

Hydrogen storage properties, structural analysis, elastic and electronic properties of K_2PdH_4

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Density functional theory is adopted to study phase transitions, structural, elastic, and electronic properties of hydrogen storage K_2PdH_4 . Firstly, the structural evolution of K_2PdH_4 is investigated under high pressure along with the hydrogen storage properties. In the ambient conditions, K_2PdH_4 crystallizes in a tetragonal structure with space group $I4/mmm$. As the pressure is increased gradually on the crystal, a phase transition is recorded to the orthorhombic structure with space group $Immm$. Subsequently, the density of states and electronic band structures are obtained for each phase. Mechanical properties such as ductility and brittleness are investigated using elastic constants which are crucial parameters for solid-state hydrogen storage materials. Moreover, several properties are analyzed using Young, shear and bulk modulus to reveal the bonding characteristics of K_2PdH_4 .

Keywords: solid-state hydrogen storage, hydrides, structural evolution.

1. Introduction

The worlds' increasing population, energy need, and heavy pollution urge the requirements for developing green and sustainable energy sources. The increase of temperature in the atmosphere along with pollution will bring disasters such as flooding, drought, migration, etc. Thus, the research world has started to focus on developing clean, cheap, and viable carbon-free technologies. Hydrogen is offered to be one of the best options among wind, solar, and nuclear energy production. Hydrogen can be an effective energy carrier in various applications such as fuel cells. The utilization of hydrogen requires a few steps: production, storage, transportation, and usage. Each step has its own benefits and disadvantages. In terms of hydrogen storage, recent studies [1–3] have focused on solid-state hydrogen storage where hydrogen is bonded to a host material. In the presented study we focused on one of these materials, namely K_2PdH_4 . The phase transitions, mechanical, electronic and hydrogen storage properties will be examined by using *ab initio* calculations. *Ab initio* calculations have been well established and proven to be effective to reveal various properties of materials before synthesizing the materials.

2. Computation method

The theoretical properties of K_2PdH_4 have been investigated by using *ab initio* calculations with the Siesta-4.0 software package [4]. The exchange-correlation energy was calculated by using the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) [5]. Troullier–Martins type pseudopotentials were used for K, Pd, and H atoms [6]. A double- ζ basis including polarized orbitals were used. As a result of the optimizations, the calculations have been carried out using a 250 Ry cut-off energy. The simulation cell consisted of 84 atoms has been used with appropriate boundary conditions. The Brillouin zone integration was performed with $10 \times 10 \times 8$ and $8 \times 10 \times 6$ k -point meshes for $I4/mmm$ and $Immm$ phases of K_2PdH_4 , respectively. These k -point meshes were utilized for the energy vs volume calculations. Structural optimizations were performed via the conjugate gradient (CG) technique using to apply external pressure to the system until the residual forces acting on all atoms were smaller than 0.01 eV/Å. The pressure was increased with an increment of 10 GPa. The structures of K_2PdH_4 at each pressure value were analyzed with the KPlot program and RGS algorithm [7, 8]. As a result of the analysis, detailed information about lattice parameters, space groups, and atomic positions of the structures was obtained.

3. Results and discussion

Firstly, the ground state properties of K_2PdH_4 tetragonal structure with the space group $I4/mmm$ at zero pressure and temperature are investigated. After the optimization of the structure, the lattice parameters of this tetragonal structure are obtained as $a = b = 6.023 \text{ \AA}$ and $c = 7.5216 \text{ \AA}$. Subsequently, the pressure has been increased gradually on this optimized structure and a sharp volume decrease is observed at 20 GPa as shown in Fig. 1, where V/V_0 represents the ratio of the volume at pressure applied to the volume at zero one. A 30.33% collapse in volume at 20 GPa pressure is determined in this figure which is a clear indication of phase transition. In addition, the discontinuity in the volume is proof that the phase transition is of the first order. The tetragonal $I4/mmm$ phase transforms into the orthorhombic $Immm$ phase at 20 GPa. The lattice parameters of this orthorhombic phase are obtained as $a = 5.168 \text{ \AA}$, $b = 4.766 \text{ \AA}$, and $c = 6.859 \text{ \AA}$.

Figure 2 demonstrates the evolution of the structure. The lattice constants of K_2PdH_4 decreases when the symmetry of the structure transforms from $I4/mmm$ to $Immm$.

