# Where do the H atoms reside in PdH$_x$ systems?

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We present an *ab initio* density-functional theory study of PdH$_x$ systems. We evaluated the total energy of PdH$_x$ systems with the H atoms occupying interstitial (octahedral and tetrahedral) sites of a Pd supercell, allowing for the relaxation of the coordinates and supercell dimensions. The majority of our calculations were based on supercells consisting of four Pd atoms, and up to four H atoms, covering the range from $x = 0.25$ to $x = 1$. In addition some larger calculations are reported. In order to compare the relative stability of systems at different values of $x$ (at fixed pressure and temperature $T = P = 0$), we computed the enthalpy of formation $\Delta H_f(x)$ of the (non)stoichiometric systems. In the regime $x = 0 \rightarrow 1$, the $\Delta H_f(x)$ decrease in a manner indicative of the existence of attractive interactions between the dissolved H atoms. Ideal-solution theory cannot be applied to this system. Furthermore, we find that tetrahedral occupation is favoured over octahedral occupation at high $x$, leading to the formation of a zincblende structure at $x = 1$. A preliminary vibrational analysis of normal modes has been performed. Inclusion of vibrational zero-point energies in a harmonic approximation leads us to conclude, tentatively, that the observed stability of octahedral site occupation is due to more favourable zero-point energies of the H atoms in those sites. The results indicate that a proper understanding of this system must take into account the quantum nature of the dissolved hydrogen.

## 1. Introduction

Palladium–hydrogen systems have been extensively studied since the discovery in 1886 by Graham [1] of the ability of Pd to absorb relatively large amounts of H ($\approx 97$)M [2–4]. Although many metals can exothermically dissolve considerable amounts of hydrogen, Pd seems to have peculiar chemical–physical properties that make it a highly attractive metal for hydrogen absorption and dissolution. According to the *Encyclopaedia Britannica*, '... at 80 °C and one atmosphere, palladium will absorb up to 900 times its own volume. The absorption causes both the electrical conductivity and magnetic susceptibility to decrease. ... it expands and becomes harder, stronger, and less ductile in the process. A metallic or alloylike hydride is formed from which the hydrogen can be removed by increased temperature and reduced pressure. ... hydrogen passes rapidly through the metal at high temperatures ...'. The phase diagram of the PdH$_x$ system exhibits a low concentration $\alpha$-phase; at room temperature $x_\alpha \approx 0.01$. Below a critical point ($T_c \approx 300$ °C, $P_c \approx 20$ atm) [2] the $\alpha$-phase can coexist with a high concentration $\beta$-phase in which

$x \approx 0.6$. The lattice parameter in the $\beta$ phase is expanded by $\approx 3\%$ compared to the pure Pd lattice. The phase coexistence curve is highly reminiscent of a liquid–vapour phase coexistence [5]. Loading of H beyond a saturation concentration of $x \approx 0.7$ requires either high hydrogen partial pressures or a decrease in temperature. The heat of formation of the monohydride PdH is only moderately exothermic, in the region of $-20$ kJ mol$^{-1}$ (0.21 eV) [5].

Since early neutron-diffraction [6–8] work, it has been assumed that the dissolved hydrogen resides atomically at the centre of octahedral sites in the face-centred cubic (FCC) lattice of Pd, leading to the formation of a rock-salt structure in the monohydride system PdH. For $\alpha$-phase (low concentration $x \approx 0.03$) at high temperature ($T \approx 600$ K) detailed quasi-elastic neutron scattering data is available [9].

Of great interest is an understanding of the physical characteristics of the host metal [10] which led to the observed phase diagram, structure and energetics for PdH$_x$ systems. In particular, the nature of the energetic interaction of H with the metal is not clear. It is undoubtedly of electronic origin [11–13], but is also dependent on the concentration of H in the host

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metal [14–16]. An understanding of the effective H–metal and H–H interactions as a function of concentration is lacking.

