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# A Neutron Diffraction Investigation of Deuterated $Pd_3P_{0.80}$

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The crystal structures of pure and deuterated $Pd_3P_{0.80}$ have been analyzed by Rietveld-type profile refinements of neutron powder diffraction intensity data. $Pd_3P_{0.80}$ crystallizes with the cementite ($Fe_3C$)-type structure, space group *Pnma* (No. 62), $Z = 4$, with random vacancies at the phosphorus positions. In $Pd_3P_{0.80}D_{0.15}$ (equilibrium composition at 296 K and 500 kPa $D_2$ pressure), the deuterium atoms occupy sites near the vacant phosphorus positions. The deuterium atoms have five palladium neighbors (average D–Pd distance 2.14 Å) in a distorted square pyramidal coordination.

## I. Introduction

The palladium phosphide $Pd_3P$ crystallizes with the cementite ($Fe_3C$)-type structure, space group *Pnma* (No. 62), $Z = 4$ (*1*). The $Pd_3P$ phase has a range of homogeneity extending from the ideal 3/1 palladium/phosphorus atomic ratio to more metal-rich compositions (*1-5*). The deviation from ideal composition is most probably associated with a variable number of vacant phosphorus sites in the structure, and the chemical formula can accordingly be written $Pd_3P_{1-x}$, $0 \leq x < 0.28$ (*5*).

Recent measurements (*6*) have shown that hydrogen and deuterium dissolve appreciably in $Pd_3P_{1-x}$ alloys; formation of these interstitial solutions leads to expansion of the unit cells. For $x = 0$ the solubility is insignificantly small but increases for larger values of $x$. In connection with studies of the thermodynamics of these solutions (*6*) it became desirable to obtain detailed information on the hydrogen and deuterium atomic positions in the crystal structure. The present neutron diffraction study was therefore undertaken.

A deuterated rather than a hydrogenated sample was chosen for investigation in order to avoid the serious experimental problems associated with the incoherent neutron scattering from hydrogen. Under the same conditions of temperature and pressure the solubility of deuterium in $Pd_3P_{1-x}$ alloys is less than that of hydrogen (*6*) but the solubilities of the two isotopes vary in a similar manner as conditions are changed. Similar solubility behavior toward the hydrogen isotopes has been found for pure palladium (see (*6*) and the references therein). In view of this similarity in isotopic solubility behavior in palladium and in the $Pd_3P_{1-x}$ alloys, and the fact that the same interstices (octahedral) are known to be occupied by both isotopes in palladium, it seems quite reasonable to assume that hydrogen and deuterium occupy

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the same crystallographic positions, not necessarily octahedral positions, in the $Pd_3P_{1-x}$ structures.

## II. Experimental Details

*II.1. Synthesis of $Pd_3P_{0.80}$.* An initial alloy of nominal composition $Pd_3P_{0.8}$ was prepared by dropping lumps of red phosphorus (Koch–Light, claimed purity 5N) into molten palladium (Johnson, Matthey & Co., spectroscopically pure) following the procedure described in (*7*). The alloy was crushed, ground to a fine powder in a tungsten carbide ball mill, and annealed in an evacuated and sealed silica tube at 1040 K for 7 days. The resulting product was again ground to a powder, stress relieved by heating at 940 K for 40 min, and checked by X-ray diffraction. The process of annealing and grinding had to be repeated until the powder diffraction patterns were free from lines belonging to palladium metal and other palladium phosphides and exhibited only perfectly sharp $Pd_3P_{0.8}$ lines. Chemical analysis was finally made by the methods described by Gullman (*5*), and the following results were obtained: Pd, 92.69 wt%, P, 7.18 wt%, corresponding to the formula $Pd_3P_{0.798}$.

*II.2. X-Ray powder diffraction work.* X-Ray diffraction films were recorded in a Hägg–Guinier type focusing camera (Philips XDC 700) using strictly monochromatized Cu$K\alpha_1$ radiation and silicon, $a = 5.431065$ Å (*8*), as internal calibration standard. Unit-cell dimensions were refined by the least-squares method using the local program CELNE (*9*). The values obtained for the final alloy were in satisfactory agreement with those interpolated from Gullman's data (*5*) for the composition $Pd_3P_{0.80}$.

Powder film intensity data were recorded using a SAAB automatic film scanner (*10, 11*) connected to an IBM 1800 computer.