It is known that a constant pressure simulation overestimates the transition pressure. It is conventional to apply a thermodynamic theorem to estimate transition pressures in these calculations. The result of such procedure is given in Fig. 3. It is known that the transition pressure is close to the pressure where the enthalpy of phases crosses each other since it does not take into account perfect boundary conditions, short time scale, etc. As Fig. 3 suggests that the transition from $I4/mmm$ phase to $Immm$ phase occurs at 5.4 GPa.

The mechanical stabilities of phases are examined via elastic constants. Their calculated values, together with the lattice parameters, are collected in Table 1. The well-known Born stability criteria are given as [9, 10] for tetragonal:

$$C_{11} - C_{12} > 0, \quad C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \\ C_{11} + C_{33} - 2C_{13} > 0, \quad 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0 \quad (1)$$

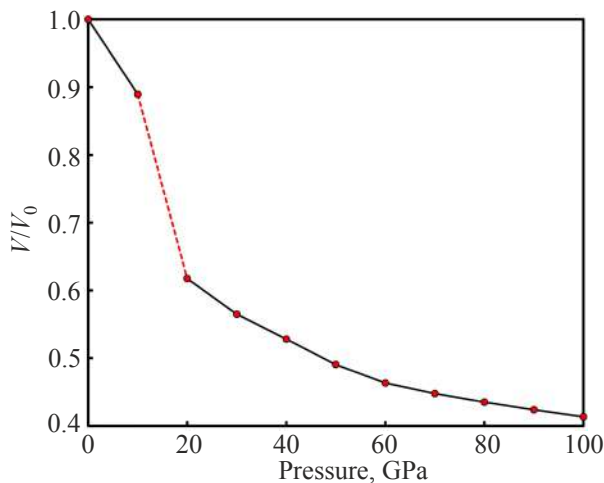


Fig. 1. Change of the volume of the unit cell under pressure applied.

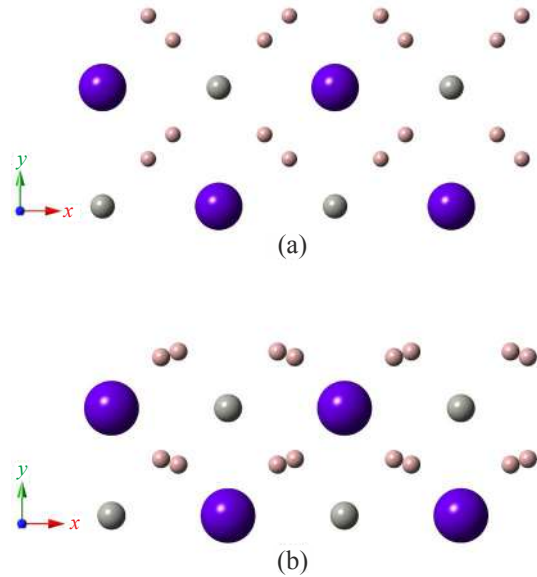


Fig. 2. Structure changes of K_2PdH_4 , (a) $I4/mmm$ at zero pressure and (b) $Immm$ at 20 GPa. K, Pd, and H atoms are represented by blue, gray and pink balls, respectively.

and for an orthorhombic structure:

$$C_{11} + C_{33} - 2C_{13} > 0, \quad C_{22} + C_{33} - 2C_{23} > 0, \\ C_{11} + C_{22} - 2C_{12} > 0, \\ C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \\ C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0, \\ 1/3 (C_{12} + C_{13} + C_{23}) < B < (C_{11} + C_{22} + C_{33}). \quad (2)$$

The fulfillment of both criteria (1) and (2) serves as a confirmation that both phases are mechanically stable.

