Original Research Article

First Principles study of electronic structure, mechanical and superconducting Properties of Palladium Hydride

ABSTRACT

The Structural, electronic and elastic properties of mono and dihydrides of Palladium are investigated by using first principles calculation based on density functional theory as implemented in Vienna ab-initio simulation package. The calculated lattice parameters are in agreement with the experimental results. A pressure-induced structural phase transition from ZB to NaCl is observed at a pressure of 11 GPa for PdH. A high superconducting transition temperature (T_c) of 18.76K is obtained for PdH_2.

Keywords: *ab-initio calculations, structural phase transition, electronic structure, elastic properties*

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1. INTRODUCTION

Palladium has been known as an excellent metallic observer of hydrogen for more than a century [1]. Electronic structure of $PdH_{0.6}$ at 100K was studied by means of photoelectron spectroscopy [2]. Behavior of d electrons and their effect on chemical bonding for diatomic transition metal hydrides of NiH and PdH were studied [3]. PdH_x is a superconductor with a transition temperature T_c of about 9 K for x=1. Band structure calculations and superconducting properties of PdH_x and PdD_x were reported [5]. Recently, both static and dynamic calculations of various properties of PdH(D) were performed [6]. Stoichiometric PdH and PdD in a diamond anvil cell have been synthesized and pressure dependence of the superconducting transition temperature was measured [7].

In this paper, structural, mechanical and electronic properties of mono and dihydrides of Palladium metal are investigated by the first principles calculation using Vienna ab-initio simulation package (VASP).

2. COMPUTATIONAL DETAILS

The total energy calculations are carried out using density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) [8], which is based on pseudo potentials and plane wave basis functions. All electron projected augmented wave (PAW) method of Blochl [9] is applied in VASP with the frozen core approximation. The generalized gradient approximation (GGA) introduced by Perdew, Burke and Ernz-erhof (PBE) [10] is employed to evaluate the electron exchange and correlation potential. The valence electron configurations are Pd $4d^{10}$ and H $1s^1$. The cutoff energy for plane waves in our calculation is 500 eV. The integration over the Birllouin Zone (BZ) is performed with a grid of special k point-mesh determined according to the Monkhorst-Pack scheme [11] with a grid size of 8x8x8 for structural optimization and total energy calculation. Iterative relaxation of atomic positions is stopped when the change in total energy between successive steps is less than 1 meV/cell. Pressure calculations are done with second order Birch Murnaghan equation of states [12, 13]. The superconducting transition temperature is obtained using the tight binding linear muffin tin orbital method (TB-LMTO) within the frame work of local density approximation (LDA) [14-17].

3. RESULT AND DISCUSSIONS

3.1 Geometric Properties

At ambient condition, the monohydride of palladium crystallize in ZB structure with the space group of *F-43m* (no.216). The wyckoff positions for Pd atom is 4a:(0,0,0) and H atom is 4c:(0.25,0.25,0.25) and contains four formula units per unit cell. The dihydrides of Pd crystallize

in CaF_2 structure with the space group of *Fm-3m* (no.225). The cubic unit cell is composed of four formula units with the metal and H atoms in 4a:(0,0,0) and 8c:(0.25,0.25,0.25) sites respectively. Here, each metal atom is surrounded by eight H atoms forming a cube and each H connects with four metal atoms to build a tetrahedron. The unit cell structures of the considered phases of mono and dihydrides of Pd atoms are given in fig. 1 (a&b).

