

First-principles study of vacancy-hydrogen interaction in PdO. Yu. Vekilova,^{1,2} D. I. Bazhanov,² S. I. Simak,¹ and I. A. Abrikosov¹¹*Division of Theory and Modeling (IFM), Linköping University, SE-581 83 Linköping, Sweden*²*Department of Physics, M. V. Lomonosov Moscow State University, 1-2 Lenin Hills, Moscow 119992, Russia*

(Received 26 March 2009; revised manuscript received 8 June 2009; published 1 July 2009)

Hydrogen absorption in face-centered-cubic palladium is studied from first principles, with particular focus on interaction between hydrogen atoms and vacancies, formation of hydrogen-vacancy complexes, and multiple hydrogen occupancy of a Pd vacancy. Vacancy formation energy in the presence of hydrogen, hydrogen trapping energy, and vacancy formation volume have been calculated and compared to existing experimental data. We show that a vacancy and hydrogen atoms form stable complexes. Further we have studied the process of hydrogen diffusion into the Pd vacancy. We find the energetically preferable position for hydrogen to reside in the palladium unit cell in the presence of a vacancy. The possibility of the multiple hydrogen occupancy (up to six hydrogen atoms) of a monovacancy is elucidated. This theoretical finding supports experimental indication of the appearance of superabundant vacancy complexes in palladium in the presence of hydrogen.

DOI: [10.1103/PhysRevB.80.024101](https://doi.org/10.1103/PhysRevB.80.024101)

PACS number(s): 61.72.Bb, 61.72.jd, 71.20.Be

I. INTRODUCTION

Studies of hydrogen storage materials are of vital importance due to the needs of hydrogen economy in finding new renewable sources of energy. The presence of hydrogen in metals influences their mechanical and thermodynamic properties. Hydrogen possesses high diffusion ability and can permeate under high hydrogen pressure into the crystal even at room temperatures. It also exhibits high chemical activity and can interact with different defects of crystal structures.¹

Pd system is of particular interest because Pd can absorb large amount of hydrogen and therefore can be used as a catalyst in heterogeneous catalysis as well as in isolating membranes.^{2,3} Thin palladium membranes have excellent hydrogen permeability and exhibit very high hydrogen selectivity.^{4,5}

It is known that any real sample has defects of crystal structure, such as vacancies, impurities, dislocations, etc. However concentration of most of these defects in a material is very low at ambient conditions. For instance, the vacancy concentration in palladium can reach a value of about 0.02–0.03 at. %.² Nevertheless, recent experiments by Fukai *et al.* showed that in the process of palladium hydrogenization large number of vacancies are created when hydrogen atoms permeate into palladium. Their concentration reaches up to 16 at. %.⁶ Fukai and co-workers experimentally determined modification of the cell parameter in systems Ni-H and Pd-H at high temperatures and high hydrogen pressure. They have assumed appearance of superabundant vacancies.⁷ They have also revealed, using scanning electron microscope (SEM), that in Pd and Ni large amount of nanopores with diameters of 20–200 nm are present.⁸

Moreover, the vacancy ordered structure $L1_2$ has been observed in Pd-H by means of x-ray diffraction analysis. It has shown superstructure lines with indices such as in a cubic unit cell.⁹ It has been proposed that this defect ordered phase is caused by the presence of superabundant vacancies. The symmetry lowering from face-centered cubic to simple cubic corresponds to an ordering in the metal lattice due to the presence of vacancy complexes in palladium structure.¹⁰

Note that a vacancy in the face-centered-cubic (fcc) or body-centered-cubic (bcc) metals is surrounded by six possible positions for absorbed atoms (octahedral sites). It has been found that in bcc Fe and fcc Pd systems six deuterium atoms can be captured by a monovacancy, and it has been assumed that in the presence of absorbed hydrogen atoms vacancies form the so-called vacancy-hydrogen clusters.^{10,11} Nordlander and co-workers¹² studied the process of multiple (up to 6) deuterium atom occupancy of vacancies in transition metals in terms of the effective-medium theory (EMT). They have calculated hydrogen trapping energy as a function of hydrogen occupancy. However, until the present work there have been no investigations of this problem from first principles, i.e., using most accurate modern theoretical tools.

