First Principles Study of the Electronic Structure, Structural Properties and Superconductivity of Nickel Hydride

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Abstract

First principles calculations are performed using a tight-binding linear muffin-tin orbital (TB-LMTO) method with local density approximation (LDA) and atomic sphere approximation (ASA) to understand the electronic properties of nickel hydride. The equilibrium geometries, the electronic band structure, the total and partial density of states (DOS) are obtained under various pressures and are analyzed in comparison with the available experimental and theoretical data. The most stable structure of NiH is the NaCl structure, NiH₂ the CaF₂ structure and NiH₃ the AlH₃ structure at normal pressure. Our result indicates that the maximum storage capacity achieved is 4.9 % for NiH₃. In particular there is no superconductivity in NiH. An increase in Tc is predicted due to the addition of H atoms. The obtained Tc values for NiH₂ and NiH₃ are 5 K and 10 K respectively at normal pressure. Also, it is found that the superconducting transition temperature (Tc) increases as the pressure increases.

Keywords: Ab initio calculations, electronic structure, phase transition, mechanical properties, superconductivity

Introduction

Many transition metals react readily with hydrogen to form stable metal hydrides [1]. Metal hydrides are of intense scientific and technological interest in the view of their potential application, e.g., for hydrogen storage, in fuel cells and internal combustion engines, as electrodes for rechargeable batteries and in energy conversion devices. Hydrides for hydrogen storage must form hydrides with a high hydrogen to-metal mass ratio, but should not be too stable, so that the hydrogen can easily be released without excessive heating [2]. A number of interesting modifications is produced in the metallic characteristics when hydrogen is added. Wimmer [3] discussed the growing importance of computations in materials science. Most transition metals form hydrides at sufficiently high pressures of hydrogen [4]. Wolf and Baranowski [5] measured the heat capacity of nickel hydride. Eckert et al. [6] determined the optical phonon density of states in nickel hydride at room temperature using incoherent-inelastic neutron-scattering techniques. Cable et al. [7] performed coherent neutron scattering measurements to determine the crystal structure and hydrogen content of nickel hydride. Vargas and Christensen [8] presented a self-consistent calculation of the electronic structure of nickel hydride. Moreover, to the best of our knowledge, the structural phase transition, hydrogen storage capacity and superconducting transition temperature of nickel hydride have been not yet reported. Recently, Kim et al. [9] investigated the
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superconductivity of ScH$_3$, LaH$_3$ and YH$_3$. Meanwhile, we have investigated the electronic structure and mechanical stability of MgH$_2$ [10]. In this paper, the band structure, the density of states (DOS), the electronic charge distribution and the structural phase transition of nickel hydride under various pressures are investigated by first principles calculation. All the possible cubic, tetragonal and hexagonal crystal systems are chosen as candidate structures of nickel hydride, including zinc blende (ZB) (space group $3m$), NaCl and CaF$_2$ (space group Fm3m), CsCl (space group Pm3m), WC (space group P6m2) and tetragonal (space group I4/mmm). Further, the superconducting transition temperature $T_c$ of NiH, NiH$_2$, and NiH$_3$ is calculated by using the McMillan formula [11]. The hydrogen storage capacity of nickel is analyzed.

**Computational details**

To compute the electronic structure and the basic ground state properties of NiH, NiH$_2$ and NiH$_3$, TB-LMTO (tight-binding linear muffin-tin orbital method) has been used [12,13]. In the LMTO scheme, the crystal potential is approximated by a series of non-overlapping atomic like spherical potentials and a constant potential between the spheres. The Schrödinger equation can be solved in both regions. These solutions are then matched at the sphere boundaries to produce muffin-tin orbitals. These muffin-tin orbitals are used to construct a basis which is energy independent, linear order in energy and rapidly convergent. Each orbital must satisfy Schrödinger’s differential equation in the region between the atoms. Here the potential is flat on a scale of 1 Ry and, since the energy range of interest begins near the point where the electron can pass between the atoms and extends upwards by about 1 Ry, it seems natural to choose orbital’s which have zero kinetic energy, i.e., satisfy the Laplace equation, in the interstitial region. In the tight-binding muffin-tin orbital the solution of Schrödinger’s equation is written as,

$$
\chi^a(E) = \begin{cases} 
|\phi(E) \rangle N^a(E) + |J^a \rangle P^a(E) & \text{for} \ r \leq w \\
|K^a \rangle & \text{for} \ r \geq w 
\end{cases}
$$