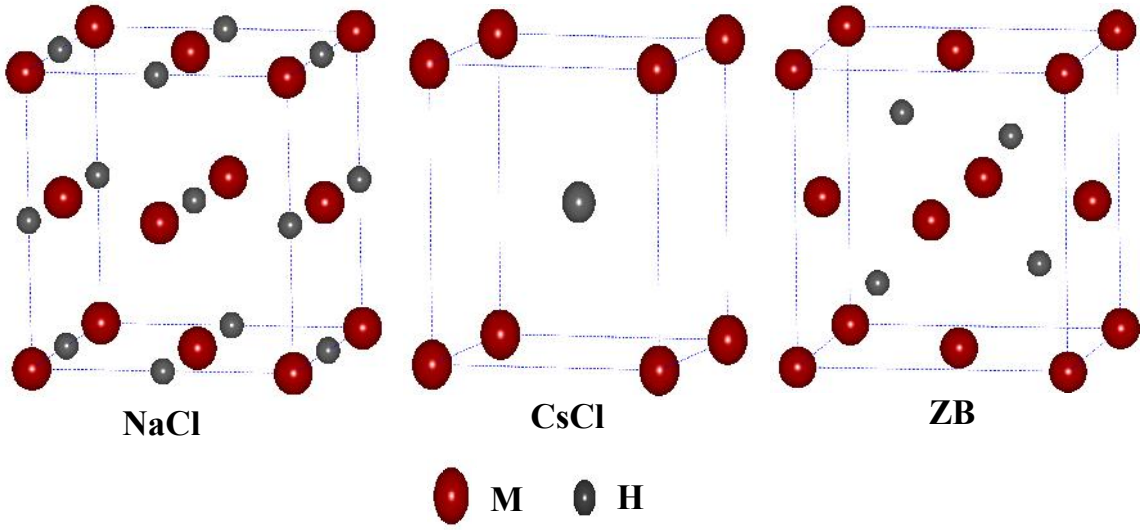

Fig. 1a The unit cell structures of the considered phases of pdh

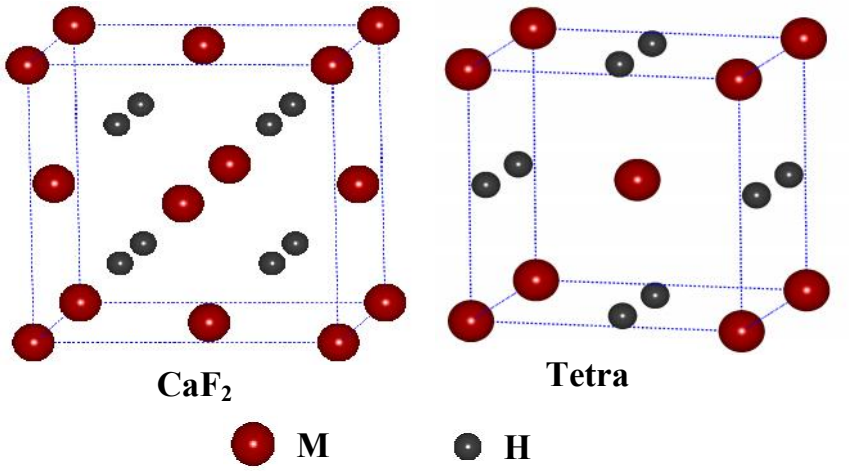

Fig. 1b The unit cell structures of the considered phases of PdH_2

3.2 Ground State Properties

The stability of mono and dihydrides of Pd are analyzed by computing the formation energy using the following relation

$$\Delta H_1 = E_{tot}(TMH) - E_{tot}(TM) - (1/2)E_{tot}(H_2) \quad (1)$$

$$\Delta H_2 = E_{tot}(TMH_2) - E_{tot}(TM) - E_{tot}(H_2) \quad (2)$$

where $E_{tot}(TMH_2)$ and $E_{tot}(TMH)$ are the energies of primitive cells of PdH_2 and PdH respectively. $E_{tot}(TM)$ and $E_{tot}(H_2)$ are the energies of a transition metal atom and a hydrogen molecule. The energy of the metal and metal hydride is calculated using VASP code, performed in the frame work of density functional theory using the generalized gradient approximation (GGA). The value of heat of formation ΔH for mono and dihydrides are calculated using Equation 1 and Equation

2 respectively. Valence electron density (VED) is defined as the total number of valence electrons divided by volume per unit cell.The computed lattice parameters a and c (Å), equilibrium volume V_0 (Å^3), valance electron density ρ (electrons/ Å^3) and cohesive energy E_{coh} (eV) for mono and dihydrides of Pd metal for different structures are given in Table 1 along with available data [18, 19].

