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Dynamic stability of palladium hydride: an *ab initio* study.

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Abstract

We present results of our *ab initio* studies of electronic and dynamic properties of ideal palladium hydride PdH and its vacancy ordered defect phase Pd₃VacH₄ with L1₂ crystal structure proposed theoretically and found experimentally. Quantum and electronic properties of these hydrides, such as phonon dispersion relations and the vacancy formation enthalpies have been studied. Dynamic stability of the defect phase Pd₃VacH₄ with respect to different site occupation of hydrogen atoms at the equilibrium state and under pressure was analyzed. It was shown that positions of hydrogen atoms in the defect phase strongly affect its stability and may be a reason for further phase transitions in the defect phase.

Introduction

Metal hydrides have been attracting attention of scientists for decades. Their physical properties are interesting from both fundamental and practical points of view. For example, hydrogen density in metal hydrides can be larger than that in liquid hydrogen [1]. This interesting fact led to the idea to consider metal hydrides as potential materials for portable fuel cell applications [2]. However, hydrogen stored in metals causes drastic microstructural changes in the host metallic matrix which can lead to undesirable changes in physical and mechanical properties of a material, such as hydrogen embrittlement. Experimental studies have also shown that hydrogenation process can considerably affect vacancy concentration in metals [3]. It was found that hydrogen charging process in palladium and nickel at 700-800° C under hydrogen pressure of about 5 GPa resulted in decreased lattice parameter [3]. This effect was explained as a result of formation of a large amount of vacancies, so-called superabundant vacancies (SAV), in the hydrides where the measured vacancy concentration was found to be 18±3%. In Ref. [4] it was shown that vacancies in these hydrides can gather together and form large pores of 20 - 30 nm in size. The existence of hydrogen-vacancy complexes was experimentally confirmed for Ni, Cu, Cr, Rh, Pt, Mn and some other transition metals [5] as well as in palladium based alloys Pd-Rh and Pd-Pt [3] proving the generality of this phenomenon. Moreover, it was found that SAVs are stable even after quenching down to ambient conditions. Thus, temperature and pressure are needed just to improve the kinetic characteristics of hydrogen in metals [5]. Recent

theoretical and experimental studies devoted to vacancy abundant hydrides have shown that SAV's formation is related to the gas pressure and high temperature [5]. Hydrogen-vacancy (VacH_n) complexes can be formed during hydrogenation process [6] and such a possibility has been confirmed theoretically [7].

Another interesting result observed experimentally for some metal hydrides is the vacancy ordering during SAV's formation. In addition to the lattice contraction, the X-Ray diffraction studies of hydrogen charged palladium [3] revealed the superlattice reflections corresponding to a new phase with a slightly smaller lattice parameter. These reflections indicated the formation of a new vacancy ordered phase Pd_3VacH_n induced by hydrogen. This structure was stable in a wide temperature range from 300° to 800° C. From symmetry considerations in Ref.[3] it was suggested that the stoichiometric formula for the defect phase Pd_3VacH_n can be written as Pd_3VacH_4 where hydrogen atoms occupy octahedral sites adjacent to the vacancies, so it has L1_2 crystal structure (Cu_3Au -type). Further Monte-Carlo simulations [8] proved this suggestion.

Nevertheless, hydrogen arrangement near vacancies in metals is still a matter of discussion. For instance, recent theoretical studies of *bcc* Fe, where the defect phase was also observed, revealed that hydrogen atoms prefer to stay near the tetrahedral interstitial positions [9].

Thus, the problem of the formation of the vacancy ordered defect phases and the effect of hydrogen on its formation is still under debates. To understand the origin of the formation and thermodynamic stability of the defect phase one should take into account quantum effects connected with the presence of hydrogen atoms in the metallic matrix, its concentration and arrangement. In this work we have performed first-principles calculations to study the dynamic stability of palladium hydride PdH and its defect phase Pd_3VacH_4 where hydrogen atoms occupy either four octahedral, or four tetrahedral sites in the palladium matrix. We have shown that dynamic stability of the defect phase Pd_3VacH_4 is strongly connected with the local environment of hydrogen atoms.