where, $r$ is any distance from the centre of the muffin-tin sphere, $w$ is the average Wigner-Seitz radius and $\alpha$ are dimensionless screening constants. Inside the MT sphere, the base field (or) unscreened field $|K^a \rangle$ is defined by

$$
|K^a \rangle = |\phi(E) \rangle N^a(E) + |J^a \rangle P^a(E)
$$

In the interstitial region, the screened field $|k^a \rangle$ is defined by,

$$
|k^a \rangle = |\phi(E) \rangle N^a(E) + |J^a \rangle P^a(E) - |J^a \rangle S^a
$$

where $\phi(E)$ is normalized to unity in its sphere such that $\langle \phi(E) \phi(E) \rangle = 0$ and $\langle \phi(E) \phi(E) \rangle = -1$.

$J^a$ is the screen field radial function and $S^a$ is the screened structure matrix. The elements of the diagonal matrices $P$ and $N$ are,

$$
P^a(E) = \frac{|\phi(E), k \rangle}{|\phi(E), J^a \rangle} = \frac{P^a(E)}{1 - aP^a(E)}
$$

$$
N^a(E) = \frac{|J^a, k \rangle}{|J^a, \phi(E) \rangle} = \left( \frac{w}{2} \right)^{1/2} P^{-1/2} (E)^{1/2}
$$

The set of energy dependent MTO’s $|\chi^a(E)\rangle$, thus equals $|k^a\rangle$ and $|k\rangle$; the linear combination $|\chi^a(E)\rangle u^a$, specified by a column vector $u^a$, is seen to be a solution of Schrödinger’s equation at energy $E$ for the MT potential if it equals the one center expansions $|\phi(E)\rangle > N^a(E)u^a$ in the spheres, i.e., if the set of linear homogeneous equations $[P^a(E) - S^a]u^a = 0$ has a proper solution. This is the generalization of the so-called tail cancellation or Kerringa-Kohn-Rostoker (KKR) condition.

The secular matrix $[P^a(E) - S^a]$ depends on the potential only through the potential functions along the diagonal and for the most localized set it...
has the TB two center form with \( S^o \) playing the role of the transfer integrals.

The screened field \( \left| k^0 \right\rangle \) is given by the superposition of bare fields \( \left| k^0 \right\rangle \) and that the relationship between the bare and screened structure matrices is,

\[
S^a = S^o \left( 1 - S^o \right)^{-1} \tag{6}
\]

The expansion co-efficient \( S^o \) forms a Hermitian matrix which is dimensionless and independent of the scale of the structure. This is the so-called (bare) canonical structure matrix.

The KKR equations have the form of an Eigen value problem if \( \alpha \) is a linear function of \( E \). This is true, if \( \alpha = \gamma \) (potential parameter) in which case the effective two center Hamiltonian is,

\[
H^\gamma_{ij} = C_i S_{ij} + \left( \sqrt{\Delta_1} \right) S^{\gamma}_{ij} \left( \sqrt{\Delta_1} \right) \tag{7}
\]

For crystals, where the matrix inversion in Eq. (7) can be performed, one may obtain from \( S^o \) (or) \( S^o \).

To obtain an Eigenvalue when \( \alpha \neq \gamma \), energy independent orbitals are needed. Now, \( \left| \chi^\gamma (E) \right\rangle \) is independent of energy, in the interstitial region and in the spheres, its first energy derivative at \( E_i \) will vanish. Therefore, the orbital base is,

\[
\left| \chi^\alpha \right\rangle = \left| \varphi \right\rangle + \left| \varphi^a \right\rangle e^{\alpha} \tag{8}
\]

In this base, the Hamiltonian matrices are,

\[
\left\langle \chi^\alpha | H - E_{\gamma} | \chi^\alpha \right\rangle = h \left( 1 + \alpha^\gamma h^\gamma \right) \tag{9}
\]

\[
\left( H - E \right) \left| \varphi (E) \right\rangle = 0 \tag{10}
\]

\( H - E_{\gamma} \) is the effective two center TB Hamiltonian. This has a shorter range. Therefore, this set of equations is used in self consistent calculations. In the interstitial region Eq. (9) becomes,

\[
\left\langle \chi^\alpha | H - E \right| \chi^\alpha \right\rangle = h \left( 1 + \alpha^o h^o \right) \tag{11}
\]

