Low Temperature Physics/Fizika Nizkikh Temperatur, 2021, vol. 47, No. 12, pp. 1135–1138

Phase transitions, elastic and electronic properties of hydrogen storage Na_2PdH_4

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Received July 8, 2021, published online October 25, 2021

Hydrogen can be absorbed by some materials at specific pressures and temperatures. This is extremely important in terms of creating carbon-free and sustainable society. In this work hydrides are good candidates to fulfill these aims. Electronic and magnetic properties of hydrides are investigated. This study considers Na_2PdH_4 as solid storage of hydrogen material. Hydrogen is highly soluble in palladium and can be stored in large amounts at ambient conditions. The structural evolution, electronic and elastic properties of Na_2PdH_4 has been investigated by means of density functional theory. The SIESTA software package is used with the generalized gradient approximation for the exchange-correlation functional and norm-conserving Troullier–Martins pseudopotentials. High-pressure computations have been carried out to reveal phase transitions. Na_2PdH_4 is transformed from *I*4/*mmm* tetragonal structure to *Immm* orthorhombic structure at 100 GPa. The electronic band structures and density of states are obtained for both phases. Mechanical stability is analyzed using the elastic constants. Moreover, several parameters such as Young's modulus, shear modulus, and their ratios are obtained and discussed.

Keywords: density functional theory, elastic properties, phase transitions, hydrogen storage.

1. Introduction

The growing world population, energy consumption increase, environmental problems, pollution due to extraction and processes of fossil fuels have led the research world to search for clean, sustainable, and cheap energy sources and methods [1]. Hydrogen technology is believed to be one of the best options to solve these problems [2–4]. Hydrogen is an energy carrier rather than a source which can be used in stationary power plants, fuel cells, and portable applications [5]. In order to make hydrogen technology viable, there are a few steps that need to be overcome. Hydrogen production, storage, transportation, and usage. Every step has its advantages and disadvantages. Hydrogen can be stored, in different ways, in pressurized-tanks as gas, liquefaction and solid-state storage. In solid state storage, hydrogen bonds a host material. Hydrides have been investigated as host materials recently [6]. Palladium (Pd) has high hydrogen solubility and can absorb a large amount of hydrogen at ambient conditions. Also, Pd membranes are commonly used as hydrogen separation membranes [7]. Ternary Pd hydrides have interesting properties since they include both ionic (alkali-hydrogen) and covalent (transition metal-hydrogen) bonding. Thus, they can depict different electronic properties from dielectric to metallic. In this study, high-pressure phase change, elastic and electronic properties of Na_2PdH_4 will be investigated by means of first-principles calculations. Additionally, hydrogen storage properties will be examined for this solid-state hydrogen storage material.

2. Computation method

First-principles calculations were used to investigate various properties of Na_2PdH_4. The exchange-correlation energy was calculated by using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [8]. Cut-off energy of 250 Ry was used in all calculations. The simulation cell consisted of 84 atoms with periodic boundary conditions. The Brillouin zone integration was performed with 10×10×8 *k*-point meshes for all phases of Na_2PdH_4, respectively. These *k*-point meshes were utilized for the energy vs volume calculations. The conjugate gradient technique was used to apply external pressure to the system. The pressure was increased with an increment of 10 GPa.

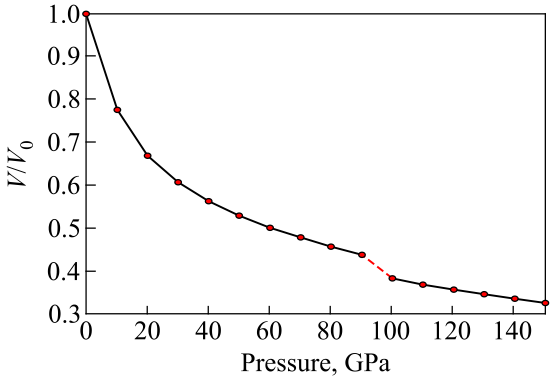

Fig. 1. Dependence of the relative volume of the unit cell of Na_2PdH_4 on the applied pressure.