Table 1 lattice parameters a and c (Å), EquilibriumV_0 (Å^3), Valence electron density (electrons/ Å^3) and cohesive energy E_c (eV)

	PdH			PdH_2	
	NaCl	ZB	CsCl	Cubic	Tetra
a	4.1440 4.07[18] 4.147[19]	4.2505	2.6746	4.475	3.7912
c	-	-	-	-	3.3552
V_0	17.820	19.240	19.130	22.40	23.46
ρ	0.6173	0.5717	0.5750	0.5357	0.5115
E_c	-4.048 -3.261[19]	-5.692	-4.02711	-4.6563	-4.0943

3.3 Structural Phase Transition

The total energy for the considered phases of mono and dihydrides of Pd is calculated as a function of reduced volume and their plots are given in Fig.2. It is noted that PdH and PdH_2 are stable in ZB and CaF_2 phases respectively. On further reducing the volume, a structural phase transition occurs from ZB to NaCl phase in PdH whereas PdH_2 is highly stable in the cubic (CaF_2) phase at ambient and as well at high pressures.

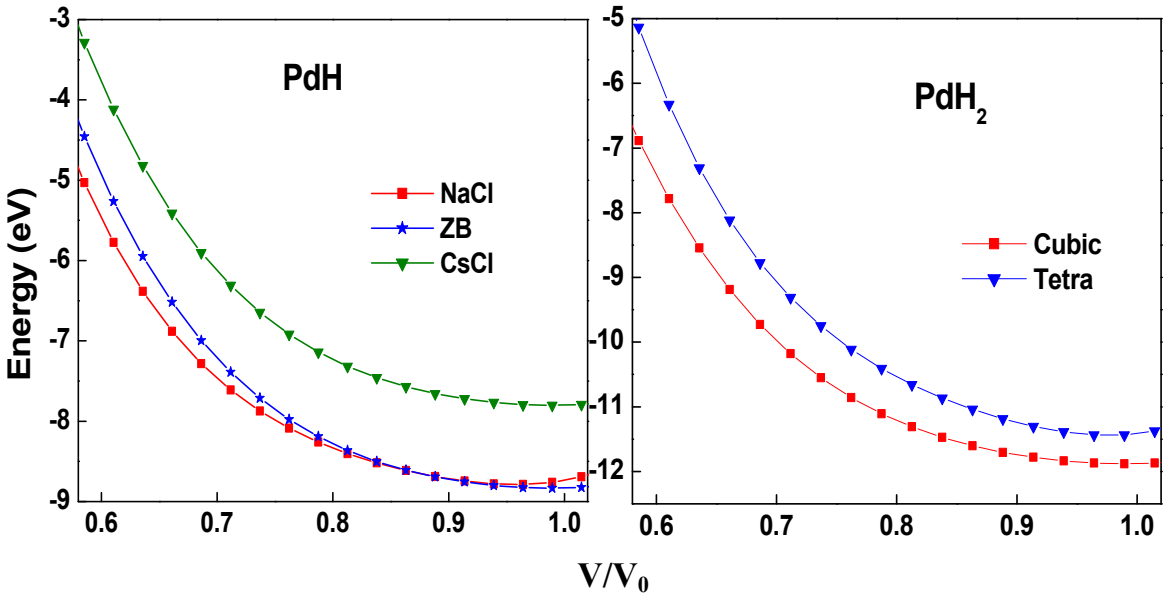

Fig.2 The total energy as a function of reduced volume for PdH and PdH_2

In order to determine the structural phase transition, enthalpy is calculated using the formula

$$H=E+PV \quad (3)$$

and is plotted in Fig.3. A pressure induced structural phase transition from ZB phase to NaCl phase is predicted at a pressure of 11GPa for PdH.

