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Formation and electronic properties of palladium hydrides and palladium-rhodium dihydride alloys under pressure

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We present the formation possibility for Pd-hydrides and Pd-Rh hydrides system by density functional theory (DFT) in high pressure upto 50 GPa. Calculation confirmed that PdH_2 in face-centered cubic (fcc) structure is not stable under compression that will decomposition to fcc-PdH and H_2. But it can be formed under high pressure while the palladium is involved in the reaction. We also indicate a probably reason why PdH_2 can not be synthesised in experiment due to PdH is most favourite to be formed in Pd and H_2 environment from ambient to higher pressure. With Rh doped, the Pd-Rh dihydrides are stabilized in fcc structure for 25% and 75% doping and in tetragonal structure for 50% doping, and can be formed from Pd, Rh and H_2 at high pressure. The electronic structural study on fcc type $Pd_xRh_{1-x}H_2$ indicates the electronic and structural transition from metallic to semi-metallic as Pd increased from $x = 0$ to 1.

As it is well known that metal hydrides are very interesting systems because of their favourable characteristics including hydrogen-storage capacity, kinetics, toxicity, cyclic behaviour, pressure and thermal response[1]. Especially, the hydrides of platinum group metals are highly attractive due to a number of favourable properties. For instance, the hydrogen absorption by palladium is reversible and therefore has been investigated for hydrogen storage[2], the catalytic properties, kinetic reversibility[3] and superconductivity[4,5] of palladium hydrides also have been investigated.

It has been reported that hydrogen atoms randomly occupy the octahedral interstices in the Pd-metal lattice with neutron diffraction studies. The limit of absorption at normal pressures is $PdH_{0.7}$, indicating that approximately 70% of the octahedral holes are occupied[6]. Hydrogen absorption in Rh requires extremely high hydrogen pressures (of the order of GPa)[7] and under normal conditions this metal can only adsorb hydrogens on the surface. Recently, rhodium dihydride was discovered as a first dihydride compound in the platinum group metals by compressing rhodium in fluid hydrogen[8]. The mechanical stability, thermodynamic and elastic properties of RhH_2 were also studied[9]. With the discovery of RhH_2, the dihydride of platinum group metals with tetrahedral sites occupied structure was considered to construct the dihydrides of palladium and Pd-Rh-H system alloys.

It is known that the addition of a second metal to palladium changes hydrogen absorption properties of system. It is a consequence of the alteration of crystal lattice structure, elastic and electronic properties[10–13]. Among various Pd alloys, the Pd-Rh system is an exceptional system because the amount of absorbed hydrogen in Pd-rich Pd-Rh alloys is larger than in case of pure Pd[14]. This is in contrast to the general rule that Pd alloys with a non-absorbing metal (e.g., Au, Ag and Pt) are characterised by a decrease in the maximum amount of absorbed hydrogen[15]. An Pd-Rh alloy containing 92.6 at.% Pd has been characterised by the highest hydrogen absorption capacity with H/M ratio exceeding 0.80[16] using cyclic voltammetry and chronoamperometry in acidic solution.

In this work, we have calculated the formation enthalpy of the hydrides (mono-, di- and tri-) of palladium and rhodium and also Pd-Rh dihydride alloys using DFT approach under high pressure to study the formation

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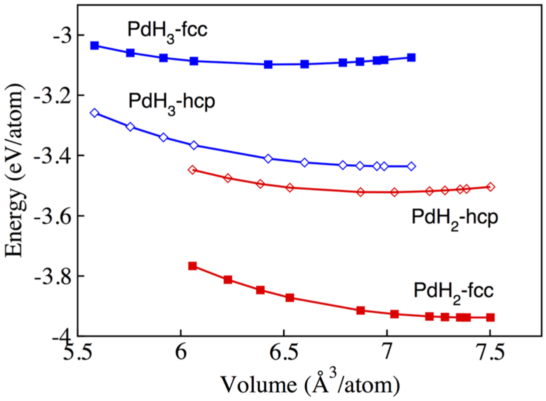

Figure 1. Total energy as a function of volume of fcc and hcp phases for both PdH_2 and PdH_3.