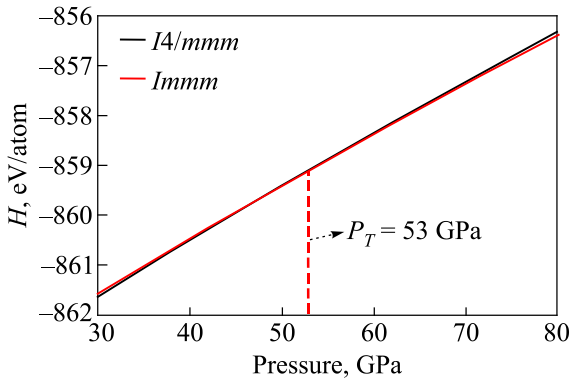

Fig. 3. (Color online) Dependence of enthalpy on pressure for two phases of Na_2PdH_4.

In order to analyze each minimization step, the KPLOT program was used which gives detailed data about cell parameters, atomic positions, and space group of an analyzed structure.

3. Results and discussion

3.1. Structural properties

Na_2PdH_4 belongs to a tetragonal structure with *I*4/*mmm* space group at zero pressure. The change in volume is determined using first-principal calculations and given in Fig. 1. V/V_0 represents a decline in volume that also represents the ratio of volume at any pressure to volume at zero pressure. The volume drops off dramatically at about 90 GPa, followed by a more rapid volume decline. A phase transition from *I*4/*mmm* phase to *Immm* phase is determined at 100 GPa. This sudden volume change suggests a first-order phase transition in Na_2PdH_4.

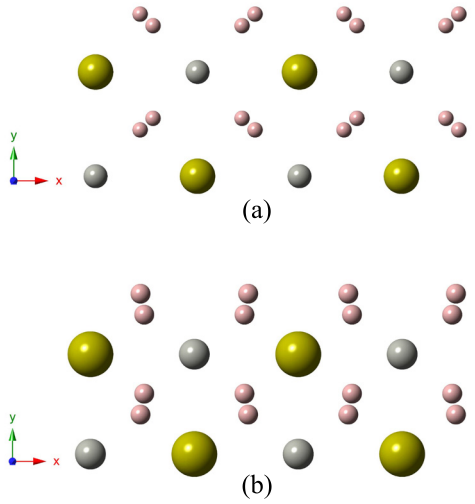

Fig. 2. Structures of Na_2PdH_4: (a) *I*4/*mmm* at zero pessure and (b) *Immm* at 100 GPa, Na, Pd, and H atoms are shown as green, grey, and pink balls, respectively.

Figure 2 indicates the structural change of Na_2PdH_4 from tetragonal *I*4/*mmm* at zero pressure to orthorhombic *Immm* at 100 GPa. This value of the pressure of a phase change can be overestimated due to several reasons such as short time scale, defects, surface effects, etc. The thermodynamic theorem is usually used to overcome these obstacles since does not include such restrictions. Thus, the energy vs volume computations are carried out to calculate the transition pressure between *I*4/*mmm* and *Immm* phases.

The predicted enthalpy pressure dependence of the phases is presented in Fig. 3. It shows that the curves cross at 53 GPa, suggesting the phase transition from *I*4/*mmm* to *Immm* phase.

3.2. Elastic properties

The lattice parameters and elastic constants of Na_2PdH_4 are also computed and given in Table 1.

The obtained values for *I*4/*mmm* phase of Na_2PdH_4 fulfil both mechanical stability criteria given in [9, 10]. Indicating that *I*4/*mmm* Na_2PdH_4 is mechanically stable material. In the contrast, *Immm* orthorhombic phase is not mechanically stable at ambient pressure.

Elastic constants can be used to improve understanding of some mechanical properties. Table 2 contains those parameters obtained from the elastic constants.

The values of bulk and shear modulus of Na_2PdH_4, make it possible to estimate that this compound will exhibit compressive strength under pressure since its bulk modulus is higher than the shear one. Additionally, the ratio of bulk modulus to shear modulus B/G is also evaluated.