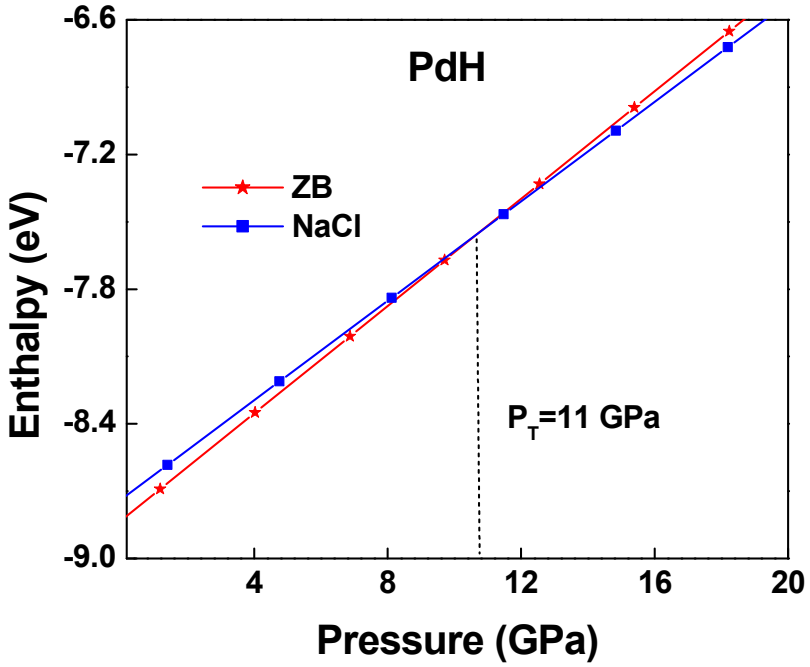

Fig.3 The enthalpy as a function of pressure of PdH

3.4 Elastic Properties

In order to calculate the elastic constants of a structure, a small strain is applied on to the structure and its stress is determined. The energy of a strained system [20, 21] can be expressed in terms of the elastic constants C_{ij} as:

$$\Delta E = \frac{E(\{e_i\}) - E_0}{V_0} = \left(1 - \frac{V}{V_0}\right)P(V_0) + \frac{1}{2}\left(\sum_1^6 \sum_1^6 C_{ij} e_i e_j\right) + O(\{e_i^3\}) \quad (4)$$

where V_0 is the volume of the unstrained lattice, E_0 is the total minimum energy at this unstrained volume of the crystal, $P(V_0)$ is the pressure of the unstrained lattice, and V is the new volume of the lattice due to strain tensor [21]. The elasticity tensor has three independent components (C_{11}, C_{12}, C_{44}) for cubic crystals. A proper choice of the set of strains $\{e_i$, i=1,2,…….,6$\}$, in Equation (4) leads to a parabolic relationship between $\Delta E/V_0$ ($\Delta E \equiv E - E_0$) and the chosen strain. Such choices for the set $\{e_i\}$ and the corresponding form for ΔE are shown in Table 2 for cubic [22]. For the stable structure of mono and dihydrides of Ni and Pd at normal pressure, the lattice was strained by 0%, ±1%, and ±2% to obtain their total minimum energies E (V). These energies and strains were fitted with the corresponding parabolic equations of $\Delta E/V_0$ as given in Table 2 to yield the required second-order elastic constants.