*II.3. Neutron powder diffraction work.* Neutron powder diffraction data were collected at the R2 reactor, Studsvik, Sweden. The neutron beam from a radial reactor channel was passed through a double-monochromator system (using the (200) planes in two copper crystals) to produce a thermal neutron flux at the specimen of $\sim 10^6$ cm$^{-2}$ sec$^{-1}$ at a wavelength of 1.552 Å. The specimen was contained in a 12-mm-diameter vanadium tube, which was connected to a vacuum system with a manometer and deuterium gas supply. Diffraction data were recorded at room temperature (296 K) in three separate runs.

The first run was made on the pure phosphide sample in steps of 0.08° and a measuring time of about 7 min per point. The step scan covered the angular range of 20°–90° in $2\theta$. The vanadium tube was then evacuated and deuterium gas admitted and allowed to reach equilibrium at 200 kPa deuterium pressure for about 48 hr. Diffraction data were then recorded in the same manner as before. Finally, the deuterium pressure was increased until equilibrium conditions were again established at 500 kPa. Data were now recorded in two consecutive runs in order to check the reproducibility of the measurements. Separate experiments have also shown that the sample should have equilibrated with deuterium gas within 48 hr under these conditions of temperature and pressure.

The absorption in the samples was measured and found to be virtually identical under the three different experimental conditions. Absorption corrections for all three sets of intensity data were applied, based on an experimental $\mu r$ value of 0.20.

## III. Structure Analyses and Refinements

*III.1. $Pd_3P_{0.80}$.* The $Pd_3P$ crystal structure was originally determined by X-ray diffraction methods for a single crystal of almost ideal stoichiometry (*1, 5*). The structure belongs to the cementite ($Fe_3C$) type, space group *Pnma* (No. 62).

With increasing $x$ in $Pd_3P_{1-x}$, the $a$ axis decreases and the $b$ axis increases. The $c$ axis increases until $x$ reaches a value of approximately 0.08. On passing this $x$ value the lattice parameters show anomalous behavior: $c$ reaches a maximum and then decreases, while $a$ and $b$ continue to decrease and increase, respectively, but with different slopes with respect to the variation in $x$ (*5*). We suspected that the lattice parameter anomaly might well be associated with some crystallographic change, e.g., the onset of ordering in the phosphorus vacancies. Heavily overexposed powder diffraction photographs for $Pd_3P_{0.80}$ revealed no sign of superstructure reflections, however. The diffraction lines for carefully stress-relieved samples were invariably very sharp with no suggestion of any splitting resulting from a lowering of the symmetry.

In the subsequent structure analyses it was assumed that the *Pnma* symmetry was retained and that the phosphorus vacancies were distributed randomly. Structure refinements of $Pd_3P_{0.80}$ were made on the basis of both X-ray and neutron diffraction data.

In the X-ray case, the structure refinement was carried out by the least-squares method using a Rietveld-type full-profile analysis of the Hägg–Guinier film data according to the technique described by Malmros and Thomas (*12*). The refinement converged in a normal manner, and the positional parameters obtained were not much different from those reported for $Pd_3P$ of almost ideal stoichiometry (*1*). Attempts to refine the structure in the lower space group *Pn2₁a* did not lead to any significant improvement.

The refinement based on the neutron diffraction data was carried out in an analogous manner using a local modification (*13*) of the full-matrix least-squares neutron powder profile analysis program of Rietveld (*14*). The values for the positional parameters agreed to within experimental error with those obtained from the X-ray refinement.

Structure data for $Pd_3P_{0.80}$ as obtained from the neutron diffraction measurement are given in Table I. The final $R$ values (for definitions, see (*12*)) were as follows: $R_{F^2} = 0.050$; $R_F = 0.038$; $R_P = 0.069$; $R_{wp} = 0.084$. For a comparison, the results from the structure analysis by X rays for $Pd_3P_{0.99}$ (*1, 5*) are also included in the table. (A misprint in the $x$ parameter value for Pd(1) in (*1*) has been corrected (*15*).)

*III.2. $Pd_3P_{0.80}D_u$.* The unit-cell dimensions for the deuterated samples were appreciably larger than those for the pure phosphide. Significant differences in intensity between corresponding reflections in the pure and deuterated phosphide were also observed in several instances.

The deuterium positions were located with a three-dimensional ($F_{obs} - F_{calc}$) Fourier synthesis using $F_{obs}$ values measured for the sample at 200 kPa $D_2$ pressure, and $F_{calc}$ values obtained from the refinement of the pure phosphide structure. The difference maps showed four large symmetry-related maxima per unit cell, situated at $y = \frac{1}{4}$ in the vicinity of the phosphorus positions. The maxima were very elongated in the direction of the $b$ axis, indicating pairwise overlap of two individual maxima with slightly different $y$ coordinates.