Addressing some aspects of this question is the topic of this paper. We have investigated the energetics of (sub)-stoichiometric $PdH_x$ systems using *ab initio* total energy calculations. A key thermodynamic quantity to be computed is the enthalpy of formation $\Delta H_f(x)$ of a $PdH_x$ system from its elemental components, Pd and $H_2$. This is a stepping stone toward computing the Gibbs energy of formation $\Delta G_f(x)$, from which one can compute the temperature and pressure dependence of the loading factor, i.e. in effect the equilibrium concentration of H as a function of the temperature $T$ and pressure $P$. Since $\Delta G_f(x) = \Delta H_f(x) - T\Delta S_f(x)$, modelling the latter also requires a hypothesis regarding the entropy of formation, $\Delta S_f(x)$. When we originally started this work, our intention was to make a mean-field approximation [5, 17, 18] for $\Delta S_f(x)$, thus giving a direct albeit approximate route to the Gibbs energy. However, as our work proceeded, it became apparent that the behaviour of $\Delta H_f(x)$ is already sufficiently complicated to merit detailed consideration on its own, before proceeding to the statistical mechanics implied by the Gibbs energy. Here we shall report largely on this issue.

The paper is organized as follows. In §2 we give technical details of the calculations. In §3 we discuss how to compute the $\Delta H_f$. In §4 we discuss aspects of the geometries for H placed in interstitial sites. In §5 we present results on results we have obtained so far. Section 6 is a discussion of the results, together with some tentative conclusions.

## 2. Method

We performed density functional theory (DFT) calculations using norm-conserving pseudopotentials and the PBE generalized gradient approximation (GGA) for non-stoichiometric $PdH_x$ compounds, covering the range of $x$ from 0 to 1. An electronic free-energy functional [19] was employed, as implemented in the CPMD code [20]. The geometric set-up consisted of a cubic supercell containing four Pd atoms in a FCC structure, together with a number of H atoms placed in interstial sites. This conveniently allows us to look at $x = 0.25, 0.5, 0.75$ and 1. Given that there are two types of FCC interstitial sites (octahedral and tetrahedral), we examined a number of possibilities of occupying these sites which are indicated in table 1. For each configuration all internal coordinates, as well as the cell volume, were relaxed.

The Pd pseudopotential was of the Troullier–Martins [21] type in the Kleinmann–Bylander representation (with the $s$ component local); the $s$ and $d$ components were generated the $[Kr]4d^{10}$ atomic electron configuration;

Table 1. Number of hydrogen atoms per cell, non-equivalent configurations $C_{neq}$, interstitial sites and point group in Schoenflies notation.

| | | Geometric configurations | | |
|---|---|---|---|---|
| $m$ | $C_{neq}$ | Interstitial site | Point group | Label |
| 1 | 1 | $\forall j, O_j$ | $O_h$ | O1 |
| | 1 | $\forall k, T_k$ | $T_d$ | T1 |
| 2 | 1 | $\forall j, O_j$ | $D_{4h}$ | O2 |
| | 3 | $T_1, T_2$ | $D_{4h}$ | T2.1 |
| | | $T_1, T_3$ | $C_{4v}$ | T2.2 |
| | | $T_1, T_7$ | $O_h$ | T2.3 |
| 3 | 1 | $\forall j, O_j$ | $O_h$ | O3 |
| | 3 | $T_1, T_2, T_4$ | $C_{4v}$ | T3.1 |
| | | $T_1, T_7, T_3$ | $C_{4v}$ | T3.2 |
| | | $T_1, T_6, T_8$ | $T_d$ | T3.3 |
| 4 | 1 | $\forall j, O_j$ | $O_h$ | O4 |
| | 5 | $T_1, T_2, T_4, T_5$ | $T_d$ | T4.1 |
| | | $T_1, T_3, T_6, T_8$ | $T_d$ | T4.2 |
| | | $T_1, T_5, T_8, T_3$ | $D_{2h}$ | T4.3 |
| | | $T_1, T_2, T_3, T_4$ | $D_{4h}$ | T4.4 |
| | | $T_1, T_3, T_5, T_7$ | $D_{4h}$ | T4.5 |

the $p$ component was generated using a singly-charged configuration $[Kr]5s^1 5p^{0.25} 4d^8$. The core radii for the $s, p, d$ components were set to $r_s = r_d = 2.2$, $r_p = 2.5$ au. The PBE functional was used both in the generation of the pseudopotential as well as in the bulk calculations. The cut-off was set to 60 Ry, sufficient to give well-converged energies and structures. In the bulk calculations, where we employed a simple cubic (four Pd-atom) supercell, we used a $8 \times 8 \times 8$ $k$-point mesh. Where possible due account was taken of symmetry in reducing the number of $k$-points to those in an irreducible wedge. For configurations with $O_h$ symmetry, this implied 20 $k$-points. We also did a number of calculations using an eight Pd-atom tetragonal cell in order to achieve the intermediate values of $x = 0.125, 0.375$ and $0.625$. In the majority of the configurations we limited here our inspection to those configurations in which all H atoms occupy the same type of site. A few 'mixed' occupation configurations were also considered, but these are still in progress.