Therefore we performed a study of the vacancy-hydrogen interactions as well as multiple hydrogen occupancy of vacancies in palladium from first principles. We calculated the vacancy formation energy in Pd and the vacancy formation energy in the presence of hydrogen, i.e., energy of the hydrogen trapping by a vacancy. We found the preferable position for hydrogen absorbed in fcc Pd in the presence of a vacancy. We also studied possibility of multiple hydrogen occupancy of the vacancy. Our results show that hydrogen is attracted by the vacancy and a vacancy-hydrogen complex forms. However, the position of the hydrogen atom in the center of the vacancy is energetically unfavorable. Moreover, we conclude that by consequently adding hydrogen atoms one reduces the vacancy formation energy, which may lead to the superabundant vacancy formation in palladium.

The paper is organized as follows. In Sec. II we present the method of calculations. In Sec. III we discuss the results on the monovacancies and single hydrogen impurities, vacancy-hydrogen complexes, hydrogen diffusion, and multiple hydrogen occupancy in fcc palladium. The conclusions are given in Sec. IV.

II. METHOD OF CALCULATION

The calculations are based on the density-functional theory and the projector-augmented-wave (PAW) method¹³

as implemented in the plane-wave code VASP.¹⁴ The exchange and correlation effects are described by the local-density approximation (LDA). This choice is based on the fact that the LDA, as will be shown below, provides a better description of the vacancy characteristics in hydrogenated Pd compared with the generalized gradient approximation (GGA). The system parameters have been calculated within the supercell approach with constant number of lattice sites. We consider fcc based supercells containing 32 or 64 lattice sites. Plane-wave energy cut off has been set to $E_{\text{cut}} = 270.98$ eV. The k points have been generated on a Monkhorst-Pack grid.¹⁵ We used $5 \times 5 \times 5$ and $4 \times 4 \times 4$ k -point meshes for 32 and 64 site supercells, respectively. In our calculations we consider relaxation of the volume for the cell with 32 atoms, while for the cell with 64 atoms the volume is fixed.

The vacancy formation volume Ω_{nv}^F has been calculated by using the following formula:^{11,16}

$$\Omega_{nv}^F = V - (N - n)\Omega_0, \quad (1)$$

where N is the number of lattice sites of the palladium supercell, n is the number of vacancies, V is the volume of the supercell with n vacancies, and Ω_0 is the volume of the defect-free supercell per atom.

The vacancy formation energy (E_f) in the system has been calculated as¹⁷

$$E_f = E_{\text{tot}}^{nv} - E_{\text{tot}} + n \frac{E_{\text{tot}}}{N}, \quad (2)$$

where E_{tot}^{nv} is the total energy of the system with N lattice sites and n vacancies and E_{tot} is the total energy of pure palladium per N -atom supercell.

Since we are going to study the influence of hydrogen on the vacancy formation process, we need to estimate the vacancy formation energy in the presence of hydrogen. We define this energy (E_f^H) as

$$E_f^H = E_{\text{tot}}^{H-nv} - E_{\text{tot}}^H + \frac{nE_{\text{tot}}}{N}, \quad (3)$$

where E_{tot}^{H-nv} is the total energy of the system with a hydrogen atom and n vacancies and E_{tot}^H is the total energy of the system with just a hydrogen atom.

The hydrogen absorption energy in palladium E_{abs} has been calculated as¹⁸

$$E_{\text{abs}} = E_{\text{tot}}^H - E_{\text{tot}} - \frac{1}{2}E^{H_2}, \quad (4)$$

where E^{H_2} is the total energy of the hydrogen molecule. We notice that the LDA overestimates binding energy of the hydrogen molecule. Further the vibrational corrections (harmonic and anharmonic) reduce substantially the binding energy but they are not taken into account in the present work.¹⁹ Therefore the absolute values of E^{H_2} and E_{abs} should be considered with care.