The difference Fourier synthesis was accordingly interpreted in terms of deuterium atoms occupying one $8d$ position in space group *Pnma*, with a $y$ parameter not very different from $\frac{1}{4}$.

The deuterium contents, as determined directly by solubility measurements described in (*6*), were $Pd_3P_{0.80}D_{0.14\pm0.01}$ and $Pd_3P_{0.80}D_{0.15\pm0.01}$ at 200 and 500 kPa $D_2$ pressure, respectively. A series of refinements was finally made, where the occupancy for the deuterium position was fixed at the values obtained from the solu-

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Pd_3P_{0.99}$, $Pd_3P_{0.80}$, AND $Pd_3P_{0.80}D_{0.15}$

| Atom | Position[a] | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|---|
| | | $Pd_3P_{0.99}$<br>$a = 5.947$ Å, $b = 7.451$ Å, $c = 5.170$ Å (*1, 5, 15*) | | | |
| Pd(1) | 8*d* | 0.1763(2) | 0.0636(3) | 0.3373(3) | 0.70 |
| Pd(2) | 4*c* | 0.0264(4) | $\frac{1}{4}$ | 0.8700(4) | |
| P | 4*c* | 0.8834(11) | $\frac{1}{4}$ | 0.4550(11) | |
| | | $Pd_3P_{0.80}$<br>$a = 5.7019(2)$ Å, $b = 7.5366(2)$ Å, $c = 5.1191(2)$ Å | | | |
| Pd(1) | 8*d* | 0.1799(3) | 0.0625(3) | 0.3325(4) | 0.79(4) |
| Pd(2) | 4*c* | 0.0245(4) | $\frac{1}{4}$ | 0.8662(6) | 1.42(7) |
| P | 4*c* | 0.8854(6) | $\frac{1}{4}$ | 0.4604(7) | 1.23(9) |
| | | $Pd_3P_{0.80}D_{0.15}$<br>$a = 5.7182(4)$ Å, $b = 7.5448(6)$ Å, $c = 5.1304(4)$ Å<br>(296 K, 500 kPa $D_2$ pressure) | | | |
| Pd(1) | 8*d* | 0.1791(3) | 0.0627(2) | 0.3316(3) | 0.80(3) |
| Pd(2) | 4*c* | 0.0249(4) | $\frac{1}{4}$ | 0.8671(5) | 1.25(6) |
| P | 4*c* | 0.8845(10) | $\frac{1}{4}$ | 0.4592(11) | 1.50(14) |
| D | 8*d* | 0.379(6) | 0.178(4) | 0.003(6) | 2.8(7) |

[a] Space group *Pnma* (No. 62).

bility measurements, and an isotropic temperature factor for deuterium was allowed to vary. The results of the final refinement of $Pd_3P_{0.80}D_{0.15}$ at 296 K and 500 kPa $D_2$ pressure are presented in Table I.(These results are insignificantly different from those obtained for the sample at 200 kPa $D_2$ pressure.) The parameters refined were the following:

*Profile parameters*: linewidth (3), $2\theta$ zero point (1); *structure parameters*: scale factor (1), lattice parameters (3), positional parameters (10), isotropic temperature factors (4). The neutron scattering lengths ($\times 10^{14}$ m) used were: Pd, 0.60; P, 0.51; and D, 0.67 (*16*). The final $R$ values (*12*) were as follows: $R_{F^2} = 0.044$; $R_F = 0.034$; $R_p = 0.061$; $R_{wp} = 0.071$.

A final Fourier difference synthesis, where the calculated contributions from all atoms including deuterium were subtracted, revealed no further significant maxima. We conclude that the deuterium atoms occupy only one type of crystallographic position in the structure.

## IV. Description and Discussion of the Structures

The cementite-type structure of $Pd_3P$ can be visualized as comprising triangular prismatic building blocks with palladium atoms at the six corners and a phosphorus atom at the centre. The prisms are packed in such a way that there is one palladium atom outside each of the three quadrilateral faces in close contact with the four palladium atoms at the face corners (*17*).

Comparison of the present structural results for $Pd_3P_{0.80}$ with those obtained earlier for $Pd_3P_{0.99}$ (Table I) suggests no major atomic rearrangement, which can explain the anomalous lattice parameter variation of $Pd_3P_{1-x}$ (*5*). In the absence of further evidence it is tentatively proposed that the lattice parameter anomaly is associated with electronic band structure effects, perhaps similar to the Fermi surface/Brillouin zone overlaps originally discussed by Jones (*18*).

