Mechanical and electronic properties of van der Waals layered hcp PdH$_2$

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Mechanical and electronic properties of palladium dihydrides (PdH$_2$) as a function of pressure were studied by ab initio calculations based on density functional theory (DFT). The ab initio random structure searching technique was employed for screening potential PdH$_2$ crystal structures under high pressure. A hexagonal close packed (hcp) phase of PdH$_2$ with space group P6$_3$mc was reported. The structure geometry and elastic constants were calculated as a function of pressure. It was found that H atoms are in the interstitial position of Pd atoms layer at 0 GPa. There is an electronic topology transition of hcp PdH$_2$ at 15 GPa. When pressure exceeds above 15 GPa, one hydrogen atom occupies the tetrahedral site and another hydrogen atom locates in the interstitial position. When the c/a ratio is between 1.765 to 1.875, the hcp PdH$_2$ is mechanically stable, and the Pd-H$_2$ bond is the major factor that limits the mechanical stability. The elastic constant $C_{44}$ is the first one that cannot satisfy the mechanical stability criteria under pressure. The anisotropy parameters are far from 1(one) shows that the hcp PdH$_2$ is a highly anisotropic structure. The electronic structure study indicates that the bonding force between Pd and H atoms along the z-axis direction increases with the increasing pressure. Also, the phonon dispersion study shows that PdH$_2$ is dynamic stability under pressure. The results suggest that hcp PdH$_2$ can be metastable in van der Waals layered structure.

Metal hydride (M-H) systems have attracted a lot of attention because of their properties, such as high hydrogen-storage capacity, fast hydrogen absorption/desorption, long-term cycle life and low toxicity$^1$. Palladium-hydrogen (Pd-H) is used to be a system to understand the hydrogen atoms bonding with the metal host lattice in the M-H systems. The phase diagram and electronic properties of Pd-H have been used as a prototype in other M-H systems$^2$. Some applications of Pd-H system have been investigated. The palladium can absorb hydrogen at ambient conditions and the dissociative adsorption of H$_2$ molecules occurs with little or no activation energy barrier on the palladium surface. The reversible hydrogen absorption property can be used for hydrogen storage$^3$. Increasing the hydrogen concentration will cause volume expansion of PdH$_x$. Based on this mechanism, a Pd based H$_2$ sensor was used to measure the hydrogen concentration$^4$. Due to the dissociative properties of H, Pd-H can be used for hydrogen-related catalytic reactions$^5$.

The hydrogen concentration affects the superconductivity of Pd-H system. PdH$_x$ is a superconductor and the transition temperature $T_c$ increased with the increase of H concentration$^x$. For the H/Pd is 0.81, a $T_c$ = 1.3 K was observed. At the highest concentration ratio of about 1.0, the $T_c$ to the superconducting state higher than 8.0 K$^7$. Recently Syed et al. found that by rapidly cooling the hydride after loading with hydrogen at elevated temperature, the $T_c$ has a remarkable increase to 54 K when the H/Pd is about 1$^6$. Tripodi et al.$^9$ have shown that, when the H/Pd is up to 1.6, the $T_c$ can go up to room temperature. Hence, the PdH$_2$ could be considered as a possible room temperature superconductor.

