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BRIEF COMMUNICATION

Neutron Powder Diffraction Investigations of Hydrogenated $Pd_3P_{0.80}$ and Pd_6P

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The thermodynamic properties of solid solutions of hydrogen and deuterium in the palladium phosphides Pd_3P_{1-x} ($0 \leq x < 0.28$) and Pd_6P have been studied previously (*1*, *2*). The results were interpreted on the basis of the crystal structures of deuterated $Pd_3P_{0.80}$ (*3*) and Pd_6P (*4*), assuming that the hydrogen atoms occupy the same crystallographic positions as those found for deuterium. Since the crystal structures of the two palladium phosphides are rather complex and contain several types of interstices which might in principle accommodate the hydrogen atoms, it seemed desirable to verify the assumed locations by neutron diffraction measurements on the hydrogenated compounds.

The synthesis of the palladium phosphides and the neutron powder diffraction work were described in detail in Refs. (*3*, *4*). Neutron powder diffraction data were recorded at room temperature (296 K) at the Swedish research reactor, R2 at Studsvik, using a thermal neutron beam at a wavelength of 1.552(1) Å (*4*). Powder intensities of $Pd_3P_{0.80}$ at 500 kPa hydrogen pressure and Pd_6P at a pressure of 800 kPa were measured in the 2θ ranges 20–91° and 8–91°, respectively, in steps of 0.08°. Refinements were performed using a local modification of the ILL-version of the Rietveld profile refinement program (*5*, *6*). The neutron scattering lengths used were Pd 6.0; P 5.1; H −3.72 fm (*7*). The hydrogen atoms were located using three-dimensional difference ($F_{obs} - F_{calc}$) Fourier maps, where the Pd and P contributions were subtracted.

$Pd_3P_{0.80}H_y$. A series of refinements were made. The correlation between the occupation and thermal parameter of the hydrogen atoms was considerable. We therefore decided to fix the occupation at a value corresponding to the formula $Pd_3P_{0.80}H_{0.17}$. This value was estimated from the hydrogen solubility measurements by Flanagan *et al.* (*1*). In the last cycles the following parameters were refined: 2θ zero-point (1), half-width parameters (3); structure parameters: scale factor (1), unit cell dimensions (3), positional parameters (10), anisotropic thermal parameters (14), isotropic temperature factor for H (1). The final agreement fac-

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tors[1] were $R_{F^2} = 1.7\%$, $R_P = 3.9\%$, $R_{wp} = 3.9\%$. The expected R-value was 2.9%. The final structural parameters are listed in Table I and the unit cell dimensions in Table II.

Pd_3P crystallizes with the cementite (Fe_3C)-type structure, space group *Pnma* (No. 62) (*8*). The structure can be described as a packing of Pd_6 triangular prisms with a phosphorus atom at the center of each prism. The deviation from the ideal composition is associated with phosphorus vacancies, leaving some of the Pd_6 prisms empty. The dissolved hydrogen atoms were found to occupy the same crystallographic positions as deuterium in $Pd_3P_{0.80}D_{0.15}$. These sites are situated near the midpoints of two of the quadrilateral faces of the empty prisms. The distance between the two pyramidal voids within the same prism is less than 1.7 Å. Since H—H distances in metal hydrides are not likely to be shorter than 2.1 Å (*9*), occupation of one void should block the adjoining void from H occupation. This hypothesis is strongly supported by the results of the solubility measurements (*1*).

Pd_6PH_z. Refinements of the following parameters were performed: profile parameter: 2θ zero-point (1); structure parameters: unit cell dimensions (4), scale factor (1), positional parameters (27), degree of occupancy of the H atoms (3), isotropic temperature factors (2). The total amount of dissolved hydrogen at 800 kPa hydrogen pressure and room temperature was refined to a value corresponding to the formula $Pd_6PH_{0.39}$. The final R-values[1] were $R_{F^2} = 2.2\%$, $R_p = 4.3\%$, $R_{wp} = 4.2\%$. The expected R-value was 3.2%. The structure parameters are listed in Table I. Unit cell dimensions of pure deuterated and hydrogenated Pd_6P are listed in Table II.

