

# First-principles study of hydrogen diffusion in transition metal Rhodium

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**Abstract.** In this study, the diffuse pattern and path of hydrogen in transition metal rhodium are investigated by the first-principles calculations. Density functional theory is used to calculate the system energies of hydrogen atom occupying different positions in rhodium crystal lattice. The results indicate that the most stable position of hydrogen atom in rhodium crystal lattice locates at the octahedral interstice, and the tetrahedral interstice is the second stable site. The activation barrier energy for the diffusion of atomic hydrogen in transition metal rhodium is quantified by determining the most favorable path, i.e., the minimum-energy pathway for diffusion, that is the indirect octahedral-tetrahedral-octahedral (O-T-O) pathway, and the activation energy is 0.8345eV.

## 1. Introduction

Research into the reaction of hydrogen with metals has attracted much attention because of potential applications as effective hydrogen storage materials [1], Ho K M *et. al* [2] studied the metal-hydrogen interactions in NbH by first-principles total energy calculations. And the transition metal-hydrogen systems have also attracted considerable interest for the unfilled *d* orbitals. Antonov V E [3] discussed the phase transformations, crystal and magnetic structures of high-pressure hydrides of *d*-metals, and obtained the conclusions that the high-pressure technique had been most effective in hydrogenation of the group VI–VIII transition metals, neither of which except Pd forms hydrides at low hydrogen pressures, and the hydrides formed at high pressures were shown to have close-packed metal sublattices with *fcc*, *hcp* or *double hcp* structures, in which hydrogen occupied octahedral interstitial positions. Then Pronsato M E *et. al* [4] investigated the electronic and bonding properties of iron monohydride using tight-binding method. We[5,6] had investigated the structural, electronic and magnetic properties of RhH alloy and PdHx with both cubic and tetrahedral structures based on *ab-initio* total energy calculations.

Hydrogen diffusion and migration in metals are important aspects to determine the behavior of hydrogen in metals. The diffusion of hydrogen in metals or alloys are also investigated by scientific workers. Diffusion of hydrogen in the  $\alpha$ -phase Pd system was investigated by electrochemical methods[7], and the concentration of hydrogen in the metal was gradually increased by control of the electrode potential. The dissolution and diffusion behaviors of hydrogen in copper were investigated based on first-principles calculations in combination[8]. The adsorption and diffusion of hydrogen on ordered Ni<sub>3</sub>Fe(111) surface and in the bulk were studied by first-principles calculations based on density functional theory[9]. The hydrides of Rh were synthesized at the Institute of Solid State Physics, Russian Academy of Sciences for the first time [10,11], and RhH had a NaCl-type crystal structure with H atoms occupying every octahedral site in the face - centered cubic of rhodium lattice with the parameter  $a = 4.010 \text{ \AA}$ . In this work, we investigate the hydrogen diffusion behaviors in face - centered cubic of rhodium structures based on *ab-initio* total energy calculation. And *ab-initio* calculations are very helpful as they are able to provide fundamental understanding of many properties and insight into microscopic details.



## 2. Computational method

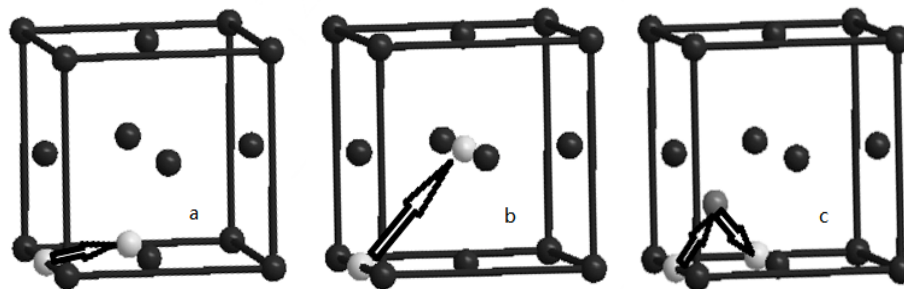
A first principles simulation is carried out using the plane wave ultra-soft pseudo-potentials (USPP) [12] method, which is based on density-functional theory (DFT)[13]. In this method, the ultra-soft pseudo-potentials are used to describe the computationally expensive core-valence interaction, and the Perdew-Wang parameterization (PW91) has been used for the GGA exchange- correlation functional in the calculations. The Monkhorst-Pack [14] special  $k$ -point sampling of the brillouin zone used in the calculations is  $8 \times 8 \times 8$ , the energy cut-off for the plane waves are set to 280eV.