The hydrogen concentration also affects the characteristics of the Pd-H system including mechanical, hydrogen storage capability and superconductivity$^{10}$. The hydrogen storage capacity of the Pd-H system increases with the increase of H concentration. For the stoichiometry PdH, palladium can absorb 935 times its volume in hydrogen gas$^{11}$. Neutron diffraction study has been performed for PdH$_x$ system. The maximum hydrogen concentration is 0.7 at room temperature and normal pressures$^{12}$. It was found that the hydrogen reduces the compression resistance in Pd-H$^{13}$, in which bulk modulus decreases from 195 GPa to 183 GPa with the increase
Pd atoms are positioned at 2b (1/3 2/3 z) and H atoms occupy the 2a (0 0 z) and 2b (1/3 2/3 z) site. The atomic hcp PdH2 at 0 GPa is shown in Fig. 2(a). The inexistence of imaginary frequencies indicates the dynamic stability compared with monohydride. Experiments show that PdH increases with the increase of pressure, except for the P63mc structure at 15 GPa as shown in Fig. 2(b). The reason for the discontinuity of zero energy is that the hcp PdH2 undergoes an isostructural phase transition when the pressure is increased to 3 GPa or higher than 95 GPa. The hcp PdH2 relative to Fm3m structure at all pressures. An energy minimum structure is confirmed. It is an hcp structure, and the space group is P63mc. The structural parameters of hcp and fcc PdH2 are discussed as a function of pressure. The elastic constants of hcp PdH2, as a function of pressure are obtained through ab initio calculations using the stress-strain method. The electronic structure of hcp PdH2 is also analyzed by band structure and DOS projected on atoms and orbitals. From the obtained results, the mechanical and electronic properties of the PdH2 are analyzed.

**Results and Discussion**

**Crystal structure.**  A global energy minimum phase of PdH2 structure was found by ab initio random structure searching technique as shown in Fig. 1. It is an hcp structure with the space group P63mc. In this structure, Pd atoms are positioned at 2b (1/3 2/3 z) and H atoms occupy the 2a (0 0 z) and 2b (1/3 2/3 z) site. The atomic symmetry of both Pd and H atoms is 3m. As shown in Fig. 1(a), at 0 GPa, Both of H atoms 2a sites (H2a) and 2b sites (H2b) are three-coordinated with Pd atoms. As the pressure increases above 15 GPa (see in Fig. 1(b)), the coordination number of H3 atoms with Pd atoms increased to four.

For comparison, the fcc PdH2 with the space group Fm3m and F43m were considered. In the Fm3m structure, Pd and H atoms are located at the Wyckoff positions 4a (0 0 0) and 8c (1/4 1/4 1/4). The atomic symmetries of Pd and H atoms are 3m and m3m, respectively. The 8c H (H8) atom occupy two tetrahedral (T) sites. In the F43m structure, Pd atoms located at the Wyckoff positions 4a (0 0 0) and the H atoms occupy the 4b (1/2 1/2 1/2) and 4c (1/4 1/4 1/4) site. The atomic symmetries of Pd and H atoms are 3m. The 4b H (H4b) and 4c H (H4c) atoms occupy octahedral (O) sites and T sites, respectively. The enthalpy differences ∆H for Pd6 mc and F43m PdH relative to Fm3m PdH2 are obtained. Figure 2 shows the enthalpy difference ∆H including zero-point energy and zero-point energy as a function of pressure. The ∆H takes positive values for the F43m structure at all studied pressure indicating that the F43m structure is unstable than the Fm3m structure. At the pressure lower than 3 GPa or higher than 95 GPa, ∆H of Pd6 mc structure takes negative values. It suggests that the hcp structure is more stable than the F43m structure in these pressure ranges. Phonon dispersion in the whole Brillouin zone of hcp PdH2 at 0 GPa is shown in Fig. 2(a). The inexistence of imaginary frequencies indicates the dynamic stability of the phases at 0 GPa.

The zero-point energy (ZPE) of the system is defined as the free energy of the system at 0 K. To improve accuracy, the zero point vibration energy was corrected in the energy calculations. The zero-point energy monotonous increase with the increase of pressure, except for the P63mc structure at 15 GPa as shown in Fig. 2(b). The reason for the discontinuity of zero energy is that the hcp PdH2 undergoes an isostructural phase transition when the pressure is about 15 GPa. The detailed discussion is carried out in the later discussion on structural parameters. The results show that the P63 mc PdH2 is, in fact, a different phase under pressure. For comparison, we have included the hcp P63mc and fcc Fm3m structures in the subsequent calculations of the structural parameters.
The structural parameters of PdH$_2$ can be obtained by full relaxation of the structure. Figure 3 shows the structural parameters as a function of pressure.