Table 2 depicts other parameters that are obtained using the elastic constants. The ductility and brittleness of materials can be evaluated using bulk to shear modulus ratio. According to Pugh's rule, if this ratio is higher than 1.75, the material is ductile otherwise it is a brittle material. It can be seen that both phases of K_2PdH_4 are ductile. The other

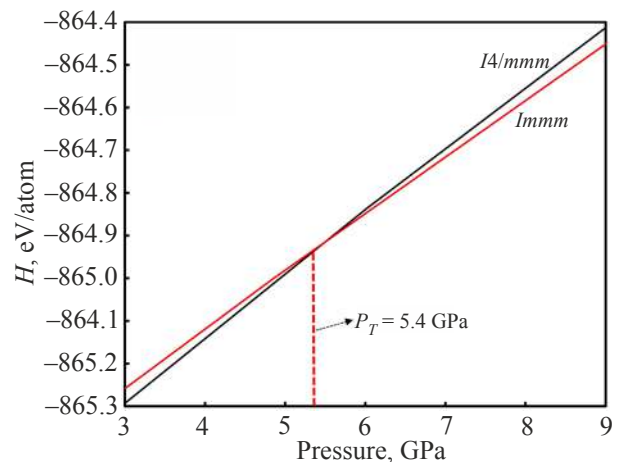


Fig. 3. The enthalpy vs pressure dependencies for tetragonal and orthorhombic modifications of K_2PdH_4 .

Table 1. The calculated lattice constants (Å) and elastic constants (GPa) of K_2PdH_4

K_2PdH_4	a , Å	b , Å	c , Å	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
$I4/mmm$	6.023	6.023	7.521	24.95	–	29.71	6.87	–	7.09	8.89	9.01	–
$Immm$	5.168	4.766	6.859	34.92	25.61	48.15	5.34	11.11	4.08	11.41	48.15	12.30

parameter, Poisson's ratio, provides information about bonding properties. It is considered that if Poisson's ratio is around 0.25, the material has dominant ionic characteristics. Thus, it can be predicted that ionic bonding seems to be dominant in both phases. Young modulus is an indicator of stiffness. As it gets higher, the stiffness of the material increases. Therefore, it can be considered that the orthorhombic phase is more rigid than tetragonal one.

The electronic band structures and density of states (DOS) of the phases are presented in Figs. 4 and 5. Zero energy corresponds to the Fermi level. As can be seen from the Fig. 4, both phases of K_2PdH_4 show a band gap in their band structures. The band gap is 2.43 eV for $I4/mmm$ phase at zero pressure and 2.14 eV for $Immm$ phase at 20 GPa pressure. Thus, both phases of K_2PdH_4 exhibit a semiconductor character.

In Fig. 5, the total and partial density of states were calculated for the obtained phases of K_2PdH_4 . The largest contribution below the Fermi energy level in both phases comes from Pd-4d electrons. Above the Fermi energy level, the largest contribution comes from K-4s electrons.

The gravimetric hydrogen density (GHD) is an important parameter for hydrogen storage materials which can be calculated as follows:

$$C_{wt\%} = \left(\frac{(H/M)M_H}{M_{\text{host}} + (H/M)M_H} \times 100 \right) \%, \quad (3)$$

where H/M is hydrogen to metal ratio, M_H is the molar mass of hydrogen and M_{host} is the molar weight of host material. The obtained GDH of K_2PdH_4 is about 2.09 wt%.