Table 2 Strain combinations in the strain tensor for calculating the elastic constants of cubic structures

Cubic crystals		
Strain	Parameters (unlisted e_i=0)	$\Delta E/V_0$
1	$e_1=e_2=\delta$, $e_3=(1+\delta)^{-2}-1$	$3(C_{11}-C_{12})\delta^2$
2	$e_1=e_2=e_3=\delta$	$(3/2)(C_{11}+2C_{12})\delta^2$
3	$e_6=\delta$, $e_3=\delta^2(4-\delta^2)^{-1}$	$(1/2)C_{44}\delta^2$

While computing these energies all atoms are allowed to relax with the cell shape and volume fixed by the choice of strains $\{e_i\}$. From the calculated C_{ij} values, the bulk modulus and shear modulus for the cubic crystals and hexagonal crystals are determined using the Voigt-Reuss- Hill (VRH) averaging scheme [23-25]. The strain energy $1/2C_{ij}e_ie_j$ of a given crystal in Equation (3) must always be positive for all possible values of the set $\{e_i\}$; for the crystal to be mechanically stable. The calculated elastic

constants C_{ij}(GPa),Young's modulus E(GPa), shear modulus G(GPa) and Poisson's ratio (v) are listed in Table 3. From tabulated values, it is found that most of the calculated elastic constants are in agreement with the available theoretical and experimental data [19, 26]. The small deviation in some elastic constants may be due to the small difference in the lattice constants calculated by different methods and also upon the various software packages used.

Table 3 Elastic moduli and elastic constants in GPa

	Pd	PdH	PdH_2
C_{11}	358.34	184.96 241.7[19]	197.67
C_{12}	206.70	130.2 190.3[19]	131.88
C_{44}	108.37	48.53 69.05[26] 25.5[19]	31.21
B	257.25	148.64 183.32[26]	153.81
G	95.35	40.01	31.88
E	254.59	110.16	89.47
v	0.335	0.38	0.40

The Born-Huang elastic stability criteria [27] for the cubic crystals are

$$C_{44} > 0,\ \ C_{11} > |C_{12}|,\ \ C_{11} + 2C_{12} > 0 \tag{5}$$

The computed values of the elastic constants for the rare earth metal hydrides satisfy Born-Huang criteria suggesting that all are mechanically stable. The Young's modulus (E) and the Poisson's ratio (v) values are two important factors necessary to find out the technological and engineering applications of a material. The Young's modulus (E) is given by

$$\mathrm{E} = \frac{9\mathrm{BG}}{(3\mathrm{B} + \mathrm{G})} \tag{6}$$

Poisson's ratio is associated with the volume change during uniaxial deformation, which is expressed as

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \tag{7}$$

The Debye temperature (θ_D) is the important parameter for determining the thermal characteristics of materials, which correlates many physical properties of materials, such as specific heat, elastic constants and melting temperature. The Debye temperature is defined in terms of the mean sound velocity ν_m and gives explicit information about the lattice vibrations [28] and it is calculated using the equation [29]

$$\theta_D = \frac{\hbar}{k_B}\left[6\pi^2 n \frac{N_A \rho}{M}\right]^{1/3} \nu_m \tag{8}$$

with $\hbar = h/2\pi$, h is Planck's constant, k_B is Boltzmann's constant, N_A is the Avogadro's number, ρ is density, M is molecular weight, n is the number of atoms in the molecule and

$$\nu_m = \left[\frac{1}{3}\left(\frac{2}{\nu_t^{\,3}} + \frac{1}{\nu_l^{\,3}}\right)\right]^{-1/3} \tag{9}$$

where

$$\nu_l = \left(\frac{B + 0.75G}{\rho}\right)^{1/2} \tag{10}$$

and

$$v_t = \left(\frac{G}{\rho}\right)^{1/2} \quad (11)$$

are the velocities of longitudinal and transverse sound waves respectively. The calculated values are listed in Table 4.

