In this chapter we have investigated the structural, electronic and magnetic properties of light lanthanide nickel intermetallic compounds CeNi, PrNi and NdNi in their orthorhombic chromium boride (CrB) structure employing the first principles method. Main emphasis is given on bulk thermodynamic properties of the compounds. Lanthanide intermetallic compounds with nickel as binary element are theoretically studied for the first time, therefore, it is expected that our results, presented here, will simulate interest in theoretical and experimental research in the emerging field of magnetic refrigeration and magneto-strictive devices.

This chapter is based on two research publications:


4.1 Introduction

Binary alloys of lanthanide elements with transition metals exhibit interesting physical properties such as good oxidation resistance, excellent strength and stiffness at elevated temperatures [1-3]. Intermetallic compounds in which the magnetism of the lanthanide atoms with their partially filled localized 4f shell is combined with that of the itinerant 3d transition metals form an important class of materials from an applications point of view. Due to their large magnetic moments and magneto-caloric effect (MCE) they also have applications in the fabrication of permanent magnets, magneto–strictive devices, magneto-optical recorders and magnetic refrigeration [4-11]. Among all transition metals nickel is one of the promising materials in its pure form or as alloying with other materials. Nickel based lanthanide intermetallics is an important class of materials due to variety of physical properties.

Lanthanide intermetallic compounds LnNi’s (Ln= Ce, Pr and Nd) are ferromagnetic binary compounds which are metallic in nature. At normal conditions, they crystallizes in base centred chromium boride phase (CrB) with space group 63-Cmcm [12-14]. The structure is also commonly known as B33 structure.

Ce-based intermetallic compounds have attracting attention due to their broad variety of physical properties originate from the changing character of Ce 4f electrons. The kondo effect in Ce-X intermetallic compounds have been investigated by Gignoux [15-16]. Among the lanthanide intermetallic compounds, PrNi is one of remarkable system. It also crystallizes into the CrB (B33) type structure (orthorhombic; space group Cmcm) with one crystallographic type of parametric sites for Pr and Ni. The lattice parameters determined from the diffraction experiment (a = 3.824 Å, b =10.497 Å, c = 4.358 Å) [17]. Gozzi et. al. [13] analysed the thermodynamic behaviour of Ni rich intermetallic compound of lanthanide series.
Later, the study on the magnetic properties of lanthanide intermetallic compounds with transition metals has been extended by experimentalists [18 - 21].

Thus literature shows that sufficient amount of work is available on the magnetic properties of lanthanide intermetallic compounds. The experimental studies of the electronic properties of some of the LnNi’s are available in [22-23]. Further despite the wide technological applications of LnNi’s (Ln= Ce, Pr and Nd), studies of the electronic and thermodynamic properties of these materials is lacking. Thus in the context of lanthanide earth intermetallic compounds, we considered it pertinent to provide theoretical study of the bulk LnNi’s (Ln= Ce, Pr, and Nd) with Ln: Ni :: 1:1.

First-principle calculations within the framework of density functional theory using the full potential linearized augmented plane wave (FP-LAPW) method are the most powerful tools for carrying out theoretical studies with high accuracy. Therefore, in this chapter we report calculations carried out with the aim of investigating the structural, electronic, magnetic and thermodynamic properties of LnNi’s in Cmcm space group. We believe that our first principle results for LnNi’s can serve as good reference data for the LnNi’s intermetallic compounds.

4.2 Computational Methodology

Full potential linearized augmented plane wave plus local orbitals methods (FP/LAPW +lo) as employed in the code WIEN2k has been applied to perform the first principles total energy calculations. The analyses of the structural, electronic, thermal and magnetic properties of the LnNi’s (Ln= Ce, Pr and Nd) are performed in the frame work of spin-polarized density functional theory (SP-DFT) [24–25] which is a quantum mechanical approach for many body problems. The augmented plane wave + lo methods expands the Kohn-Sham orbitals in the atomic like orbitals inside
the muffin tin (MT) spheres and plane waves in the interstitial region. The generalized gradient approximation (GGA) with spin polarisation for the exchange–correlation interaction given by Perdew, Burke and Ernzerhof (PBE) [26] has been used. This scheme of approximation was preferred here due to their capability to give superior results in case of magnetic systems. In this method, the basis set inside each muffin-tin sphere is split into two parts: core subset and valence subset. The states under core region are treated as spherically symmetric of the potential and are assumed to have a spherically symmetric charge density confined inside the muffin-tin spheres. For the valence part, the wave functions inside the atomic sphere are expanded up to \( l_{\text{max}} = 10 \). A degree of convergence was achieved by considering the full potential linear augmented plane wave basis functions up to \( R_{\text{MT}} K_{\text{max}} = 8 \) where \( R_{\text{MT}} \) signifies the smallest radius of the muffin tin spheres and \( K_{\text{max}} \) is the maximum value of the wave vectors.