The set of \( \left| \chi^\alpha \right\rangle \) is thus complete to first order in \( (E - E_{\gamma}) \) and it can yield energy estimates correct to the third order. A Von-Barth and Hedin [14] parameterization scheme has been used for the exchange correlation potential within the local density approximation (LDA). The accuracy of the total energies obtained within the density functional theory, often using LDA, is in many cases sufficient to predict which structure at a given pressure has the lowest free energy [15]. The atomic sphere approximation (ASA) has been used in the present work. The Wigner-Seitz sphere is chosen in such a way that the sphere boundary potential is at its minimum and the charge flow is in accordance with the electronegativity criteria. The s, p and d partial waves are included. The tetrahedron method [16] of the Brillouin zone (k-space) integration has been used to calculate the density of states. The configurations of Ni 4s3d8 and H 1s1 are treated as the valence electrons. Pressure calculations are done with second order Birch Murnaghan equation of states [17].

\[
P = \frac{3}{2} B \left( \frac{V}{V_0} \right)^{\frac{3}{2}} - \left( \frac{V}{V_0} \right)^{\frac{3}{2}} \times 
\left\{ 1 + \frac{3}{4} \left( \frac{B'}{B} - 4 \right) \left( \frac{V}{V_0} \right)^{\frac{3}{2}} - 1 \right\} \tag{12}
\]

where \( B \) and \( B' \) are the bulk modulus and the first derivative of the bulk modulus respectively.

### Results and discussion

**Geometric and mechanical property**

At ambient conditions nickel hydride crystallizes with a fcc structure in the space group Fm3m (225). The Wyckoff positions for the Ni and H atoms are 4a:(0,0,0) and 4b:(0.5,0.5,0.5) respectively and contains four formula units per unit cell. The primitive unit cells of NiH, NiH\(_2\) and NiH\(_3\) are shown in Figure 1.

Valence electron density (VED) is defined as the total number of valence electrons divided by volume per unit cell which is an important factor for analyzing super hard materials. The
equilibrium volume $V_0$ (Å$^3$), lattice parameters $a$ (Å), $c$ (Å), total energy (Ry), density of states (DOS) at the Fermi level $N(E_F)$ (DOS(States/Ry.Cell)), radius of the Wigner-Seitz cell ($R_{WZ}$), band energy $E_B$ (Ry), Fermi energy $E_F$ (Ry) obtained from the TB-LMTO method are listed in Table 1. The calculated VEDs are 0.698 electrons/Å$^3$ for ZB-NiH, 0.912 electrons/Å$^3$ for NaCl-NiH, 0.766 electrons/Å$^3$ for CsCl-NiH, 0.926 electrons/Å$^3$ for CaF$_2$-NiH$_2$, 0.621 electrons/Å$^3$ for hexagonal-NiH$_2$ and 0.455 electrons/Å$^3$ for tetragonal-NiH$_3$. It is worth noticing that all VEDs for NaCl-NiH and CaF$_2$-NiH$_2$ structure are similar to Ni metal (0.917 electrons/Å$^3$). The equilibrium volumes per formula unit are 15.761 Å$^3$ for ZB-NiH, 12.057 Å$^3$ for NaCl-NiH, 14.367 Å$^3$ for CsCl-NiH, 12.953 Å$^3$ for CaF$_2$-NiH$_2$, 19.336 Å$^3$ for Hexagonal NiH$_3$ and 26.364 Å$^3$ for Tetragonal NiH$_3$, which are higher than that of Ni metal (10.9 Å$^3$) due to the additional H atoms.

![Figure 1](image)

**Figure 1** Primitive unit cells of NiH, NiH$_2$ and NiH$_3$.

<table>
<thead>
<tr>
<th></th>
<th>NiH</th>
<th>NiH$_2$</th>
<th>NiH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>CsCl</td>
<td>ZB</td>
</tr>
<tr>
<td>$a$</td>
<td>3.64</td>
<td>2.431</td>
<td>3.98</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.912</td>
<td>0.766</td>
<td>0.698</td>
</tr>
<tr>
<td>$R_{WZ}$</td>
<td>2.134</td>
<td>2.263</td>
<td>1.852</td>
</tr>
<tr>
<td>$E_B$</td>
<td>−2.468</td>
<td>−2.671</td>
<td>−2.105</td>
</tr>
<tr>
<td>$E_F$</td>
<td>9.6290</td>
<td>16.2913</td>
<td>13.5624</td>
</tr>
<tr>
<td>$E$(total)</td>
<td>−3038.89</td>
<td>−3038.82</td>
<td>−3038.86</td>
</tr>
</tbody>
</table>