The bond angle of Pd–H–Pd as a function of pressure is shown in Fig. 3(a). At 0 GPa, the inlayer angles Pd–H$_{2a}$–Pd and Pd–H$_{2b}$–Pd of hcp structure are smaller than the angle Pd–H$_{8c}$–Pd of fcc structure, the interlayer angle Pd–H$_{2b}$–Pd is bigger than the Pd–H$_{8c}$–Pd. When the pressure is less than 15 GPa, the inlayer and the interlayer Pd–H$_{2b}$–Pd angles have a slight change with the increase of pressure. All the Pd–H–Pd bond angles changed significantly at 15 GPa due to the influence of the interlayer bonding force. The Pd–H$_{2a}$–Pd has a sharp increase at 15 GPa which makes it bigger than the Pd–H$_{8c}$–Pd. The hcp lattice parameter a has a slight increase at 15 GPa. As the pressure increases, the distance between Pd and H atoms decreases, the c/a ratio of hcp structure decreases, and the lattice parameter c increases. The distance between two H atoms increases with the increase of pressure.

Figure 2. The enthalpy differences and zero-point energy as a function of pressure (a) $\Delta H$ for hcp and F43m PdH$_2$ relative to Fm3m PdH$_2$; (b) zero-point energy.

Figure 3. Structural parameters of PdH$_2$ as a function of pressure: (a) bond angle of Pd–H–Pd; (b) distance between Pd and H atoms; (c) c/a ratio of hcp structure and lattice parameter a and c; (d) distance between two H atoms.
the PdH₂ is further compressed, the inlayer Pd-H₂-Pd and interlayer Pd-H₂-Pd decrease and inlayer Pd-H₂-Pd increases. The H₂ atom occupies the ideal T sites at 115 GPa. Figure 3(b) shows the distance between Pd and H as a function of pressure. The Pd-H distance decreases with the increase of pressure. The Pd-H₂ distance and Pd-H₂ distance are equal to 1.87 Å and less than the Pd-H₂ distance which is 2.00 Å at 0 GPa. When the pressure is lower than 15 GPa, the Pd-H₂ and Pd-H₂ are similar in size. In addition, Pd-H₂ and Pd-H₂ are still less than the Pd-H₂. Pd-H₂ is smaller to the Pd-H₂ and the difference for Pd-H₂ relative to Pd-H₂ increases with the increase of pressure. When the pressure exceeds 15 GPa, the Pd-H₂ is similar to the Pd-H₂ in size. The Pd-H₂ is larger than the Pd-H₂, and the difference for Pd-H₂ relative to Pd-H₂ decreases with the increase of pressure. The interlayer Pd-H₂ distance is almost two times bigger than Pd-H₂ and Pd-H₂ at 0 GPa. The interlayer bonding force between Pd and H is very weak. When the external pressure is applied, the c-axis is rapidly compressed. The interlayer bonding force between Pd and H increases with the increase of pressure. The interlayer bonding force between Pd and H increases significantly around 15 GPa. All of the Pd-H distance tends to 1.7 Å as the pressure up to 150 GPa.

As is shown in Fig. 3(c), the c/a ratio decreases dramatically from 2.718 to 1.875 with the increase of pressure from 0 GPa to 15 GPa. As the PdH₂ is further compressed, the decrease of c/a ratio becomes slower with the increase of pressure. This indicates that the interlayer bonding force between Pd and H atoms is significantly enhanced when the pressure reaches above 15 GPa. The c/a ratio almost tends to an ideal value of 1.613 as the pressure exceeds 100 GPa. The c/a ratio changes with the pressure, indicating that the hcp PdH₂ is highly anisotropic. The lattice parameter a of both hcp and fcc PdH₂ decreases with the increase of pressure, except a slight increase at around 15 GPa. When pressure is lower than 15 GPa, the c decreases rapidly compared to a with the increase of pressure. With further increase in pressure, the decrease of c becomes slower. Pressure affects the distance between the two H atoms. As is shown in Fig. 3(d), the H-H distance decreases with the increase of pressure. The hcp H₂-H₂ distance is always less than fcc H₂-H₂ distance. The H₂-H₂ distance is closer to H₂-H₂ distance at a pressure below 15 GPa than the pressure above 15 GPa.