The 4f electronic states in lanthanides and its compounds are found in strongly correlated state. To analyse their electronic state, GGA is not sufficient to describe them accurately. To overcome this discrepancy, additional Coulomb’s repulsion parameter (\( U \)) was taken into account to introduce the many body effects within the 4f electronic structure of lanthanide compounds.

The optimized values of muffin-tin radii (\( R_{\text{MT}} \)) of Ce, Pr, Nd are 2.28, 2.3, 2.3 a.u. (atomic units) while the sphere size for Ni atom is 2.0 a.u. in all the cases. The k-points used in the calculations were based on 10\( \times \)10\( \times \)10 Monkhorst – Pack [27] scheme. The iteration process was repeated until the calculated total energy and charge of the crystal converges to less than \( 10^{-4} \) Ry and \( 10^{-3} \) e\(^-\), respectively. We carried out optimization of the total energy of the structures of all the compounds with respect to the different values of unit cell volume using Murnaghan’s equation.
of state (EOS) [28] in order to obtain the equilibrium structural parameters (viz., lattice constants, bulk modulus and first order pressure derivative of bulk modulus).

The temperature effects for ground state of CeNi, PrNi and NdNi have been determined by combining the first-principles calculation and taking account the phononic effect within quasi harmonic Debye model [29]. This model generates the thermal equation of state $V(P, T)$, to determine behaviour of material with respect to changes in the pressure and temperature. Through the quasi-harmonic Debye model, one could calculate the thermal quantities at any temperatures and pressures of present compound from the calculated $E-V$ data at $T=0$ K and $P=0$ GPa. The standard thermodynamic relations are then used to derive other macroscopic properties. The effect of pressure on the cell volume has also been analysed at $T=0$ K and $T=300$ K. Also the compressibility of the materials has checked through analysing the behaviour of bulk modulus with rise in pressure and different temperature values.

4.3 Structural Optimization

The geometry optimization was performed by calculating the total energy as a function of the three variables, $b/a$, $c/a$ and $V$. Here $a$, $b$, $c$ is related to lattice parameters and $V$ represents volume of unit cell. For the $b/a$ and $c/a$ ratio optimization the crystal energy is calculated for a grid of cell volumes $V$ and $b/a$ and $c/a$ ratio values. Each point in the grid involves the minimization with respect to the internal cell geometry. To attain optimized values of $c/a$ and $b/a$ ratio, total energy of the crystal structure has been calculated for a set of cell volumes. Using the best fitted $c/a$ and $b/a$ ratio, the lattice coordinates for $Ce$, $Pr$, $Nd$ and $Ni$ atoms have also been optimized. The geometry of the crystal structures is relaxed by using data from the literature [17, 31]. LnNi’s (Ln= Ce, Pr and Nd), the three intermetallic...
compounds exhibits CrB structure ($B33$), having 2 formula units ($fu$) per unit cell [30, 31]. Within the crystal structure all the three Ln atoms Ce, Pr, Nd and Ni occupy identical Wyckoff positions 4c and the atomic position for Ce, Pr, Ni atoms is $(0, y_1, \frac{1}{4})$ and that for Ni atom is $(0, y_2, \frac{1}{4})$.

The optimized results for internal parameters and $y$ coordinates of Ce, Pr, Nd and Ni atoms are used to analyse the ground state structural properties of the intermetallic compounds. Using obtained coordinates, we compute optimized values of total energy corresponding to different unit cell volumes. The obtained sets of calculated data are fitted to the Murnaghan’s *equation of state* [28] which is as follows

$$E_T(V) = \frac{B_0 V}{B_0'} \left[ \frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] + E_0 - \frac{V_0 B_0}{B_0' - 1},$$

4.1

The fit provides values of the equilibrium volume $V_0$, bulk modulus $B_0$ and pressure derivative of bulk modulus $B_0'$.