Calculation details

Ab initio total energy calculations were carried out in the framework of the density functional theory [10,11]. Phonon calculations were performed using the density functional perturbation theory [12]. They are implemented in state-of-the-art *Quantum ESPRESSO* [13] package. Ultrasoft pseudopotentials [14] were used to describe the ionic cores. Exchange correlation effects were treated within the local density approximation [15] as it gives the vacancy formation energy in bulk palladium, 1.82 eV, close to experimental value 1.85 eV [16]. Plane waves basis set with the cutoff energy up to 40 Ry was chosen to describe electron wave functions in a periodic crystal and plane waves with the kinetic energy up to 800 Ry to describe the augmented charge. To perform the integration over the Brillouin zone the 12x12x12 Monkhorst-Pack *k*-point grid was used [17]. Phonon spectra calculations were carried out using fast Fourier transformation of real-space interatomic force constants matrix obtained via dynamic matrices calculated for the 4x4x4 *q*-point grid [18].

In our work we considered the vacancy ordered phase Pd_3VacH_4 (Cu_3Au -type structure) with hydrogen atoms occupying either four tetrahedral or four octahedral sites. To study the formation enthalpies of the defect phases Pd_3VacH_4 and compare them with the formation enthalpy of the ideal hydride PdH we used following formulas:

$$\Delta H_{ideal} = \frac{E(\text{Pd}_4\text{H}_4)}{4} - E(\text{Pd}) - \frac{E(\text{H}_2)}{2}, \quad (1)$$

for the ideal hydride PdH and

$$\Delta H_{SAV} = \frac{E(Pd_3VacH_4)}{4} - \frac{3}{4} E(Pd) - \frac{E(H_2)}{2}, \quad (2)$$

for the defect phase Pd_3VacH_4 , respectively. In formulas (1) and (2) $E(Pd_4H_4)$, $E(Pd_3VacH_4)$, $E(Pd)$ and $E(H_2)$ are the total energies of the corresponding systems. Enthalpies of formation of ideal and defect hydride were evaluated per one hydrogen atom.

Results and discussion

The first-principles atomic structure and phonon spectra calculations of palladium and ideal palladium hydride were performed in order to compare obtained results with other theoretical and experimental data. The calculated equilibrium lattice parameters for palladium $a_0=3.88$ Å and ideal PdH of NaCl-type $a_0=4.06$ Å are very close to experimental values 3.89 Å [19] and 4.07 Å [3], respectively. The calculated phonon dispersion curves for palladium are shown in Fig.1 and it can be seen that the spectrum is in very good agreement with results of inelastic neutron scattering experiments [20] performed along all high symmetry directions $\Delta[100]$, $\Sigma[110]$, $\Lambda[111]$ for the *fcc*-crystal. One can see from Fig.1 that there is a slight change of the slope of the acoustic mode near the $q=1/3[110]$. Such a kind of peculiarity in the phonon spectrum, which is known as the Kohn anomaly, was also found experimentally [20] and theoretically [21].

It is well known that palladium hydride adopts the *fcc* structure [22] where hydrogen atoms occupy octahedral sites of palladium matrix (Fig.2). The calculated enthalpy of formation of ideal PdH turned out to be -0.53 eV which is almost two times lower than the value of -0.25 eV obtained in Ref.[23]. The discrepancy between the results can be explained by the use of different approximations applied for the exchange-correlation energy: we used the LDA, while in Ref.[23] the GGA was applied. In the present work the phonon spectrum of palladium hydride calculated for the equilibrium lattice parameter was also analyzed in order to study its dynamic stability (Fig.3). It can easily be seen from Fig.3 that the calculated spectrum has no peculiarities or softening for the acoustic modes and as a result we can conclude the ideal PdH is dynamically stable in its ground state. However, the optical and acoustic parts are not separated by an energy gap observed experimentally [24]. In order to understand the origin of this discrepancy we performed additional calculations of phonon dispersion curves for the lattice parameter of 3.98 Å which corresponds to the pressure of 15.2 GPa in our calculations. New phonon spectrum shown in Fig.4 also does not reveal any peculiarity for the acoustic modes. The comparison with the results obtained in coherent neutron inelastic scattering experiments [24] showed a very good agreement between experimental and theoretical results in the acoustic part of the spectrum while for the optical parts there is still some disagreement along all high symmetry directions. Such kind of disagreement between theoretical and experimental optical modes was found previously for some carbides and nitrides of transition metals [25-27]. This disagreement between experimental and theoretical optical modes may be caused by the hydrogen anharmonicity.

