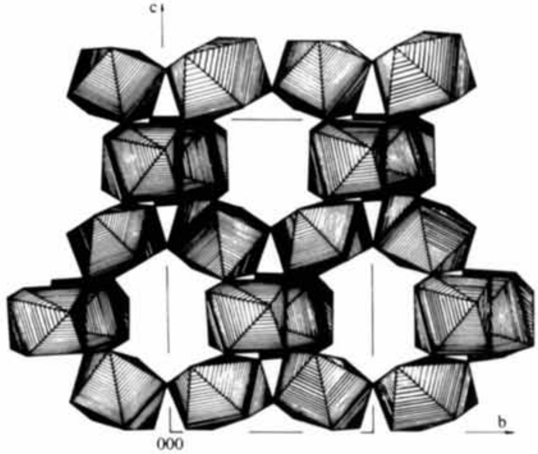

Fig. 3. The three-dimensional network of polyhedra showing the channels between the F(1) corners of the polyhedra parallel to **a** at **b** $\simeq 0$, **c** $\simeq \frac{3}{8}$; **b** $\simeq \frac{1}{2}$, **c** $\simeq \frac{7}{8}$ and parallel to **b** at **a** $\simeq 0$, **c** $\simeq \frac{5}{8}$; **a** $\simeq \frac{1}{2}$; **c** $\simeq \frac{1}{8}$.

Geometrical parameters of the $ZrF_6(H_2O)$ dodecahedron are compared with the hard-sphere model (Hoard & Silverton, 1963; Kepert, 1965, 1978) in Table 3. The shape of the dodecahedron is defined by the angles θ_A, θ_B made by the bonds M–A, M–B with the unique axis and the ratio of the bond lengths. The occurrence of an infinite network of polyhedra instead of discrete polyhedra, and dissimilar ligands [F, O(W)] together with the ligand repulsions cause the departure of the dodecahedron from ideality. A more stable structure can often be obtained by distortion of the structure based on the hard-sphere model and this is observed here.

Molecular packing

The structure consists of a three-dimensional network of $ZrF_6(H_2O)_2$ polyhedra sharing six corners (Fig. 2) through atoms O(W), O(W^{iv}), and F(2), F(2^{i}), F(2^{ii}), F(2^{iii}). F(1) and F(1^{i}) are disposed at free corners of the polyhedron. Fig. 3 shows the three-dimensional network of polyhedra. The water molecule is surrounded by eight F atoms arranged at the corners of a cube at distances O(W)$\cdots$F 2·479 (3), 2·547 (3), 2·576 (3) and 2·595 (3) Å. A trifurcated O(W)–H$\cdots$F hydrogen bond might be expected.

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Neutron Powder Diffraction Investigation of Pure and Deuterated Palladium Phosphide Pd_6P

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Abstract

A structure proposal for Pd_6P has been refined by the Rietveld method from neutron powder diffraction profile data to a weighted profile R_{wp} value of 0·055, based on 1000 measured points in the profile. The space group is $P2_1/c$ with a = 5·6740 (4), b = 9·4409 (6), c = 8·2100 (6) Å, β = 110·414 (4)°, U =

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412·2 (1) Å^3 (296 K) and $Z = 4$; all atoms are on 4(*e*) positions. An alternative structure proposal based on the same space group and *a* and *b* axes but with $c =$ 8·1916 (6) Å, $\beta =$ 110·065 (4)° refined to $R_{wp} =$ 0·058. For both alternatives, the structure can be described as a packing of Pd_6 triangular prisms, half of which are filled with P atoms. From neutron diffraction data recorded at D_2 pressures of 200, 500, and 750 kPa (296 K), the positions and the degrees of occupancy were determined for the dissolved D atoms. These were found to occupy one 2(*d*) and one 4(*e*) position. The 2(*d*) position is surrounded octahedrally by six Pd atoms, and the 4(*e*) position by five Pd atoms in a distorted square-pyramidal configuration. The variation in occupancy with D_2 pressure for the two sites indicates that only the 2(*d*) position is occupied at low pressures; occupation of the 4(*e*) position starts at pressures around 50 kPa. A survey of possible interstitial sites for D indicates that the D atoms prefer positions as far as possible from the P atoms. Possibilities for further occupation of sites by D atoms at higher D_2 pressures are considered.

Introduction

Recent investigations have shown that hydrogen and deuterium can be dissolved to a considerable extent in palladium phosphides. The thermodynamics and crystallography of these solid solutions are currently being studied; the solutions in the Pd_3P_{1-x} phase have so far been investigated in some detail (Flanagan, Biehl, Clewley, Rundqvist & Andersson, 1980; Andersson, Rundqvist, Tellgren, Thomas & Flanagan, 1980).

The occurrence of the compound Pd_6P was first reported by Gullman (1966). The crystal structure was examined by X-ray powder diffraction methods by Andersson, Kaewchansilp, del Rosario Casteleiro Soto & Rundqvist (1974). The major features of the Pd atomic arrangement were derived, but the location of the P atoms could not be determined satisfactorily.

