Ab initio studies on the mechanic and magnetic properties of PdH_x*

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Based on *ab initio* total energy calculations, the structural, electronic, mechanic, and magnetic properties of PdH_x are investigated. It is found that bulk modulus of PdH_x is larger than the metal Pd with the hydrogen storage except Pd_4H_2. The calculated results for the magnetic moments show that the hydrogen addition weakens the magnetic properties of the PdH_x systems. A strong magneto-volume effect is found in PdH_x structures as well as Pd. The transition from paramagnetism to ferromagnetism is discussed. The corresponding densities of states for both structures are also shown to understand the magnetic behaviour.

Keywords: palladium hydride, electronic structure, magnetic moments

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1. Introduction

Much attention has been attracted to metal–hydrogen systems due to their basic physical properties and technological applications. The palladium–hydrogen system is a kind of the most extensively studied metal–hydrogen systems.[1−5] Neutron-diffraction studies[2] have shown that hydrogen atoms in β-phase PdH are located at the octahedral positions of the fcc Pd lattice. When hydrogen goes into fcc palladium, it occupies octahedral interstitial sites within the slightly expanded metal lattice.[3] Wu *et al.* studied four kinds of PdH_x hydrides (x = 0.25, 0.5, 0.75, and 1.0) with the hydrogen atoms doped in the octahedral sites of the Pd bulks,[4] and concluded that the lattice constants are expanded by 1.98%, 3.01%, 4.01%, and 5.99% with respect to the pure Pd's value of 3.89 Å (1 Å=0.1 nm), respectively. Wang *et al.*[5] studied the total energies of various ordered structures of PdH (in which hydrogen occupies the octahedral sites within the fcc Pd lattice) using the pseudopotential method and a plane-wave basis within the local-density functional approximation. Their calculated results show that the lattice constant is expanded by 4.2% to 4.11 Å for PdH with H filling up all octahedral sites.

Theories predicted that both the bulk Rh and Pd metals can be ferromagnetic by 13%–16% and 5%–6% lattice expansions, respectively.[6,7] In the previous work,[8,9] we have studied the structural stability, mechanical and the magnetic properties of rhodium hydride (RhH) in both NaCl-type cubic and ZrH-type tetragonal structures, and found a strong magneto-volume effect. The lattice expansion can be induced by doping impurity atoms into the lattice[10] or by depositing it as a film onto a substrate with a larger lattice dimension.[11,12] Theories suggested that magnetic moments are nonzero and size-dependent.[13] However, there is little information about the mechanic and magnetic properties of PdH_x.

In this paper, we investigate the structural stability, mechanic and magnetic behaviour of PdH_x based on *ab initio* total energy calculation. The structural, electronic, and magnetic properties are reviewed by analysing the computed electronic structure, total energies, and magnetic moments.

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2. The model and the computational method

Let us consider the PhH_x systems with $x = 0$, 0.25, 0.50, 0.75 and 1.0; all of them have fcc unit-cell containing four palladium atoms. The PhH_x structures can be produced by filling hydrogen atoms into four octahedral sites in the cubic cell: Filling one to four hydrogen atoms separately into the corresponding sites construct sequentially Pd_4H_1 ($x = 0.25$), Pd_4H_2 ($x = 0.5$), Pd_4H_3 ($x = 0.75$) and Pd_4H_4 ($x = 1$) structures.

In the calculations, the projector augmented wave (PAW) approach[14,15] with the generalized gradient approximation (GGA) has been employed, as implemented in the highly efficient Vienna *ab initio* simulation package (VASP),[16,17] which has been applied widely.[18] The Perdew–Wang parameterization (PW91) has been used for the GGA exchange-correlation functional in the calculations.[19,20] The energy cutoff for the plane waves are set to 400 eV. The k-point meshes for Brillouin zone sampling are constructed using the Monkhorst–Pack scheme[21] and a $12 \times 12 \times 12$ k-point mesh is used for all systems to calculate the total energy. Spin-polarized calculations have been performed to take into account the effect of magnetism. Convergence criterion for energy is set to 10^{-6} eV. The total energies as a function of the volume are calculated to estimate lattice constants.