Discontinuous change of bond length, bond angle, c/a, lattice parameter a, and the crystal symmetry remains unchanged at 15 GPa, indicating that there is an isostuctural phase transition of hcp PdH₂. For hcp PdH₂, a = 2.973 Å and c/a = 2.718 at 0 GPa and a = 3.034 Å and c/a = 1.875 at 15 GPa.

**Mechanical properties.** Elastic constants are the quantities to characterize the elasticity of materials which determine the response of materials to external forces. Elastic constants Cᵢⱼ of hcp PdH₂ as a function of pressure are listed in Table 1. It shows that all of the Cᵢⱼ increases monotonously with the increase of pressure. The magnitude of all the C₁₁, C₁₂, C₁₃ and C₃₃ are greater than the magnitude of the applied pressure except for the C₄₄. The smaller increasing rate in the value of C₄₄ leads to that the shear deformation increase faster than before with the increase of pressure. It implies that the pressure reduces the stability of the structure.

| P (GPa) | C₁₁ (GPa) | C₁₂ (GPa) | C₁₃ (GPa) | C₃₃ (GPa) | C₄₄ (GPa) |
|--------|----------|----------|----------|----------|----------|
| 0      | 154.8    | 54.3     | 14.2     | 21.0     | -3.8     |
| 5      | 187.3    | 73.0     | 42.9     | 46.1     | -2.2     |
| 10     | 213.4    | 92.0     | 66.3     | 61.8     | 0.9      |
| 15     | 229.5    | 148.5    | 111.3    | 116.0    | 20.2     |
| 20     | 248.2    | 162.8    | 128.7    | 148.1    | 24.2     |
| 50     | 354.0    | 241.9    | 202.5    | 250.7    | 37.2     |
| 100    | 483.4    | 361.0    | 302.7    | 442.3    | 46.8     |
| 150    | 588.2    | 482.3    | 427.3    | 558.3    | 58.1     |

Table 1. Elastic constants Cᵢⱼ (GPa) of PdH₂ as function of pressure P (GPa).

| P (GPa) | C₁₁ (GPa) | C₁₂ (GPa) | C₁₃ (GPa) | C₃₃ (GPa) | C₄₄ (GPa) |
|--------|----------|----------|----------|----------|----------|
| 0      | 154.8    | 54.3     | 14.2     | 21.0     | -3.8     |
| 5      | 187.3    | 73.0     | 42.9     | 46.1     | -2.2     |
| 10     | 213.4    | 92.0     | 66.3     | 61.8     | 0.9      |
| 15     | 229.5    | 148.5    | 111.3    | 116.0    | 20.2     |
| 20     | 248.2    | 162.8    | 128.7    | 148.1    | 24.2     |
| 50     | 354.0    | 241.9    | 202.5    | 250.7    | 37.2     |
| 100    | 483.4    | 361.0    | 302.7    | 442.3    | 46.8     |
| 150    | 588.2    | 482.3    | 427.3    | 558.3    | 58.1     |
When the pressure is lower than 13 GPa or higher than 29 GPa, the slip of PdH$_2$ will occur between the \{001\} plane. The projection of Pd-H$_2$\textsuperscript{a} and Pd-H$_2$\textsuperscript{b} bond in the \{001\} plane is along the [120] and [110] direction. The strain along the [120] and [110] direction is related to $C_{11}$ and $C_{11} - C_{12}$. Therefore, the Pd-H$_2$\textsuperscript{b} bond is the major factor that limits the mechanical stability of hcp PdH$_2$.