The interaction between hydrogen and hydrogen-vacancy complex can be studied by estimation of the trapping energy. Cumulative hydrogen trapping energy of m hydrogen atoms, E_{tr}^{mH-v} , has been calculated by using the following expression:

$$E_{\text{tr}}^{mH-v} = E_{\text{tot}}^{mH-v} - E_{\text{tot}}^v - m(E_{\text{tot}}^H - E_{\text{tot}}), \quad (5)$$

where m is the number of H atoms and E_{tot}^{mH-v} is the total energy of the system with m hydrogen atoms and a vacancy. Accordingly, the trapping energy $\Delta E_{\text{tr}}^{mH-v}$ when the number of hydrogen atoms is increased from $m-1$ to m is defined as¹¹

$$\Delta E_{\text{tr}}^{mH-v} = E_{\text{tr}}^{mH-v} - E_{\text{tr}}^{(m-1)H-v} - (E_{\text{tot}}^H - E_{\text{tot}}). \quad (6)$$

III. RESULTS

A. Monovacancies and a single hydrogen impurity

We have carried out calculations of a monovacancy in palladium bulk to study the effect of the point defects on the atomic structure. The presence of a vacancy in a palladium supercell leads to reduction in the lattice constant. For the 32 site supercell this reduction is $\Delta a = a_v - a_0 = -0.02$ Å, where $a_v = 3.836$ Å is the palladium lattice constant in the presence of the vacancy and $a_0 = 3.854$ Å is the lattice constant of pure palladium. This result is in a good agreement with existing experimental and theoretical data.²⁰ Relaxation of atomic positions in the first coordination shell of the vacancy is ~ 0.07 Å (i.e., 1.82% of $a = 3.854$ Å). From Eq. (1) the vacancy formation volume Ω_{1v}^F and the relative vacancy formation volume Ω_{1v}^F/Ω_0 have been calculated. As a result of these calculations, the following values have been obtained $\Omega_{1v}^F = 7.85$ Å and $\Omega_{1v}^F/\Omega_0 = 0.55$. We find that due to the presence of the vacancy, the volume of palladium is decreased as expected.

The monovacancy formation energy in palladium has been calculated. Our results are presented along with the available data from literature in Table I, where FP stands for full potential, ASA stands for atomic sphere approximation, LMTO stands for linear muffin-tin orbital, KKR stands for Korringa-Kohn-Rostocker, and US stands for ultrasoft pseudopotential methods, respectively. We note that in our work we used the LDA for the calculations.

Despite the common believe that the GGA approximation for the exchange and correlation functionals improves the results of calculations, the performance of the GGA in solids is in fact controversial.²⁴ The vacancy problem has been pointed out as an internal surface problem.²⁵ There are reasons to believe that, due to cancellation of errors, the LDA gives a better approximation to the true jellium surface energy than the GGA and even some many-body calculations.²⁵⁻²⁷ In order to underline this point the vacancy formation energy has been calculated both within the LDA ($E_f = 1.52$ eV) and the GGA ($E_f = 1.05$ eV). Taking into account experimental E_f (see Table I), it is clear that the LDA better describes vacancy characteristics in Pd. Our conclusion agrees with the one of Matsson *et al.*^{22,28} where the failure of the current GGA functionals to predict vacancy

TABLE I. Theoretical and experimental values of vacancy formation energy E_f in fcc palladium crystal.

Measurements and calculations	Method [Ref.]	Approximation	Vacancy formation energy, E_f (eV)
Our calculations	PAW	LDA, 32 sites	1.52
	PAW	LDA, 64 sites	1.41
Theory	FP-LMTO [21]	LDA	1.65
	US [22]	LDA	1.5 ^a
	US [22]	GGA	1.2 ^a
	KKR-ASA [17]	LDA	1.43
Experiment	[23]		1.7
	[20]		1.5

^aThe values uncorrected for the DFT intrinsic surface error.

formation energies was attributed to an intrinsic surface error of this approximation. Therefore we use the LDA in the present study.