In the present paper, the results of a neutron powder diffraction study of both pure and deuterated Pd_6P are reported. The ordering of the P atoms has been determined, as well as the interstitial sites occupied by D atoms dissolved in the phosphide.

Experimental

Synthesis and chemical characterization

An initial alloy of nominal composition Pd_6P was prepared by dropping lumps of red phosphorus (Koch-Light, claimed purity 5*N*) into molten palladium (Johnson, Matthey & Co., spectroscopically pure) according to the technique described by Carlsson, Gölin & Rundqvist (1973). The product was ground to a fine powder by means of a tungsten carbide ball mill, sealed into an evacuated silica tube and annealed at 1030 K for 7 days. The alloy was again ball-milled, and the powder was stress-relieved by heating at 920 K for 15 min and examined by X-ray powder diffraction. The process of ball-milling and annealing was repeated until the diffraction films showed no trace of lines from neighbouring phases in the Pd–P system, and exhibited only sharp Pd_6P lines. Chemical analysis of the final product by the methods described by Gullman (1966) gave the following result: Pd 95·18, P 4·62 wt%, corresponding to a Pd/P atomic ratio of 6/1·000.

X-ray powder diffraction

X-ray powder diffraction films were recorded at room temperature (296 K) in a Philips XDC 700 focusing camera using strictly monochromatized Cu $K\alpha_1$ radiation and zone-refined silicon, $a =$ 5·431065 Å (Deslattes & Henins, 1973), as an internal calibration standard. Unit-cell dimensions were refined using the local least-squares program *CELNE* (N. O. Ersson, unpublished).

Neutron powder diffraction

Neutron powder diffraction data were recorded at the R2 reactor, Studsvik, Sweden. The neutron beam from a radial reactor channel was passed through a double-monochromator system [using the (220) planes in two copper crystals] to produce a thermal neutron flux at the specimen of approximately 10^4 mm^{-2} s^{-1} at a wavelength of 1·552 Å. The powder specimen, weighing about 30 g, was contained in a 12 mm diameter vanadium tube which was connected to a vacuum system with a manometer and a high-purity deuterium gas supply. Diffraction data were measured at room temperature (296 K) by scanning the angular range 8–88° in 2θ in steps of 0·08° with a measuring time of about 7 min per point. Data were collected under four different conditions of deuterium pressure. The first run was made on pure Pd_6P. The vanadium container was then evacuated, and deuterium gas was admitted and allowed to reach equilibrium with the phosphide for about 48 h at 200, 500, and 750 kPa D_2 pressure. After equilibration, diffraction data were recorded in two consecutive runs. The two recordings were found to give identical results within counting statistics at each pressure. Neutron absorption in the sample was also measured and found to be almost identical for the four pressures. Absorption corrections were applied based on an experimental μr value of 0·20. The recordings were summed pairwise to give four final data sets.

Structure analysis

In a previous investigation of the Pd_6P structure by X-ray powder diffraction methods (Andersson *et al.*, 1974), the reflections were indexed with a monoclinic cell of dimensions $a = 2{\cdot}837$, $b = 9{\cdot}441$, $c = 7{\cdot}695$ Å, $\beta = 90{\cdot}20°$. A structure was proposed on the basis of the space group $C2/c$ (No. 15), with 12 Pd atoms occupying one 8(*f*) and one 4(*e*) position, and two P atoms randomly occupying one 4(*e*) position.

This structure proposal was in good agreement with the X-ray intensity data, indicating that at least the arrangement of the Pd atoms was essentially correct. The proposal of a disordered P sublattice appeared somewhat unsatisfactory for crystal-chemical reasons and was also less reliably established, although no experimental evidence in favour of an ordered P arrangement could be detected in the X-ray diffraction data.

The neutron powder diffraction profile of Pd_6P contained a number of small low-angle peaks with no counterparts in the X-ray data. Indexing of these reflections required a larger unit cell than that originally derived from X-ray diffraction. Overlaps among the reflections caused by the closeness of the original monoclinic angle to 90° made the indexing of the neutron diffraction peaks ambiguous. When the structural considerations were restricted to a choice of the smallest unit cell and the highest space-group symmetry consistent with the observed intensity data, two possibilities presented themselves: one unit cell with dimensions $a = 5{\cdot}674$, $b = 9{\cdot}441$, $c = 8{\cdot}192$ Å, $\beta = 110{\cdot}07°$, and another with $a = 5{\cdot}674$, $b = 9{\cdot}441$, $c = 8{\cdot}210$ Å, $\beta = 110{\cdot}41°$, both having $P2_1/c$ (No. 14) space-group symmetry and twice the volume of the original X-ray cell.