Table 4 Density ρ (g/cm^3), longitudinal velocity v_l (km/s), transverse velocity v_t (km/s), average velocity v_m (km/s) and Debye temperature θ_D (K) for mono and dihydrides of Pd

	Pd	PdH	PdH_2
ρ	12.007	9.267	8.034
v_l	5.644	4.645	4.943
v_t	2.797	2.038	1.992
v_m	3.139	2.301	2.256
θ_D	381.59	322.25	343.74

3.5 Electronic Structure

In order to understand the electronic structure, total density of states (DOS) for the transition metal (Pd) and for the stable structure of mono and dihydrides of Pd are given in Fig.4. The Fermi level is indicated by a dotted vertical line. In the mono-hydrides, the hydrogen character is isolated within the lowest peak, which is a single occupied band holding two electrons. This lowest band possesses significant hydrogen character, in addition to a characteristic free electron tail and some metal character. Along the series, the number of electrons in the d-state increases steadily with the increase in the atomic number. These results indicate that a strong hybridization between the H-1s and M-d states. The central part of the density of states (DOS) is characterized by two regions. The lower region arises from the hybridization of p and d states of the transition metal, and the upper region is highly dominated by 4d states. The valence states are separated by a wide gap from the occupied states, indicating covalent behavior. Above the Fermi level the empty conduction states are present with a mixed s, p, and d characters. Therefore at ambient pressure all these three hydrides show metallic behavior.