Elastic anisotropic is also a fundamental parameter regarding mechanical properties. In this work, the $c/a$ value changes with pressure. It means that the structure is always varying with the applied pressure. When the $c/a$ value is in 1.765–1.875, the PdH$_2$ is mechanically stable. Here, we have discussed the anisotropy parameters of PdH$_2$ with $c/a$ 1.827. For an isotropic medium, $\Delta P = \Delta S_1 = \Delta S_2 = 1$. PdH$_2$ is anisotropic. For PdH$_2$, the compressional anisotropy $\Delta P = 0.60$. The PdH$_2$ is more easily compressed in the [001] direction than the [100] direction. The shear anisotropy $\Delta S_1$ and $\Delta S_2$ are 1.43 and 0.57, respectively. Due to the small $C_{44}$, the shear anisotropy is large. It indicates that the largest shear deformation occurs in \{100\} plane and the slip is most likely to occur between planes parallel to \{001\} plane. All the anisotropy parameters are far away from 1(one), which means that the hcp PdH$_2$ is highly anisotropic. The results indicate that the Pd-H bonds are stronger in the layer which is parallel to the \{001\} plane than between the layers.

**Table 2.** The calculated bulk modulus $B$ (in GPa), shear modulus $G$ (in GPa), $B/G$, Young’s modulus $E$ (in GPa) and Poisson’s ratio $\nu$ of PdH$_2$ as a function of pressure $P$ (in GPa).

| $P$ (GPa) | $B$ (GPa) | $G$ (GPa) | $B/G$ | $Y$ (GPa) | $\nu$ |
|-----------|-----------|-----------|-------|-----------|-------|
| 0         | 37.8      | 6.4       | 5.9   | 18.2      | 0.42  |
| 5         | 64.0      | 11.0      | 5.8   | 31.1      | 0.42  |
| 10        | 82.9      | 16.1      | 5.2   | 45.3      | 0.41  |
| 15        | 131.0     | 27.7      | 4.7   | 77.7      | 0.40  |
| 20        | 154.6     | 31.7      | 4.9   | 89.1      | 0.40  |
| 50        | 242.4     | 45.8      | 5.3   | 129.3     | 0.41  |
| 100       | 369.2     | 58.9      | 6.3   | 167.9     | 0.42  |
| 150       | 488.2     | 59.3      | 8.2   | 171.9     | 0.44  |

**Figure 4.** The mechanical stability criteria of hcp PdH$_2$. The fill parts indicate that the stability condition is satisfied.

1.875. When the pressure is lower than 13 GPa or higher than 29 GPa, the slip of PdH$_2$ will occur between the \{001\} plane.

The projection of Pd-H$_2$\textsuperscript{a} and Pd-H$_2$\textsuperscript{b} bond in the \{001\} plane is along the [120] and [110] direction. The strain along the [120] and [110] direction is related to $C_{11}$ and $C_{11} - C_{12}$. Therefore, the Pd-H$_2$\textsuperscript{b} bond is the major factor that limits the mechanical stability of hcp PdH$_2$.

Electronic structure. The fat band along the high-symmetry directions of the BZ for PdH$_2$ at different pressure are shown in Fig. 5. The d-band on Pd atom has the main contribution to the electronic structure. The flat bands near the Fermi level suggest that the hcp PdH$_2$ is potential superconducting material. The band moves to lower energy with the increase of pressure. It also shows that two type-I Dirac point appears at K and H high-symmetry points indicating that the hcp PdH$_2$ is a topological-like structure. When the pressure increase from 0 GPa to 15 GPa, the gap between Dirac point appears. As the pressure increases from 0 GPa to 15 GPa, the flat band of H$_{16}$ and H$_{17}$ along $\Gamma$ to A point move from $-1.00$ to 0.93. The anti-bonding was formed at 15 GPa.

This sudden change in electronic structure at 15 GPa is due to the electronic topological transition of Fermi surface morphology. There are flat bands along with the high-symmetry directions [100] and [110] in the BZ. With the increase of pressure, the flat bands move to high energy because the partially occupied Pd 4d states were excited to a higher energy state. The flat bands move to the Fermi level at 40 GPa. When the pressure is higher than 40 GPa, the flat bands move across the Fermi level.

The density of states (DOS) projected on atoms and orbitals for PdH$_2$ at different pressure is shown in Fig. 6. This figure shows a pressure-induced metal to semimetal transition in the PdH$_2$. It is seen that the Pd 4d states
have the main contribution to the total DOS at around Fermi level. The H$_2$ a 1s and H$_2$ b 1s states have a similar contribution to the DOS at around the Fermi level at 0 GPa, as shown in Fig. 6 (0 GPa).