We obtain the possible filling positions of hydrogen in face - centered cubic of rhodium by comparing the binding energy of the hydrogen atom in interstitial sites of Rh. Define a formula to calculate the binding energy of the hydrogen atom:

$$E_{\text{int}} = E_{\text{cell+H}} - E_{\text{cell}} - E_{\text{H}} \quad (1)$$

Where  $E_{\text{cell+H}}$  is the total energy of the system when a hydrogen atom embedding to interstitial site,  $E_{\text{cell}}$  is the energy of the pure face - centered cubic of rhodium cell, and  $E_{\text{H}}$  is the energy of one hydrogen atom. The energy is obtained in the same calculation method and accuracy for all the systems. The whole system is most stable when the binding energy of the hydrogen atom is the lowest.

The most possible diffusion pathway of hydrogen atom is from an octahedral position to the adjacent octahedral position. We calculate the activation energies for H diffusion in Rh along three possible pathways, as shown in Figure 1. The hydrogen atoms both migrate linearly from an original octahedral site to its neighbor octahedral site (the O-O path) for the first two pathways, and the hydrogen atom moves between two octahedral sites in the same panel via an adjacent tetrahedral site intermediate (the O-T-O path) for the third pathway, as shown in Figure 1(c).



**Figure 1.** Pathway of H diffusion in fcc Rh from (a) original O site(1/2,0,0) to edge O site(0,1/2,0), (b) original O site(1/2,0,0) to body-centered O site(1/2,1/2,1/2), (c) original O site(1/2,0,0) to edge O site(0,1/2,0) via a T site(1/4,1/4,1/4). The black spheres is Rh atoms, the white and gray spheres are single H atom in octahedral and tetrahedral sites respectively.

H atom must overcome a potential barrier when migrating along the diffusion pathway and the maximum point for the potential barrier is identified as the saddle point, which is generally located at the midpoint of migration path in high-symmetric configurations. The activation energy for H diffusion ( $Q_{\text{H}}$ ) in Rh is calculated as the energy difference[15]:

$$Q_{\text{H}} = E_{\text{sad}} - E_0 \quad (2)$$

where  $E_{\text{sad}}$  and  $E_0$  are the total energies of the cells for the saddle point and for the equilibrium site, respectively.

## 3. Results and discussions

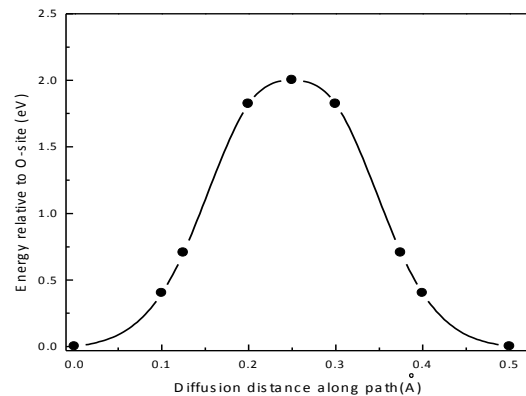
In order to find the equilibrium lattice parameters and the most stable adsorption position of this system, we calculate the total energies with both octahedral and tetrahedral structures. By total energy minimization, lattice parameter of the fcc rhodium structure is estimated to be 3.8966 Å, which is in good agreement with the experimental value, 4.010 Å reported by Somenkov *et al.* [16]. The calculated binding energies for hydrogen in different interstitial sites are shown in Table 1. It can be

see that the binding energy of hydrogen atom in octahedral site is lower than that in tetrahedral site, that is the octahedral site is the global minimum, the tetrahedral site being higher in energy by 0.5423eV, so the most stable position of hydrogen atom in fcc rhodium locates at the octahedral interstice, and the tetrahedral interstice is the second stable site. Then we study the diffusion path between octahedral sites that is the optimum geometry for the fully lattice for hydrogen.

**Table 1.** Binding energy for H in different interstitial sites

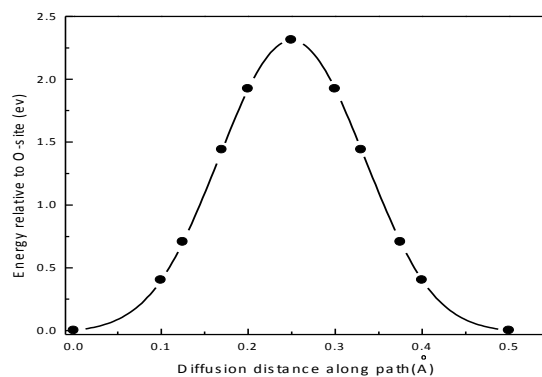
$E/\text{eV}$		$\Delta E/\text{eV}$
octahedral site	tetrahedral site	
-2.0411	-1.4988	0.5423

To estimate the activation energy for hydrogen interstitial diffusion between octahedral sites in fcc rhodium, we calculate the energy variation of the whole system with diffusion distance along the pathway. Nine images are used for both the first direct pathways from original octahedral site(1/2,0,0) to edge octahedral site(0,1/2,0), and the second one from original octahedral site(1/2,0,0) to body-centered octahedral site(1/2,1/2,1/2), as shown in Figure 2 and 3, respectively. We can see that the saddle point is explicitly located at the midpoint of the migration paths for both two paths, which turns out to be a common feature in many high-symmetry configurations[17].



