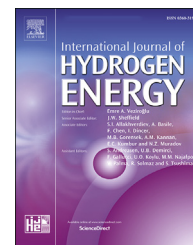




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## Accounting for the thermo-stability of PdH<sub>x</sub> (x = 1–3) by density functional theory

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### ABSTRACT

We calculate the formation enthalpies of PdH<sub>x</sub> (x = 0–3) by cluster expansion (CE) and calculations based on density functional theory. CE predicts the stable palladium hydride structures PdH, PdH<sub>2.67</sub>, and PdH<sub>2.75</sub>. The band structures and density of states indicate that the amount of hydrogen in the palladium lattice does not alter the metallic character of the palladium significantly. However, all PdH<sub>x</sub> structures with x > 1 have greater formation enthalpies than that of the given reaction path 4PdH<sub>2</sub> = 2PdH + 2Pd + 3H<sub>2</sub> and thus they are thermodynamically unstable. The shorter bond length of Pd–H and the smaller bond angle of Pd–H–Pd imply a higher cohesive energy in zincblende (ZB) PdH than that in rocksalt (RS) PdH. Bader charge analysis shows a stronger electronegativity of H atoms in ZB-PdH than that in RS-PdH. This results in a stronger Pd–H bond in ZB-PdH than that in RS-PdH. Thus ZB-PdH has lower formation enthalpy than that of RS-PdH. However, regarding the dynamic stability, we conclude that hydrogen atoms prefer to occupy the octahedral sites of the palladium lattice because of the lower zero-point energy and vibration free energy than that of occupying the tetrahedral sites.

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### Introduction

Hydrogen is the simplest, lightest, and most abundant natural element, but less than 1% of Earth's hydrogen is present in the atmosphere as hydrogen molecules [1,2]; the majority is in the form of terrestrial H<sub>2</sub>O [2,3]. As clean and sustainable energy,

hydrogen energy is an ideal candidate for effectively alleviating the problem of air pollution and greenhouse effect, as well as reducing the dependence on imported oil for these countries which are short of natural resources [4]. However, the greatest challenge in the practical application of hydrogen energy is storing and transporting highly dense hydrogen. Therefore, it is imperative to search for safe and reliable

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hydrogen-storage materials. The transition metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au all have the capacity to absorb hydrogen [5], making them candidate materials for hydrogen storage. Among these transition metals, palladium (Pd) has the best hydrogen-absorption performance, with an H/Pd ratio reaching 0.70 at ambient temperature and atmospheric pressure [6,7]. Because of this characteristic, Pd is often called the “metal sponge.” This unique property of palladium metal has brought up a lot of reports on palladium-hydrogen and palladium alloy-hydrogen systems. In nanocrystalline, polycrystalline and epitaxial Pd films, the effect of microstructure on the behavior of absorbed hydrogen were investigated by Čížek et al. [8] and an increase of the defect density in all Pd films was observed due to the hydrogen-induced plastic deformation. Pivak et al. [9] found that highly adhesive Pd thin films exhibits a much larger hysteresis on hydrogen cycling than weakly adhesive films, and in Pd/Ti films, the hydrogen absorption and desorption induces a rearrangement and pile-up of the materials. By Monte Carlo and Molecular Dynamics simulations, Ruda et al. [10] investigated the hydrogen absorption in Pd thin-films and demonstrated that hydrogen absorption properties are sensitive to the nanofilm's thicknesses and to the orientation of their exposed surfaces. Theoretical calculations on thermodynamics of hydrogen in Pd nanoparticles indicate that the formation enthalpy and entropy decrease with particle size towards the corresponding bulk values, and H atoms are segregated to the subsurface of the particles forming a shell structure [11].