Applied pressure reduces the distance between two layers of PdH$_2$. As is shown in Fig. 6 (15 GPa), the interaction between Pd and H due to the two peaks at around the Fermi level. The Pd d$_{z^2}$ states produce the main contribution to the DOS at around Fermi level. Above the Fermi level, the first peak shows that the H$_2$ b 1s states contribute more to DOS than the H$_2$ a 1s states. The first peak below the Fermi level shows that the H$_2$ a 1s and H$_2$ b 1s states almost have the same contribution to the DOS. The Pd d$_{z^2}$ states interact with the H 1s states lead to an increase in interlayer bonding force between Pd and H.

The peaks around the Fermi level move towards the Fermi level as the increase of pressure. As can be seen in Fig. 6 (40 GPa), the peak is on the Fermi level. This peak is derived from the flat zone along with the high-symmetry directions [100] and [110] in the Brillouin zone. It suggests that the hardness of the material is strengthened.

As the PdH$_2$ is further compressed, as in Fig. 6 (70 GPa), the peak moves above the Fermi level. The DOS has a minimum value at the Fermi level. The results show a phase transition from metal to semimetal in the PdH$_2$ under pressure.

The DOS of both H$_2$ a and H$_2$ b 1s states are flat at around Fermi level at 0 GPa. However, they are not flat as the PdH$_2$ is compressed. When the pressure was applied, some small peaks for H 1s states can be found at around Fermi level because of the Pd 4d states interact with other states. Hybridization of Pd d$_{z^2}$ states and H 1s states increases the bonding force between layers of PdH$_2$. These results indicate that the PdH$_2$ is more stable under pressure than at 0 GPa.

Conclusions

In conclusion, a palladium hydride (PdH$_2$) with high hydrogen concentration is reported. The mechanical and electronic properties of PdH$_2$ were investigated by the ab initio calculations. We have reported elastic parameters such as bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio within Hill approximation. It has been found that the hcp PdH$_2$ is mechanically stable when the c/a ratio is between 1.765 to 1.875. The Pd-H$_2$ bond is the major factor that limits the mechanical stability of this structure. The analysis of mechanical stability and anisotropy also shows that the interatomic forces of hcp PdH$_2$ are weaker between the layers which is parallel to the [001] plane than in the layer. Therefore, the cause of PdH$_2$ structural instability is the slip between [001] planes. Our study shows that the PdH$_2$ is dynamic stable at 0 GPa and the interatomic forces between layers increases with the increase of pressure. The results also show that there is an electronic topology transition of hcp PdH$_2$ at 15GPa. Our results suggest that PdH$_2$ can be stabilized in a metastable form.

Figure 5. Electronic fat band for PdH$_2$ at the different pressure. The Fermi level is set to be at zero. The size of the symbol represents the weight of projection on orbitals.
Methods. The structural and elastic constants of PdH$_2$ have been studied by performing first principles calculations. The calculations were achieved based on the density functional theory (DFT)$^{23}$. The ab initio random structure searching technique$^{24}$ was used to find potential PdH$_2$ crystal structures at ambient and high pressure. The random search study was performed at 0, 50, and 100 GPa, with 1, 2, 3, and 4 PdH$_2$ units per simulation cell. The ab initio random structure searching technique generated unit cells of random shapes with reasonable volumes by calculating the ground state structure as well as determining the positions of PdH$_2$ formula in the cells. A plan-wave basis-set energy cutoff of 260 eV and an initial Brillouin Zone (BZ) sampling grid of $2\pi \times 0.07$ Å$^{-1}$ were found to be sufficient for the initial searches. The generalized gradient approximation (GGA) with the

Figure 6. DOS projected on atoms and orbitals for PdH$_2$ at the different pressure. The Fermi level is set to be at zero.
Perdew-Burke-Ernzerhof (PBE)\(^\text{25}\) parameterization for the exchange-correlation functional and ultrasoft pseudopotential\(^\text{26}\) were used for the structure searches by CASTEP code\(^\text{27}\).