Table 1 Equilibrium volume $V_0$ (Å$^3$), lattice parameters $a$ (Å), $c$ (Å), Valence electron density $\rho$ (electrons/Å$^3$), the radius of the Wigner-Seitz cell ($R_{WZ}$), Fermi energy $E_F$ (Ry), band energy $E_B$ (Ry), density of states (DOS) at the Fermi level $N(E_F)$ (DOS(States/Ry.Cell)) and total energy $E$(total) (Ry).
Young’s modulus $E$ and Poisson’s ratio $\nu$ are two important factors for technological and engineering applications. The Young’s modulus, Poisson’s ratio, bulk modulus and shear modulus are calculated using the following expressions:

$$E = \frac{9BG}{3B + G}$$

(13)

$$\nu = \frac{3B - 2G}{2(3B + G)}$$

(14)

$$B = -V_0 \frac{dP}{dV}$$

(15)

$$G = \frac{C_{11} - C_{12}}{2}$$

(16)

The stiffness of the solid can be analyzed using the Young’s modulus ($E$) value. Bulk modulus $B$, Young’s modulus $E$ (GPa), shear modulus $G$ (GPa), Poisson’s ratio $\nu$ and the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ (GPa) are calculated for NaCl-NiH which is more stable than the other phases and are listed in Table 2.

The elastic constants $C_{ij}$ should satisfy the well known Born-Huang criteria for the stability of cubic crystals [18].

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

(17)

From Table 2, it is seen that the obtained elastic constants of cubic NaCl-NiH satisfy the Born-Huang criteria, suggesting that it is mechanically stable. The computed elastic moduli are in agreement with the available theoretical data [3]. The Young’s modulus of Ni is calculated as 254 GPa by Erich Wimmer [3]. It is found that the Young’s modulus of NiH is less than Ni. It shows that the stiffness of NiH is less than Ni. Poisson’s ratio reflects the stability of the crystal against shear. The ratio can formally take values between $-1$ and 0.5, which corresponds to the lower limit, when the volume remains unchanged. The obtained Poisson’s ratio of NaCl-NiH is 0.4. Hence, the NaCl – NiH is stable at normal pressure.

<table>
<thead>
<tr>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
<th>$\nu$</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>212.64</td>
<td>45</td>
<td>126.1</td>
<td>0.4</td>
<td>272.64</td>
<td>182.64</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 2 Elastic moduli and elastic constants for NaCl-NiH.

Electronic structure

The band structure of nickel hydrides is computed for various reduced volumes and the band structures for the reduced volume $V/V_0 = 1.0$ and 0.4 are given in Figure 2. From Figure 2, it is seen that, at normal pressure, the band structure has 6 valence bands (bottom most) corresponding to 11 valence electrons which comes from $4s^23d^8$ of the Ni atom and $1s^1$ state electrons of the H atom. Above the Fermi level the empty conduction bands are present with mixed s, p, and d characters. The empty conduction bands are highly overlapping with the valence bands and there is no band gap. Hence, at normal pressure, nickel hydride is a metal. At high pressure the bands get dispersed.

To understand the correlation between the electronic and mechanical properties, we have computed the density of states under equilibrium geometries. The total DOS of NiH, NiH$_2$ and NiH$_3$ are shown in Figure 3. From Figure 3, it is observed that, the spike near $-0.5$ Ry. is due to s state electrons of the H atom. The highest spike near the Fermi level is expected to be essentially Ni 3d-like states. The Fermi level is shifted by adding the H atoms one by one.
Figure 2 Band structures of nickel hydrides at $V/V_0 = 1.0$ and 0.4.
Electrons in the s, p and d shells of Ni and H at different pressures for NaCl-NiH are given in Table 3. From Table 3, it is found that as the pressure increases, a fraction of 4s state electrons are transferred to 4p and 3d states of the Ni atom. Similarly a portion of 1s electrons are transferred to 2p and 3d states of the H atom.