The following example illustrates the ambiguous situation in detail. The powder diffraction profile contained a peak at $\theta = 8{\cdot}37°$ with a half-width of $0{\cdot}23°$, corresponding to a d spacing of 5·33 Å. Using the cell with $\beta = 110{\cdot}07°$ for indexing, the position of the peak would correspond to the two reflections: 100 at $\theta = 8{\cdot}372°$ and $\bar{1}01$ at $\theta = 8{\cdot}391°$. Using the second cell for indexing, 100 would lie at $\theta = 8{\cdot}391°$ and $\bar{1}01$ at $\theta = 8{\cdot}372°$. If $P2_1/c$ symmetry is correct, the $\bar{1}01$ reflection should be extinct. An experimental distinction between the alternative 100 diffraction angles was precluded on account of the large half-width of the observed peak. Neither could such distinctions be made for higher-angle reflections due to increased line-broadening and overlap. In the subsequent structure analysis, the choice of unit cell was therefore provisionally left open.

It was probable that the superstructure reflections were due to an ordering in the P arrangement. As discussed in the following, this removes several of the unsatisfactory structural features which arose from the original assumption of disorder.

The Pd atom arrangement can be described as a packing of Pd_6 triangular prisms. The prisms share triangular faces to form infinite columns running in the **a** direction. If P atoms were distributed randomly at the centres of these prisms, there would seem to be no structural reason why the occupation should be restricted to exactly one half of the available positions. The composition of the compound shows no measurable deviation from the ideal Pd/P atomic ratio 6/1, however.

Furthermore, a random distribution would lead to the occasional occurrence of P—P distances between adjacent prisms of only 2·837 Å. Such P—P distances would be abnormally short for a metal-rich transition-metal phosphide structure, where the P atoms normally tend to keep as far away as possible from one another. In $Pd_{15}P_2$ (Andersson, 1977) and Pd_3P (Rundqvist & Gullman, 1960), for instance, the shortest P—P distances exceed 3·5 Å.

The doubling of the 'neutron cell' along the **a** direction as compared to the 'X-ray cell' indicates that every second Pd_6 prism within a given column should be filled with P in a perfectly regular manner. This ordering scheme would eliminate the abnormally short P—P distances mentioned above, and at the same time explain the strict stoichiometry of the compound.

Further consideration of the ordering of the P atoms between different prism columns in conformity with $P2_1/c$ symmetry provided a structure proposal in good agreement with the observed superstructure peak intensities. The proposal involved six sets of Pd atoms on 4(*e*) positions, and one set of P atoms, also on a 4(*e*) position.

Refinement of the structure model was made for both unit cells employing a local version (Thomas, 1977) of the Rietveld full-profile least-squares program (Rietveld, 1969). The positional parameters for P converged readily, while the convergence for the Pd parameters was slow. This is probably due to the high pseudosymmetry of the Pd sublattice, which results in strong correlations between the parameters during the initial least-squares cycles. Very good agreement was finally reached between observed and calculated intensity profile data for both refinements.

The results of the two alternative refinements are given in Table 1. The parameters refined were as follows: profile parameters: linewidth (3), 2θ zero-point (1), wavelength (1); structure parameters: scale factor (1), positional parameters (21), isotropic temperature factors (2) (one for Pd and one for P). Values for the unit-cell dimensions as obtained from the X-ray powder diffraction measurements were used to refine the zero-point and wavelength parameters. The neutron scattering length used for Pd was 6·0 fm and for P 5·1

Table 1. *Crystallographic data for* Pd_6P, $Pd_6PD_{0\cdot15}$, $Pd_6PD_{0\cdot22}$ *and* $Pd_6PD_{0\cdot26}$

Space group $P2_1/c$; two alternative cells (see text). Positional parameters for Pd and P are $\times 10^4$ and for D(2) $\times 10^3$.