In order to obtain the relationship between corresponding pressures and volumes for every phase the above equation is modified to give pressure

$$P = \left( - \frac{\partial E}{\partial V} \right)_{\text{eq}},$$

which leads to the following expression

$$P(V) = \frac{B_0}{B_0'} \left( \frac{V_0}{V} \right)^{B_0'} - 1$$

(4.2)

Here pressure $P$ is defined as the negative derivative of total energy. Other variables used in the equation are the bulk modulus $B_0 = (\frac{\partial P}{\partial V})_{\text{eq}}$, $B_0' = (\frac{\partial B}{\partial P})_T$ is the first order pressure derivative of bulk modulus and $V_0$ is the equilibrium cell volume. This energy optimization provides the equilibrium lattice constants of the structure.
4.4 Results and Discussion

4.4.1 Structural Properties

The optimized atomic positions of Ln atoms and Ni atoms in B33 structure are given in *Table 4.1* along with earlier reported data. The unit cell structure of LnNi in B33 structure is represented in *Figure 4.1*.

An understanding of the structural properties and stability of a given structure is important and prerequisite to any further investigation of its properties. The values of optimized internal structure parameters ‘y’ describing the position of Ln atom and the ratio b/a and c/a are used to investigate the structural properties. The calculation was done using PBE-GGA exchange correlation functional. By fitting the total energy versus volume data in the Murnaghan’s EOS, we obtained the lattice parameters, the bulk modulii and their first order pressure derivative. The calculated results for these compounds are shown in *Table 4.2*. The available experimental data have also been included for the sake of comparison and reliability of the present results. For the present set of systems under analysis there is no theoretical values are available for comparison. It is clear from *Table 4.2* that the calculated results for CeNi, PrNi and NdNi in CrB structure are in reasonable agreement with experimental data [12, 32, 36-38], implying the competency and accuracy of the present work.

4.4.2 Magnetic Properties

Lanthanide intermetallic compounds are, in general magnetic materials. The spin orbit interactions for most of the lanthanide compounds are very strong, because of the reason that the net magnetic moments have both spin and orbital components. The magnetic domains of Ni atom are anti parallel coupled to the magnetic moments...
of Ln atoms. This is due to the exchange interactions between the 4f electrons of lanthanide atoms and 3d electrons of transition elements. The spin polarised self consistent calculations are performed to give an overview about magnetic behaviour in present set of compounds. The calculated total (M) and local (m) magnetic moments for CeNi, PrNi and NdNi compounds in orthorhombic CrB structure are listed in Table 4.3 along with available experimental data for comparison. The main contribution to the total magnetic moment in all the compounds is due to 4f systems i.e. Ce, Pr and Nd. The contribution from 3d Ni element is negative and negligible. The negative magnetic moments give conclusion that 3d electronic states of Ni are anti parallel to 4f states of Ln atoms.

4.4.3 Electronic Properties

The spin polarised self consistent calculations have been done by using GGA+U scheme. In lanthanide compounds, the 4f electronic states are very narrow hence having high order of hindrance originates coulomb repulsion between highly localised f electrons. In these systems, single particle GGA is no longer sufficient to give exact description of 4f electronic states. To fulfil this purpose, coulomb repulsion factor (U) is added to GGA scheme. The band structures of CeNi, PrNi and NdNi in their ground states have been calculated and are shown in Figure 4.2 with clear description about spin majority and spin minority states. From the compounds it has been noticed that GGA+U scheme has significant effect on the energy levels of occupied and unoccupied 4f electronic states. To understand the role of Ln and Ni ions in the intermetallic compounds we studied the electronic band structure. The description of the electronic states in all the three intermetallic compounds is given individually in the following sections.
**Band Structure of CeNi**

To compute the accurate position of 4f states in CeNi compound the GGA+U scheme is opted. The value of parameter $U$ is taken as the default value of the WIEN2K program i.e. 6.5 eV and $J=0.9$ eV which is closed to the available result for CeN compound [33]. The effect of $U$ is clearly observed in the electronic band structure shown in Figure 4.2. The 4f electronic states for CeNi are shifts towards 4 eV below Fermi level ($E_F$) in spin up channel, while the partially occupied 4f states (in the spin down channel) are found to be located around 2.0 to 5.0 eV above Fermi level.