Pd_6P crystallizes in space group $P2_1/c$, with all atoms in 4*e* positions (*4*). The structure can be described in terms of infinite columns of Pd_6 triangular prisms sharing triangular faces. Half of these prisms are filled with phosphorus atoms. In accordance with the results obtained from deuterated Pd_6P, the dissolved H atoms occupy one of three structurally different octahedral interstices and one distorted square-

TABLE I

STRUCTURAL PARAMETERS FOR $Pd_3P_{0.80}H_{0.17}$ AND $Pd_6PH_{0.39}$

$Pd_3P_{0.80}H_{0.17}$

Atom	x	y	z	B^a (Å²)
Pd(1)	0.1782(2)	0.0639(2)	0.3325(2)	0.8(1)
Pd(2)	0.0255(3)	¼	0.8655(4)	1.1(1)
P	0.8853(4)	¼	0.4579(6)	1.6(2)
H	0.355(6)	0.137(4)	0.005(7)	4.8(1.2)

$Pd_6PH_{0.39}$

Atom	x	y	z	n
Pd(1)	0.9652(23)	0.8625(7)	0.9451(7)	
Pd(2)	0.5280(22)	0.1372(8)	0.0684(11)	
Pd(3)	0.7781(21)	0.8699(8)	0.5750(8)	
Pd(4)	0.7099(23)	0.1325(8)	0.4326(10)	
Pd(5)	0.8676(25)	0.5781(6)	0.7516(12)	
Pd(6)	0.6150(26)	0.4163(8)	0.2547(11)	
P	0.8832(21)	0.2588(4)	0.7474(12)	
H(1)	½	0	½	0.20(1)
H(2)	0.381(19)	0.098(8)	0.224(8)	0.13(1)
H(3)	0.249(50)	0.006(25)	0.970(22)	0.06(2)

B_{iso}(Å²): Pd 0.48(2), P 0.75(7), H fixed at value for D in $Pd_6PD_{0.26}$, 3.8 Å².

[a] The B-value for all atoms except H is the mean of B_{11}, B_{22}, and B_{33}.

[1] See NAPS document No. 04171 for 9 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE II

UNIT CELL DIMENSION IN ÅNGSTROMS

Compound	a	b	c	$\beta°$	U (Å^3)
$Pd_3P_{0.80}$(3)	5.7019(2)	7.5366(2)	5.1191(2)	—	220.0
$Pd_3P_{0.80}D_{0.15}$(3)	5.7182(4)	7.5448(6)	5.1304(4)	—	221.3
$Pd_3P_{0.80}H_{0.17}$	5.7144(3)	7.5364(4)	5.1271(3)	—	220.8
Pd_6P(4)	5.6740(4)	9.4409(6)	8.2100(6)	110.414(4)	412.2
$Pd_6PD_{0.26}$(4)	5.6870(4)	9.4654(7)	8.2196(8)	110.431(9)	414.6
$Pd_6PH_{0.39}$	5.6846(2)	9.4638(4)	8.2097(5)	110.431(7)	413.9

pyramidal site. This pyramidal site is situated at the midpoint of one of the quadrilateral faces of the empty prisms. In addition to these two positions, hydrogen occupation of a third position in one of the remaining octahedral sites (position 4*e*) was indicated by the difference Fourier maps and the subsequent refinements. A projection of the structure of Pd_6PH_z along the *a*-axis is shown in Fig. 1.

The results confirm the previous assumption that hydrogen and deuterium occupy the same crystallographic positions when dissolved in $Pd_3P_{0.80}$. For the solutions in Pd_6P, the two sites occupied by deuterium were also found to be occupied by hydrogen. In addition, hydrogen occupation of a third site was indicated. This position was earlier predicted to be the most likely one for further occupation at higher pressures (*4*).

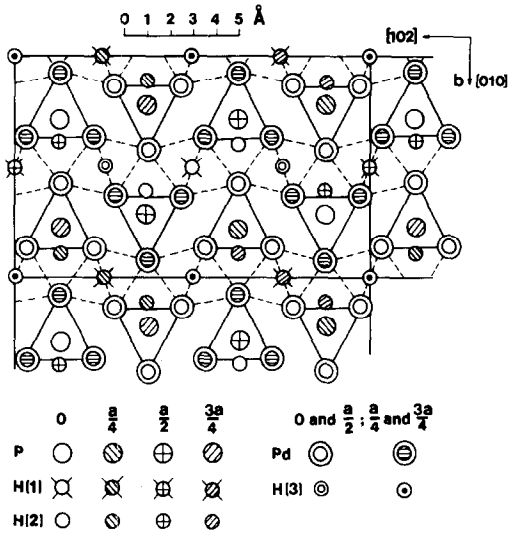

FIG. 1. The Pd_6PH_z structure projected on a plane perpendicular to the *a* axis. Infinite columns of Pd_6 prisms sharing triangular faces appear as triangles in the projection. The approximate heights of the atoms above the projection plane are indicated.

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