

DYNAMICAL STABILITY OF PALLADIUM HYDRIDE: *ab initio* STUDY

Isaeva L.E.^{(1,*), Bazhanov D.I.}^{(1), Isaev E.I.}^{(2,3), Ereemeev S.V.}^{(4), Kulkova S.E.}^{(4), Abrikosov I.A.}⁽³⁾

⁽¹⁾ M.V.Lomonosov Moscow State University, Leninskie Gory 1, bld.2, Moscow 119992, Russia

⁽²⁾ Theoretical Physics Department, Moscow State Institute of Steel and Alloys (Technological University), Leninskii prospect 4, Moscow 119049, Russia

⁽³⁾ Department of Physics, Chemistry and Biology (IFM), Linkoping University, SE-581 83 Linkoping, Sweden

⁽⁴⁾ Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences, Akademicheskii prospect 2/1, 634055 Tomsk, Russia

*Fax: 7 (495) 939 4610 E-mail: leyla_isaeva@yahoo.com

Introduction

We carried out the first-principle's study of electronic and dynamical properties of ideal palladium hydride PdH and its defect phase Pd₃VacH_x with L1₂ group symmetry proposed theoretically and experimentally. Quantum and electronic properties of these hydrides, such as phonon relations, density of states, formation enthalpies have been studied. We analyzed the influence of external pressure and concentration of hydrogen atoms on dynamical stability of the defect phase. The performed calculations have shown that position of hydrogen atoms in the unit cell can be responsible for further phase transitions in the defect phase.

Results and discussions

The first-principles calculations were based on density functional theory [1]. In the present study we used VASP [2] and Quantum Espresso packages [3]. To describe electron-ion interaction ultrasoft pseudopotentials proposed by Vanderbilt were used [4]. Exchange correlation effects were treated in the framework of the local density approximation [5] as it gives the vacancy formation energy in palladium bulk 1.82 eV close to experimental value 1.85 eV. For the integration over Brillouine zone we used 12x12x12 *k*-points mesh generated according to Monkhorst-Pack scheme [6]. Phonon spectra calculations were carried out using real-space interatomic force constants matrices derived via the linear response method. In our work we considered several possible hydrogen occupations in the unit cell of vacancy-ordered phase Pd₃Vac («Vac» is vacancy).

The formation enthalpies of Pd₃VacH_x ΔH_{SAV} phases were calculated using the second formula in

order to compare them with the formation enthalpy of the ideal palladium hydride PdH ΔH_{Ideal} :

$$\Delta H_{Ideal} = \frac{E(Pd_4H_4)}{4} - E(Pd) - \frac{E(H_2)}{2}$$
$$\Delta H_{SAV} = \frac{E(Pd_3VacH_x)}{x} - \frac{3E(Pd)}{x} - \frac{E(H_2)}{2}$$

Pd₃VacH₄ phase were supposed to be the most stable between Pd₃VacH_x phases according to experimental and theoretical studies [7,8]. The dynamical stability of this phase were studied using phonon spectra calculations at lattice parameter 3.92 Å which correspond to the pressure -0.2GPa close to equilibrium state. As it can be seen from Fig.1 (right top corner) phonon relations represents soft modes near high symmetry points M(0.0,0.5,0.5) and R(0.5,0.5,0.5). Such peculiarities in the considered phonon spectra is unstable at the given pressure. Thus we performed series of phonon spectra calculations at pressure range from -11GPa to 21GPa corresponding to the lattice parameter range from 3.80 Å to 4.00 Å. But it was found that atomic frequency achieves its lowest absolute value at the equilibrium state. Thus, occupation of octahedral sites by hydrogen atoms makes this phase dynamically unstable. However, such location of hydrogen atoms may be not correct. There are other possibilities of hydrogen atoms arrangement and concentration in the unit cell. We performed phonon spectra calculations for x=4 and 8, where x is hydrogen concentration, thus, they occupy half or full tetrahedral sites of the Pd₃Vac cell. Phonon relations of Pd₃VacH₄ and Pd₃VacH₈ does not show any peculiarities such as soft modes, and this means that in harmonic approximation these phases are dynamically stable.