Table 1. The calculated lattice constants (Å) and elastic constants (GPa) of Na_2PdH_4

Na_2PdH_4	a, Å	c, Å	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
*I*4/*mmm*	5.405	6.528	46.24	–	44.22	7.69	–	8.59	7.09	8.96	–
Immm	4.059	4.701	382.35	378.75	44.22	7.69	–99.01	10.01	174.56	200.33	217.77

Table 2. The calculated bulk modulus B, shear modulus G, B/G ratios, Poisson's ratios σ, and Young's moduls E of Na_2PdH_4

Na_2PdH_4	B, GPa	G, GPa	B/G	σ	E, GPa
*I*4/*mmm*	20.74	11.28	1.83	0.27	28.65
Immm	244.09	13.52	18	0.47	39.84

Based on the 4.01 (>1.75) value of B/G given in Table 2, Na_2PdH_4 belongs to a ductile material. The bonding properties of Na_2PdH_4 are evaluated via Poisson's ratio. If the Poisson's ratio is about 0.1, the solid characterized by covalent bonding, a value of about 0.25, indicates dominant ionic bonding. For Na_2PdH_4 ionic bond predominate. Young's modulus of material determines its stiffness. The higher E value the stiffer the material. So, Na_2PdH_4 is a stiff material.

3.3. Electronic properties

The electronic band structure of Na_2PdH_4 along the high symmetry directions in the Brillouin zone calculated GGA is given in Figs. 4(a) and 4(b). The Fermi energy level is set to zero by extracting Fermi energy value from electronic band energies and shown as dot lines in Fig. 4(a) and 4(b). As it is clearly seen there are band gaps between valence and conduction band, 2.08 eV for *I*4/*mmm* phase and 1.10 eV for *Immm* phase of Na_2PdH_4, indicating that Na_2PdH_4 is an insulator. In order to better understand the electronic characteristics of Na_2PdH_4, the total and partial density of states (DOS) is presented in Fig. 5. As can be seen from the total and partial densities of the states, the main contribution to valence band is provided by Pd-4*d* states.

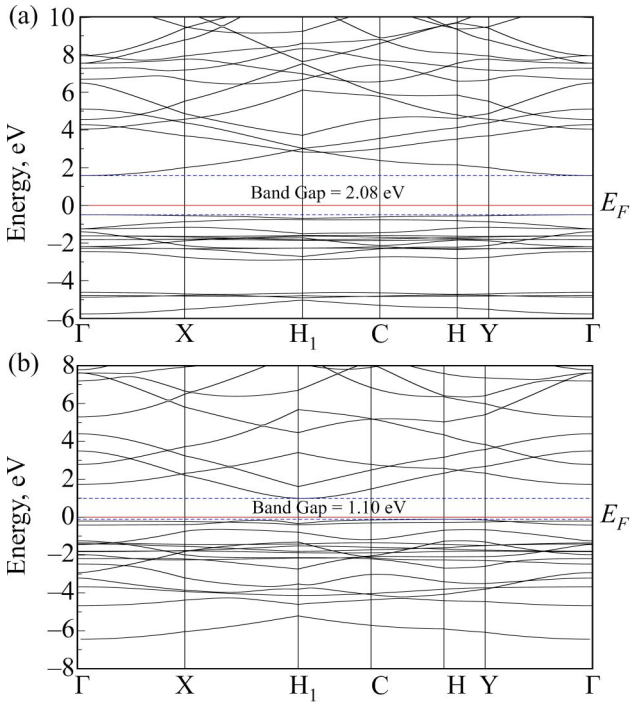

Fig. 4. The calculated electronic band structures of Na_2PdH_4 at zero pressure (a) and at 100 GPa (b).