The deuterium sites found in deuterated $Pd_3P_{0.80}$ correspond to positions near the midpoints of two of the quadrilateral faces of the triangular prisms. A projection of the structure on (010) is shown in Fig. 1, where four of the triangular prismatic building blocks are indicated. Interatomic distances are listed in Table II.

If the deuterium atoms were distributed entirely randomly over the whole set of 8*d* positions, D–P distances of only 0.6 Å would occur in many instances. Such distances are unreasonably short, since normal H–P or D–P covalent bond distances are of the order of 1.5 Å. Accordingly, deuterium sites can only be occupied in those prisms where the central phosphorus position is vacant. The distance between the two deuterium sites within the same prism is less than 1.1 Å. Available crystal structure data for transition metal hydrides and deuterides indicate that hydrogen and deuterium atoms are always at least 1.9 Å apart. It is therefore likely that the deuterium atoms in $Pd_3P_{1-x}$ avoid D–D contacts as short as 1.1 Å. Occupation by deuterium of one site in an empty prism would accordingly exclude a simultaneous occupation of the second site within the same prism.

TABLE II

INTERATOMIC DISTANCES SHORTER THAN 3.6 Å IN $Pd_3P_{0.80}D_{0.15}$

| | | | |
|---|---|---|---|
| Pd(1)–D | 2.05(3) | Pd(2)–2D | 2.14(3) |
| –D | 2.10(3) | –2D | 2.21(3) |
| –D | 2.22(3) | –P | 2.241(6) |
| –P | 2.294(5) | –P | 2.241(6) |
| –P | 2.367(5) | –2Pd(1) | 2.822(2) |
| –P | 2.617(3) | –2Pd(1) | 2.880(3) |
| –D | 2.74(3) | –2Pd(1) | 2.907(3) |
| –Pd(2) | 2.822(2) | –2Pd(1) | 2.909(2) |
| –D | 2.82(3) | –2Pd(2) | 3.101(2) |
| –Pd(1) | 2.826(5) | –P | 3.142(6) |
| –Pd(1) | 2.842(3) | –2Pd(1) | 3.213(3) |
| –2Pd(1) | 2.852(2) | –2D | 3.38(3) |
| –Pd(2) | 2.880(3) | | |
| –Pd(2) | 2.907(3) | D–P | 0.58(3)[a] |
| –Pd(2) | 2.909(2) | –D | 1.09(6)[a] |
| –2Pd(1) | 2.979(1) | –Pd(1) | 2.05(3) |
| –D | 3.05(3) | –Pd(1) | 2.10(3) |
| –Pd(2) | 3.213(3) | –Pd(2) | 2.14(3) |
| –D | 3.55(3) | –Pd(2) | 2.21(3) |
| | | –Pd(1) | 2.22(3) |
| P–2D | 0.58(3)[a] | –Pd(1) | 2.74(3) |
| –Pd(2) | 2.241(6) | –Pd(1) | 2.82(3) |
| –Pd(2) | 2.241(6) | –D | 3.02(6) |
| –2Pd(1) | 2.294(5) | –Pd(1) | 3.05(3) |
| –2Pd(1) | 2.367(5) | –Pd(2) | 3.38(3) |
| –2Pd(1) | 2.617(3) | –P | 3.51(3) |
| –Pd(2) | 3.142(6) | –Pd(1) | 3.55(3) |
| –2D | 3.51(3) | | |
| –2P | 3.575(7) | | |

[a] Interatomic contacts of this type never occur in the real structure.

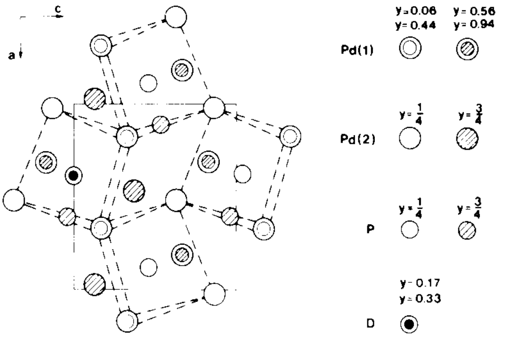

FIG. 1. The crystal structure of $Pd_3P_{1-x}D_u$ projected on (010). Four of the triangular prismatic building blocks are indicated. Deuterium sites are shown in one triangular prism, where the central phosphorus position is vacant.

On the basis of this structural argumentation we propose that the deuterium atoms dissolved in $Pd_3P_{1-x}$ can occupy a maximum of one site per vacant phosphorus position, the solubility limit corresponding to the formula $Pd_3P_{1-x}D_x$.