The partial DOS of NaCl-NiH is shown in Figure 4.
Table 3 Electrons in s, p and d shells of Ni and H at different pressures for NaCl-NiH.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>Ni</th>
<th>H</th>
<th>Q-valence</th>
<th>Ni</th>
<th>H</th>
<th>Q-valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.521</td>
<td>0.747</td>
<td>8.776</td>
<td>10.044</td>
<td>0.742</td>
<td>0.181</td>
</tr>
<tr>
<td>45.158</td>
<td>0.512</td>
<td>0.788</td>
<td>8.736</td>
<td>10.036</td>
<td>0.729</td>
<td>0.198</td>
</tr>
<tr>
<td>138.167</td>
<td>0.497</td>
<td>0.822</td>
<td>8.704</td>
<td>10.023</td>
<td>0.719</td>
<td>0.217</td>
</tr>
<tr>
<td>406.324</td>
<td>0.465</td>
<td>0.846</td>
<td>8.701</td>
<td>10.010</td>
<td>0.711</td>
<td>0.231</td>
</tr>
</tbody>
</table>

Figure 4 Partial density of states of NiH at normal pressure. Vertical dotted line indicates the Fermi level.
It is observed that the electrons from the p and d state electrons of the Ni and H atoms contribute much to the DOS in the lower-energy region. The highest spike is due to the 3d state electrons of Ni atom. As the pressure increases, the height of the spike decreases. The charge density distribution for NaCl-NiH is shown in Figure 5. It is clearly seen that charge strongly accumulates between the Ni and H atoms, which means that a strong directional bonding exists between them.

**Figure 5** Charge density plot of NaCl-NiH at normal pressure.

**Energetics and phase diagram**

The energy-V/V₀ curves corresponding to the three different phases of NiH and NiH₂ are shown in Figures 6 and 7, where V/V₀ is the ratio between the volume at any pressure and the equilibrium volume. It is observed that at normal pressure, the thermodynamically stable phase of NiH and NiH₂ are NaCl and CaF₂ structures respectively. A pressure induced structural phase transition from NaCl phase to ZB phase is observed for NiH and CaF₂ to a tetragonal phase is observed for NiH₂.

In order to calculate the transition pressure, the Gibb’s free energy is calculated for the two phases using the expression.

\[ G = E_{\text{tot}} + PV - TS \quad (18) \]

Since the theoretical calculations are performed at 0 K, the Gibb’s free energy will be equal to the enthalpy (H)

\[ H = E_{\text{tot}} + PV \quad (19) \]

**Figure 6** Structural phase transition between the different phases of NiH.

**Figure 7** Structural phase transition between different phases of NiH₂.

At a given pressure, a stable structure is one in which the enthalpy has its lowest value. The transition pressures are calculated at which the enthalpies of the two phases are equal. The enthalpy versus pressure plots of NiH and NiH₂ are shown in Figures 8 and 9. From Figure 8, it is seen that, there is a phase transition from the NaCl to ZB phase at a pressure of 24 GPa. Similarly, from Figure 9, a phase transition is found from CaF₂ to tetragonal phase at a pressure of 64 GPa.
The superconducting transition temperature ($T_c$ K) of NiH, NiH$_2$ and NiH$_3$ are estimated using McMillan equation [11].

$$ T_c = \frac{\theta_D}{1.45} \exp \left( \frac{1.04(1 + \lambda)}{1 - \mu^* (0.62\lambda)} \right) $$  \hspace{1cm} (20)

where $\theta_D$ is the Debye temperature (in energy units) and $\mu^*$ is the electron-electron interaction parameter, which is estimated using the relationship,

$$ \mu^* = \frac{0.26 N(E_F)}{1 + N(E_F)} $$  \hspace{1cm} (21)

The electron-phonon coupling constant

$$ \lambda = \frac{N(E_F) < I^2 >}{M < \omega^2 >} $$  \hspace{1cm} (22)

where $N (E_F)$ is the density of states at the Fermi level, $<I^2>$ is the square of the electron phonon matrix element averaged over the Fermi energy.

$$ < I^2 > = \sum_{l} \left\{ \frac{2(1+1)}{2(1+2)(2l+3)} \right\} M_1 \sum_{l} \left\{ \frac{N(E_F)N(E_{F,l})}{N(E_F)\omega_l} \right\} $$  \hspace{1cm} (23)

