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Elastic, Electronic, Dynamic and Thermodynamic Properties of $YbPdH_3$

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Abstract: A comprehensive computational investigation has been carried out for $YbPdH_3$ via first principles calculations for the first time. Structural, electronic and thermodynamic properties are obtained. The obtained lattice constant of $YbPdH_3$ is in a good agreement with the existing literature. Subsequently, the elastic constants are obtained and used to compute several parameters such as anisotropy, hardness, Cauchy pressure, shear and Young modulus, machinability index and Poisson's ratio. According to Born stability criteria, $YbPdH_3$ is mechanically stable material. Cauchy pressure and Poisson's ratio indicates ductile nature. The anisotropy factor indicates anisotropic nature almost in every direction for Young modulus, shear modulus, linear compressibility and Poisson's ratio. The machinability index (B/C_{44}) is found to be 2.88 whereas Vickers hardness of $YbPdH_3$ is computed via Chen's model as 2.965. The electronic band structure of $YbPdH_3$ demonstrates metallic characteristics since there is no band gap between valence and conduction band. The thermodynamic properties such as Debye temperature, Debye vibrational energy, vibrational free energy, entropy, heat capacity and melting temperature of $YbPdH_3$ are also obtained. The heat capacity seems to reach its Dulong-Petit limit at about 300 K.

$YbPdH_3$'ün Elastik, Elektronik, Dinamik ve Termodinamik Özellikleri

Anahtar Kelimeler
İlk prensip hesaplamaları, sertlik, elastik özellikler, işlenebilirlik, anizotropi.

Öz: $YbPdH_3$ için ilk kez ilk prensip hesaplamaları yoluyla kapsamlı bir hesaplamalı araştırma yapıldı. Yapısal, elektronik ve termodinamik özellikler elde edildi. $YbPdH_3$'ün elde edilen örgü sabiti mevcut literatürle iyi bir uyum içindedir. Daha sonra elastik sabitler elde edildi ve anizotropi, sertlik, Cauchy basıncı, kayma ve Young modülü, işlenebilirlik indeksi ve Poisson oranı gibi çeşitli parametreleri hesaplamak için kullanıldı. Born stabilite kriterlerine göre $YbPdH_3$ mekanik olarak stabil bir malzemedir. Cauchy basıncı ve Poisson oranı sünek yapıyı gösterir. Anizotropi faktörü Young modülü, kayma modülü, doğrusal sıkıştırılabilirlik ve Poisson oranı için neredeyse her yönde anizotropik doğayı göstermiştir. İşlenebilirlik indeksi (B/C_{44}) 2.88 olarak bulunurken $YbPdH_3$'ün Vickers sertliği Chen modeliyle 2.965 olarak hesaplandı. $YbPdH_3$'ün elektronik bant yapısı, değerlik ve iletim bandı arasında bant aralığı olmadığından metalik özellikler göstermektedir. $YbPdH_3$'ün Debye sıcaklığı, Debye titreşim enerjisi, titreşim serbest enerjisi, entropi, ısı kapasitesi ve erime sıcaklığı gibi termodinamik özellikleri de elde edilmiştir. Isı kapasitesi yaklaşık 300 K'da Dulong-Petit sınırına ulaşmış gibi görülmüştür.

1. Introduction

To date, several hydrides have been under investigation for several reasons such as superconductivity and hydrogen storage. $YbPdH_3$ is a perovskite type hydride which contains hydrogen in its structure. It might be a possible candidate for hydrogen storage. Its application can be carried out both as conducting material or storage material. Hydrogen storage requires a couple of conditions such as cost, safety, high concentration storage capacity, kinetic etc. In general, there are two types of hydrogen storage methods, these are physisorption and chemisorption. While physisorption is based on weak

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interaction between the host material and hydrogen molecules, chemisorption is based on the chemical reaction of the host material and hydrogen and a new hybrid phase is formed. Recently, hydrogen storage in perovskite hydrides with high gravimetric density has been extensively investigated alongside metal hydrides. There are very few studies exist in literature on $YbPdH_3$ [1, 2], in which only electronic properties were investigated. In this study, a thorough investigation on $YbPdH_3$ has been done to reveal its extensive properties.