		$\beta = 110\cdot4°$				$\beta = 110\cdot1°$			
		Pd_6P	$Pd_6PD_{0\cdot15}$	$Pd_6PD_{0\cdot22}$	$Pd_6PD_{0\cdot26}$	Pd_6P	$Pd_6PD_{0\cdot15}$	$Pd_6PD_{0\cdot22}$	$Pd_6PD_{0\cdot26}$
a (Å)		5·6740 (4)	5·6846 (4)	5·6858 (4)	5·6870 (4)	5·6740 (4)	5·6847 (4)	5·6857 (4)	5·6870 (4)
b (Å)		9·4409 (6)	9·4611 (7)	9·4632 (7)	9·4654 (7)	9·4409 (6)	9·4621 (7)	9·4642 (7)	9·4667 (7)
c (Å)		8·2100 (6)	8·2181 (8)	8·2192 (8)	8·2196 (8)	8·1916 (6)	8·2020 (8)	8·2020 (8)	8·2029 (8)
β (°)		110·414 (4)	110·414 (9)	110·431 (9)	110·431 (9)	110·065 (4)	110·109 (9)	110·105 (9)	110·117 (9)
U (Å^3)		412·2 (1)	414·2 (1)	414·4 (1)	414·6 (1)	412·2 (1)	414·3 (1)	414·5 (1)	414·7 (1)
Pd(1)	x	9669 (20)	9619 (19)	9653 (25)	9612 (20)	9617 (18)	9617 (19)	9612 (22)	9615 (20)
	y	8635 (7)	8623 (7)	8615 (7)	8602 (6)	8633 (7)	8620 (7)	8614 (7)	8606 (6)
	z	9445 (7)	9376 (12)	9398 (12)	9391 (10)	9423 (12)	9413 (11)	9408 (12)	9411 (10)
Pd(2)	x	5265 (19)	5349 (16)	5301 (23)	5307 (22)	5359 (18)	5341 (19)	5346 (22)	5361 (20)
	y	1381 (7)	1355 (8)	1360 (8)	1357 (7)	1371 (8)	1348 (8)	1353 (8)	1353 (7)
	z	684 (10)	746 (10)	711 (13)	716 (11)	740 (12)	717 (11)	717 (12)	733 (10)
Pd(3)	x	7756 (18)	7715 (16)	7766 (21)	7750 (19)	7736 (19)	7750 (18)	7776 (21)	7761 (20)
	y	8696 (8)	8701 (9)	8698 (9)	8690 (8)	8709 (8)	8704 (9)	8700 (9)	8704 (8)
	z	5752 (8)	5689 (11)	5724 (13)	5726 (11)	5703 (12)	5728 (10)	5723 (11)	5725 (10)
Pd(4)	x	7070 (18)	7168 (17)	7150 (21)	7154 (18)	7098 (18)	7134 (19)	7133 (21)	7132 (20)
	y	1315 (7)	1333 (7)	1324 (7)	1318 (6)	1334 (8)	1337 (7)	1331 (7)	1335 (7)
	z	4326 (10)	4415 (11)	4389 (12)	4395 (11)	4357 (12)	4392 (11)	4387 (11)	4389 (10)
Pd(5)	x	8702 (20)	8686 (19)	8702 (24)	8599 (20)	8674 (18)	8694 (18)	8719 (22)	8691 (21)
	y	5777 (5)	5795 (6)	5794 (6)	5794 (6)	5781 (6)	5797 (6)	5795 (7)	5797 (6)
	z	7527 (12)	7496 (13)	7483 (13)	7481 (11)	7468 (10)	7475 (10)	7481 (11)	7470 (10)
Pd(6)	x	6127 (19)	6101 (17)	6154 (24)	6250 (24)	6131 (17)	6108 (15)	6145 (19)	6133 (19)
	y	4156 (6)	4174 (6)	4170 (8)	4173 (7)	4165 (6)	4180 (6)	4180 (8)	4179 (7)
	z	2529 (12)	2546 (14)	2566 (13)	2560 (11)	2572 (11)	2571 (10)	2567 (12)	2562 (10)
P	x	8845 (18)	8870 (17)	8846 (23)	8761 (22)	8886 (16)	8892 (17)	8863 (21)	8847 (19)
	y	2608 (4)	2606 (4)	2614 (5)	2614 (5)	2613 (4)	2607 (4)	2612 (5)	2613 (5)
	z	7519 (11)	7467 (13)	7486 (15)	7481 (13)	7504 (13)	7483 (14)	7474 (15)	7476 (13)
D(1)	x	–	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	–	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	y	–	0	0	0	–	0	0	0
	z	–	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	–	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	N	–	0·117 (5)	0·157 (6)	0·169 (6)	–	0·120 (5)	0·155 (6)	0·166 (5)
D(2)	x	–	(*a*)	335 (20)	311 (10)	–	(*a*)	316 (18)	306 (10)
	y	–	(*a*)	74 (13)	83 (8)	–	(*a*)	87 (13)	84 (8)
	z	–	(*a*)	225 (15)	226 (9)	–	(*a*)	213 (11)	205 (6)
	N	–	0·033 (5)	0·063 (6)	0·091 (6)	–	0·030 (5)	0·065 (6)	0·094 (5)
Pd B_{iso} (Å^2)		0·70 (2)	0·63 (2)	0·71 (2)	0·68 (2)	0·70 (2)	0·63 (2)	0·71 (2)	0·68 (2)
P B_{iso} (Å^2)		0·91 (8)	0·80 (8)	0·72 (9)	0·53 (9)	0·95 (8)	0·84 (8)	0·81 (9)	0·60 (8)
D B_{iso} (Å^2)		–	3·7 (6)	4·2 (6)	3·8 (5)	–	3·9 (7)	4·0 (6)	3·6 (5)
R_{wp} (%)		5·5	5·2	5·7	5·3	5·8	5·4	6·0	5·6
R_I (%)		3·8	2·6	3·2	2·6	3·9	2·5	3·4	2·7

(*a*) Fixed at the values from $Pd_6PD_{0\cdot26}$.

fm (*International Tables for X-ray Crystallography*, 1974).