The stable structure of PdH\(_2\) was studied by ab initio lattice dynamics with a supercell approach, as implemented in the Vienna ab initio Simulations Package (VASP) code\(^\text{28}\) and the phonopy package\(^\text{29}\). The structure was done using the projector augmented-wave (PAW)\(^\text{30}\) method and GGA was used to describe the electronic exchange-correlation effects. The calculation used \(2 \times 2 \times 2\) supercells, with consisting of 48 atoms, for P\(_6\)/mc PdH\(_2\) by using a plane-wave basis-set energy cutoff of 700 eV and sampling the BZ with fixed k-mesh \(13 \times 13 \times 4\).

The geometry relaxation and elastic constants calculations were performed using the VASP code. The exchange-correlation functional was described within the GGA of PBE. The outer electron configuration is \(4p^{6}5s^{1}4d^{10}\) for Pd. The plane-waves kinetic energy cut-off was set to be 900 eV. The “High” precision setting was used to avoid wrap around errors in the calculations. The vdW-DF\(^\text{31}\) functional was used to include the van der Waals interactions in the PBE functional. In a weakly bonded layered system, this function can calculate accurately equilibrium spacing and binding energy compare to the vdW-DF function\(^\text{32}\). The van der Waals (vdW) forces include attraction and repulsions between atoms, molecules, and surfaces, as well as other intermolecular forces. They differ from covalent and ionic bonding in that they are caused by correlations in the fluctuating polarizations of nearby particles. For the sparse systems, including soft matter, van der Waals complexes, and layered materials, which have interparticle separations, the vdW forces are important for the interactions of nonlocal and long-ranged.

For the structural optimization and self-consistent calculations, the energy and forces convergence criterion of the electronic self-consistency were chosen as \(10^{-4} \text{ eV}\) and \(10^{-3} \text{ eV/Å}\) per atom. The k-meshes were generated automatically to divide the BZ in each direction. A k-mesh \(17 \times 17 \times 17\) was generated by Gamma method for fcc PdH\(_2\) and a \(22 \times 22 \times 22\) was generated by Monkhorst-Pack method for fcc PdH\(_2\). These settings ensure a high convergence of 1 meV per unit cell in the total energy and accurate values of the forces in the atoms. For calculations of the hcp PdH\(_2\), electronic band and DOS, the k-mesh was increased to \(27 \times 27 \times 27\).

Ab initio calculations were performed for enthalpies as a function of pressure. The enthalpy \(H\) at 0 K can be obtained by using the expression:

\[
H = E_0 + E_{ZPE} + PV
\]  

where \(E_0\) is the total energy, \(E_{ZPE}\) is the zero-point energy, \(P\) is the hydrostatic pressure and \(V\) is the volume.

For the hcp PdH\(_2\), the elastic constants were calculated by using VASP software based on the strain-stress approach\(^\text{33}\). The number of k-mesh was increased to \(27 \times 27 \times 27\) for elastic constants calculations. A 0.01 Å positive and negative displacement was applied for each atom. For an hcp crystal, there are five independent elastic constants, \(C_{11}, C_{12}, C_{44}, C_{33}\) and \(C_{14}\). According to Hooke’s law, the stress-strain relationship can be written as:

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\tau_{12} \\
\tau_{23} \\
\tau_{13}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix} \begin{bmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\gamma_{12} \\
\gamma_{23} \\
\gamma_{13}
\end{bmatrix}
\]

where \(C_{66} = 1/2 (C_{11} - C_{12})\). The elastic tensor is determined by performing six finite distortions of the lattice and deriving the elastic constants from the strain-stress relation.