**Band Structure of PrNi**

In case of PrNi compound the occupied 4f states in spin up channel are situated between 4.0 – 5.0 eV below $E_F$ and the partially occupied 4f states are placed within the region of 3.0 to 5.5 eV above $E_F$, as shown in second row of Figure 4.2. The splitting of 4f electronic states is observed at $U=7.0$ eV and $J=0.9$ eV which resemble with the available data for PrN compound [34].

**Band Structure of NdNi**

The electronic band structure is calculated for NdNi compound by performing same analysis as used in previous two cases. From last row of Figure 4.2, which presents the electronic behaviour of NdNi compound, it is clearly noticed that the range of occupied 4f states in spin up channel is in between 5 eV and 5.5 eV. The partially occupied 4f states are placed within the region of 3 to 5.5 eV above $E_F$. The splitting of 4f states are analyse at $U=7.2$ eV and $J=0.9$ eV.
**Density of States**

In order to provide better understanding of electronic energy states, we have also analysed the density of states. The total density of states (DOS) and spin-projected DOS for individual atoms of compounds CeNi, PrNi and NdNi are presented in Figures 4.3, 4.4 and 4.5, respectively. The projected DOS provides a more clear idea about the depicted band structures for the present set of compounds (plotted in Figures 4.3 – 4.5).

From the view of Figures 4.3(a), 4.4(a) and 4.5(a), it seems that the bands lie within the region from -4.0 eV to -6.0 eV are due to main contribution from Ce, Pr and Nd 4f states. The Figures 4.3(b)–4.5 (b) represent the clear view about the position of 4f states of CeNi, PrNi and NdNi, respectively. On the analyses of Figures 4.3(c)–4.5(c) and Figures 4.3(d)–4.5(d), a strong hybridisation of 5d electronic states of Ce, Pr, Nd with 3d Ni states have been also been observed. This strong hybridisation is effectively dominate in the total DOS of the compounds (Figures 4.3 (a), 4.4 (a) and 4.5 (a)) results in the increase in peaks in total DOS near Fermi level. The strong hybridisation between 4f states of Ce, Pr and Nd atoms and 3d states Ni are the cause of decrease in width of 5d states of lanthanide atoms (Ce, Pr and Nd). The present results on total and partial DOS indicates to presence of itinerant electrons near Fermi level. There is no photoemission data is available for CeNi, PrNi and NdNi compounds. Some details on photoelectron spectroscopy and photoemission data have been available on GdNi [35, 36]. A unified study on the basis of experiment and spin polarised DFT calculations have also been performed to investigate the screening effects on Gd resonant photoemission in a set of GdNi alloy films with varying concentration of Gd. The compound is belonging to the
same series hence we have compared our present results with the data available. Spin-polarised calculation performed by Wu et al [37] reported that the DOS of bulk Gd have been lying below -6 eV which is well agreeable to the present study. Addition of Ni atom to the pure Gd element causes some additional itinerant energy states near Fermi level resulting in the increase in DOS. The present CeNi, PrNi and NdNi compounds results analysis agrees well with above mentioned results.

4.4.4 Thermal Properties

Thermal properties of CeNi, PrNi and NdNi compounds are computed using Gibbs Program [29]. On varying the temperature and pressure of the system affects the density which results to the thermal expansion or contraction within the system. The effects of temperature and pressure on CeNi, PrNi and NdNi have been analysed upto the 0K to 1000K (temperature range) and 0 GPa to 30 GPa (pressure range). The corresponding results to for thermodynamic properties are observed and are listed in Table 4.4. Various parameters like thermal expansion coefficient (α), Gruneisen parameter (γ), Debye temperature (θ_D) and Entropy (S) for the compounds described above, have been presented in Figures 4.7–4.12. Their analysis is presented in the following sections.