$<\omega^2>$ is the average of the phonon frequency squared and $M$ is the atomic mass.

$$ <\omega^2> = 0.5 \theta_D^2 $$  \hspace{1cm} (24)

The computed values of $\lambda$, $\mu^*$ and $T_c$ as a function of pressure for NiH, NiH$_2$ and NiH$_3$ are given in Table 4. The estimated superconducting transition temperature ($T_c$) is 1.52 K for NiH. The $T_c$ value increases with an increase in pressure. The computed superconducting transition temperature for the normal pressure is compared with the available theoretical work [19]. Thus, our results conclude there is no superconductivity in NiH at normal pressure. But, it is found that due to the addition of hydrogen atoms, the superconducting transition temperature increases [20]. The estimated $T_c$ for NiH$_2$ and NiH$_3$ are 5.5 K and 10 K at normal pressures respectively. For NiH$_3$, the $T_c$ value at 578.4 GPa ($V/V_0 = 0.6$) is computed as 25.571 K. Hence the addition of hydrogen atoms increases the $T_c$ value of nickel hydride. Also, it is found that the $T_c$ value increases as the pressure increases.
Table 4 $\lambda$, $\mu^*$ and $T_c$ values as a function of pressure for NiH, NiH$_2$ and NiH$_3$.

<table>
<thead>
<tr>
<th>V/V$_0$</th>
<th>NiH</th>
<th>NiH$_2$</th>
<th>NiH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$</td>
<td>$\mu^*$</td>
<td>$T_c$ (K)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.427</td>
<td>0.107</td>
<td>1.528</td>
</tr>
<tr>
<td>0.8</td>
<td>0.4725</td>
<td>0.100</td>
<td>1.633</td>
</tr>
<tr>
<td>0.6</td>
<td>0.508</td>
<td>0.0697</td>
<td>1.887</td>
</tr>
</tbody>
</table>

Hydrogen storage in nickel hydride

Hydrogen fuel, which can be readily produced from renewable energy sources, contains at least three times larger chemical energy per mass 142 MJ Kg than any chemical fuel, thus making a hydrogen fuel cell an attractive alternative to the internal combustion engine for transportation [21]. Elements, especially those in group I - IV and some transition metals, have their hydride and amide/imides forms. There is, therefore, still plenty of scope for further exploring metal-H system for hydrogen storage. In our study, we have analyzed the storage capacity of Ni by adding hydrogen atoms one by one. The formation energy, density of H/unit cell and storage capacity of NiH, NiH$_2$ and NiH$_3$ is given in Table 5. From the table, we see that the formation energy for NiH, NiH$_2$ and NiH$_3$ are negative. It shows that the formation is possible. The highest hydrogen storage obtained for NiH$_3$ is 4.9 %.

Table 5 Storage capacity of hydrogen in Ni.

<table>
<thead>
<tr>
<th></th>
<th>Formation Energy</th>
<th>Density of H/unit cell</th>
<th>Weight % of Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiH$_1$</td>
<td>$-0.17$</td>
<td>9.7</td>
<td>1.6</td>
</tr>
<tr>
<td>NiH$_2$</td>
<td>$-0.25$</td>
<td>19.4</td>
<td>3.3</td>
</tr>
<tr>
<td>NiH$_3$</td>
<td>$-0.15$</td>
<td>29.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Conclusion

The band structure, density of states, structural phase transition, charge density and superconducting transition temperature under various pressures are investigated based on first principles calculation under the framework of tight-binding theory within the local density approximation. At normal pressure, the thermodynamically stable phase of NiH is the NaCl structure and for NiH$_2$, the CaF$_2$ phase is more stable. At certain high pressures, it is found that a structural phase transition occurs from NaCl to ZB for NiH and from CaF$_2$ to a tetragonal phase for NiH$_2$. Electronic structure calculations show that NiH presents obvious metallic features. Our results conclude, that there is no superconductivity in NiH. But, due to the addition of hydrogen atom we observe superconductivity in NiH$_2$ and NiH$_3$. The estimated $T_c$ values for NiH$_2$ and NiH$_3$ are 5.5 K and 10 K respectively. Also, it is found that as the pressure increases, the $T_c$ value also increases in NiH, NiH$_2$ and NiH$_3$. The maximum hydrogen storage capacity achieved is 4.9 % for NiH$_3$. We hope that this work can stimulate further experimental research on nickel hydride.

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References