In order to gain insight into the vibrational modes of the $PdH_x$ system, we also performed a vibrational analysis on the optimized structures using a finite-difference method. Analyses of this type have been presented before (e.g. see [22]). Briefly, the dynamical matrix $D_{i\alpha, j\beta}$ is computed by displacing each Cartesian component $x_{i\alpha}$ of each atom $i$ in the super-cell by a finite amount $\pm\delta x_{i\alpha}$, and computing the resulting forces $F_{j\beta}$ by

performing the self-consistent minimization of the total energy functional. Then

$$-D_{i\alpha,j\beta} = \frac{1}{(m_i m_j)^{1/2}} \frac{\partial F_{j\beta}}{\partial x_{i\alpha}} \qquad (1)$$

$$\approx \frac{1}{(m_i m_j)^{1/2}} \frac{F_{j\beta}(\delta x_{i\alpha}) - F_{j\beta}(-\delta x_{i\alpha})}{2\delta x_{i\alpha}}, \qquad (2)$$

where $m_i$ is the mass of atom $i$. For a system of $N$ atoms this gives a $3N \times 3N$ symmetric matrix, whose eigenvalues ($\omega_i^2$) and eigenvectors yield the vibrational frequencies and normal modes. Of the $3N$ modes, three should correspond to translational modes with zero frequency. In practice, because of small numerical inaccuracies associated with computing the forces in a self-consistent procedure, there is an error of about $10\,\text{cm}^{-1}$ in the frequencies. These errors can be systematically reduced by increasing the threshold of the SCF procedure. Structures for which all modes $\omega_i^2 > 0$, the corresponding structure is a minimum; the presence of imaginary modes implies a saddle point. With this we could verify if our structures were indeed proper minima.

## 3. Enthalpy of formation

In order to compare the relative energies of the PdH$_x$ systems as a function of $x$, it is convenient to compute the enthalpy of formation $\Delta H_f(x)$ for the following reaction:

$$n\text{Pd} + \frac{m}{2} H_2 \rightleftharpoons n\text{PdH}_x, \qquad (3)$$
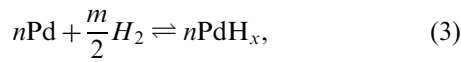
where $x$ is the loading factor, defined as

$$x = \frac{m}{n}. \qquad (4)$$

$\Delta H_f(x)$ per atom of Pd is defined as

$$\Delta H_f(x) = \frac{H(\text{PdH}_x)}{n} - \mu_{\text{Pd}} - x\mu_{\text{H}}, \qquad (5)$$

where $\mu_{\text{Pd}}$ and $\mu_{\text{H}}$ are the chemical potentials at $T = P = 0$ for Pd and H, and $H(\text{PdH}_x)$ is the enthalpy of the PdH$_x$ supercell. $\Delta H_f(x)$ measures the stability of a PdH$_x$ system with respect to the elements in their standard state at $T = 0$ and pressure $P$.

The enthalpy function $H(x, P) = E(x, V) + PV$ was computed at $P = 0$ by minimizing the total energy $E(x, V)$ with respect to the supercell volume $V$ to obtain the equilibrium volume $V_0$, thus satisfying

$$P = -\left(\frac{\partial E}{\partial V}\right)_x \Big|_{V=V_0} = 0. \qquad (6)$$

For a given configuration of H atoms in the Pd host, we computed the energy–volume curve at a series of $V$ and found the minimum $V_0$ using polynomial interpolation. For a given concentration $x$ of H atoms, there are a number of possible ways of occupying the interstitial sites. We found that the energy–volume curves, and hence the $V_0$, depend rather sensitively on the actual distribution of the H atoms, even at a given $x$. The majority of our computational effort, therefore, has been obtaining $E(x, V)$ curves for the numerous combinations. The minimum lattice parameters so obtained, together with their bulk modulus, defined as

$$B = -V\left(\frac{\partial^2 E}{\partial V^2}\right)_x, \qquad (7)$$

are given in table 2.