A calculation of interatomic distances for both structure alternatives revealed no abnormal features; the differences between the two sets of interatomic distances were very small. In fact, taking into account the probable underestimation of the standard deviations resulting from the Rietveld procedure (see Sakata & Cooper, 1979), the differences were hardly significant. However, as seen from Table 1, the agreement between observation and calculation was somewhat better for the structure based on the 110·41° monoclinic angle. The hypothesis that the choice of the larger monoclinic angle is correct is further supported by the results from the refinements of the deuterated samples (see below). Here, the R_{wp} reliability factors were consistently lower for the 110·41° alternative.

The structure proposal based on the cell with the 110·41° monoclinic angle should thus be preferred to that based on the 110·07° angle. The evidence is close to the limits of experimental error, however, and it would be desirable to carry out a complete single-crystal neutron diffraction analysis to resolve the question more definitively. Extensive attempts to grow

Pd_6P single crystals even of the size required for X-ray measurements have previously been unsuccessful (Andersson *et al.*, 1974), however. No further attempt was made in the present study.

Determination of the deuterium atomic distribution

With the intensity data from the sample deuterated at 750 kPa D_2 pressure, and the results from the pure Pd_6P structure analysis, a three-dimensional Fourier difference synthesis was calculated by subtracting the Pd and P contributions. Significant maxima were observed corresponding to the occupation by D atoms of the 2(*d*) position [designated as the D(1) site in the following] and a 4(*e*) position [designated D(2)]. Structure refinements were again performed on the basis of both unit-cell alternatives.

The results of the refinements are summarized in Table 1.* As already mentioned, the structure alternative based on the unit cell having the larger monoclinic angle gives somewhat better agreement with the experimental data. In addition to the parameters refined in the case of pure Pd_6P, the following new parameters were refined: unit-cell dimensions (4), (2θ zero-point and wavelength were fixed at the values obtained for pure Pd_6P), positional parameters for D(2) (3), an isotropic temperature factor common for D(1) and D(2) (1), and an occupancy parameter (1). The sum of the two occupancies for D(1) and D(2) was constrained to the values obtained by direct solubility measurements (Flanagan, Bowerman, Rundqvist & Andersson, 1981).

Only one occupancy parameter was thus refined. The experimental solubility values obtained at 200, 500 and 750 kPa D_2 pressure correspond to the formulae $Pd_6PD_{0\cdot15}$, $Pd_6PD_{0\cdot22}$ and $Pd_6PD_{0\cdot26}$, respectively, with an estimated uncertainty of ±0·01 in the deuterium contents. In the case of the 200 kPa recording, the D(2) positional parameters oscillated considerably during the refinement (without actually diverging). They were therefore held fixed at the values obtained from the 750 kPa refinement in the final cycles.

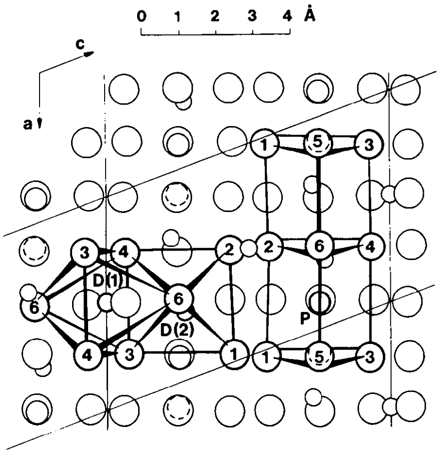

Fig. 1. The Pd_6PD_z structure projected on (010). Large circles: Pd, medium circles: P, small circles: D. The triangular-prismatic Pd surrounding of P, the octahedral Pd surrounding of D(1), and the square-pyramidal Pd surrounding of D(2) are indicated.

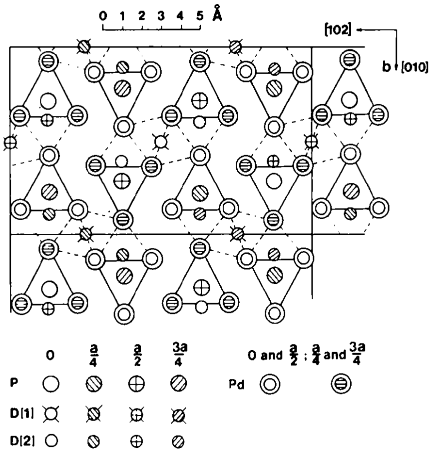

Fig. 2. The Pd_6PD_z structure projected on a plane perpendicular to the *a* axis. The approximate heights of the atoms above the projection plane are indicated. Infinite columns of Pd_6 prisms sharing triangular faces appear as triangles in the projection.