Compounds	Space Group	Lattice constant (Å)		B_0(GPa)	
		Present work	Expt.	Present work	Expt.
Rh	$Fm\bar{3}m$	3.8327	3.8031[21]	264.5	270.4[22]
Pd	$Fm\bar{3}m$	3.9486	3.8898[21]	171.7	180.8[22]
RhH	$Fm\bar{3}m$	4.040(8)	4.020[23]	233.9	
PdH	$Fm\bar{3}m$	4.134(7)	4.090[24]	177.0	130.0[25] ($PdH_{0.7}$)
RhH_2	$Fm\bar{3}m$	4.3583	4.3395[8]	190.8	194.3^h
$Pd_{0.25}Rh_{0.75}H_2$	$Fm\bar{3}m$	4.3583	4.3395[8]	175.9	
$Pd_{0.5}Rh_{0.5}H_2$	P4/nbm	a = 4.3167, c/a = 1.05		165.0	
$Pd_{0.75}Rh_{0.25}H_2$	$Fm\bar{3}m$	4.4429		158.0	
PdH_2	$Fm\bar{3}m$	4.4701		151.5	
PdH_2	P6/mmm	a = 2,9485, c/a = 0.94		159.2	
RhH_3	$Fm\bar{3}m$	4.5220		182.9	
PdH_3	$P6_3/mmc$	a = 3.0785, c/a = 2.23		126.4	

Table 1. Crystal structure properties of Rh, Pd, RhH, PdH, $Pd_xRh_{1-x}H_2$, RhH_3 and PdH_3 together with available experimental data.

possibility. The electronic structure of Pd-Rh dihydride alloys are also analysed by total and partial density of states calculation. The concentration of Pd in Pd-Rh dihydride system alloys is 25%, 50% and 75%, respectively.

Results and Discussion

Crystal Structure. The total energy of Pd-Rh-H compounds as a function of volume are shown in Fig. 1. The results show that the PdH_2 compound in fcc phase is energetically more stable than in hcp phase for the volume range from 7.5 $Å^3$/atom to 6.1 $Å^3$/atom. PdH_3 in hcp phase is more stable than fcc phase for the volume range of 7.1 $Å^3$/atom to 5.6 $Å^3$/atom.

In our calculations, the metal hydride are stabilized in fcc and hcp structures. For monohydride compound PdH, the crystal structure is fcc in space group Fm3m and the hydrogen atom resides in a octahedral sites. For dihydride compounds PdH_2 and RhH_2, the crystal structures are same with monohydrides, but the hydrogen atom resides the tetrahedral sites. The trihydride compound RhH_3 is stabllized in fcc structure, in which the hydrogen atoms are occupied in both tetrahedral and octahedral sites. but PdH_3 is stabllized in hcp structure in space group of $P6_3/mmc$.

Table 1 shows the lattice parameters and bulk modulus of all the compounds compared with experimental data. The bulk modulus are obtained by fitting B-M equation of state with fixed $B_0' = 4$. The bulk modulus B_0 for Rh-hydrides are larger than Pd-hydrides. As the insertion of H in the octahedral sites of Pd leads to an expansion of the lattice constant from Pd to PdH, the bulk modulus are increased as hydrogen concentration increased. With Rh doped, the bulk modulus of $Pd_xRh_{1-x}H_2$ are increased with various Rh concentration from 0% to 100%.