Hydrogen storage materials and technology are crucial to promoting hydrogen use and fuel cell energy in stationary and portable power sources and transportation. The bottleneck of using hydrogen as an energy carrier is storing hydrogen in an efficient way. A couple of hydrogen storage methods have been proposed and investigated last a few decades such as gaseous form in high pressure, liquid form in low temperature and solid-state storage. High pressure gaseous form is limited to heavy tanks, poor safety and possible leakage. High strength materials should be reinforced for pressure vessels which brings extra costs and limited gravimetric hydrogen density.

Moreover, compressing gases leads to release of heat including hydrogen, therefore a pre-cooling system of hydrogen is required when compressing. Liquid form requires low temperature which leads to addition of cooling system that decreases the efficiency of it. This procedure requires a good thermal insulation of the tank, otherwise the heat transfer between the tank and environment will lead to release of hydrogen (boil-off) from the valves. To sum up, both ways bring extra costs, strict regulations, and safety concerns, especially for mobile applications. Thus, explosion, flammability, toxicity etc. are not desired for hydrogen storage. Compared to these two methods, solid state hydrogen storage provides superior safety and allows to operate at appropriate pressure and temperature. The biggest obstacle to the use of hydrogen as a fuel is the lack of materials with suitable gravimetric density. To overcome this problem, an interactive approach is needed where materials can be synthesized with sufficient storage capacity at higher densities. Hence, it is crucial to carry out a theoretical computation for this capacity. Along with various parameters, gravimetric hydrogen density (GHD) is a significant parameter is computed for hydrides for hydrogen. The GHD of $YbPdH_3$ is obtained as follows [3]:

$$C_{wt\%} = \left(\frac{(H/M)M_H}{M_{Host}+(H/M)M_H} \; x \; 100 \right) \% \qquad (1)$$

In the equation H/M donates for hydrogen to metal ratio, M_H donates for molar mass of hydrogen and M_{Host} donates for molar weight of host material. The GHD value of $YbPdH_3$ is computed as 1.06 wt.%.

2. Materials and Methods

Quantum Espresso code was utilised to carry out calculations. The plane wave pseudopotential approach was adopted within the Quantum Espresso [4, 5]. The GGA (generalized gradient approximation) by Perdew, Burke, and Ernzerhof (PBE) was used to treat electronic exchange correlation potentials [6]. The cut-off energy for the maximum plane wave was adopted as 60 Ry while the basis cut-off was taken as 600 Ry for the electronic charge density. A 8×8×8 k point grid was used to integrate Brillouin-zone. The smearing parameter is taken as σ= 0.01 Ry for integration up to Fermi level [7]. Stress-strain approach within thermos-pw program was adopted to compute elastic constants within Quantum Espresso. The thermodynamic properties under constant volume were obtained by using the Gibbs2 code with semi-harmonic approximation (QHA). The thermodynamic properties were obtained using the energy-strain method applied in the thermo-pw code.

3. Results

3.1 Physical Properties

$YbPdH_3$ crystalizes in cubic structure with the space group $Pm\bar{3}$ m (No. 221), its crystal structure representative is given in Figure 1. The computed lattice constant for $YbPdH_3$ is found as 3.696 Å which is the similar value given in Materials Project (3.66 Å). The mechanical properties of materials are generally evaluated by stiffness (elastic) constants $C_{ij.}$ The stiffness constants help to understand the material's behavior such as hardness, ductility, bonding, machinability, brittleness, anisotropy and mechanical stability. In general, mechanical stability evaluation of materials are carried out by examining the material's respond in any application under static stress via elastic stiffness.

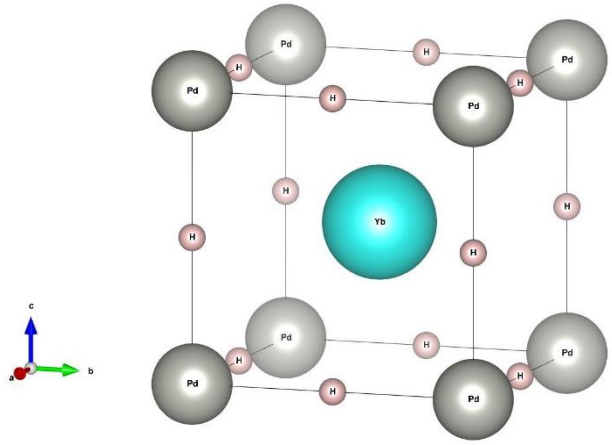

Figure 1. The crystal structure representative of $YbPdH_3$.