This is in good agreement with the experimental solubility data reported in (*6*), assuming that hydrogen and deuterium behave similarly in the phosphide structure.

The hydrogen solubility, as measured at constant temperature and hydrogen pressure for a series of $Pd_3P_{1-x}$ alloys, increases from zero at $x = 0$ to progressively larger values when $x$ increases. This feature is expected since an increasing number of hydrogen sites becomes available as the number of vacant phosphorus positions increases. The hypothesis that the second hydrogen site is blocked by a hydrogen atom occupying one of the two possible positions within the same prism is also supported by the solubility data (*6*). For a given value of $x$, the hydrogen solubility increases asymptotically to the limiting composition $Pd_3P_{1-x}H_x$ when the hydrogen pressure increases, the solubility data following closely the values calculated from a "blocking model without overlap" according to Speiser and Spretnak (*19*). The "overlap" effect between hydrogen or deuterium atoms in different prisms is probably very small, since D–D distances between different prisms exceed 3 Å.

The atomic environment of a deuterium atom is illustrated stereoscopically in Fig. 2. The deuterium atom has five near palladium neighbors: four at the corners of the quadrilateral prism face, and the fifth outside the midpoint of the face. The arrangement can be described as a distorted square pyramidal coordination, with an average D–Pd distance of 2.14 Å.

In palladium and a number of palladium alloys, the dissolved hydrogen and deuterium atoms have a regular octahedral coordination of palladium atoms. It is interesting to observe that there are four slightly distorted octahedral interstices per unit cell between the palladium atoms in $Pd_3P$. The size of these holes is similar to that of the octahedral holes in pure palladium or in palladium hydride. The present study does not indicate any deuterium occupation of the octahedral holes in $Pd_3P_{0.80}$, however. Neither is there any sign of occupation of the tetrahedral holes in the structure, nor of the square pyramidal hole at the third quadrilateral face of the $Pd_6$ triangular prisms. These interstices may play an important role in the diffusion of deuterium and hydrogen atoms through the structure.

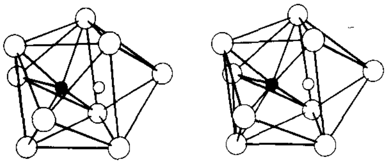

FIG. 2. The palladium atom environment of a deuterium atom in $Pd_3P_{1-x}D_u$. The deuterium atom (solid circle) has five near palladium neighbors in a distorted square pyramidal arrangement. The nearest deuterium site (small open circle) is vacant.

Filling the vacant prisms in $Pd_3P_{1-x}$ with hydrogen (8*d* positions) or with phosphorus atoms (4*c* positions) is accompanied by an increase of the unit-cell volume, but the lattice parameter variation is distinctly different in the two cases. This difference may be explained by simple structural arguments following an earlier geometric analysis of the cementite-type structure by Aronsson and Rundqvist (*17*).

For decreasing $x$, the $a$ and $c$ axes increase in $Pd_3P_{1-x}$, while the $b$ axis decreases (for $x$ values around 0.2). This means that the expansion of the triangular prismatic building blocks is mainly confined to two of the quadrilateral faces. (The projections of these two faces on the *ac* plane are indicated in Fig. 1.) The palladium atoms situated outside the midpoints of the two faces (the "waist atoms") are in bonding contact with the four palladium atoms (the "prism atoms") situated at the corners of each face. When the quadrilateral faces expand, the "waist atoms" tend to retain their contacts with the "prism atoms" by moving closer toward the faces. This is achieved by the contraction of the $b$ axis. The "waist atoms" are at considerably larger distances from the central phosphorus atom than the "prism atoms," and the interaction between phosphorus and the "waist atoms" is presumably of minor importance.

Upon hydrogenation the three unit-cell edges of $Pd_3P_{1-x}$ increase, and the quadrilateral faces of the prisms expand. The "waist palladium atoms" would presumably tend to move closer toward the faces as in the phosphorus case, but such movement is now counteracted by the hydrogen atoms at the midpoints of the faces. The Pd–H interaction thus causes an expansion of the *b* axis, although only approximately one-half of that of the *a* and *c* axes.

The contraction of the *b* axis on filling the phosphorus sites, as opposed to the expansion of *b* on filling the hydrogen sites, is thus explained by negligible Pd–P interaction in contrast to a bonding Pd–H interaction for those palladium atoms situated outside the two crucial quadrilateral faces of the triangular prismatic building blocks.

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