetry of the structure and the rather long axes the powder photograph with Cu- $K\alpha_1$ radiation was very complex, and therefore the photograph with Cr- $K\alpha_1$ radiation was indexed. A least-squares program⁸ for refining the unit cell dimensions was used. The axes and the monoclinic angle were determined with the standard deviations of 0.0005 Å and 0.005°, respectively. Indexed powder diffraction data for the sample with nominal composition Pd_{4.75}P are to be found in Gullman's paper.² All the lines, except two belonging to the phase Pd₆P, could be indexed on the basis the unit cell of Pd_{4.8}P.

The single-crystal diffraction patterns showed that the crystal has the Laue symmetry $2/m$. Systematic absences were only observed for $0k0$ reflexions when *k* is odd. This indicated a 2_1 -axis parallel to the unique axis. Thus the possible space groups are $P2_1/m$ and $P2_1$. The unit cell volume indicated a cell content of eighteen palladium atoms.

Using F_o -values for the eight layer lines, a three-dimensional Patterson function was calculated. An attempt was made to interpret the Patterson function in terms of the higher symmetry $P2_1/m$. From spatial considerations some at least of the palladium atoms in the cell should occupy fourfold positions. Three sets of fourfold palladium sites and three sets of twofold metal sites could then be determined, so that the positions and the heights of the main maxima could be explained on the basis of the space group $P2_1/m$.

On the basis of the structure proposed a three-dimensional electron density function was computed. This function contained peaks with the expected positions and heights, but in addition three peaks appeared, which were much lower than the palladium peaks. These maxima could all be explained by atoms in $2(e)$ positions.

If these peaks represented phosphorus atoms situated in $2(e)$ positions, the composition of the phase would be Pd₃P. But the alloy, which was found to be a single-phase in the X-ray powder examination, had a much lower phosphorus content (about 17 at-%). This can be attained if the phosphorus sites are only partly filled. This effect should be revealed by the heights of the assumed phosphorus peaks. Two electron density calculations were then carried out, one using observed F -values and the other with calculated structure factors. A scale-factor for the ρ_{obs} calculation was obtained from the ratio between the peak heights for the $2(e)$ palladium atoms in the ρ_{obs} and the ρ_{calc} maps by assuming that the palladium positions were fully occupied. After the scale-factor correction the following ratios K between the heights of the phosphorus peaks in the ρ_{obs} and the ρ_{calc} maps were obtained: peak 1, $K = 0.60$; peak 2, $K = 0.61$; peak 3, $K = 0.80$.

From this preliminary examination it seemed that two of the phosphorus sites are about half-filled, and the third filled to about 80%. This would mean that the three independent twofold positions are probably occupied by only about 3.8 phosphorus atoms per unit cell. A close re-inspection of the Weissenberg films did not reveal the presence of any superstructure reflexions. It was therefore assumed in the subsequent refinements that the vacancies on the three twofold positions are completely random.

A preliminary refinement on the basis of the symmetry $P2_1/m$ was made. The parameters for the atoms were refined using a full matrix program.⁵ Ten very strong reflexions showed extinction effects and were excluded in the refinements. The parameters refined were the positional parameters and the individual isotropic temperature factors for each atom, and eight scale factors, one for each layer line. The program minimizes the function $w||F_o| - |F_c||^2$, where w stands for the weight of a reflexion according to Cruickshank *et al.*⁹ $w = 1/(a + |F_o| + c|F_o|^2)$. The constants were given the values $a = 30$ and $c = 0.0065$.

However, the possibility that the space group is $P2_1$ still remained. A further refinement according to this space group was therefore made. The result showed small but significant deviations from the symmetry $P2_1/m$, and the symmetry is therefore most probably $P2_1$.

A least-squares refinement was finally carried out using a program written by Busing, Martin, and Levy,¹⁰ allowing the degree of occupation of the phosphorus sites to be varied and refined. The result indicated that two

of the phosphorus positions are filled to 54 % and 60 %, respectively, and the third to 90 %. The standard deviations for the three degrees of occupation were 8 %. The two first positions deviate significantly from being completely filled.