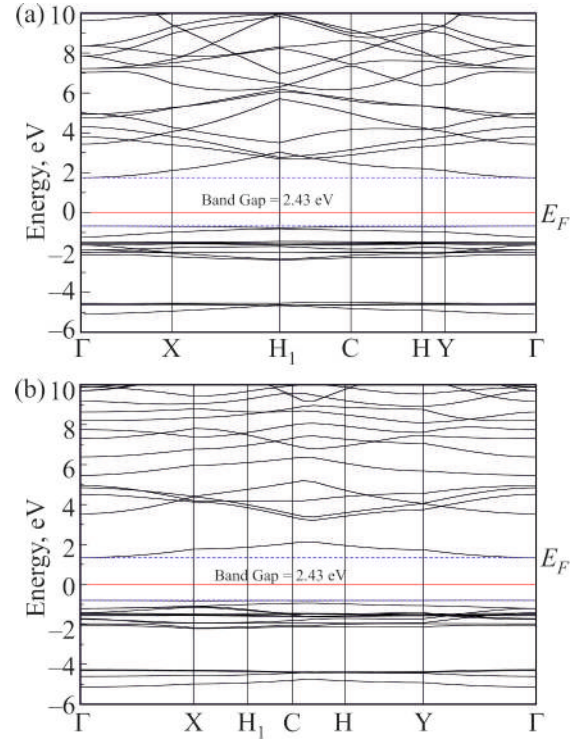
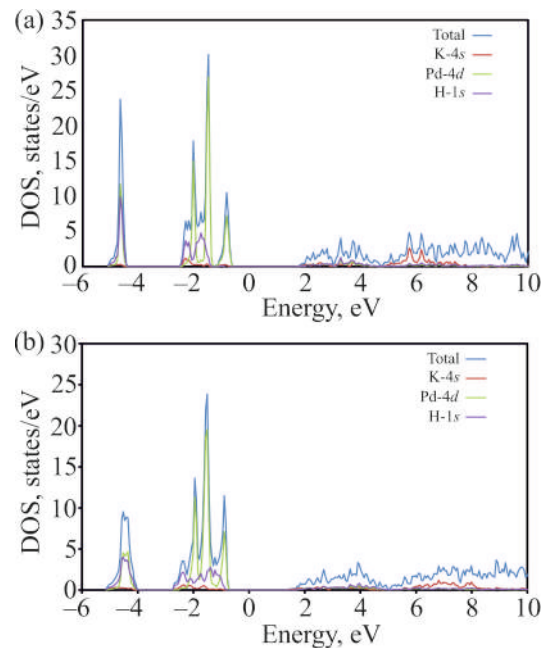
In addition to GHD of K_2PdH_4 , the hydrogen desorption temperature is predicted for evaluating the applicability of K_2PdH_4 using the following equation:

$$\Delta H = T_d \times \Delta S, \quad (4)$$

where ΔH and ΔS are the enthalpy and entropy changes of the dehydrogenation reaction, and hydrogen desorption temperature is represented by T_d . The hydrogen entropy change is previously determined as 130.7 J/mol·K, so the predicted desorption temperature is 312.74 K.

 Table 2. The calculated bulk modulus B , shear modulus G , B/G ratios, Poisson's ratios σ , and Young's modulus E of K_2PdH_4

K_2PdH_4	B , GPa	G , GPa	B/G	σ	E , GPa
$I4/mmm$	14.78	7.67	1.94	0.28	19.50
$Immm$	20.11	7.86	2.55	0.32	20.86


 Fig. 4. The calculated electronic band structures of K_2PdH_4 at zero pressure (a) and at 20 GPa (b).

 Fig. 5. (Color online) The calculated partial and total DOS of K_2PdH_4 obtained at zero pressure (a) and at 20 GPa (b).

4. Conclusion

This study investigates phase transition, mechanical, electronic, and hydrogen storage properties of K_2PdH_4 . It is found that K_2PdH_4 undergoes a phase transition at 5.4 GPa. The mechanical stability examination based on the Born stability criteria has shown that both the tetragonal and orthorhombic phases of K_2PdH_4 are mechanically stable. According to obtained B/G ratio values for two structural phases of the material, the K_2PdH_4 is a ductile material. The electronic band structures of the phases show a band gap between conduction and valence band. Additionally, the gravimetric hydrogen density and hydrogen desorption temperature of K_2PdH_4 have been predicted. The GHD is found as 2.09 wt% and the hydrogen desorption temperature is found as 312.74 K.

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Властивості зберігання водню, структурний аналіз, пружні та електронні властивості K_2PdH_4

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Теорія функціоналу густини використовується для вивчення фазових переходів, структурних, пружних та електронних властивостей накопичувача водню K_2PdH_4 . Досліджено структурну еволюцію K_2PdH_4 під високим тиском разом із властивостями накопичення водню. В умовах навколишнього середовища K_2PdH_4 кристалізується у тетрагональній структурі з просторовою групою $I4/mmm$. При поступовому збільшенні тиску на кристал спостерігається фазовий перехід до орторомбічної структури з просторовою групою $Immm$. Отримано густину станів та структуру електронних зон для кожної фази. Механічні властивості, такі як пластичність та крихкість, досліджуються за допомогою пружних констант, які є вирішальними параметрами для твердотільних матеріалів щодо зберігання водню. Деякі властивості аналізуються за допомогою модуля Юнга, зсуву та об'ємного модуля для виявлення характеру зв'язку у K_2PdH_4 .

Ключові слова: твердотільне накопичення водню, гідриди, структурна еволюція.