The calculated total energy E as a function of the cell volume V can be fitted to an integrated form of the Birch[22] equation of state. Thus, for a given crystal with a unit-cell of volume V and consisting of n atoms, the theoretical strength can be estimated as follows:[23]

$$\sigma_{\rm th} = n\frac{{\rm d}E}{{\rm d}V}\bigg|_{V=V_i}. \tag{1}$$

The bulk modulus reflects its axial stiffness, and can be determined by the second-order derivative of the E–V curve at the equilibrium point of the energy curve as

$$B = V\frac{{\rm d}^2E}{{\rm d}V^2}\bigg|_{V=V_0}, \tag{2}$$

where V_i and V_0 are the volumes of a unit-cell at the inflection point of the energy curve, and at the equilibrium point of the energy curve, respectively. Once the unit-cell expands or contracts, the energy must be changed by changing the bonds between atoms. Therefore the variation of the energy with volume is obtained by altering the lattice constant.

3. Results and discussion

In order to find the ground-state spin configurations and the equilibrium lattice constants of these systems, the total energies of the PdH_x ($x = 0$, 0.25, 0.5, 0.75 and 1.0) structures are calculated and the results as functions of the cell volume for $x = 0$, 0.25 and 0.5, as examples, are shown in Fig. 1. The lattice constants and cell volumes can be determined by minimizing the total energy. The calculated results for five kinds of structures with different hydrogen contents $x = 0$, 0.25, 0.5, 0.75 and 1.0 are listed in Table 1. It is seen that the calculated lattice constants and cell volumes increase with the hydrogen content. The results are in good agreement with those of the experiments[2] and previous theory.[4]

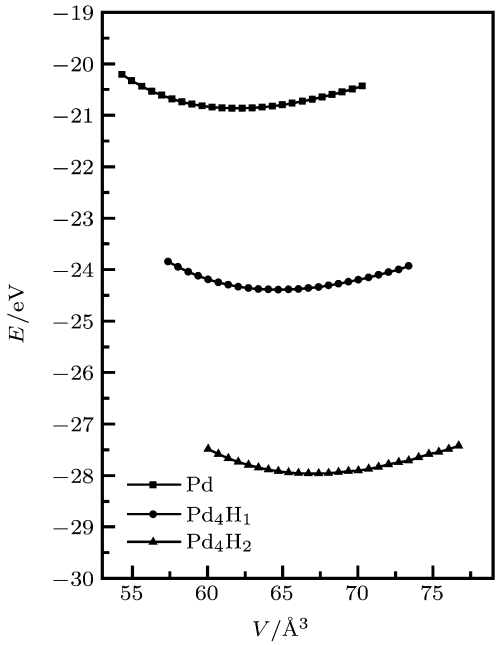


Fig. 1. Total energies as functions of the cell volume for Pd ($x = 0$), Pd_4H_1 ($x = 0.25$) and Pd_4H_2 ($x = 0.5$).

The strength is an important property of materials. However, there are less experimental and theoretical reports on the theoretical strength of Pd as well its hydrides, to our best knowledge. It is hoped that the *ab initio* calculations for the strength of materials will bring a deeper insight into mechanical properties of them. The theoretical strength and bulk modulus of PdH_x can be obtained from the total energy using Eqs. (1) and (2). The results of bulk modulus and theoretical strength are shown in Table 1, together with the corresponding experimental and previously calculated values for comparison.[24–26] The variation of cell volumes is small in the calculation here, so the bulk modulus of Pd is lower than the experimental and other theoretical values. It is interesting that some metal hydrides have larger modulus than the

host metal such as the yttrium hydride,[27] but others have smaller modulus as the titanium hydride.[28] Our calculated results show that the bulk modulus B of PdH_x is larger than that of the metal Pd, except Pd_4H_2 ($x = 0.5$). The bulk modulus increases with the hydrogen addition for $x < 0.5$, but decreases sharply at $x = 0.5$, and then increases with the increase of hydrogen.