**Debye Temperature**

Debye temperature (θ_D) has inherent relationship related to the vibrational motion of the atoms within a crystal lattice. It is the temperature above which the crystal behaves classically, because the thermal vibrations become more important than the quantum effects. The effect of increasing temperature on Debye temperature with increase in pressure is studied and plotted in Figures (4.7(b), 4.9(b) and 4.11(b))
for CeNi and PrNi and NdNi respectively. *Figure 4.7(b)* plotted for CeNi compound, shows that at P= 0 K, the Debye temperature is nearly constant for temperature in the range 200 K, above this temperature value it starts decreasing with rising in temperature. Similar variation is found in *Figure 4.9(b)* for PrNi and *Figure 4.11(b)* for NdNi compounds. These figures also show plots of Debye temperature as a function of at temperature different pressure values. The Variation is almost linear and the Debye temperature increases with the applied pressure.

**Thermal Expansion**

The coefficient of thermal expansion ($\alpha$) measures the fractional change in volume per degree change in temperature at constant pressures. *Figures 4.7(a)* represents the variation in thermal expansion with temperature at different pressures for CeNi. On plotting, thermal expansion coefficient as a function of temperature it is evident that it increases linearly from T=0 K to T=1000 K. Within lower range of temperature $\alpha$ shows abrupt increase up to 600 K and after this the curve becomes linear with almost constant value. As the pressure increases the thermal expansion decreases rapidly and the effect of temperature becomes less prominent. Similar trend are also found for PrNi and NdNi compounds and their plots are shown in *Figures 4.9(a) and 4.11(a)* respectively.

**Specific Heat Capacities**

The specific heat of a substance is defined as the heat energy absorbed by one unit mass of the substance to raise its temperature by one degree. While measuring the specific heat either volume or pressure is kept constant, hence we have two values; specific heat at constant volume ($C_v$) and specific heat at constant pressure
(Cp). The variation of specific heat with temperature is shown through three plots corresponds to three intermetallic compounds, Figure 4.7(c) is for CeNi and Figure 4.9(c) for PrNi and Figure 4.11(c) for NdNi. These plots for Cv and Cp with increasing temperature show that at lower temperatures the Cv and Cp are same but after a certain temperature (~ 300 K), Cv exceeds Cp as a result of thermal expansion of the crystal lattice.

**Entropy**

As the temperature of material increases the particle vibrate more vigorously, so the entropy of the system also increases, as shown in Figures [4.8(d), 4.10(d), and 4.12(d)] for CeNi, PrNi and NdNi, respectively.

**Gruneisen Parameter**

Figures 4.8(e), 4.10(e), and 4.12(e) display temperature dependence of Gruneisen parameter (γ), respectively, for CeNi, PrNi and NdNi. The variation in the Gruneisen parameter with increase in temperature is very almost linear. Further the change in Gruneisen parameter decreases with the increase in pressure. Hence we can conclude that Gruneisen parameter describes the effect of changing temperature on the dynamics of the crystal.

### 4.4.5 Effect of Pressure and Temperature on Structural Properties

An understanding of the modifications of structural parameters of a material under pressure or temperature is desirable for their scientific relevance. Exertion of pressure enhances the interlayer coupling and has a strong influence on the crystal structure. As pressure is exerted, the original volume of the material reduces by a
fraction the original value and this causes a reduction in the inter-atomic distance. Hence, there are significant changes in bonding and electronic properties. Figures 4.6(a-c) represent the volume-pressure diagram for CeNi, PrNi and NdNi at T=0K and T=300K. The volume of the unit cell decreases with increase in pressure. This behaviour is found to be similar at both the temperature values. As the temperature of the material is raised its volume increases.

The Bulk modulus of material indicates its compressibility on applying pressure. This property of the material helps us to understand, characterize and predict mechanical properties of the material under extreme conditions. Since the absolute value of bulk modulus can affect the behaviour of any material, therefore, its variation with applied pressure has its own importance. The dependence of the bulk modulus on the pressure at T= 0K and T=300K are shown in Figures 4.6(d-e) for the three compounds CeNi, PrNi and NdNi in B33 structure. As the volume decreases, the lattice “stiffens” due to shrinkage of orbitals and this causes an increase of the bulk modulus with increasing pressure. These plots show that the bulk modulus decreases linearly with increasing temperature. The compressibility increases with increasing temperature at given pressure and decreases with pressure at given temperature.