Table 2. Weight analysis for the last cycle of refinement.
 $\Delta = |F_o - F_c|$

$\sin^2\theta$ -interval	$w\Delta$	Number of reflexions	F_o -interval	$w\Delta$	Number of reflexions
0.00–0.45	1.15	483	0–33	0.71	107
0.45–0.57	0.94	268	33–41	0.81	108
0.57–0.65	0.85	159	41–45	0.85	108
0.65–0.71	0.90	70	45–50	0.86	107
0.71–0.77	0.70	43	50–55	0.76	108
0.77–0.82	1.20	31	55–63	0.83	108
0.82–0.86	0.49	6	63–76	1.03	107
0.86–0.90	0.46	9	76–93	1.02	108
0.90–0.94	1.23	6	93–123	1.42	108
0.94–0.97	2.06	2	123–301	1.70	108

After the last cycle of refinement the largest shifts of the parameters were less than 10 % of the magnitudes of the standard deviations. The discrepancy factor $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ was 0.107 for the 1077 observed independent F -values, which was taken as a final proof that the structure determination of $\text{Pd}_{4.8}\text{P}$ is correct.

The final structure data for $\text{Pd}_{4.8}\text{P}$ quenched from 750°C are as follows: Space group $P2_1$, $a = 5.004 \pm 0.0005 \text{ \AA}$, $b = 7.606 \pm 0.0005 \text{ \AA}$, $c = 8.416 \pm 0.0005 \text{ \AA}$, and $\beta = 95.63 \pm 0.005^\circ$. $U = 318.8 \text{ \AA}^3$.

Table 3.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B \text{ \AA}^2$	$\sigma(B)$
Pd_I	0.1350	0.0009	0.4333	—	0.2857	0.0006	0.33	0.06
Pd_{II}	0.1232	0.0009	0.0669	0.0006	0.2774	0.0006	0.30	0.06
Pd_{III}	0.3534	0.0009	0.4375	0.0015	0.6234	0.0006	0.30	0.06
Pd_{IV}	0.3503	0.0010	0.0622	0.0015	0.6255	0.0007	0.64	0.08
Pd_V	0.2442	0.0008	0.4377	0.0015	0.9643	0.0006	0.41	0.06
Pd_{VI}	0.2519	0.0009	0.0683	0.0016	0.9511	0.0007	0.65	0.08
Pd_{VII}	0.1277	0.0005	0.7445	0.0016	0.4732	0.0004	0.65	0.04
Pd_{VIII}	0.3061	0.0005	0.7486	0.0016	0.1463	0.0003	0.52	0.03
Pd_{IX}	0.3936	0.0007	0.7413	0.0017	0.8170	0.0004	0.90	0.05
P_I	0.0224	0.0031	0.7567	0.0075	0.9342	0.0021	0.39	0.19
P_{II}	0.0946	0.0033	0.2393	0.0068	0.7688	0.0021	0.86	0.22
P_{III}	0.4347	0.0024	0.2374	0.0053	0.4224	0.0015	0.97	0.17

All atoms are situated in $2(a)$ positions. The y -parameter of Pd_I is arbitrarily fixed. The sites P_I, P_{II}, and P_{III} are occupied by phosphorus atoms to $54 \pm 8\%$, $60 \pm 8\%$ and $90 \pm 8\%$, respectively.

Interatomic distances are given in Table 4. A list of observed and calculated structure factors can be obtained from this Institute on request.

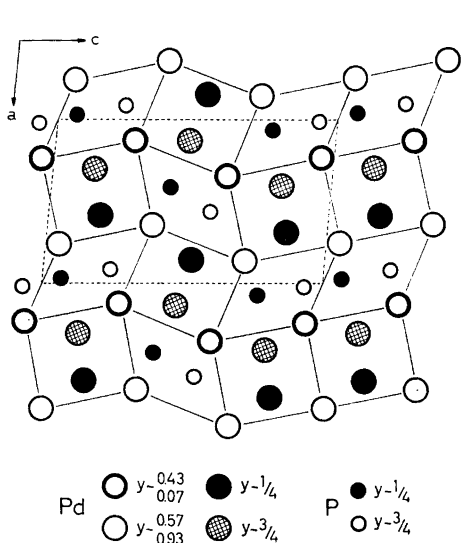


Fig. 1. The crystal structure of Pd_{4.8}P projected on (010).

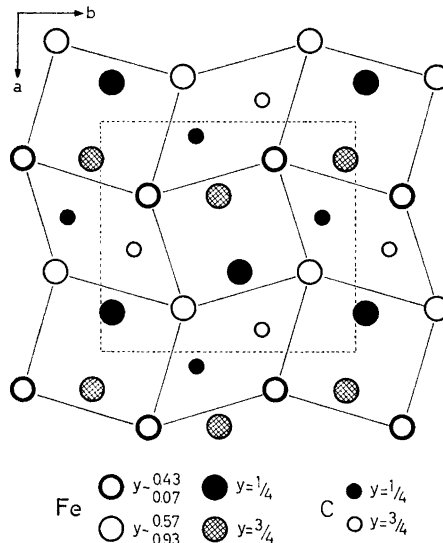


Fig. 2. The crystal structure of Fe₃C projected on (001).