Now we are going to analyze the phonon dispersion curves for the defect phase Pd_3VacH_n with different local atomic hydrogen arrangements. First, we analyzed lattice dynamics properties of the Pd_3VacH_4 where hydrogen atoms occupy four octahedral sites as it was suggested by Fukai *et.al.* [3]. The schematic atomic structure of this phase is shown in Fig.5. This defect phase was found to be the most energetically favourable according to Refs.[3,23]. In order to find the equilibrium lattice parameter of this phase we performed series of total energy calculations. The obtained lattice parameter

was found to be 3.92 Å which is close to experimental value 4.02 Å [3]. According to our LDA calculations the formation enthalpy of Pd₃VacH₄ is -0.40 eV and it is almost two times lower than GGA based result -0.15 eV obtained recently in [23]. The discrepancy can be ascribed again to the use of different approximations to the exchange-correlation energy implemented in the calculations.

Phonon dispersion curves calculated for the equilibrium lattice parameter 3.92 Å were used to analyze the dynamic stability of this phase (Fig.6). From Fig.6 one can see that the spectrum represents softening of acoustic modes near high symmetry points M(0.0,0.5,0.5) and R(0.5,0.5,0.5).

Generally, such peculiarities in phonon spectra are connected with phase transitions in the considered system and its dynamic instability. In order to investigate the stability of this structure under pressure we performed a series of phonon spectra calculations in a pressure range from -11 GPa to 21 GPa corresponding to the lattice parameter range from 4.00 Å to 3.80 Å in our case. The obtained spectra also have shown softening of acoustic branches at high symmetry points M(0.0,0.5,0.5) and R(0.5,0.5,0.5). It can be seen from Fig.7 that imaginary vibrational frequency, which comes from heavy palladium atoms, at R(0.5,0.5,0.5) point achieves its lowest absolute value at the equilibrium lattice parameter. These results allow us to conclude that the occupation of the octahedral interstitial positions by hydrogen atoms results in dynamic instability of the phase and can give rise to further phase transitions.

Since several theoretical studies predicted that hydrogen atoms can occupy tetrahedral sites adjacent to the vacancy in metals [9], we have also studied such kind of occupation for the vacancy ordered defect phase, Pd₃VacH₄. The considered defect phase with four hydrogen atoms located in the tetrahedral sites is presented in Fig.8. Equilibrium lattice parameter was found to be 4.04 Å which is very close to the experimental value for Pd₃VacH₄ phase, 4.02 Å [3]. The formation enthalpy of this phase was found to be -0.25 eV. Though, calculated phonon dispersion relations for the equilibrium lattice parameter, 4.04 Å, at high symmetry M(0.0,0.5,0.5) point show a soft mode with frequency of -0.37i THz, it can be easily stabilized by quite small lattice expansion (for example, due to temperature). For instance, lattice expansion less than 1% changes drastically the mode, as it becomes positive (see Fig.9) stabilizing the defect phase. Note that we used the LDA which usually underestimates the lattice parameter, and this fact might also be a reason for the lattice parameter expansion used in this work. One can see from Fig.10 that the calculated phonon dispersion relations for the lattice parameter of 4.05 Å do not show any soft (imaginary) modes. This might indicate that the thermal expansion can also play an important role in the dynamic stability of the vacancy ordered defect phase Pd₃VacH₄.