Table 1. Calculated equilibrium lattice constants (a), magnetic moment (M), total energy (E), bulk modulus (B) and theoretical strength (σ_{th}) compared to experimental and other calculational data for PdH_x.

		a/Å	M/μ_B	E/(eV/cell)	B/GPa	σ_{th}/GPa
		3.95	0.14	–20.866	166.4	25.6
Pd	expt.	3.89[a]			188[a]	
	calculation	3.98[a] 3.86[b]			209[a] 201.1[b]	
$PdH_{0.25}$		4.01	0.063/0.048	–24.390	177.4	32.6
$PdH_{0.5}$		4.07	0	–27.965	163.8	22.9
$PdH_{0.75}$		4.11	0	–31.508	169.0	16.3
PdH		4.15	0	–34.950	176.5	19.1
	calculation	4.1[c]			195[c]	

[a]Ref. [24]; [b]Ref. [25]; [c]Ref. [26]

Now let us turn to consider the magnetic properties of PdH_x. We have calculated the magnetic moments of PdH_x ($x = 0$, 0.25, 0.5, 0.75, and 1.0) for different cell volumes. The calculated results at the equilibrium points for PdH_x are listed in Table 1. It is shown that the ferromagnetic orders are established at the equilibrium lattice constants in Pd and Pd_4H_1 structures. The calculation gives the magnetic moment of 0.14 μ_B for fcc Pd structure. As for the Pd_4H_1 structure, which contains two different Pd sites, the nearest neighbour and next-nearest neighbour distances of Pd–H have to be considered. There are three nearest neighbouring Pd atoms and one next-nearest neighbouring Pd atom with the H atom in a unit cell. The nearest neighbouring distance of Pd–H is $\frac{1}{2}a$ (a is the lattice constant) and the corresponding Pd atom gives the magnetic moments of 0.048 μ_B, the next-nearest neighbouring distance is $\frac{\sqrt{3}}{2}a$ and the corresponding magnetic moments is 0.063 μ_B. Otherwise, there are no magnetic moments at the equilibrium points for $x = 0.5$, 0.75, and 1.0.