Description and discussion of the structures

Interatomic distances for Pd_6P and $Pd_6PD_{0\cdot26}$ (in both cases based on the unit cell with a monoclinic angle of 110·4°) are listed in Table 2. A projection of the structure along the monoclinic axis is shown in Fig. 1. The structural architecture is illustrated more conveniently by projecting the structure on a plane almost perpendicular to the **a** direction, corresponding to the (100) plane of the original X-ray-determined subcell. This projection is shown in Fig. 2, and can be compared with the analogous projection in the paper of Andersson *et al.* (1974). In Fig. 2, the repeat distance along [102] corresponds to a doubling of *c* for the original subcell. The columns of Pd_6 triangular prisms running in the **a** direction appear as triangles in the projection.

As pointed out by Andersson *et al.* (1974), the Pd atomic arrangement is very similar to the metal-atom network in the Re_3B-type structure (Aronsson,

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* Powder diffraction data for Pd_6P, $Pd_6PD_{0\cdot15}$, $Pd_6PD_{0\cdot22}$ and $Pd_6PD_{0\cdot26}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36147 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *less than* 3·6 Å *in* Pd_6P *and* $Pd_6PD_{0\cdot26}$ (*based on the unit cell with* $\beta = 110\cdot4°$)

E.s.d.'s are in parentheses.

	Pd_6P	$Pd_6PD_{0\cdot26}$
Pd(1)–D(2)		1·75 (6)
P	2·28 (1)	2·26 (1)
P	2·61 (1)	2·67 (1)
Pd(1)	2·72 (1)	2·81 (1)
Pd(2)	2·76 (2)	2·77 (2)
Pd(4)	2·82 (1)	2·79 (1)
Pd(6)	2·82 (1)	2·83 (1)
Pd(5)	2·83 (1)	2·85 (1)
Pd(3)	2·83 (1)	2·80 (1)
Pd(3)	2·84 (1)	2·82 (1)
Pd(2)	2·91 (2)	2·92 (2)
Pd(5)	2·93 (1)	2·97 (1)
Pd(6)	2·94 (1)	2·89 (1)
Pd(5)	3·08 (1)	3·04 (1)
D(2)		3·27 (7)
Pd(2)–D(2)		2·13 (6)
P	2·27 (1)	2·22 (2)
Pd(3)	2·77 (1)	2·80 (1)
Pd(4)	2·80 (1)	2·82 (1)
Pd(4)	2·80 (1)	2·83 (1)
Pd(2)	2·81 (1)	2·80 (1)
Pd(6)	2·83 (1)	2·82 (1)
Pd(6)	2·84 (1)	2·87 (1)
Pd(5)	2·86 (1)	2·80 (1)
Pd(5)	2·86 (1)	2·84 (1)
Pd(6)	2·98 (1)	3·02 (1)
D(1)		3·49 (1)
D(2)		3·55 (7)
Pd(3)–D(1)		1·92 (1)
D(2)		1·94 (7)
P	2·21 (1)	2·26 (1)
Pd(4)	2·71 (1)	2·69 (1)
Pd(4)	2·72 (1)	2·76 (1)
Pd(5)	2·81 (1)	2·88 (1)
Pd(6)	2·84 (1)	2·83 (1)
Pd(6)	2·86 (1)	2·90 (1)
Pd(5)	2·92 (1)	2·91 (1)
Pd(4)	2·96 (1)	2·93 (1)
Pd(5)	3·08 (1)	3·06 (1)
D(2)		3·57 (7)
Pd(4)–D(1)		1·93 (1)
P	2·30 (1)	2·31 (1)
D(2)		2·40 (6)
P	2·75 (1)	2·68 (1)
Pd(6)	2·80 (1)	2·88 (1)
Pd(5)	2·81 (1)	2·84 (1)
Pd(5)	2·89 (1)	2·89 (1)
Pd(6)	2·90 (1)	2·86 (1)
Pd(6)	3·02 (1)	3·05 (1)
D(2)		3·47 (7)
Pd(5)–P	2·23 (1)	2·28 (1)
Pd(6)	2·73 (2)	2·75 (2)
Pd(6)	2·95 (2)	2·94 (2)
P	2·99 (1)	3·01 (1)
D(2)		3·05 (6)
D(2)		3·37 (7)
D(2)		3·43 (6)
D(1)		3·46 (1)
D(1)		3·58 (1)
Pd(6)–D(2)		1·61 (8)
D(1)		2·12 (1)
P	2·27 (1)	2·23 (1)
D(2)		3·60 (7)
P–D(2)		2·94 (6)
D(1)		3·44 (1)
D(2)		3·46 (7)
D(2)		3·48 (6)
D(1)–2Pd(3)		1·92 (1)
2Pd(4)		1·93 (1)
2Pd(6)		2·12 (1)
2D(2)		2·27 (7)
2P		3·44 (1)
2Pd(5)		3·46 (1)
2Pd(2)		3·49 (1)
2Pd(5)		3·58 (1)
D(2)–Pd(6)		1·61 (8)
Pd(1)		1·75 (6)
Pd(3)		1·94 (7)
Pd(2)		2·13 (6)
D(1)		2·27 (7)
Pd(4)		2·40 (6)
P		2·94 (6)
Pd(5)		3·05 (6)
Pd(1)		3·27 (7)
Pd(5)		3·37 (7)
Pd(5)		3·43 (6)
P		3·46 (7)
Pd(4)		3·47 (7)
P		3·48 (6)
Pd(2)		3·55 (7)
Pd(3)		3·57 (7)
Pd(6)		3·60 (7)