The chemical potentials of the pure systems (at $T = P = 0$) are given as follows:

$$\mu_{\text{Pd}} = \text{Energy per Pd atom in relaxed pure Pd cell.} \qquad (8)$$

$$\mu_{\text{H}} = \frac{\mu_{\text{H}_2}}{2} = \frac{1}{2}\left(E^{(0)}(\text{H}_2) + \frac{1}{2}\hbar\omega_0\right). \qquad (9)$$

In the total energy of H$_2$ we include the (calculated) zero-point energy of the molecular stretching mode $\omega_0 = 4428\,\text{cm}^{-1}$ and $E^{(0)}$ is the energy of an isolated H$_2$ molecule.

## 4. Geometries

The investigated configurations are indicated in table 1 and figures 1 and 2. There are four octahedral sites in the supercell. We sequentially occupied the sites with H atoms; because of symmetry, the order in which the sites are filled is immaterial. Two H atoms placed in neighbouring O sites are $a/2^{1/2} \approx 2.8\,\text{Å}$ apart in distance, whereas their distance to the six neighbouring Pd atoms is $a/2 \approx 2\,\text{Å}$ (the precise values depending on the lattice constant appropriate to the $x$ under consideration).

Tetrahedral site occupation is more complex. There are eight tetrahedral sites to consider, shown in figure 2, which form the corners of a cube of dimension $a/2$. The distance from the centre of a T site to the nearest neighbour Pd atoms is $3^{1/2}a/4 \approx 1.8\,\text{Å}$. Therefore, in T-site occupation, the H atoms are closer to the Pd atoms, as compared to the O-site occupation, and are coordinated to four rather than six Pd atoms. The distance between H atoms in nearest neighbour T sites is $a/2 \approx 2\,\text{Å}$; in the next-nearest neighbour configuration it is $a/2^{1/2} \approx 2.8\,\text{Å}$. The occupation of two T sites can be done in three distinct ways (labelled T2.1, T2.2 and T2.3 in table 1), corresponding to nearest neighbour

Table 2. Computed heat of formation and bulk properties of $PdH_x$ system.

| $m$/atom/cell | $x$ | Label | Lattice constant/Å | $\frac{a-a_0}{a_0}$/% | $B$/kbar | $\Delta H_f$/meV |
|---|---|---|---|---|---|---|
| 1 | 0.25 | O-1 | 4.02 | 1.36 | 1694 | $-35$ |
| 2 | 0.50 | O-2 | 4.07 | 2.50 | 1726 | $-83$ |
| 3 | 0.75 | O-3 | 4.11 | 3.54 | 1763 | $-122$ |
| 4 | 1.00 | O-4 | 4.15 | 4.50 | 1788 | $-143$ |
| 1 | 0.25 | T-1 | 4.05 | 1.96 | 1593 | $-31$ |
| 2 | 0.50 | T-2.1 | 4.11 | 3.61 | 1557 | $-78$ |
|  |  | T-2.2 | 4.12 | 3.79 | 1562 | $-103$ |
|  |  | T-2.3 | 4.14 | 4.25 | 1486 | $-68$ |
| 3 | 0.75 | T-3.1 | 4.18 | 5.23 | 1510 | $-112$ |
|  |  | T-3.2 | 4.20 | 5.76 | 1469 | $-122$ |
|  |  | T-3.3 | 4.19 | 5.53 | 1520 | $-167$ |
| 4 | 1.00 | T-4.1 | 4.24 | 6.86 | 1457 | $-128$ |
|  |  | T-4.2 | 4.26 | 7.25 | 1593 | $-217$ |
|  |  | T-4.3 | 4.26 | 7.27 | 1486 | $-159$ |
|  |  | T-4.4 | 4.23 | 6.29 | 1474 | $-96$ |
|  |  | T-4.5 | 4.27 | 7.48 | 1555 | $-153$ |
| Pd |  |  | 3.97 |  | 1708 |  |
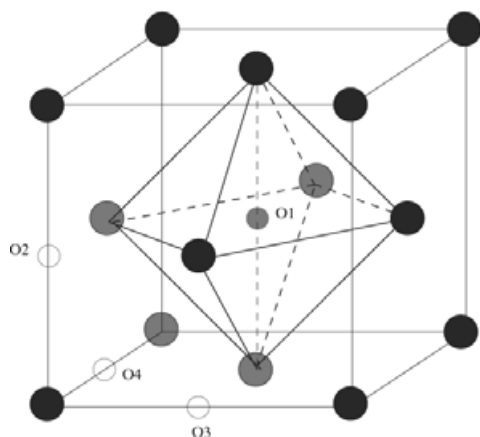