The computation of elastic stiffness is explained in refs [8, 9]. The computed various parameters by using elastic stiffness are presented in Tables 1, 2 and 3.

There are three elastic stiffness are given for a cubic structure known as C_{11}, C_{12}, C_{44}. Max Born suggested a stability criteria for mechanical stability as [10]:

$$(C_{11} - C_{12}) > 0,\ C_{11} > 0,\ C_{44} > 0,\ (C_{11} + 2C_{12}) > 0 \quad (2)$$

Equation 2 can lead to;

$$C_{12} < B < C_{11} \quad (3)$$

The computed elastic stiffness of $YbPdH_3$ satisfy the conditions given in Equation 2 and 3. Therefore, it can be concluded that $YbPdH_3$ is mechanically stable material. Elastic stiffness of materials can also provide information about material's resistance along difference directions. The value of C_{11} is an indication of material's response towards linear compression along [100]. Since C_{11} value is greater than that of C_{12} and C_{44}, resistance to linear compression is greater for $YbPdH_3$.

B of the materials indicate resistance of them towards fracture whereas G shows resistance towards plastic deformation. Higher C_{44} value also implies higher G which increases plasticity [11]. From Table 2, it can be predicted that $YbPdH_3$ has some plasticity and stiffness. Cauchy pressure (C_p) provides information about angular characteristics of materials. More positive C_p implies predominance of ionic bonding whereas more negative C_p indicates covalent bonding predominance. It is stated by Pettifor [12] that Cauchy pressure ($Cp = C_{12} - C_{44}$) can tell about bonding characteristics of the materials along with the fracture. In the case of negative Cauchy pressure, the material tends to show directional bonding characteristics with angular or covalent bonding and brittle nature. In the case of more positive Cauchy pressure, the material tends to exhibit metallic and ductile nature. The C_p of $YbPdH_3$ is computed as 58.23 GPa which suggests predominance of ionic bonding within $YbPdH_3$. In addition, C_p can give an idea about brittleness and ductility of given material. Positive C_p indicates ductility [13].

The ductility and brittleness of the materials can be analyzed by using Pugh's criteria [14] and Frantsevich's rule [15]. Pugh's criteria distinguish materials based on the B/G ratio. Higher B/G ratio displays ductility and lower B/G ratio implies brittleness; the borderline is specified as 1.75. According to Frantsevich, materials with σ, lower than $\sigma \sim 0.26$ are brittle and higher than 0.26 are ductile. As can be seen from Table 2 that, the computed B/G ratio is 5.51 and σ is 0.41 which suggests the ductile nature of $YbPdH_3$.

B/C_{44} ratio is defined as machinability index [17], if C_{44} is low, machinability index is high which is the case for softer materials. If the hardness of the material is high, machinability index is lower. Hardness of the material is computed using the Chen's model [18] and presented in Table 3.

Table 1. The calculated lattice constants (a, $Å$), Bulk modulus (B, GPa), elastic constants (C_{11}, C_{12}, C_{44}, GPa) and Cauchy Pressure (C_P) of $YbPdH_3$.

Material	a	B	C_{11}	C_{12}	C_{44}	C_{12}-C_{44} (C_p)
$YbPdH_3$	3.696	95.57	103.95	91.39	33.16	58.23
$YbPdH_3$	3.710 [1, 16]					

Table 2. The calculated Bulk modulus (B,GPa), Shear modulus (G, GPa), B/G ratios, Poisson's ratios (σ) and Young's modulus (E, GPa) of $YbPdH_3$.

Material	B	G	B/G	σ	E
$YbPdH_3$	95.57	17.32	5.51	0.41	48.77

Table 3. The computed anisotropy factor (A), melting temperature (Tm, K), Vickers hardness (H_v^G, H_v^E, GPa) and machinability index (B/C_{44}) of $YbPdH_3$.