The bulk modulus and shear modulus are used to describe the material’s response to compress and shear stress. Here, we use the Hill approximations\(^\text{34}\), which are an average of the Voigt\(^\text{35}\) and Reuss\(^\text{36}\) elastic constants, to calculate the bulk modulus \(B\) and shear modulus \(G\). The Voigt and Reuss approximations, labeled with subscripts \(V\) and \(G\), are defined by:

\[
B_V = \frac{1}{9} \left(2C_{11} + 2C_{12} + 4C_{13} + C_{33}\right)
\]

\[
G_V = \frac{1}{30} \left(3C_{11} + 12C_{13} + 12C_{44} + 2C_{44} + 2C_{66}\right)
\]

where \(S_{ij}\) represents the elements of elastic compliance matrix which is equal to the reciprocal of elastic constant matrix. Then, the bulk modulus \(B\) and shear modulus \(G\) were obtained by:

\[
B = 0.5(B_V + B_R)
\]

\[
G = 0.5(G_V + G_R)
\]

The \(G\) represents the resistance to plastic deformation and the \(B\) represents the resistance to fracture. The value of \(B/G\) is used to characterize the ductility of the material\(^\text{37}\). The material behaves in a ductile nature if \(B/G > 1.75\), otherwise a brittle nature.
Young's modulus $Y$ describes the response to linear stress. Poisson's ratio $\nu$ measures the phenomenon of deformation perpendicular to the loading direction when the material is compressed or stretched. The bond sorting can use the value of the $\nu$. The $\nu$ is very small than 0.25 for a covalently bonded compound. While, for a typical ionic compound, the $\nu$ is nearly 0.25 or more. Young's modulus and Poisson's ratio\(^6\) were calculated with the expressions:

\[
Y = \frac{9B/(3B/G + 1)}{\nu = (3B/G - 2)/(6B/G + 2)}
\]  

A crystalline structure is mechanical stable, if elastic energy is always positive. Elastic constants are used to determine the mechanical stability. At 0 GPa, the mechanical stability criteria for hcp structure are featured as\(^5\):

\[
\begin{align*}
C_{11} & > 0 \\
C_{11} - |C_{12}| & > 0 \\
C_{33}(C_{11} + C_{12}) - 2C_{13}^2 & > 0
\end{align*}
\]

At the compression, the mechanical stability criteria are pressure related\(^4\):

\[
\begin{align*}
C_{44} - P & > 0 \\
C_{11} - |C_{12}| - 2P & > 0 \\
(C_{33} - P)(C_{11} + C_{12}) - 2(C_{13} + P^2) & > 0
\end{align*}
\]

where $P$ is external pressure.

The mechanical stability criteria show the response of the material to axial and tangential strain. The $C_{44} - P > 0$ is related to shear strain in (100) face. The $C_{11} - C_{12} - 2P = C_{66} - P > 0$ is related to shear strain in (001) face. The $C_{11} - P > 0$ and $C_{33} - P > 0$ are related to the axial strain along the [100] and [001] direction, respectively. The $C_{11} - |C_{12}| - 2P > 0$ is related to the coupling strain along the [100] and [120] directions, which is same as the strain along the [100] direction. The $(C_{33} - P)(C_{11} + C_{12}) - 2(C_{13} + P^2) > 0$ is related to the coupling strain along the [100] and [001] directions. The $(C_{33} - P)C_{11} + C_{12} - 2(C_{13} + P)^2 > 0$ is related to the coupling strain along the [100], [120] and [001] directions.

Elastic anisotropy is a fundamental parameter for mechanical properties. For an hcp crystal, the elastic anisotropic is described by the following formulas\(^4\):

\[
\begin{align*}
\Delta_P &= C_{33}/C_{11} \\
\Delta_S1 &= (C_{11} + C_{33} - 2C_{13})/4C_{44} \\
\Delta_S2 &= 2C_{44}/(C_{11} - C_{12})
\end{align*}
\]

where $\Delta_P$ is anisotropy for compressional wave, $\Delta_S1$ and $\Delta_S2$ are anisotropy for shear wave, polarized perpendicular to the basal plane and polarized in the basal plane, respectively. These three parameters characterize the anisotropy of the three main acoustic modes. The acoustic anisotropy in turn indicates the anisotropy of the elastic constants.

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Author contributions
W.L. and R.A. designed the project. Z.L. did the calculations and wrote the manuscript. W.L., H. L. and R.A. analysed the results. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information

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