Figure 1. Four octahedral sites (O1–O4) of the FCC lattice.
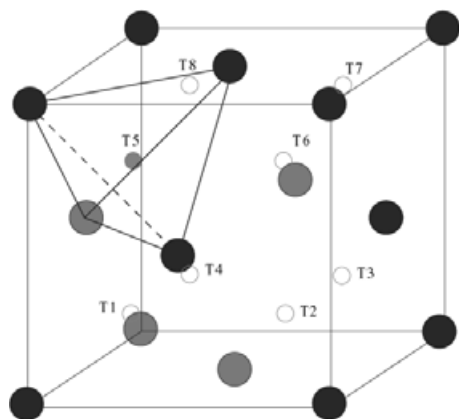


Figure 2. Eight tetrahedral sites (T1–T8), which form the corners of a cube of dimension $a/2$.
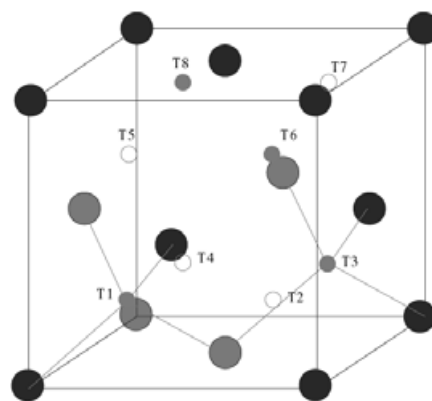


Figure 3. The zincblende structure formed at $x = 1$.

occupation, next-nearest neighbour and third-neighbour occupation, respectively. Each of these situations turn out to have rather different energies. Similarly, the occupation of three tetrahedral sites can be done in three distinct ways: either all three H atoms lie in a {001} plane or in a {011} plane or in a {111} plane. These are designated T3.1, T3.2 and T3.3, respectively. The occupation of four tetrahedral sites can be done in five distinct ways, the zincblende structure (in which four sites themselves form a tetrahedron) being one of them (see figure 3), designated T4.2 in table 1.

## 5. Results

### 5.1. Octahedral occupation

We sequentially occupied the octahedral sites with H atoms, from 1 to 4. The resulting enthalpy of formation
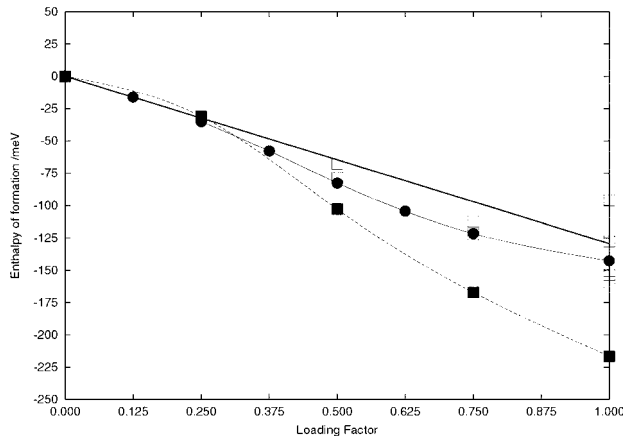
Figure 4. Enthalpy of formation $\Delta H_f$ for PdH$_x$ systems as a function of $x$. The circles refer to octahedral occupation and the squares to tetrahedral occupation. The open squares correspond to the higher energy combinations of tetrahedral site occupation. The solid straight line is $\Delta H_f^{id}$ obtained from the slope of a $x = 0.125$ calculation, which is the lowest $x$ we probed.



Figure 5. The relative change in equilibrium volume as a function of $x$ for octahedral (circle) and tetrahedral (square) occupation.