Material	A	Θ	Tm	H_v^G	H_v^E	B/C_{44}
$YbPdH_3$	5.28	206.34	1167.3	0.164	2.965	2.88

By adopting elastic stiffness B, G, E, H_v^G, H_v^E and B/C_{44} are obtained. The calculated hardness values for $YbPdH_3$ are; $Hv^G = 0.164$ and $Hv^E = 2.965$thus, it can be predicted that $YbPdH_3$ is not a hard material. In general, materials with Vickers hardness value above 10 GPa is defined as hard material and materials with a hardness value greater than 40 GPa are defined as super hard materials [19].

As well as elastic properties, melting temperatures (Tm) can also be obtained by using elastic constants. Tm provides an idea about practicability and reliability of the materials. For a cubic structure, Tm can be computed by using $Tm = 553 + 5.91\ C_{11}$ relation [18]. The computed Tm for $YbPdH_3$ is 1167.3 K which suggests that this material can be used for high temperature applications.

Debye temperature (Θ) is also a significant value which describes the temperature at which the vibration wavelengths of atoms are equal to the unit cell length [20]. Θ is a parameter that can be used with the inherent properties of the elastic lattice vibrations and can be computed through the average elastic wave velocity (Vm). Several thermodynamic properties can be obtained using Θ such as specific heat capacity, thermal expansion and thermal conductivity. Θ of $YbPdH_3$ is obtained as 206.34 K.

Deformation do not occur for brittle materials; however, it is expected for ductile materials before fracture. The crystal anisotropy can have an effect on plastic deformation and fracture. Anisotropy of the

materials affect the physical properties in different directions. Thus, the anisotropy factor of $YbPdH_3$ has been computed by using $A= 2C_{44} / C_{11}-C_{12}$ relation [21]. The calculated anisotropy factor is given as 5.28 in Table 3 which indicates anisotropic characteristics of $YbPdH_3$. The 2D and 3D dimensional change of E, linear compressibility, G and σ is computed using the ELATE program and given in Figure 2. $YbPdH_3$ exhibits anisotropic behaviour almost in every direction.

Linear compressibility in xy plane seems to be isotropic, and other properties are anisotropic in all directions.

Similar anisotropic behaviours were observed for $LiCaH_3$ and $NaCaH_3$ previously [22].

3.2 Electronic Properties

The electronic properties of $YbPdH_3$ have also been investigated. The electronic band structure and total (TDOS) and partial densities of states (PDOS) are given in Figure 3 and Figure 4.