Summary

By means of the DFT based first-principles calculations the ground state properties and thermodynamic stability of vacancy ordered defect phase Pd₃VacH₄ were studied. The obtained results revealed that the site occupation of hydrogen atoms adjacent to the vacancies in the defect phase of palladium hydride can strongly affect its dynamic stability. It was found that hydrogen occupation of tetrahedral sites stabilizes the vacancy ordered defect phase, while it is not the case when hydrogen atoms occupy octahedral sites. The obtained results also indicate that quantum nature of dissolved hydrogen should be taken into account for proper understanding of the formation and dynamic stability of the vacancy-ordered defect phase.

Acknowledgments

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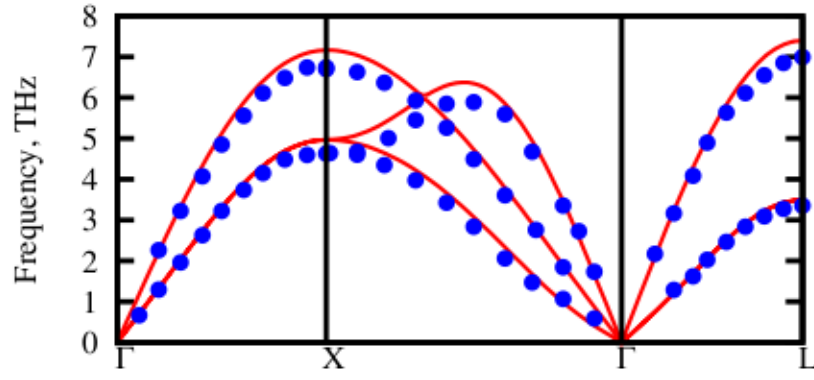


Fig.1 Phonon spectrum of palladium. Solid line represents our theoretical result, while blue circles stand for experimental data taken from Ref.[20].

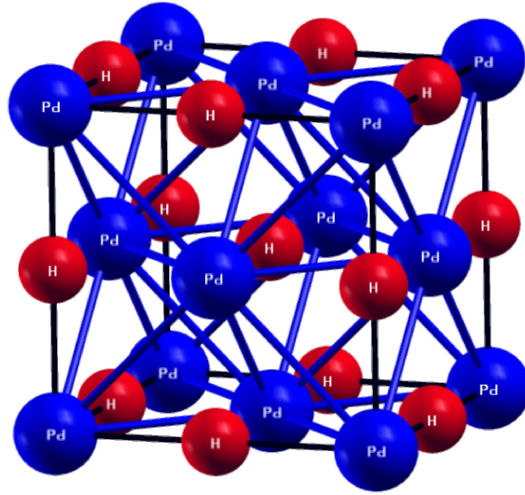


Fig.2 Schematic atomic structure of stoichiometric palladium hydride PdH.

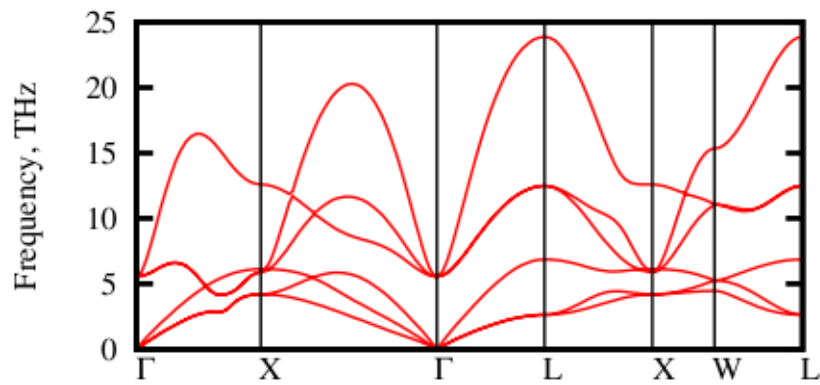


Fig.3 Phonon dispersion relations calculated for PdH at the equilibrium lattice parameter.