$\Delta H_f(x)$ is given in table 2 and in figure 4. The addition of one H atom to the pure four-atom Pd supercell lowers the energy by about 35 meV with respect to the elements in their standard state. Addition of a second H atom to a neighbouring octahedral site leads to a further lowering of 48 meV, bringing the total to $-83$ meV. This is 13 meV *more* than would have been expected on the basis of an ideal-solution model which assumes the H atoms do not interact with each other. Thus these energies suggest that *attractive* interaction exists between H atoms in neighbouring sites. Increasing the number of H atoms to three brings a further lowering of 39 meV, bringing the total to $-122$ meV, whilst adding the fourth and final hydrogen lowers the energy by 21 meV, yielding a total $-142$ meV.

The solid line in figure 4 is the result of extrapolating the $\Delta H_f$ from the $x \to 0$ limit, based on a calculation of $\Delta H_f$ at $x = 0.125$, which is the lowest concentration we could achieve by doubling the supercell size in one dimension. According to ideal solution theory, we would expect:

$$\Delta H_f^{id} = x \times \left( \frac{\partial \Delta H_f}{\partial x} \right) \Bigg|_{x=0}. \qquad (10)$$

A deviation below this line is indicative of an attractive interaction between the solute particles, i.e. the H atoms. The form of the variation of $\Delta H_f(x)$ with $x$ suggests the existence of an inflexion point, with the maximum change in $\Delta H_f(x)$ arising when $x \approx 0.5$.

The insertion of H in the octahedral sites leads to an expansion of the lattice parameter [23–25] of the PdH$_x$
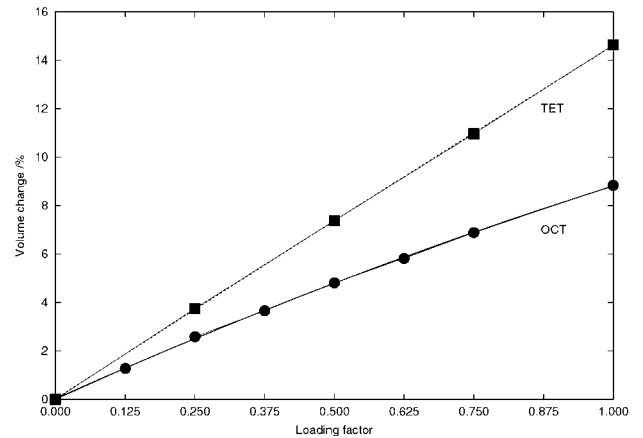
system (table 2 and figure 5). Interestingly, the bulk modulus also shows a general trend to increase (table 2). Given that the bulk modulus measures the elastic strength of the lattice, this implies the unusual coincidence with the lattice expanding and simultaneously strengthening with the addition of H. Since the expansion of the lattice is expected to weaken the Pd–Pd bonds, the implication must arise that the newly formed H–Pd bonds are sufficiently strong to lead to an overall enhancement of $B$ of the PdH$_x$ solid. The formation of strong H–Pd bonds is consistent with the negative heats of formation reported above.

It is also noteworthy that $\Delta H_f$ decreases continuously with $x$. This implies that at $T = 0$, the formation of the monohydride PdH$_1$ should be more favourable than those with $x < 1$.

### 5.2. Tetrahedral occupation

The enthalpies of formation of the tetrahedral occupation are given in figure 4 and table 2. Placing one H atom in a tetrahedral site lowers the energy by 31 meV with respect to the elements. This is marginally smaller than the corresponding octahedral site occupation. The lattice parameter $a = 4.05$ Å is slightly larger than the corresponding $a = 4.02$ Å when an octahedral site is occupied. It is noteworthy that the tetrahedron surrounding the H atom internally expands, leading to a Pd–H distance of 1.80 Å, larger than $3^{1/2}a/2 = 1.75$ Å in the unrelaxed tetrahedron, i.e. the tetrahedron containing the H atom expands uniformly outwards by 0.05 Å. Thus the H atom placed in a tetrahedron site causes both a larger global expansion of the lattice parameter, as well as a local distortion, than the corresponding O site. Nevertheless, the overall $\Delta H_f$ is

only marginally smaller for a single T occupation than O occupation.

Placing now a second H atom in a T site brings a large lowering of energy. Given the three distinct choices (T2.1, T2.2, T2.3), the T2.2 configuration in particular lowers the energy by 71 meV, leading to an overall $\Delta H_f$ of $-102$ meV. The lattice now expands to $a = 4.12$ Å. The equilibrium H–Pd bond lengths are 1.818 Å, resulting from an outward relaxation of 0.034 Å of the tetrahedra containing the H atoms. As with octahedral site occupation, the enhancement of the heat of formation in going from $x = 0.25$ to $x = 0.5$ is an attractive interaction between the H atoms. In the case of the T2.2 configuration, the two H atoms being placed along a face-diagonal, they share a single bridging Pd atom, leading to the formation of Pd–H–Pd–H–chains.