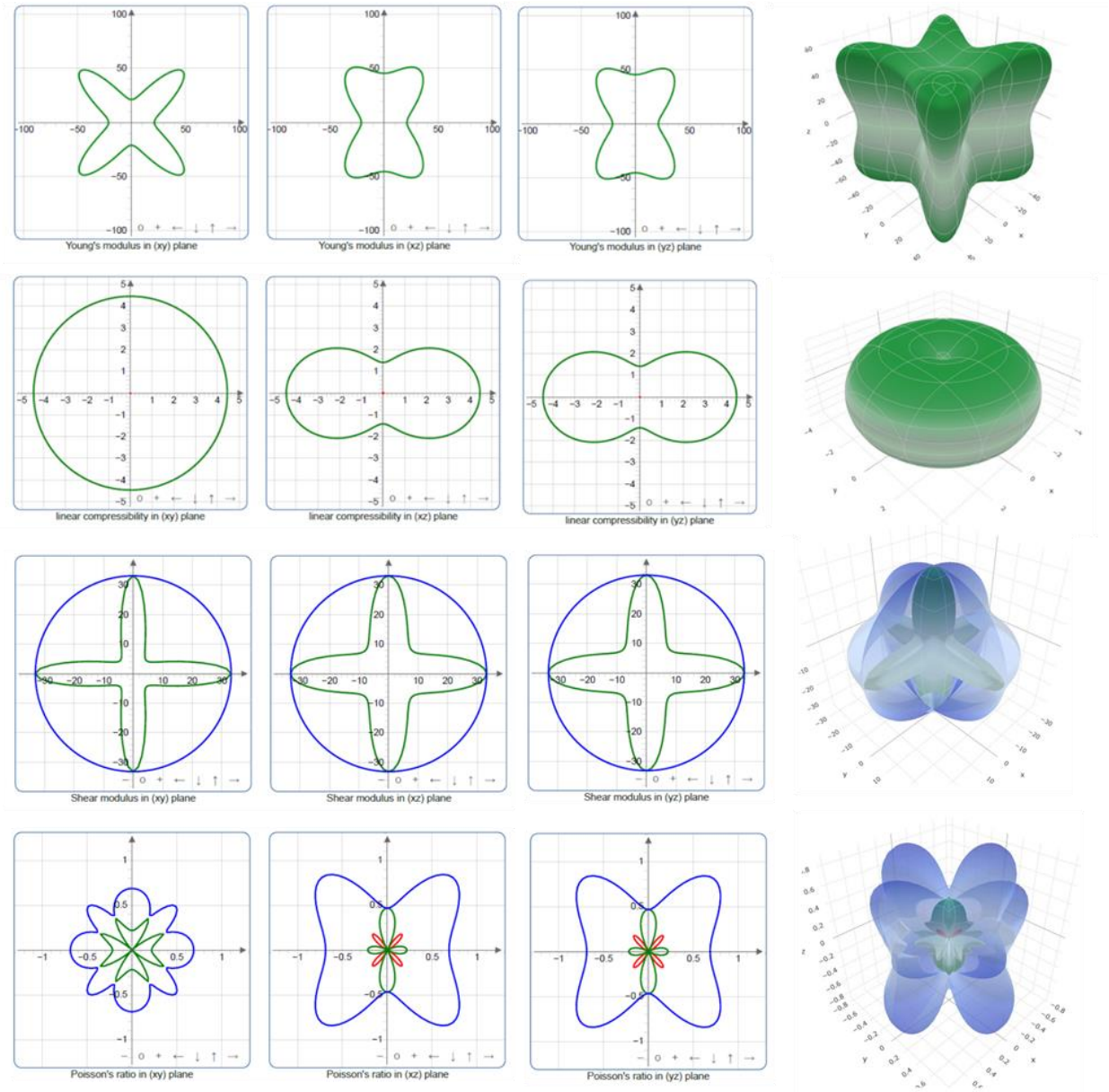

Figure 2: The 2D and 3D directional change of Young Modulus, linear compressibility, Shear modulus and Poisson's ratio of $YbPdH_3$.

The band gap describes the region between valence and conduction band where electrons cannot occupy. Figure 3 demonstrates no band gap around Fermi energy level (set to 0 eV) since valence and conduction band overlaps, thus it can be easily predicted that $YbPdH_3$ shows metallic behaviour. Figure 4 displays detailed contributions to the conductivity of $YbPdH_3$. The contribution of d states of Pd is dominated in the valence band along with s states of H, whereas d states of Yb dominate to the conduction band.

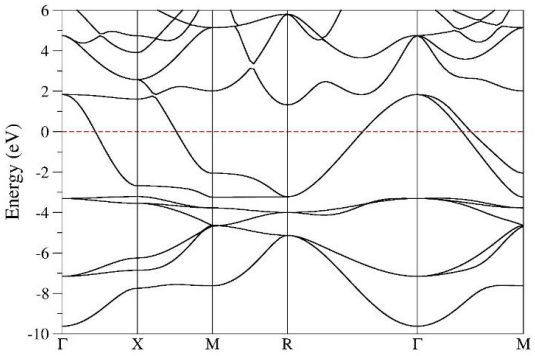

Figure 3. Electronic band structure of $YbPdH_3$.

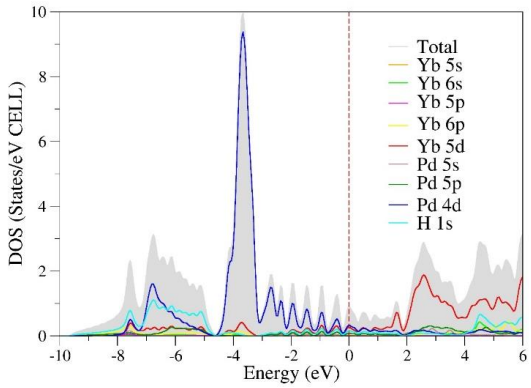

Figure 4. The TDOS and PDOS of $YbPdH_3$.

3.3 Thermodynamic Properties

The thermodynamic properties are computed for $YbPdH_3$. The internal energies of $YbPdH_3$ are shown in Figure 5. Debye vibrational energy seems to increase linearly with the increasing temperature. Debye vibrational free energy in Figure 5b seems to be more negative as the temperature increases. Materials with more negative Debye vibrational free energy seem to have better thermal response since they will have better thermodynamic stability at high temperatures.