Formation possibility driven by high pressure. The enthalpy deferences for Pd-H and Rh-H systems are shown in Fig. 2(a). For PdH and RhH, the enthalpy energy differences is regarding to the chemical reaction equations:

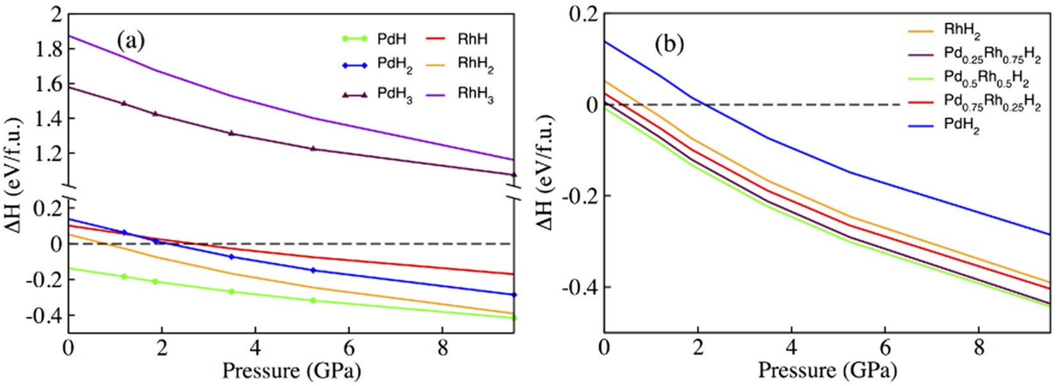

Figure 2. (**a**) The formation enthalpy difference for Pd-H and Rh-H systems. (**b**) The formation enthalpy for $Pd_xRh_{1-x}H_2$ alloy system. The combined enthalpy of the stable constituent elements establish the reference line corresponding to each compound expressed with dash. $ReferenceLine = \sum [xH(Pd) + (1-x)H(Rh) + 2H(0.5H_2)]$.

$$2PdH = 2Pd + H_2 \tag{1}$$

$$2RhH = 2Rh + H_2 \tag{2}$$

The PdH has the negative enthalpy of formation, which is consistent with the knowledge that the formation of PdH should be favourable under pressure[17]. The PdH_2 also should be formed under pressure higher than 2.1 GPa due to the negative enthalpy of formation. The formation properties for RhH and RhH_2, which both compounds can be formed under pressure, are in good aggreement with the recent work of rhodium dihydride[8]. Whereas for the trihydirde compounds, the positive enthalpy of formation for PdH_3 and RhH_3 suggest that they are unfavourable to be formed even with compressing upto 10 GPa.

The formation enthalpy of $Pd_xRh_{1-x}H_2$ system as a function of pressure is shown in Fig. 2(b). As is shown, the negative enthalpy of formation for $Pd_{0.5}Rh_{0.5}H_2$ in the range of pressure suggests it can be formed even at ambient pressure. While for $Pd_{0.25}Rh_{0.75}H_2$ and $Pd_{0.75}Rh_{0.25}H_2$, the formation enthalpy convert to negative at 0.1 GPa and 0.4 GPa, respectively. Therefore they are more favour to be formed when pressure respectively above 0.1 GPa and 0.4 GPa. Besides, with pressure increasing, the decrease trend of negative formation enthalpy for $Pd_xRh_{1-x}H_2$ suggests they are more likely to be formed with compressing.

The enthalpy difference of Pd-Rh-H were carried out in total enthalpy between production compound $Pd_xRh_{1-x}H_2$ and the sum enthalpy of reaction compounds Pd, Rh, and H_2:

$$\Delta E = E(Pd_xRh_{1-x}H_2) - [xE(Pd) + (1-x)E(Rh) + E(H_2)] \tag{3}$$

Consider the reaction of Pd and H_2, PdH as a product of reaction, will compete with PdH_2 in all range of pressure. To make a further investigation, three reaction paths of PdH_2 are figured out which respectively is

$$PdH_2 = Pd + H_2 \tag{4}$$

$$2PdH_2 = 2PdH + H_2 \tag{5}$$

$$4PdH_2 = 2PdH + 2Pd + 3H_2 \tag{6}$$

Figure 3 shows the reaction enthalpy of PdH_2 with compression upto 50 GPa. The enthalpy of reaction 5 keeps positive in the range of pressure, which suggests PdH and H_2 is more favourable competing with PdH_2. Whereas the reaction 6 suggests a decrease trend on the reaction enthalpy with pressure increase, and the reaction enthalpy convert to negative at 5.5 GPa. In this case, the PdH_2 is more likely to be formed than PdH, Pd and H_2 when pressure above 5.5 GPa. Therefore, summarising the three reactions above, we conclude that PdH_2 is metastable and will directly dissociate into PdH and H_2.