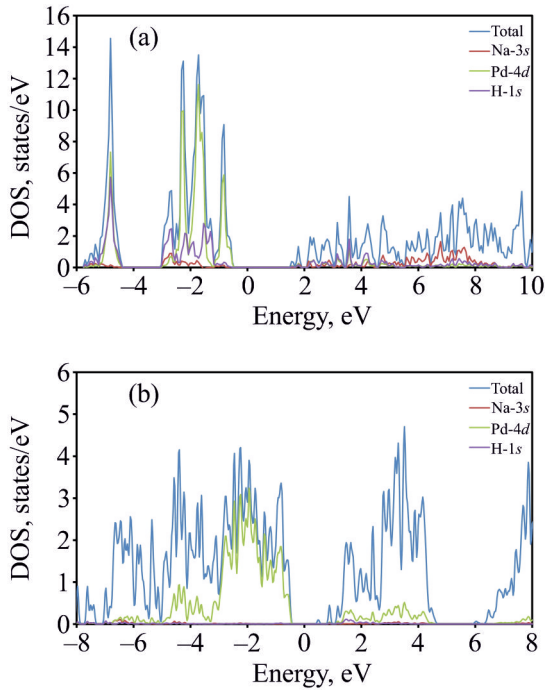

Fig. 5. (Color online) The calculated partial and total DOS of Na_2PdH_4 at zero pressure (a) and at 100 GPa (b).

3.4. Hydrogen storage properties

Gravimetric hydrogen density (GHD) is calculated as follows:

$$C_{\text{wt\%}} = \left(\frac{\left(H/M\right) M_H}{M_{\text{host}} + \left(H/M\right) M_H} \times 100 \right) \%, \qquad (1)$$

where H/M is hydrogen to metal ratio, M_H is molar mass of hydrogen and M_{host} is molar weight of host material. The obtained GDH of Na_2PdH_4 is about 2.51 wt%.

In order to evaluate the applicability of Na_2PdH_4, in addition to GHD, a hydrogen desorption temperature can be predicted using the following equation:

$$\Delta H = T_d \times \Delta S, \qquad (2)$$

where ΔH and ΔS are the enthalpy and entropy changes during the dehydrogenation reaction, respectively, T_d is the hydrogen desorption temperature. The hydrogen entropy change was previously determined as 130.7 J/mol·K [11], therefore, the temperature of hydrogen desorption is estimated as 271.34 K.

Conclusion

This study has examined structural evolution, elastic, electronic, and some hydrogen storage properties of Na_2PdH_4. The GDH of Na_2PdH_4 is found to be 2.51 wt%. Hydrogen desorption temperature is found at about 271 K. Evaluation of stability criteria indicates that Na_2PdH_4 is a ductile material. Both structural phases have a band gap which suggests a non-metallic behavior of Na_2PdH_4.

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Фазові перетворення, пружні та електронні властивості водневмісного Na_2PdH_4

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Водень може адсорбуватися деякими матеріалами при певних тисках та температурах. Це особливо важливо з точки зору створення безвуглецевої та екологічно раціональної спільноти. Гідриди виявляються добрими кандидатами для здійснення цих цілей. Досліджено електронні та магнітні властивості гідридів. В них Na_2PdH_4 розглядається як твердий матеріал, що вміщує водень. Водень, який добре розчинюється у паладії та може зберігатися у великих кількостях за умов навколишнього середовища. Структурну еволюцію, електронні та пружні властивості Na_2PdH_4 досліджено за допомогою теорії функціонала густини. Використано пакет програм SIESTA у режимі узагальненого градієнтного наближення для обмінно-кореляційного функціонала та псевдопотенціалами Троуллера–Мартіна, які зберігають норму. Обчислювання при наявності великого зовнішнього тиску проведено для виявлення фазових перетворень. Na_2PdH_4 переходить від тетрагональної *I*4/*mmm* до орторомбічної *Immm* структури при тиску 100 ГПа. Структуру електронних зон та густину станів встановлено для обох фаз. Механічну стійкість проаналізовано по значенню пружних констант. Крім того, декілька параметрів, таких як модуль Юнга, модуль зсуву, та їхнє відношення було одержано та обговорено.

Ключові слова: теорія функціонала густини, пружні властивості, фазові переходи, накопичення водню.