Entropy of $YbPdH_3$ rises with the temperature as shown in Figure 6a. This is expected since as the temperature increases the kinetic energy and motion of atoms increase. Also, the entropy is zero at zero temperature which obeys the third law of thermodynamics. In addition, entropy can be related to vibrational free energy since vibrational free energy is obtained entropy. The more negative vibrational free energy, the higher entropy [23].

The heat capacity of $YbPdH_3$ is given in Figure 6b. As can be seen from the figure that there is a sharp increase in heat capacity with the temperature between 0-150 K. After that, a slight increase can be observed up until 250 K. Around 300 K, the heat capacity reaches its Dulong-Petit limit about 120 $JNmol^{-1}K^{-1}$.

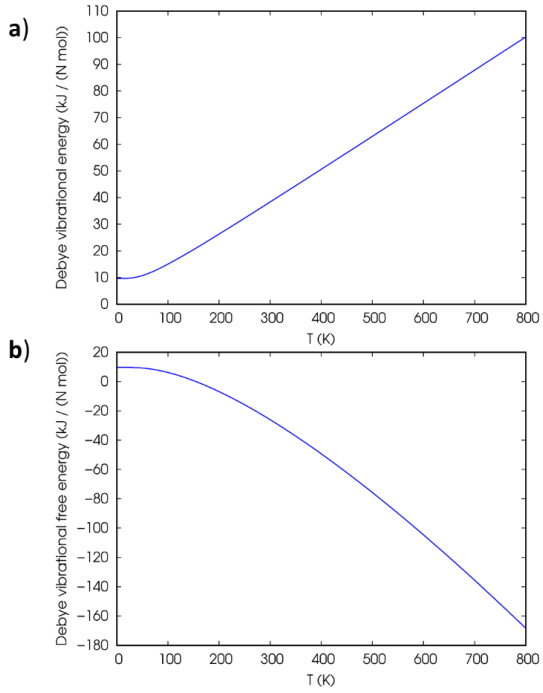

Figure 5. Debye vibrational energy (a) and free energy (b) of $YbPdH_3$.

4. Discussion and Conclusion

The development of viable solid-state hydrogen storage materials primarily relies on the theoretical study of new materials and their properties. In this context, first principles calculations form the basis and allow discovery of new materials. In this sense, the structural, elastic, mechanical, anisotropic behavior and thermodynamic properties of $YbPdH_3$ has been investigated by means of first principles calculations. The mechanical stability is evaluated by using elastic constants and Born stability criteria, the result indicates mechanical stability for $YbPdH_3$.

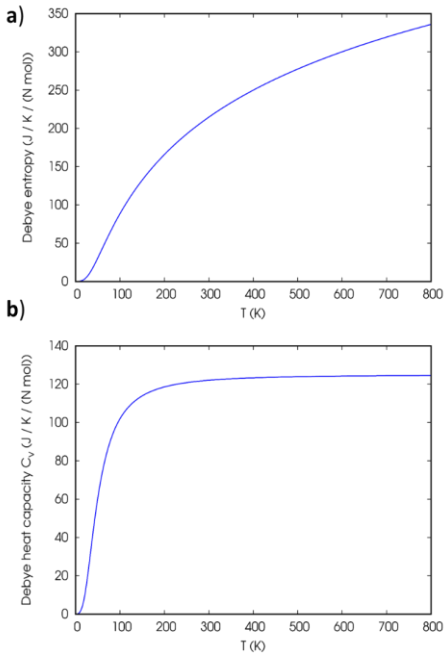

Figure 6. Debye entropy (a) and heat capacity (b) of $YbPdH_3$.

Along with elastic constants several parameters such as Cp, G, E, σ, Θ, machinability index, hardness and Tm of $YbPdH_3$ are obtained. According to obtained values, $YbPdH_3$ is a ductile and anisotropic material. The electronic band structures show a metallic character with the highest contribution to the conduction band Pd 4d states. In addition, Debye vibrational energy, vibrational free energy, entropy and heat capacity of $YbPdH_3$ are obtained. As far as the author's knowledge these properties have been studied for the first time for $YbPdH_3$.

Declaration of Ethical Code

In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.

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