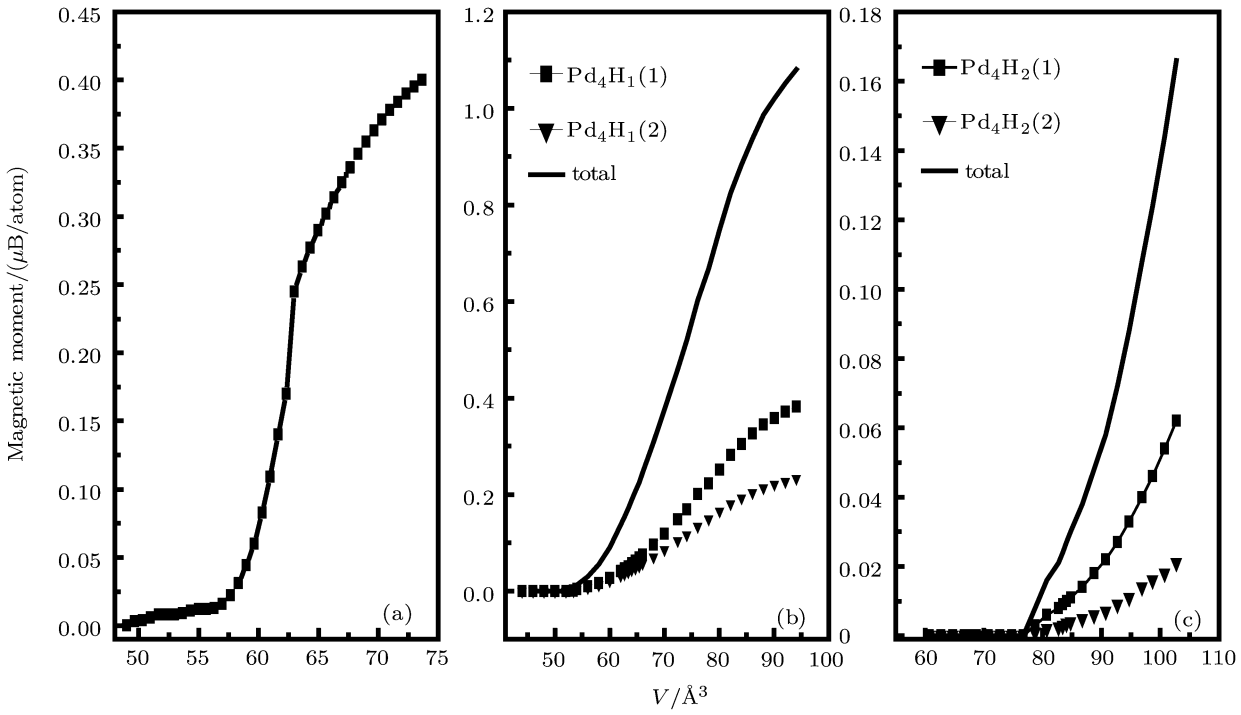


Fig. 2. Magnetic moment as a function of cell volume for (a) Pd, (b) Pd_4H_1 and (c) Pd_4H_2 ($Pd_4H_1(1)$, $Pd_4H_2(1)$ and Pd_4H_1 (2), $Pd_4H_2(2)$ represent next-nearest neighbouring Pd atoms and nearest neighbouring Pd atoms with H atoms, respectively. Solid line shows the total magnetic moments in one unit-cell).

The magnetic moments of Pd, Pd_4H_1 and Pd_4H_2 structures as functions of the cell volume are shown in Fig. 2 for analysing the volume effect of the magnetic properties of the systems. There are two nearest neighbouring and two next-nearest neighbouring Pd atoms in a unit cell of Pd_4H_2 structure. The total magnetic moments of a unit cell in Pd_4H_1, as well as in Pd_4H_2, have been calculated by summing up magnetic moments of the four Pd atoms in the cell.

A transition from "low magnetic moment—low cell volume" to "high magnetic moment–large cell volume" is revealed in the figures. The similar behaviour has also been found in earlier investigations on the magnetic moment versus atom volume in Fe-nitrides,[29] and it also resembles the characteristic given in our previous calculation for NaCl-type cubic and ZrH-type tetrahedral structures of RhH.[8] We have also calculated the magnetic moments of Pd_4H_3 ($x = 0.75$) and PdH ($x = 1$) structures as functions of the cell volumes, but cannot find an onset of magnetic moment until the cell volume expands about 100%. The above-mentioned results show a strong magneto-volume effect: the magnetic moments increase with the expansion of cell volume in these structures. Otherwise, the cell contraction results in the reduction of the magnetic moment, which tends to zero at a certain volume. It is expected that the hydrogen addition weakens the magnetic properties of PdH_x systems.

The calculated results indicate that for the magnetic transition metal Pd and its hydride Pd_4H_1, the onset of magnetic behaviour occurs at a unit-cell volume below the equilibrium volume, say 49.0 Å^3 for Pd ($x = 0$) and 53.4 Å^3 for Pd_4H_1 ($x = 0.25$). Moreover, the onset occurs at an expanded unit-cell volume of 78.7 Å^3 for the Pd_4H_2 structure. It follows that the unit-cell volume of magnetic transition increases with the increase of the hydrogen content x in PdH_x. Once the content becomes large enough (say $x \geq 0.75$), the magnetic transition is in fact impossible, since the calculated onset unit-cell volume is well over twice the equilibrium value of volume, and the lattice should be all broken.