Electronic Structure Properties. The density of state (DOS) of Pd-Rh-H compounds are calculated at equilibrium volume, as shown in Fig. 4(a). The electronic structure indicated a mixture of metallic and covalent bonding. Below Fermi level there are only occupied states by metal Rh or Pd, and hydrogen electron located in a deeply lower valence band and above fermi level states. In the doped hydrides $Pd_xRh_{1-x}H_2$, *d*-electron of Palladium shows a strong itinerant electronic properties than Rhodium. By replace 25%, 50%, 75% and 100% Rh atoms with Pd in fcc RhH_2, the fermi surface shift to lower energy from 8.24 eV for RhH_2 to 8.06 eV, 7.78 eV, 7.62 eV and 8.03 eV for fcc type PdH_2, respectively. The DOS of PdH_2 shows a semimetallic property in which the electronic states around fermi level is less than 0.06.

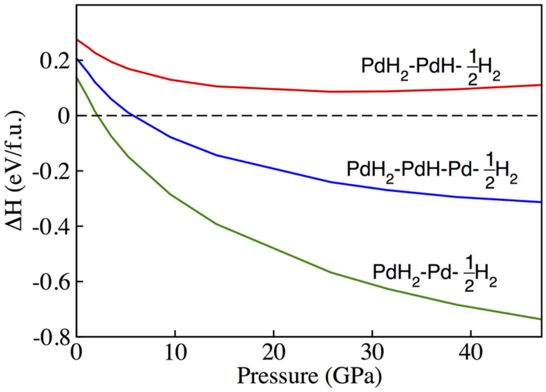

Figure 3. Reaction enthalpy of PdH_2 according to the three reactions paths: (**a**) $PdH_2 = Pd + H_2$; (**b**) $2PdH_2 = 2Pd + H_2$; (**c**) $4PdH_2 = 2PdH + 2Pd + 3H_2$.