Next, we have investigated the properties of a single hydrogen impurity in Pd. Hydrogen occupies the octahedral site of the fcc lattice leading to the lattice expansion. We have found that this expansion Δa is equal to 0.01 Å for 32 site supercell. Thus, hydrogen absorption energy is equal to $E_{\text{abs}} = -0.49$ eV in the LDA and $E_{\text{abs}} = -0.12$ eV in the GGA. The latter compares well to the previous theoretical result ($E_{\text{abs}}^{\text{theor}} = -0.126$ eV in GGA).¹⁸

Since our results are in good agreement with different experimental and theoretical data, it is obvious that our models and approximations are reliable for the studied system. We can now proceed to the discussion of our results on hydrogen-vacancy interaction, which is the main subject of the present work.

B. Vacancy-hydrogen complexes: Hydrogen diffusion path into the vacancy

First we have studied the hydrogen diffusion path from an octahedral site into the vacancy. The Pd-vac-H system was simulated by a 32 site supercell including one Pd vacancy and one hydrogen atom in the nearest octahedral position. To study the diffusion path we have displaced pointwise the hydrogen atom toward the vacancy. The supercell was fully relaxed for every step except the hydrogen atom, which was allowed to relax only in the directions perpendicular to the octahedral site—vacancy path. As a result we have defined the energetic properties of hydrogen diffusion (Fig. 1). It shows that the hydrogen is attracted by the vacancy and therefore the vacancy-hydrogen complex forms. On the other hand it is clearly seen that the position of the hydrogen atom in the center of the vacancy is energetically unfavorable. The results of our calculations of the energy barrier for hydrogen diffusion reveal the preferable position for hydrogen near the vacancy, at the distance of 1.564 Å from the vacancy along the direction [100].

We have also reexamined our results by using the 64 site supercells in order to estimate possible influence of long-range interactions between the vacancies through the peri-

odic boundary conditions on the process of hydrogen absorption in palladium. We have calculated the hydrogen trapping energy [Eq. (5)]. This value is equal to -0.22 eV for both the 32 and 64 site supercells. It shows that for our purposes it is sufficient to use the 32 site supercell.

Further we have examined, using Bader's analysis,^{29,30} the charge transfer between the diffusing hydrogen atom and the Pd surrounding. Bader's method offers a simple definition of space in the crystal associated with each particular atom based purely on the electronic charge density distribution, which is rather useful for charge analysis. The "border" of an atom is calculated as the zero flux surface, i.e., the surface on which the charge density attains minimum on the path perpendicular to the surface. As typically the charge density reaches a minimum between atoms, this is a natural way to separate atoms from each other. The charge enclosed within the Bader volume within the zero flux surface is a good approximation to the total electronic charge of an atom.^{29,30}

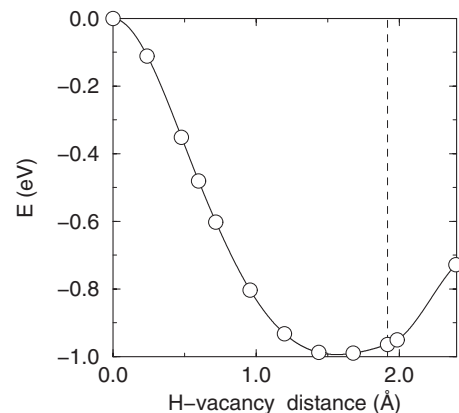


FIG. 1. Variation in the total energy in the 32 site supercell with one vacancy and 1 interstitial H atom as a function of hydrogen distance to the vacancy. Hydrogen atom is moved from the octahedral site, whose position is marked with a dashed line, toward the vacancy center. The total energy is given relative to the energy of the system where hydrogen is placed in the center of the vacancy (point zero). The estimated energy minimum corresponds to the H-vacancy distance equal to 1.564 Å.