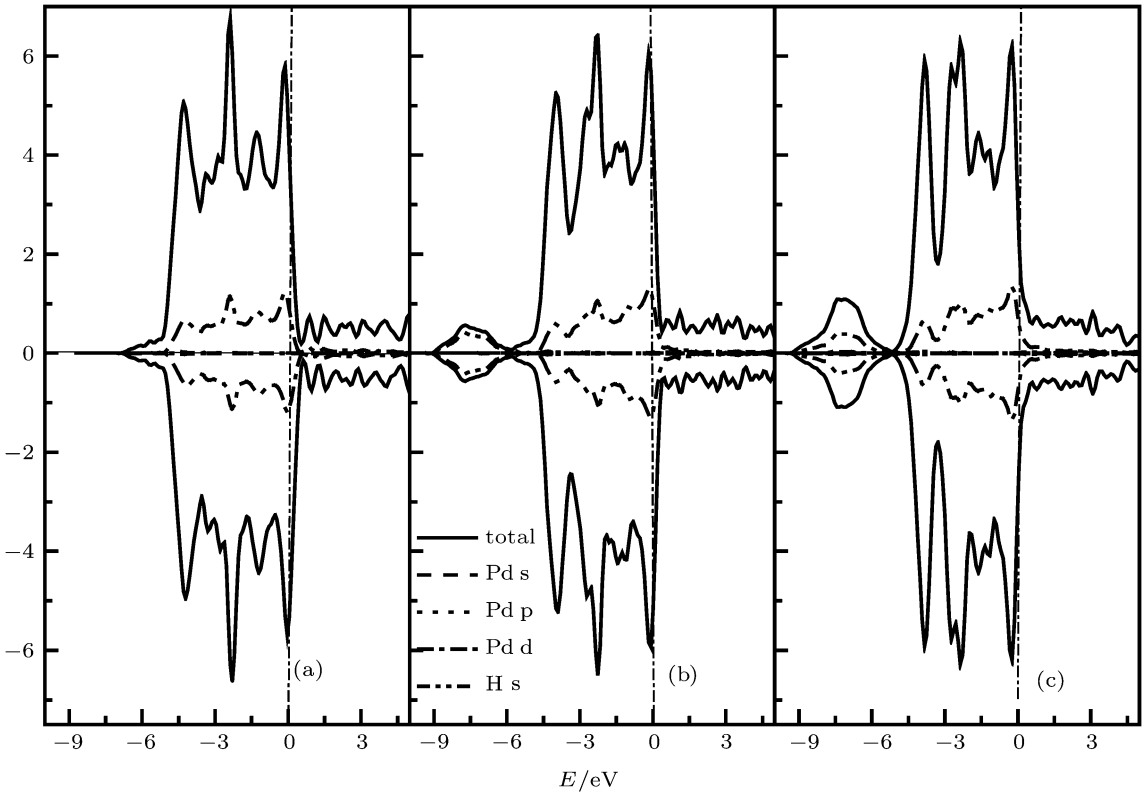


Fig. 3. Spin-dependent total DOS for (a) Pd, (b) Pd_4H_1 (c) Pd_4H_2 in equilibrium geometry. The zero energy is set at Fermi level (denoted by the vertical dot-dashed lines).

To understand the mechanism of magnetic property, the spin-dependent total density of states (DOS) is calculated for five structures, but only structures of Pd, Pd_4H_1 and Pd_4H_2 with respective equilibrium lattice

constants are displayed in Fig. 3. There is a split between spin-up and spin-down in the total DOS, which induces magnetic ordering in both structures. From the partial electronic DOS, one can see that the DOS near the Fermi level is mainly contributed by the 4d electrons of Pd, but the 1s electrons of H are located in the energy range from –9.0 eV to –6.0 eV in the Pd_4H_1 structure and –9.0 eV to –5.0 eV in the Pd_4H_2 structure. The differences between the two systems in the structure and H sites result in the different features of the DOS at the Fermi level E_F, which influence the structural stability and the magnetic moment. It is also found that the highest DOS peak decreases with hydrogen addition for $x < 0.5$, and reduces to the lowest value at x= 0.5, then increases with the increase of hydrogen. This law shows that anti-bond state appears and weakens the reaction among atoms in this structure, which is the reason why the bulk modulus is lowest at $x = 0.5$.

4. Conclusion

In summary, we have investigated the structural, electronic, mechanic and magnetic properties of PdH_x (x = 0, 0.25, 0.5, 0.75, and 1.0) based on *ab initio* total energy calculations. The calculated results for the bulk modulus are in good agreement with the experimental data and other calculations. The theoretical strength of the above structures has been obtained for the first time. A strong magneto-volume effect is found in PdH_x and Pd. The calculated unit-cell volume of magnetic transition increases considerably with the hydrogen content in PdH_x, and no magnetic property can be found for $x \geq 7.5$. The results provide a basic understanding of the 4d transition metal and its hydrides.

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