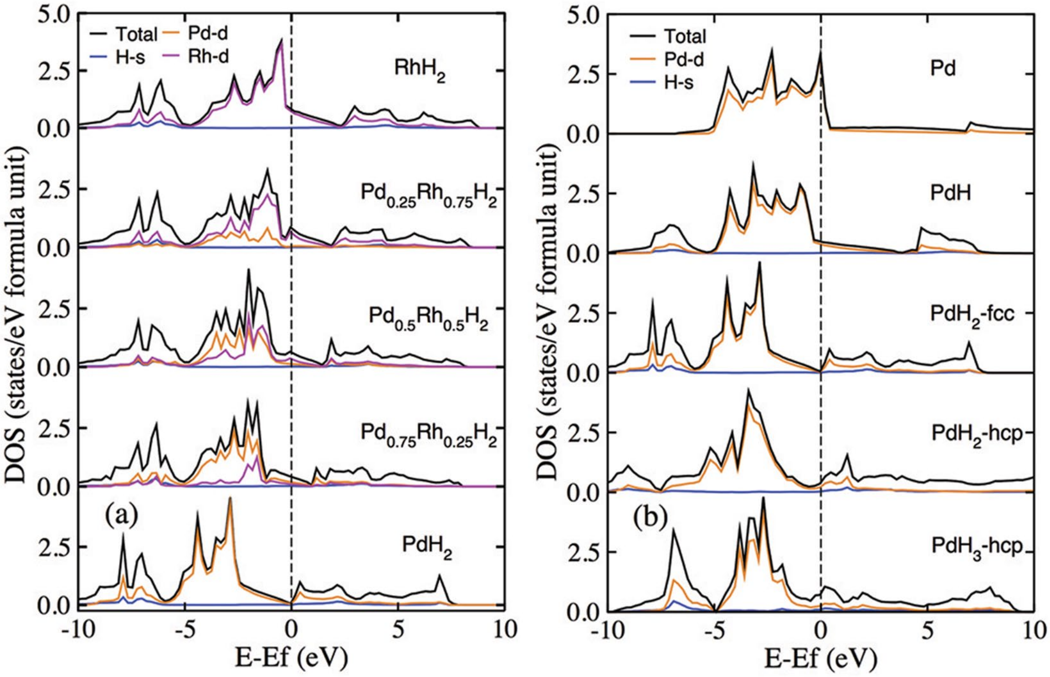

Figure 4. (**a**) Density of state of Pd-Rh-H system at ambient pressure. (**b**) Density of state of palladium hydrides at ambient pressure.

Figure 4(b) shows the electronic density of states as a function of hydrogen concentration on PdH_x series while x goes from 0 to 3. In PdH due to the number of H-filled Pd octahedra, the hybridized band H_s/Pd_d appeared and partially filled on the range of $-6.2 \sim -7.9$ eV. In additional, the valence/conduction band on the fermi level is dominated by the 4*d* orbitals of the palladium atoms in PdH, but the fermi level shifted from 8.94 eV for pure Pd to 8.86 eV for PdH. The electronic states on fermi level are decreased from 3.32 to 0.51 states/eV/f.u.

When hydrogen number increases to 2, two structures fcc and hcp PdH_2 are considered. The dispersion of the density of states for fcc PdH_2 mainly followed the curve on fcc PdH, in which fermi level shift from 8.86 eV for PdH to 8.03 eV for PdH_2. The observed difference is the electronic property that changed from metallic to "near insulator" owing to the density of states on fermi level tends to zero. For hcp PdH_2 that electron dispersion is following the curve on hcp PdH_3, in which hydrogen s orbital contributes to the valence/conduction band on the fermi level.

Conclusion

In conclusion, three different types of palladium and rhodium hydrides and Pd-Rh-H dihydride alloys have been investigated by first principle calculation. We have found that PdH_2 is not stable and dissociate to PdH and H_2 at ambient and even higher pressure. While when palladium is involved in the reaction, PdH_2 can be easy formed from lower pressure around 10 GPa. With Rh doping alloy hydrides $Pd_xRh_{1-x}H_2$ is formed from fcc metal Pd and Rh in H_2 atmosphere at even lower pressure. The electronic density of states investigations show that the $Pd_xRh_{1-x}H_2$ has metallic properties whereas PdH_2 semimetallic property.

Methods

The DFT calculations are carried out by employing the Vienna Ab-initio Simulation Package(VASP)[18] implementing the Projector Augmented Wave method. The generalized gradient approximation[19] was used for the correlation energy function[20] with the Perdew Burke Ernzerhof parameterisation. The valence electron configurations for Pd and Rh were $4p^65s^14d^9$ and $4p^65s^14d^8$, respectively. The relaxation convergence for ions and electrons are 10^{-2} and 10^{-6} eV, respectively. The electronic wave function was expanded in a plane wave with an energy cut-off 800 eV. For energy formation calculation, the 24 × 24 × 24 Monkorst-Pack(MP) K mesh for Brillouin zone integration was used for the structure optimisation and static calculation. For DOS calculations, the K mesh was increased to 32 × 32 × 32 for fcc compounds, and 15 × 15 × 7 mesh for hcp PdH_3, respectively.

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Author Contributions

W.L. and R.A. designed the project, analysed the results and review the manuscript. X.Y. did the calculation and wrote the manuscript. H.L. and T.K. reviewed the manuscript.

Additional Information

Competing Interests: The authors declare that they have no competing interests.