DESCRIPTION OF THE Pd_{4.8}P STRUCTURE

From Figs. 1 and 2 showing the structures of Pd_{4.8}P and Fe₃C, respectively, it can be seen that these structures are similar in many ways. As in the cementite structure, the metal atoms in Pd_{4.8}P are nearly in a state of close packing.

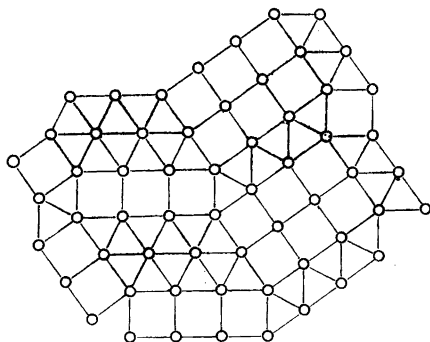


Fig. 3. The layer of palladium atoms parallel to (130) in Pd_{4.8}P.

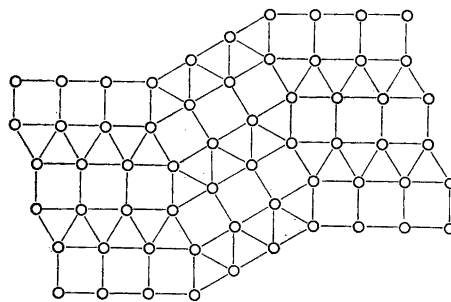


Fig. 4. The layer of iron atoms parallel to (103) in Fe₃C.

Table 4. Interatomic distances and their standard deviations (Å units) in Pd₄8P. Distances shorter than 3.8 Å listed. (Since all atoms are situated in the same type of crystallographic position, the distances between non-equivalent atoms are listed only once in order to reduce the size of the table).

	Dist.	S.d.		Dist.	S.d.			
Pd _I	-Pd _{II}	: 2.789	0.005	Pd _{II}	-Pd _V	: 2.780	0.008	
	-Pd _{IV}	: 2.789 (2)	0.008		-Pd _{III}	: 2.784	0.007	
	-Pd _V	: 2.821	0.007		-Pd _{III}	: 2.845	0.007	
	-Pd _{VI}	: 2.832	0.008		-Pd _{VIII}	: 2.850	0.011	
	-Pd _{VIII}	: 2.840	0.011		-Pd _{VI}	: 2.883	0.007	
	-Pd _{VII}	: 2.848	0.011		-Pd _{VII}	: 2.886	0.008	
	-Pd _{VII}	: 2.905	0.008		-Pd _{IX}	: 2.940 (2)	0.008	
	-Pd _{III}	: 2.945	0.007		-Pd _{VII}	: 2.954	0.011	
	-Pd _{IX}	: 2.975	0.008		-Pd _{IV}	: 3.038	0.008	
	-Pd _{IX}	: 3.071	0.008		-P _{III}	: 2.29	0.025	
	-P _{III}	: 2.34	0.028		-P _I	: 2.35	0.038	
	-P _I	: 2.36	0.036		-P _{II}	: 2.73	0.048	
	-P _{II}	: 2.62	0.047		-P _I	: 3.73	0.039	
Pd _{III}	-Pd _{IX}	: 2.824	0.015	Pd _{IV}	-Pd _{VII}	: 2.819	0.010	
	-Pd _{VII}	: 2.837	0.014		-Pd _{VIII}	: 2.831	0.010	
	-Pd _{VIII}	: 2.843	0.010		-Pd _{VI}	: 2.833	0.008	
	-Pd _{IV}	: 2.847 (2)	0.009		-Pd _{VII}	: 2.906	0.015	
	-Pd _{VII}	: 2.869	0.010		-Pd _{IX}	: 2.922	0.015	
	-Pd _V	: 2.967	0.007		-Pd _{VII}	: 3.142	0.009	
	-Pd _{VII}	: 3.159	0.009		-P _{III}	: 2.24	0.027	
	-P _{III}	: 2.34	0.029		-P _{II}	: 2.28	0.035	
	-P _{II}	: 2.40	0.036		-P _{III}	: 2.74	0.038	
	-P _{III}	: 2.56	0.038					
Pd _V	-Pd _{VI}	: 2.741	0.009	Pd _{VI}	-Pd _{VIII}	: 2.794	0.010	
	-Pd _{IX}	: 2.756	0.015		-Pd _{IX}	: 2.831	0.010	
	-Pd _{VI}	: 2.813	0.017		-Pd _{IX}	: 2.850	0.016	
	-Pd _{VIII}	: 2.823	0.014		-Pd _{VIII}	: 2.933	0.015	
	-Pd _{VI}	: 2.833	0.008		-Pd _{VIII}	: 3.147	0.009	
	-Pd _{IX}	: 2.878	0.010		-P _{II}	: 2.11	0.036	
	-Pd _{VIII}	: 2.898	0.009		-P _I	: 2.27	0.039	
	-Pd _{VIII}	: 3.164	0.009		-P _I	: 2.63	0.053	
	-P _I	: 2.16	0.039					
	-P _{II}	: 2.30	0.037					
	-P _I	: 2.67	0.053					
	-P _{II}	: 3.74	0.035					
Pd _{VII}	-Pd _{VIII}	: 2.976	0.004	Pd _{VIII} -Pd _{IX}	: 2.850	0.011		
	-Pd _{IX}	: 3.065	0.004		-P _I	: 2.17	0.017	
	-P _{II}	: 2.22	0.018		-P _{II}	: 2.20	0.017	
	-P _{III}	: 2.28	0.012		-P _{II}	: 3.02	0.017	
	-P _{III}	: 3.03	0.012		-P _{III}	: 3.74	0.013	
Pd _{IX}	-P _I	: 2.19	0.017	P _I	-P _{II}	: 2.63	0.025	
	-P _{III}	: 2.27	0.013		-P _{III}	: 3.60	0.021	
	-P _I	: 3.21	0.016					
				P _{II}	-P _{III}	: 3.52	0.021	