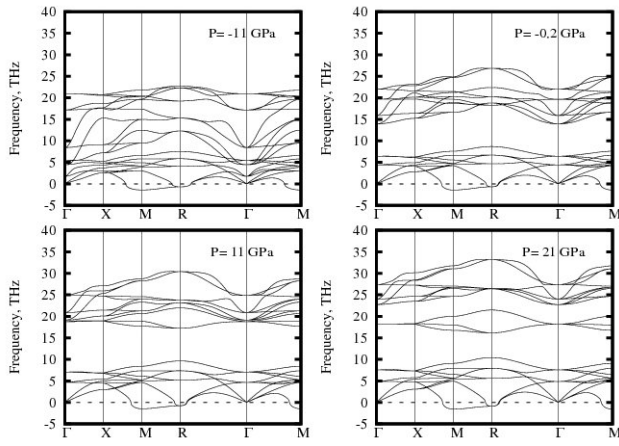


Fig.1 Phonon spectra for the defect phase Pd₃VacH₄ in the pressure range from -11GPa to 21GPa.

It is well known that palladium and silver can easily form Pd₃Ag alloy. This fact lead us to the idea that substitution of one Pd atom by copper or silver atom can stabilize the defect phase. According to our calculations both Pd₂AgH₄ and Pd₂CuH₄ are tetragonal with a=b=3.987 Å, c=3.911 Å for Pd₂AgH₄ and a=b=3.924 Å and c=3.668 Å for Pd₂CuH₄ respectively. It turned out that these hypothetical hydrides both exhibit softness of B-1g mode at M(0,0,0.5,0.5) point with imaginary frequencies of -1.52 THz and -0.76 THz for Pd₂AgH₄ and Pd₂CuH₄ respectively. It is worth to mention that soft modes are mostly from heavy metals. That means that the possibility of stabilization of the defect phase of palladium hydride by alloying elements at ambient conditions is questionable. To solve this problem we calculated the B-1g mode Gruneisen parameter which estimates the anharmonic effect of hydrogen atoms vibration. Calculated Gruneisen parameters for silver atom in Pd₂AgH₄ $\gamma_M=2.3$ and for copper atom in Pd₂CuH₄ is $\gamma_M=0.3$. Using this values we can find corrections to squared frequency of considered impurity atom using formula:

$$\omega^2 - \omega_0^2 = -6\omega_0^2 \alpha T \gamma_M,$$

where ω_0 is an atomic frequency at equilibrium cell volume, α is linear coefficient of thermal expansion and T is a temperature change. Taking into account that for pure palladium α is $11.7 \cdot 10^{-6} \text{ K}^{-1}$ [9] we can estimate the difference $\omega^2 - \omega_0^2$ for $\Delta T=300\text{K}$:

$$(\omega^2 - \omega_0^2)_{Cu} = 0.03 \text{ THz}^2$$

$$(\omega^2 - \omega_0^2)_{Ag} = 0.02 \text{ THz}^2$$

As far as $\omega_{0,Cu}^2 = -0.581 \text{ THz}^2$ and $\omega_{0,Ag}^2 = -2.306 \text{ THz}^2$ we can conclude that substitution of palladium atom by silver or copper atoms can not stabilize the alloys at room temperature. But we have to emphasize again that all calculations were performed in harmonic approximation.

Conclusions

Using ab initio method we have studied phonon spectra of palladium, ideal palladium hydride and its defect phase Pd₃VacH_x for hydrogen atoms concentrations $x=4$ and $x=8$. We have shown that the defect phase Pd₃VacH₄ with hydrogen atoms occupying all octahedral sites is dynamically unstable. While defect phases Pd₃VacH₄ and Pd₃VacH₈ with hydrogen atoms occupying half or full tetrahedral sites were found to be stable according to calculated phonon spectra. We conclude that hydrogen atoms arrangement and concentration in the hydride unit cell can affect strongly on its dynamical stability. Calculated Gruneisen parameter for Pd₂Ag(Cu)VacH₄ phases shows that substitution of one of palladium atom by copper or silver atom can not stabilize the defect phase.

This work was supported by Russian Foundation for Basic Research (grants N 07-02-01452, 07-02-01226) and The Royal Academy of Sciences, Sweden.

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