4.5 Conclusions

This chapter deals with first principle calculations of structural, magnetic and electronic properties of three lanthanide intermetallic compounds CeNi, PrNi and NdNi. The present results on structural properties like lattice constants and cell volume are in good agreement with the experimental data. The results for bulk modulus and first order pressure derivative of bulk modulus have also been reported.
The calculated total magnetic moments and individual magnetic moments of atoms increase as we move from Ce through Pr to Nd. The reason for this increase is due to increasing number of $f$ electrons. The small and negative values of magnetic moments for Ni atom in these intermetallic compounds are due to the anti parallel ordering with respect to Ln atoms. The Coulomb repulsion ($U$) parameter in GGA+$U$ method shows metallic nature of all the compounds with the proper splitting of $f$-bands in spin up and spin down states. Strong $3d$-$5d$ hybridisation below Fermi level increases the peaks of total DOS (due to presence of itinerant electrons) and decreases the band width of $5d$ bands. In this investigation we have shown that application of pressure can significantly influence the structural and electronic properties of a compound. Thus with proper control of the pressure, we can modify the material properties of these intermetallic compounds. We have also calculated the effect of temperature and pressure on the different thermal parameters as these are essential for crystal growth. The efforts made in present chapter are extensively dedicated to the theoretical investigation on scantly studied LnNi intermetallic compounds. Such class of intermetallic is very important from technical point of view and hence requires more experimental as well as theoretical attention.
References


### Table 4.1

*Optimized atomic positions for B33 structures of CeNi, PrNi and NdNi compounds*

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Positions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeNi</td>
<td>(0, 0.145, 0.25)</td>
<td>PW</td>
</tr>
<tr>
<td></td>
<td>(0, 0.13, 0.25)</td>
<td>[38]</td>
</tr>
<tr>
<td>PrNi</td>
<td>(0.0, 0.145, 0.25)</td>
<td>PW</td>
</tr>
<tr>
<td></td>
<td>(0.0, 0.14, 0.25)</td>
<td>[32]</td>
</tr>
<tr>
<td>NdNi</td>
<td>(0.0, 0.143, 0.25)</td>
<td>PW</td>
</tr>
</tbody>
</table>

*PW-Present Work*

### Table 4.2

*Structural parameters, lattice constants (in Å), equilibrium cell volume (in Å³), bulk modulus (in GPa), first order pressure derivative of bulk modulus in CrB phase.*

<table>
<thead>
<tr>
<th>Structural Parameters</th>
<th>CeNi</th>
<th>Ref.</th>
<th>PrNi</th>
<th>Ref.</th>
<th>NdNi</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>4.00</td>
<td>3.79[a]</td>
<td>3.90</td>
<td>3.82[b]</td>
<td>3.87</td>
<td>3.81[d]</td>
</tr>
<tr>
<td>$b$</td>
<td>11.54</td>
<td>10.54[a]</td>
<td>10.10</td>
<td>10.55[b]</td>
<td>9.78</td>
<td>10.51[d]</td>
</tr>
<tr>
<td>$b/a$</td>
<td>2.78</td>
<td>-</td>
<td>2.59</td>
<td>-</td>
<td>2.44</td>
<td>-</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.36</td>
<td>-</td>
<td>1.13</td>
<td>-</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>$V_{0}/2fu$</td>
<td>177.68</td>
<td>174.79[a]</td>
<td>172.56</td>
<td>-</td>
<td>169.63</td>
<td>172.62[e]</td>
</tr>
<tr>
<td>$B_0(GPa)$</td>
<td>69.78</td>
<td>-</td>
<td>65.59</td>
<td>-</td>
<td>62.75</td>
<td>-</td>
</tr>
<tr>
<td>$B_0'$</td>
<td>4.65</td>
<td>-</td>
<td>4.46</td>
<td>-</td>
<td>4.17</td>
<td>-</td>
</tr>
<tr>
<td>$E_{0}/2fu(Ry)$</td>
<td>-20772.42</td>
<td>-</td>
<td>-21527.25</td>
<td>-</td>
<td>-22301.81</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3  Total magnetic moment (M) per formula unit (M/fu in µB) and magnetic moments in interstitial sites and Ln atom (Ce, Pr and Nd in µB) and Ni (Ni in µB) in Cmcm phase