Bäckman & Rundqvist, 1960) which crystallizes in the orthorhombic space group *Cmcm*. In Re_3B, all triangular-prismatic interstices are filled with B atoms. In Pd_6P, the orthorhombic symmetry is broken by the ordering of the vacant and filled triangular prisms. The accompanying geometrical distortion of the unit cell is very small, however; the monoclinic angle of the subcell deviates by only 0·2° from 90°. The empty prisms are appreciably smaller than the filled ones; the contraction along the prism axis is of the order of 0·2 Å.

The two D positions found in the present study have considerably different atomic environments. The D(1) position is surrounded by six Pd nearest neighbours in a somewhat distorted octahedral configuration. The average Pd–D(1) distance is 1·99 Å, which may be compared with the corresponding distance of 1·945 Å for the octahedral interstices in pure Pd.

The D(2) atoms are surrounded by five Pd nearest neighbours in a distorted square-pyramidal arrangement. The atoms Pd(1), Pd(2), Pd(3) and Pd(4) are at the corners of one of the three quadrilateral faces of each vacant Pd_6 triangular prism, and Pd(6) is situated outside the quadrilateral face. This coordination closely resembles that in $Pd_3P_{0\cdot80}$ (Andersson *et al.*, 1980), where the dissolved D atoms also occupy distorted square-pyramidal sites adjacent to empty Pd_6 triangular prisms. The average of the five Pd–D(2) distances in $Pd_6PD_{0\cdot26}$ is 1·96 Å, compared to the corresponding value of 2·14 Å for $Pd_3P_{0\cdot80}D_{0\cdot15}$.

A plot of the D occupation of the two sites as a function of $p^{1/2}$, where p is the D_2 pressure, is shown in Fig. 3. The D(2) occupation varies almost linearly, consistent with an ideal solubility behaviour for monatomic deuterium. The deviation from an ideal linear behaviour is appreciable for the D(1) occupation, however. If the curve for D(2) occupation is extrapolated linearly towards lower D content, zero occupation is found at a pressure of around 50 kPa. It thus appears that the D(1) site alone is occupied in the lower pressure range. At pressures above 50 kPa, the

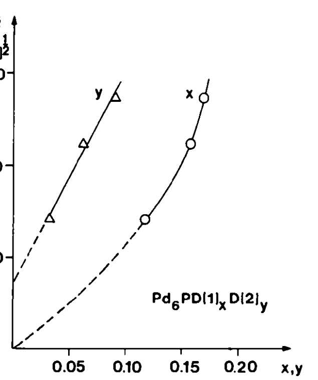

Fig. 3. The occupancies x and y for the D(1) and D(2) positions in the $Pd_6PD(1)_xD(2)_y$ structure plotted as functions of $p^{1/2}$ (p = D_2 pressure) at 296 K.

D(2) position starts to become filled. It is conceivable that even additional interstices between the Pd atoms in the structure might become occupied by D atoms when the pressure is raised beyond the values employed in the present study. There are, in fact, several types of interstices, which might in principle accommodate dissolved D atoms. In addition to the 2(*d*) sites, there are, for instance, six further octahedral holes per unit cell, corresponding to the 2(*c*) position and a 4(*e*) position at approximately (0·25, 0·00, 0·00). In the so-called filled Re_3B-type structures, where the octahedral holes are structurally equivalent, all octahedral sites are filled. Taking V_3AsC as a representative example (Boller & Nowotny, 1967), the larger As atoms occupy all the triangular-prismatic interstices between the V atoms, while the smaller C atoms occupy all the octahedral holes.

The occupation of only the 2(*d*) octahedral holes by D in Pd_6P (at least at pressures below 750 kPa) may be related to the P–D interactions since the Pd surroundings are quite similar for all three types of octahedral hole. While a D atom at 2(*d*) has no P neighbour closer than 3·4 Å, D atoms in the 4(*e*) octahedral holes would have one P neighbour at a considerably shorter distance, about 2·9 Å, and D atoms at 2(*c*) would have two P neighbours at about 2·9 Å. It thus appears that the D atoms tend to avoid close contact with the P atoms, and therefore preferentially occupy the 2(*d*) site.