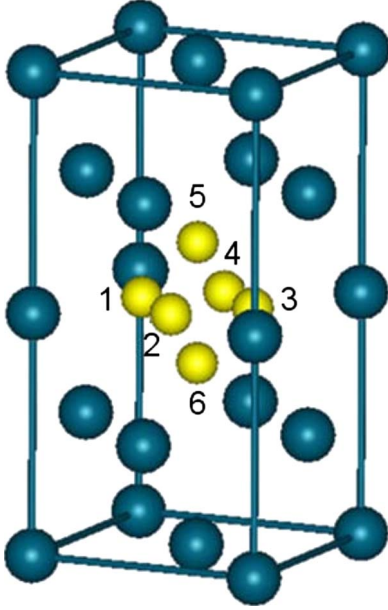


FIG. 2. (Color online) Vacancy- $n\text{H}$ complex in fcc Pd. Dark circles represent Pd atoms, small light circles represent hydrogen positions. In 1H-v cluster hydrogen occupies position 1. For 2H-v there are two different possible configurations: two hydrogen atoms in positions 1 and 2 (the compact cluster) or in 1 and 3 (the linear configuration). For 3H-v cluster three hydrogen atoms are placed in positions 1-2-3 or 1-2-5.

According to the Bader analysis total electron count related to hydrogen in fcc Pd is close to 1 in the calculated energetically favorable position of H and decreases on the path to the vacancy site, where it attains its minimum value of ~ 0.9 electrons. Therefore we conclude that within the LDA approximation the most energetically preferable position for hydrogen in Pd in the presence of a vacancy corresponds to the neutral rather than ionized state of hydrogen.

C. Multiple hydrogen occupancy

As it has been discussed above, the calculated vacancy formation energy E_f in palladium is equal to 1.52 eV for the 32 atom supercell. We have also calculated, using Eq. (3), the vacancy formation energy in the presence of hydrogen ($E_f^H = 1.301$ eV). The difference between these two numbers comes to $\Delta E_f = 0.22$ eV and shows that the process of hydrogen absorption into palladium reduces the energy required for the vacancy formation.

As mentioned above, a vacancy in an fcc metal is coordinated by six octahedral positions. In order to check the possibility for multiple hydrogen occupancy of the vacancy in Pd, which has been predicted experimentally and in semiempiric calculations,¹² we study in this section multiple hydrogen absorption process into the vacancy. Following our previous results we have studied interactions between the single vacancy and up to six hydrogen atoms in different possible configurations. We have defined, using Eq. (5), the interaction energy of $m\text{H-v}$ ($m=1, \dots, 6$) complexes, where m is the number of hydrogen atoms.

TABLE II. Total energy difference between different vac- 2H and vac- 3H clusters. See text for the description of particular systems.

System	ΔE_{tot} (eV)
<i>Pd-2H-v-linear-Pd-2H-v-compact</i>	-0.044
<i>Pd-2H-v-linear-Pd-H₂-v-molecule</i>	-1.053
<i>Pd-3H-v-tetra-Pd-3H-v-triangle</i>	-0.02

We have examined several possible hydrogen complexes with different shapes and containing different number of atoms (Fig. 2). Hydrogen atoms occupied the calculated energetically preferable positions, that is, where coordinates were optimized for all occupations similar to the case of a single hydrogen occupation discussed in the previous section. We have considered two possible constructions of the 2H-v cluster, first, the one where the hydrogen atoms occupy positions 1 and 2 (see Fig. 2) near the vacancy (the compact cluster) and, second, with the hydrogen atoms at positions 1 and 3 (the linear cluster). Also we have compared our total energy calculation of the linear 2H-v cluster with the cluster $\text{H}_2\text{-v}$ containing the hydrogen molecule placed in one of the hydrogen sites (H_2 situated on the line 1-3, with the center of mass in 1, with the initial distance between the H atoms corresponding to the equilibrium distance in a freestanding H_2 molecule). In the 3H-v cluster the H atoms occupy positions 1-2-3 (triangle) or 1-2-5 (tetracluster).

Further we have increased the number of atoms up to 6 (the 4H-v cluster with the hydrogen atoms in positions 1-2-3-4, the 5H-v cluster with the hydrogen atoms in positions 1-2-3-4-5 and the 6H-v cluster with the hydrogen atoms in positions 1-2-3-4-5-6). The results are collected in Tables II and III.