Being very small atomically, the H atoms absorbed in Pd occupy the interstices of the Pd lattice. For monohydride compound PdH, the exact position of the hydrogen atoms was a matter of long dispute [12]. The site occupation of H atoms in the palladium were first studied in 1948 [13,14]. Smith [14] thought that the H atoms were absorbed on the surfaces of the Pd atoms and were located in a massive “rift network” in the bulk of the Pd, and would therefore not be located within the Pd lattice. By contrast, based on diffraction experiments, Davis [15] proposed that the H atoms should be arranged in the tetrahedral interstices of the Pd lattice. In 1957, Worsham et al. [16] used neutron diffraction to give the first suggestion that H atoms occupy the octahedral interstices of the Pd lattice. Later, further neutron diffraction results by Maeland [17] and Skögl [18] supported that assessment. Therefore, it has been widely supposed that the H atoms occupy the octahedral interstices of the Pd lattice.

Although there are many experimental investigations [8–18] about Pd-H systems, such as palladium hydrides structures, site occupation of hydrogen in palladium lattice, as well as hydrogen absorption and desorption properties in palladium thin-films. However, these studies are based on low hydrogen content ( $x_{\text{H}} < 1$ ), while on high hydrogen content, the experimental reports about Pd-H systems are unavailable. Some theoretical papers [19–22] discussed the electronic structure and phase stability of several palladium hydrides structures on high hydrogen content, but these investigations are not systematic. Thus in the present study, we calculate the formation enthalpies of various alloy configurations and use cluster expansion (CE) to search the ground-state structures. We investigate the electronic structures of the ground states using calculations based on density functional theory (DFT).

We use the charge density and Bader charge analysis to investigate how Pd and H form chemical bonds. Apart from the Pd–H bond length and the Pd–H–Pd bond angle, the local atomic configuration and site occupation of H in the Pd lattice also have appreciable influences on the electron transfer between Pd and H. Furthermore, we compared the stabilities of rocksalt (RS) PdH and zincblende (ZB) PdH regarding both thermodynamic and dynamic stability.

## Computational details

We used CE implemented in the Alloy Theoretic Automated Toolkit (ATAT) [23] to predict the stable stoichiometries and structures of PdH<sub>x</sub> ( $x = 0–3$ ). The structure relaxation and the formation-enthalpy calculations were performed using the QUANTUM ESPRESSO package [24] with the ultrasoft pseudopotentials (USPPs) [25] from the Garrity–Bennett–Rabe–Vanderbilt (GBRV) pseudopotentials library [26] and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [27] for the exchange–correlation potential. A plane-wave cutoff energy of 600 eV was set for the convergence of the energy eigenvalues. For structure relaxation, the convergence threshold on the pressure and the self-consistent field energy tolerance were set to less than 0.05 GPa and  $1.4 \times 10^{-5}$  eV, respectively. The Monkhorst–Pack grids [28] for the Brillouin-zone integrations were determined automatically for different alloy configurations, and the KPPRA parameter [29,30] was set to 8000. The KPPRA parameter and the number of atoms were used to determine the k-points of the entire reciprocal space. The k-points were equally distributed in each basis vector direction of the reciprocal space. For the phonon calculations, a threshold of  $1.0 \times 10^{-16}$  eV for self-consistency and a  $4 \times 4 \times 4$  q-point grid [31] were used to calculate the phonon dispersion curves and phonon density of states.

## Results and discussion

### Formation enthalpies and ground-state structures

The metal Pd has a face-centered cubic (FCC) structure with space group no. 225. The Pd atoms occupy the 4a (0, 0, 0) sites of the FCC lattice while the H atoms occupy the interstitial sites. In our CE calculations, we considered two types of interstices for FCC structures, namely octahedral (O) (1/2, 1/2, 1/2) and tetrahedral (T) (1/4, 1/4, 1/4). Using CE, we searched 453 configurations and found three intermediate ground states at H compositions  $x_{\text{H}} = 1, 2.67, \text{ and } 2.75$  as shown in Fig. 1. Each configuration has been confirmed by DFT calculations. The formation enthalpies of all configurations are negative, indicating that it is easy for H to enter the Pd lattice and form PdH<sub>x</sub> alloys. The information about the crystal structures of these PdH<sub>x</sub> varieties with low formation enthalpies (marked in Fig. 1) are given in Table 1. The lattice symmetry and parameters clearly change appreciably as the hydrogen composition is increased. This indicates that H atoms entering the interstices of the Pd lattice cause large lattice distortion. In Table 1, we compared our results to the available literature data, it

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