**Figure 2.** Activation energies for H interstitial diffusion in Rh along the first direct pathway from original O site(1/2,0,0) to edge O site(0,1/2,0).

In the first direct path from original octahedral site(1/2,0,0) to edge octahedral site(0,1/2,0), the calculated activation energy for H diffusion in fcc rhodium is 2.0008 eV, which is lower than the value in the second path from original octahedral site(1/2,0,0) to body-centered octahedral site(1/2,1/2,1/2), indicating that the potential barrier of path 2 is larger than that of path 1, and it is easier for H diffusion in fcc rhodium along the first direct path from original octahedral site(1/2,0,0) to edge octahedral site(0,1/2,0).



**Figure 3.** Activation energies for H interstitial diffusion in Rh along the second pathway from original O site(1/2,0,0) to body-centered O

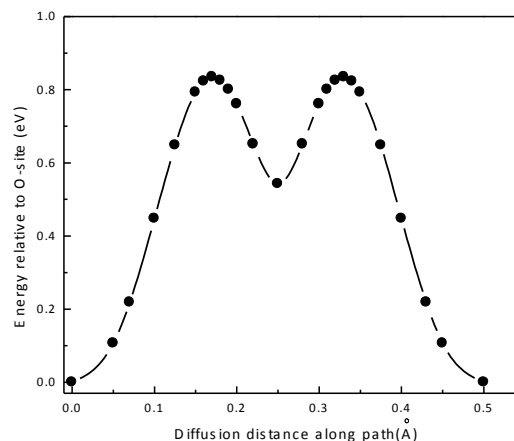
site(1/2,1/2,1/2)

The calculated diffusion activation energies for hydrogen interstitial diffusion in Rh for the first two direct pathways are listed in Table 2.

**Table 2.** Calculated results of activation energy for H interstitial diffusion in Rh via three different pathways

Diffusion pathway	Activation energy /eV
The first O-O path	2.0008
The second O-O path	2.3105
The third O-T-O path	0.8345

Then we compare the direct and indirect path between the two octahedral sites, For the third path, that is an indirect O-T-O pathway, as many as twenty one images are used to find the saddle point accurately, and the energy variation with diffusion distance along this pathway is calculated, shown in Figure 4. We can see that the midpoint of this diffusion path corresponding to the tetrahedral site is not the saddle point as found in the first two direct O-O paths but the local minimum point, that is, it is locally stable but globally metastable. From the structure of image for the saddle point, we find that it lies symmetrically at the centroid of the triangle of fcc rhodium atoms shared by the octahedron and its adjacent tetrahedron.



**Figure 4.** Activation energies for H interstitial diffusion in Rh along the third path from original O site(1/2,0,0) to edge O site(0,1/2,0) via a T site(1/4,1/4,1/4).

The calculated activation energy for H diffusion along the third path is 0.8345 eV, also shown in Table 2, which is much lower than the value along the first path. We compare the activation energies of H diffusion along the first pathway and the third pathway, both of which can be denoted for H diffusion with the same initial octahedral site and the final one. It can be found that the activation energy for H diffusion in the indirect O-T-O pathway is about 1.1663 eV lower than that in the direct O-O path, therefore, the energetically most favorable pathway for H diffusion in fcc rhodium is the indirect O-T-O pathway.

From a chemical point of view, the role of the interstitial atom is to debilitate the Rh-Rh nearest-neighbor (NN) interaction. As noted above, the repulsive forces among Rh atoms induced by the hydrogen atom passing through the saddle point of the indirect O-T-O path are smaller than those in the direct O-O path, so that the indirect O-T-O mechanism for hydrogen diffusion in fcc rhodium is not only energetically but also geometrically more favorable.

#### 4. Conclusion

With the use of the DFT-based first principle method, we have investigated the diffusion behavior of hydrogen atom in face-centered cubic structure of rhodium. The calculated results indicate that the most stable position of hydrogen atom in fcc rhodium locates at the octahedral interstice. By comparing the activation energy of hydrogen diffusion along the different paths, find that the most

favorable pathway for H diffusion in fcc rhodium is the indirect O–T–O pathway, with the activation energy of 0.8345 eV.

### Acknowledgment

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