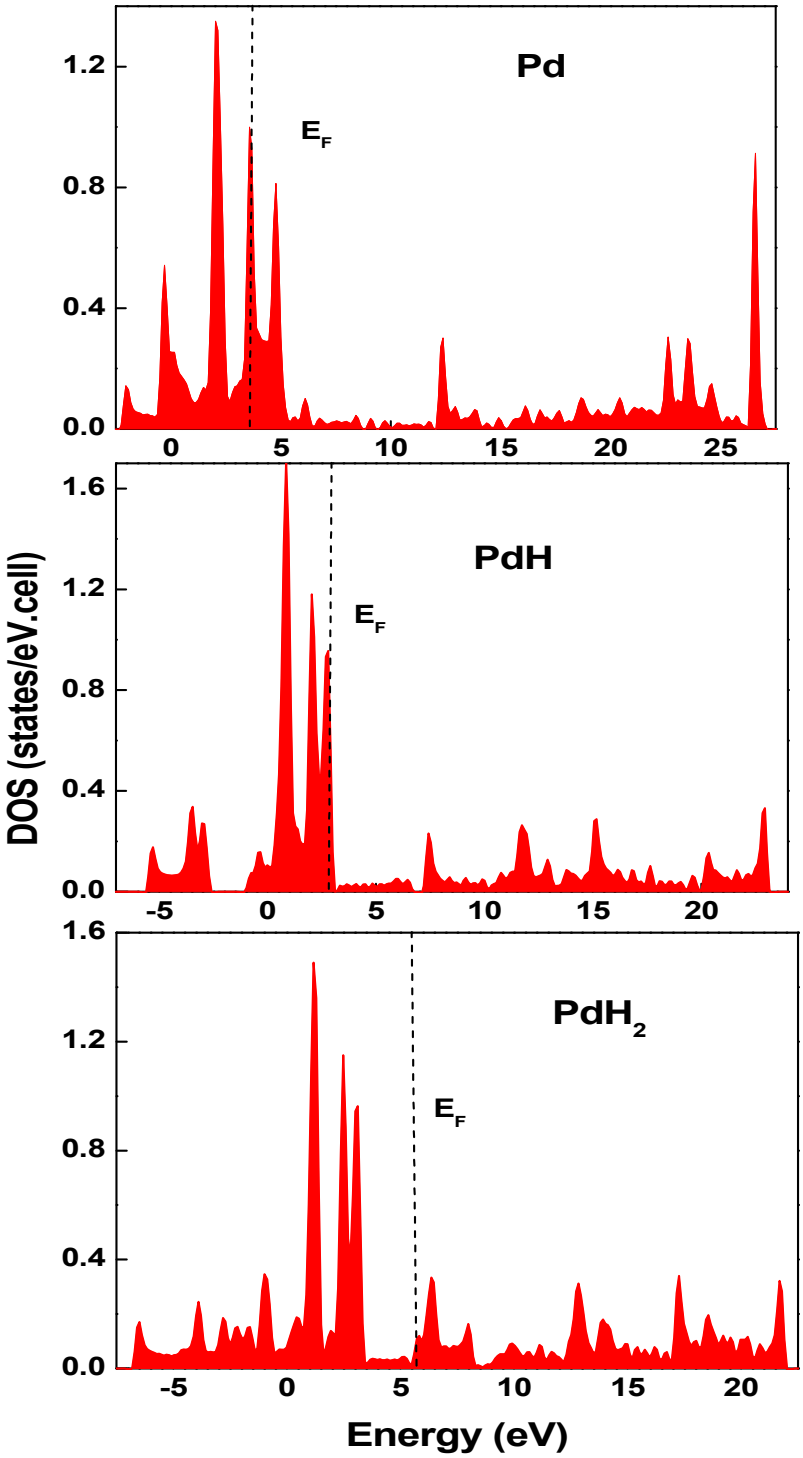

Fig.4 Density of States of Pd metal, mono and dihydrides of Pd at normal pressure

3.6 Charge Density Analysis

The charge density distribution for PdH and PdH_2 containing M^+ and H^- ion is shown in Fig.5. It is observed that the voids (i.e charge depletion regions) are narrow between H ions and broad between the metal ions. On increasing the M-ion atomic number the M-H bonding becomes stronger and these voids change their shape. It is also found that the light colored areas indicate electron gain, whereas

the darker areas indicate electron loss. Because the electron gain on hydrogen is so much greater than on the transition metal, the minimum and maximum values of electron gain and loss were truncated, in order to keep enough resolution around the transition metals. Electron gain on the hydrogen position is substantial, indicating that the hydrogen does not insert as a bare proton. Near the transition metal there are both regions of positive and negative charge difference, corresponding to the loss or gain of *d* occupation. Significant loss off d state electrons is observed, which is due to the formation of a bonding-antibonding pair between the direct overlapping of hydrogen *s* with metal *d* orbitals. A more detailed understanding of which *d* orbital's gain occupation can be obtained from the total density of states. It is clearly seen that charge strongly accumulates between Pd and H atoms, which means that a strong directional bonding exists between them. We can also see that the charge around the Pd site is very much d-like, while that around H site is s-like.

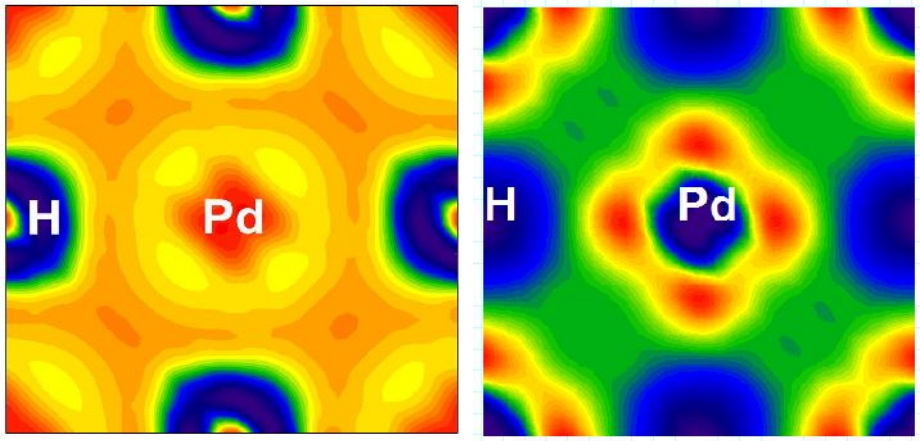

Fig.5 Charge density distribution of mono and dihydrides of Pd

3.7 Superconducting Transition Temperature (T_c K)

One of the important applications of the electronic structure calculations is the determination of the electron-phonon coupling constant, which in turn can be used to estimate the superconducting transition temperature T_c. The superconducting transition temperature is estimated by using the McMillan equation modified by Allen and Dynes [30],