The palladium atoms at $y \sim 1/4$ and $y \sim 3/4$ are surrounded by 12 neighbours at an average distance of 2.92 Å, while the other palladium atoms have eleven neighbours. According to Lipson and Petch¹¹ the Fe₃C structure is built up of successive layers of metal atoms parallel to (103). Each layer (see Fig. 4) consists of a slightly corrugated array of squares and triangles linked to each other. As shown in Fig. 3, Pd_{4.8}P is built up of similar corrugated layers of metal atoms parallel to (130), which is the strongest reflexion.

Alternately the structure can be considered as an array of metal atom squares and triangles at $y \sim 0$ and $y \sim \frac{1}{2}$. The difference between the Fe₃C and Pd_{4.8}P arrays is that in the latter structure squares also share edges with other squares. Between these layers there are rectangular arrays at $y \sim \frac{1}{4}$ and $y \sim \frac{3}{4}$.

The three non-equivalent phosphorus sites are surrounded by nine metal atoms; six of these are placed at the corners of a distorted triangular prism. The remaining three metal atoms are situated outside the rectangular sides of the prism, and two of these metal atoms are somewhat closer to the centre of the prism than the third.

This type of coordination is very common with metal-rich transition metal phosphides,¹² and closely resembles that found in Pd₃P.¹³

The structure refinement showed the phosphorus sites (P_I and P_{II}) near the corners of the unit cell to be only about 50 % filled. The reason for the occurrence of the vacancies may be explained in the following way. In metal-rich phosphides of the transition metals, there is a tendency for the phosphorus atoms to avoid close contacts, the P—P distances generally being larger than 2.9 Å.¹² If the P_I and P_{II} sites are occupied to more than 50 %, P_I—P_{II} distances of only 2.63 Å must inevitably occur. If, however, the degree of occupation is 50 % or less, the P_I and P_{II} atoms may be arranged in several alternative ways without any short P_I—P_{II} distances occurring. All these arrangements imply that the four P_I and P_{II} sites near one corner of each unit cell are occupied by only two phosphorus atoms separated in the y direction by half the y translation. Since there is no obvious reason why certain sites should be preferred, the occupation of the P_I and P_{II} sites in different unit cells and near different corners in the same unit cell should be entirely random. This is in complete accord with the absence of superstructure reflexions. The P_{III} sites can be completely filled with phosphorus atoms without any short P—P distances occurring. If P_I and P_{II} are half-filled, and P_{III} is fully occupied by phosphorus atoms, the resulting composition of the compound would be Pd_{4.5}P, which is probably the limiting composition at the phosphorus-rich side. Gullman's phase analysis indicated a more palladium-rich composition (Pd_{4.8}P), and this result is not contradicted by the present structure refinement, which yielded an occupation of about 90 % for the P_{III} site.

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