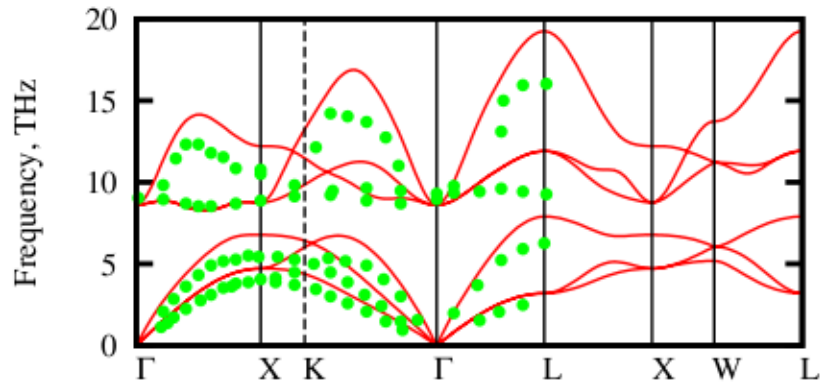


Fig.4 Phonon dispersion relations calculated for PdH under pressure 15.2 GPa. Solid lines represents our theoretical result, while green circles stand for experimental data taken from Ref.[24].

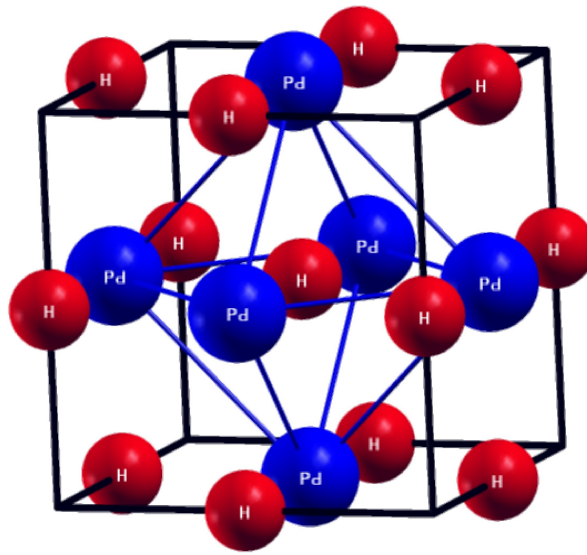


Fig.5 Atomic structure of the defect phase Pd_3VacH_4 . Hydrogen atoms occupy octahedral interstitial positions.

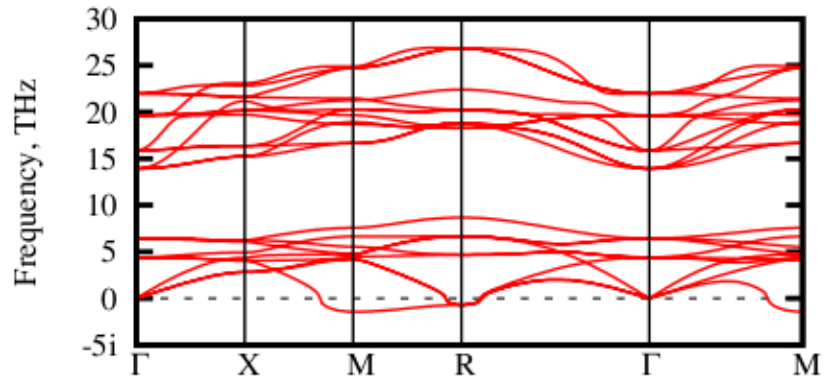


Fig.6 Phonon dispersion relations calculated for the defect phase Pd_3VacH_4 . Hydrogen atoms occupy octahedral interstitial positions.