The trigonal-prismatic interstices between the Pd atoms are evidently not suitable for D occupation since, for both Pd_6P and $Pd_3P_{0\cdot80}$, the D atoms enter square-pyramidal positions near the quadrilateral faces rather than the empty centres of the prisms. Each Pd_6 prism is surrounded by three distorted square-pyramidal interstices. If a D atom is assumed to occupy a pyramidal interstice outside one of the Pd_6 prisms centred by a P atom, the D–P distance would be abnormally short: about 0·6 Å. Accordingly, only pyramidal sites associated with empty Pd_6 prisms can accommodate D atoms. There are altogether 12 such sites per unit cell, corresponding to three 4(*e*) positions. For any particular empty Pd_6 prism, the presence of a D atom at one of the pyramidal sites blocks the occupation of the other two pyramidal sites within the same prism. The distances between adjacent pyramidal sites are of the order of 1·5 Å. This particular type of blocking actually occurs in Pd_3P_{1-x}, as shown by a statistical thermodynamic analysis of the experimental solubility data for hydrogen and deuterium (Flanagan *et al.*, 1980).

The preference for the D(2) pyramidal site may again be connected with P–D interactions. The D–P distances are somewhat larger for the D(2) position than would be the case for the other two pyramidal sites. The differences are not very pronounced, however, and other factors, such as differences in Pd–D interactions, might also be significant.

In addition to the interstices already mentioned, there are 40 tetrahedral interstices per unit cell, of which 16 have two faces in common with octahedral interstices, and the remaining 24 share two faces with square-pyramidal interstices. The centres of the latter 24 tetrahedra are all rather close to neighbouring P atoms, the distances being of the order of 2·4 Å. D occupation of these tetrahedral voids therefore appears less likely. D occupation of those tetrahedra which share one face with the D(1) octahedra is probably blocked, since otherwise very short D–D distances would occur. Amongst the remaining eight tetrahedral interstices associated with the 4(*e*) octahedral holes, four have their centres much closer to a P atom than the other four.

As a result of this analysis of the various interstitial sites in Pd_6P, it appears that the most likely sites for further D occupation at higher pressures would be the 4(*e*) octahedral holes; alternatively, one set of 4(*e*) tetrahedral holes adjoining these octahedral holes. A simultaneous occupation of adjoining octahedral and tetrahedral sites would be prevented by blocking, *i.e.* occupation of both sites would lead to D–D distances which would be too small.

Blocking may be important even with respect to the simultaneous occupation of the D(1) and D(2) sites. The distance between these positions is about 2·3 Å. If blocking occurs, and no further sites in addition to D(1) and D(2) are occupied, the maximum solid solubility of deuterium (or hydrogen) in Pd_6P would correspond to a composition between $Pd_6PD_{0\cdot5}$ [all D(1) positions occupied and all D(2) positions blocked] and Pd_6PD [D(2) fully occupied and D(1) entirely blocked]. Measurements at a hydrogen pressure of 5000 kPa actually indicate a hydrogen content corresponding to the approximate formula $Pd_6PH_{0\cdot6}$ (Flanagan, Bowerman, Rundqvist & Andersson, 1981).

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Structure of Medaite, $Mn_6[VSi_5O_{18}(OH)]$: The Presence of a New Kind of Heteropolysilicate Anion

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Abstract

A manganese(II) vanadatopentasilicate, medaite $(Mn_{5.774},Ca_{0.190},Fe_{0.035})[(V_{0.815},As_{0.185})Si_5O_{18}(OH)]$, which crystallizes in the monoclinic space group $P2_1/n$, with $a = 6.712\ (1)$, $b = 28.948\ (8)$, $c = 7.578\ (2)$ Å, $\beta = 95.40\ (2)^\circ$, $Z = 4$, $V = 1465.9$ Å^3, $D_o = 3.70$ (flotation in Clerici solution), $D_c = 3.727$ Mg m^{-3}, has recently been found in nature as a new mineral. Computer-controlled four-circle diffractometer data (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator) were analysed; $F(000) = 1588$, μ(Mo $K\alpha$) = 6.7 mm^{-1}. The final R index = 0.059 for 3350 independent reflections. The structure contains a vanadatopentasilicate anion (with some substitution of As for V) $[VSi_5O_{18}(OH)]^{12-}$, comprising six tetrahedra linked together to form a chain fragment. This ion is another representative of a new series of heteropolysilicate ions, the conformation of which resembles polyphosphates. It can be considered to be an extended relative of a similar ion $[AsSi_3O_{12}(OH)]^{8-}$, recently observed for another new mineral, tiragalloite, which occurs in the same locality.

Introduction

Some interesting new minerals have recently been found in an old manganese mine at Molinello near Chiavari (Liguria), as small orange-yellow to brown grains intimately intergrown with rhodochrosite, quartz, parsettensite, *etc.* (Gramaccioli, Griffin & Mottana, 1979, 1980*a*,*b*). The solution of the crystal structure of one of these minerals showed it to be a

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