Going now on to three H atoms, we found that the T3.3 was the most stable of the three distinct geometries, lowering the energy with respect to T2.2 by 64 meV, i.e. with a $\Delta H_f = -167$ meV. T3.3 consists of the three H atoms being placed along the face diagonals of a cube to form $T_d$ symmetry.

Finally, addition of the fourth H atom in the zincblende configuration leads to the most stable structure of all, having $\Delta H_f = -216$ meV. In this structure, four corners of a cube which form a tetrahedron are occupied. Note that in this $x = 1$ structure, the energy is about 74 meV more stable than the corresponding rock-salt structure obtained from O-site occupation. The overall expansion in the lattice constant is roughly 7% in the zincblende structure compared to the pure Pd lattice, considerably greater than $\approx 4\%$ when the octahedral sites are occupied.

## 6. Discussion

The above results indicate that, at least from the point of the total energy $T = 0$ calculations, the occupation of T sites must be considered favourable compared to that of O-site occupation. This result contradicts the widely held belief that the H atoms reside in octahedral sites. Firstly, neutron diffraction unambiguously supports the notion of a rock-salt structure, which implies octahedral occuption. Further evidence against tetrahedral occupation is that the lattice constant expands with $x$ at a rate which is much too rapid; by contrast, the rate of lattice expansion seen for O-site occupation nicely matches experiment. Thus, it seems unlikely that the T sites are indeed more stable than the O site. What, then, has gone wrong?

In attempting to resolve this paradox, we next considered a vibrational analysis. The rationale for this stems from the fact that the H atoms can possess a considerable amount of zero-point energy (ZPE), which in the harmonic approximation can be represented as

$$E_{ZPE} \approx \sum_i \frac{1}{2}\hbar\omega_i, \qquad (11)$$

where $\omega_i$ are frequencies associated with the harmonic modes and the sum extends over all modes of the crystal, which in practice we shall truncate over the modes which principally involve H motion. These frequencies are likely to be rather different in the two types of sites, since both the H–Pd bond lengths are different, as are the available volumes in the two sites. Both features favour the octahedral sites. Longer Pd–H bonds will give rise to lower frequencies for the modes which principally involve the H atoms.

The full set of vibrational calculations are still in progress. Below we report only a set of two, corresponding to occupation of a single O or T site. Due to symmetry, there are three degenerate modes. For O sites, we obtained $\omega = 345$ cm$^{-1}$ and for the T sites we obtained $\omega = 957$ cm$^{-1}$. Taking into account that these modes are three-fold degenerate, we arrive at a rough estimate of the zero-point energy per H: 64 meV (O) and 177 meV (T). The former value compares quite favourably with inelastic neutron scattering measurements of $68.5 \pm 2$ meV [7]. Thus the zero-point energies of the H atoms in O sites are stabilized by roughly 110 meV per H atom compared to T-site occupation. Recall that at $x = 1$, the energetic difference between the most stable T configuration and the most stable O configuration was about 75 meV per supercell, making it about 18 meV per H atom. Therefore a difference in ZPE of 110 meV per H atom is easily sufficient to tip the balance in favour of the O sites. Of course this assumption (i.e. in effect the Einstein oscillator assumption) that the vibrational frequencies are independent of $x$ is crude. Calculations are currently in progress to compute the vibrational frequencies at higher values of $x$. The extent to which the occupation of neighbouring interstitial sites affects the vibrational modes will then be taken into account. However, the preliminary indications are that it is the quantum effects, manifest in the proton zero-point energies, may play a decisive role in determining the stability of O-site occupation in PdH systems.

In summary, we have reported a study of the energetics in PdH$_x$ systems from the view point of *ab initio* total energy calculations, by considering possible occupation of octahedral and tetrahedral sites of the Pd lattice. Unexpectedly, we found that the occupation of T sites, particularly in the zincblende structure, is energetically favourable. A preliminary vibrational analysis suggests that the observed stability of octahedral sites arises through lower zero-point

energies associated with vibrational modes of the H atoms residing in the octahedral sites.

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