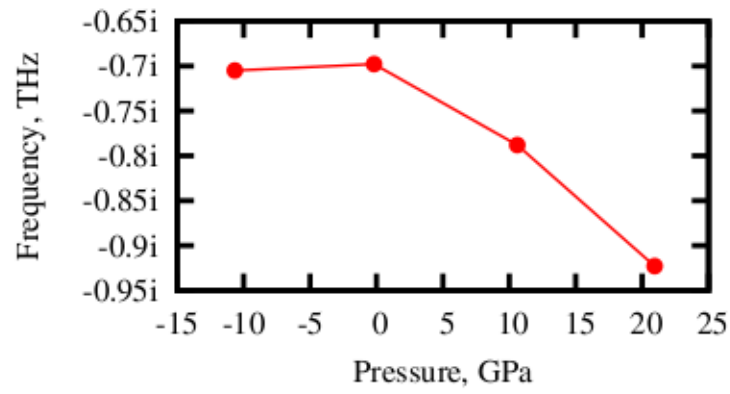


Fig.7 Pressure dependence of the soft mode at high symmetry point $R(0.5,0.5,0.5)$.

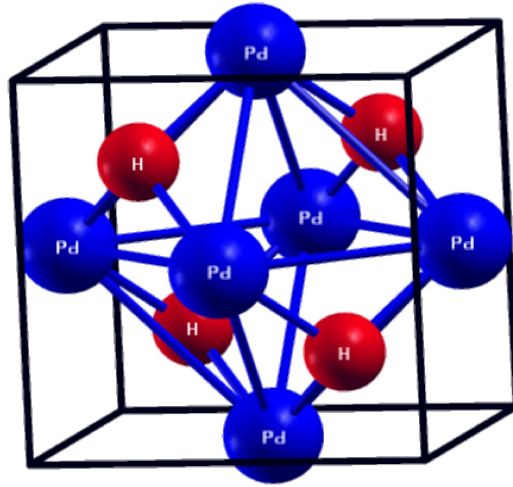


Fig.8 Atomic structure of the defect phase Pd_3VacH_4 . Hydrogen atoms occupy tetrahedral interstitial positions.

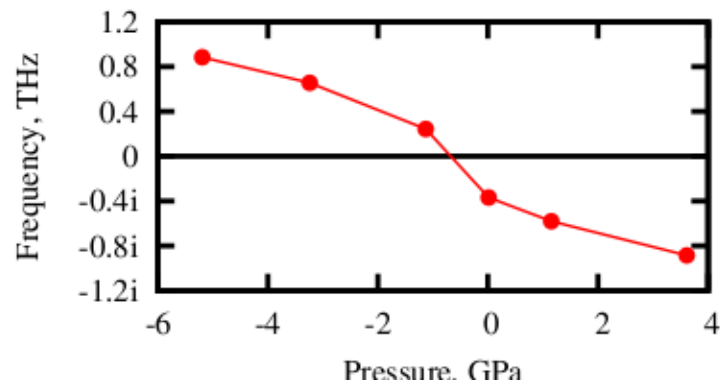


Fig.9 Pressure dependence of the soft mode at high symmetry point $M(0.0,0.5,0.5)$.

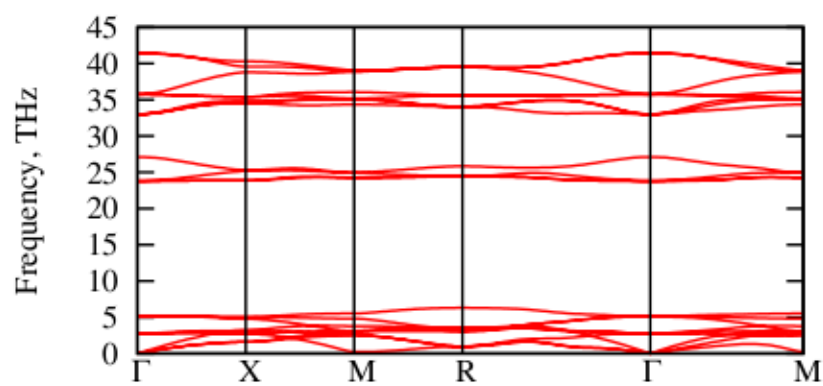


Fig.10 Phonon dispersion relations for the defect phase Pd_3VacH_4 calculated at the lattice parameter 4.05\AA . Hydrogen atoms occupy tetrahedral interstitial positions.