From Table II one can see that two hydrogen atoms and a vacancy prefer to form the linear rather than compact cluster configuration. The presence of the hydrogen molecule in palladium bulk is unfavorable being more than 1 eV higher in energy than the linear cluster with H atoms in positions 1 and 3 in Fig. 2. For the 3H-v cluster the tetrahedral shape turns out to be more energetically preferable.

One may see from Table III the calculated trapping energy for a m th hydrogen atom by the $(m-1)\text{H-v}$ cluster ($\Delta E_{\text{tr}}^{m\text{H-v}}$)

TABLE III. Calculated trapping energy for a m th hydrogen atom by the $(m-1)\text{H-v}$ cluster ($\Delta E_{\text{tr}}^{m\text{H-v}}$) as well as the cumulative trapping energy for trapping m hydrogen atoms in a vacancy ($E_{\text{tr}}^{m\text{H-v}}$).

System	$\Delta E_{\text{tr}}^{m\text{H-v}}$ (eV)	$E_{\text{tr}}^{m\text{H-v}}$ (eV)
<i>Pd-1H-v</i>	-0.23	-0.23
<i>Pd-2H-v</i>	-0.24	-0.47
<i>Pd-3H-v</i>	-0.16	-0.63
<i>Pd-4H-v</i>	-0.16	-0.79
<i>Pd-5H-v</i>	-0.19	-0.98
<i>Pd-6H-v</i>	-0.18	-1.16

as well as the cumulative trapping energy for trapping m hydrogen atoms in a vacancy (E_{tr}^{mH-v}). Negative energy indicates that the addition of hydrogen atoms is energetically favorable. The cumulative hydrogen trapping energy [Eq. (5)] increases in its absolute value with increasing number of hydrogen atoms in $mH-v$ cluster. At the same time the hydrogen trapping energy [Eq. (6)] varies rather weakly as a function of hydrogen occupancy. With increasing number of H atoms the trapping energy tends to become less negative, but it is still negative for all occupations considered in this work. However, H is attracted to $(m-1)H-v$ complexes for $m \geq 1$. The trapping energy is also close to the difference between the vacancy formation energy and the vacancy formation energy in the presence of a hydrogen atom discussed above in this section. The results are in good agreement with those from Ref. 12. Our first-principles study therefore supports the possibility of the multiple occupation of a vacancy in fcc Pd by H atoms. Moreover, we conclude that by adding more hydrogen atoms one reduces the vacancy formation energy, which may lead to the superabundant vacancy formation in palladium.

IV. CONCLUSIONS

Interaction between H atoms and vacancies in Pd has been studied from the first-principles. We have found the preferable position for the hydrogen atom in palladium near the vacancy which is at the distance of 1.564 Å from the

vacancy along the direction [100]. We have calculated the hydrogen trapping energy to be -0.23 eV, and we have found, in agreement with the experimental data, that a numerical estimation of interactions in $H-v$ complexes is important.

We have compared two different possible positions for two hydrogen atoms to be placed near the vacancy, in the form of the hydrogen molecule and in the form of two single atoms close to the vacancy. We have shown that a more preferable situation is in the case of two separated atoms near the vacancy.

The multiple hydrogen occupancy of vacancies has been investigated. Calculations show that in the process of palladium hydrogenization vacancies and hydrogen atoms prefer to form the $mH-v$ complexes. We have calculated the hydrogen trapping energy and the vacancy formation energy in the presence of hydrogen. The substantial reduction in this energy with adding hydrogen is observed. This supports the idea of the superabundant vacancy formation reported in experiments on hydrogenated palladium.

ACKNOWLEDGMENTS

We are grateful to the Swedish Research Council (VR) and the Göran Gustafsson Foundation for research in Natural Sciences and Medicine for financial support. O. Yu. V. and D. I. B. acknowledge RFBR Grant No. 07-02-01452. The calculations have been done at Swedish Infrastructure of Computer resources (SNIC).

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