$$T_c = \frac{\omega_{\log}}{1.2}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \quad (12)$$

where λ is the electron- phonon coupling constant, μ* is the electron - electron interaction parameter and ω_{log} is the average phonon frequency. The average of the phonon frequency square is,

$$<\omega\log^2> = 0.5\,\theta_D^2 \quad (13)$$

The variation of θ_D with pressure in terms of 'E_F' and the lattice constant 'a' is given as,

$$\theta_D(P) = \frac{\sqrt{E_F}}{\sqrt{E_F{}^o}}\frac{a_o}{a}\theta_D \quad (14)$$

But, in this case θ_D is taken as constant for various pressures. $\theta_D{}^o$, a^o and $E_F{}^o$ are Debye temperature, lattice constant and Fermi energy corresponding to normal pressure. The electron - phonon coupling constant λ can be written as [31]

$$\lambda = \frac{N(E_F)<I^2>}{M<\omega^2>} \quad (15)$$

where N (E_F) is the density of states at the Fermi energy. M is the atomic mass.
$<I^2>$ is the square of the electron - phonon matrix element averaged over the Fermi energy. $<I^2>$ (in Rydbergs) can be written as [32],

$$< I^2 >= 2\sum_l \left\{ \frac{(l+1)}{(2l+1)(2l+3)} \right\} M^2{}_{l,l+1} \left\{ \frac{N_l(E_F) N_{l+1}(E_F)}{N(E_F)^2} \right\} \quad (16)$$

where $M_{l,\ l+1}$ are the electron-phonon matrix elements which can be expressed in terms of the logarithmic derivatives.

$$D_l = \left. \frac{d \ln \phi_l}{d \ln r} \right|_{r=s} \quad (17)$$

is evaluated at the sphere boundary,

$$M_{l,l+1} = -\phi_l \phi_{l+1} \left[(D_l(E_F) - 1)(D_{l+1}(E_F) + l + 2) + (E_F - V(S))S^2 \right] \quad (18)$$

where Φ_l is the radial wave function at the muffin-tin sphere radius corresponding to the Fermi energy. The logarithmic derivative of the radial wave function at the sphere boundary (D_l), the muffin-tin potential at the sphere boundary (V(S)) and the radius of the muffin-tin sphere (S) are taken from the output of TB-LMTO program.

The electron – electron interaction parameter μ* is estimated using the relation [33],

$$\mu^* = \frac{0.26 N(E_F)}{(1 + N(E_F))} \quad (19)$$

The calculated λ, μ* and T_c values for PdH and PdH_2 at normal pressure is given in Table 5. The estimated superconducting Transition Temperature (T_c) is 8.86 K for PdH. It is compared with the available experimental and theoretical work [34, 35, 5].

Table 5 λ, μ* and T_c values for mono and dihydrides of Pd

	PdH			PdH_2		
	λ	μ*	T_c(K)	λ	μ*	T_c(K)
Present	0.378	0.083	8.86	1.007	0.047	18.78
Expt.			8.0[34]			
			9.1[35]			
Others	0.54[5]	0.085[5]	7.9[5]			

4. CONCLUSION

The structural, electronic and elastic properties of mono and dihydrides of Pd are investigated in detail based on first-principles calculation. Our results suggest that PdH is stable in ZB phase and PdH_2 is highly stable in the CaF_2 phase at normal pressure. A pressure induced structural phase transition from ZB phase to NaCl phase for PdH is predicted at a pressure of 11GPa. The calculated superconducting Transition Temperature of PdH and PdH_2 is 8.86K and 18.76 at normal pressure.

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