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Magnetic Sites (µB) (Present Work)</th>
<th>Expt. Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interstitial Ln Ni Total (M) MM/fu</td>
<td></td>
</tr>
<tr>
<td>CeNi</td>
<td>0.17 1.07 -0.87 2.47 1.23 2.46[12], 2.54[38]</td>
<td></td>
</tr>
<tr>
<td>PrNi</td>
<td>0.83 2.18 -0.14 4.89 2.44 -</td>
<td></td>
</tr>
<tr>
<td>NdNi</td>
<td>0.75 3.26 -0.09 6.45 3.23 -</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4  Calculated results for thermal properties (volume, V_0/2 fu), bulk modulus (B_0), pressure derivative of bulk modulus (B'_0), thermal expansion coefficient (α), specific heat capacities (Cv, Cp), Gruneisen parameter (γ), Debye temperature (θ_D) and entropy (S) of CeNi, PrNi and NdNi in orthorhombic CrB phase at P= 0 GPa.

<table>
<thead>
<tr>
<th>Properties</th>
<th>CeNi T=0 K</th>
<th>PrNi T=0 K</th>
<th>NdNi T=0 K</th>
<th>CeNi T=300 K</th>
<th>PrNi T=300 K</th>
<th>NdNi T=300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_0/2fu (a.u^3)</td>
<td>585.36</td>
<td>549.53</td>
<td>578.9</td>
<td>584.1</td>
<td>555.26</td>
<td>564.97</td>
</tr>
<tr>
<td>B_0(GPa)</td>
<td>116.31</td>
<td>160.26</td>
<td>130.67</td>
<td>128.58</td>
<td>192.03</td>
<td>190.66</td>
</tr>
<tr>
<td>B'_0</td>
<td>4.32</td>
<td>4.61</td>
<td>4.15</td>
<td>3.84</td>
<td>3.83</td>
<td>3.85</td>
</tr>
<tr>
<td>α (10^5/K)</td>
<td>0</td>
<td>1.10</td>
<td>0</td>
<td>1.55</td>
<td>0</td>
<td>0.79</td>
</tr>
<tr>
<td>C_v(J/mol K)</td>
<td>0</td>
<td>40.62</td>
<td>0</td>
<td>48.46</td>
<td>0</td>
<td>49.41</td>
</tr>
<tr>
<td>C_p(J/mol K)</td>
<td>0</td>
<td>40.91</td>
<td>0</td>
<td>50.20</td>
<td>0</td>
<td>51.58</td>
</tr>
<tr>
<td>γ</td>
<td>2.127</td>
<td>2.134</td>
<td>2.52</td>
<td>2.69</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>θ_D (K)</td>
<td>624.56</td>
<td>621.89</td>
<td>234.58</td>
<td>228.98</td>
<td>334.77</td>
<td>334.05</td>
</tr>
<tr>
<td>S (J/mol/K)</td>
<td>0</td>
<td>75.13088</td>
<td>0</td>
<td>80.71</td>
<td>0</td>
<td>82.26</td>
</tr>
</tbody>
</table>
Figure 4.1  Pictorial representation of orthorhombic CrB (B33) structure. The pink coloured spheres represents the positions of Ln atom (Ln= Ce, Pr, Nd atom while yellow spheres are for Ni atom.
Figure 4.2 The electronic band structure for CeNi, PrNi and NdNi in ground state CrB phase, in spin up states and spin down states at ambient conditions (i.e. $=0$ GPa and $T=0$K). [Both spin channels are mentioned clearly in each compound along with compounds name].
Figure 4.3  
Total and partial DOS (including 4f and 5d states of Ce atom and 3d states of Ni atom) for CeNi compound in orthorhombic-Cmcm CrB structure.
Figure 4.4  Total and partial DOS (including 4f and 5d states of Pr atom and 3d states of Ni atom) for PrNi compound in orthorhombic-Cmcm CrB structure.
Figure 4.5  Total and partial DOS (including 4f and 5d states of Nd atom and 3d states of Ni atom) for NdNi compound in orthorhombic-Cmcm CrB structure.
Figure 4.6 Pressure dependence on unit cell Volume and bulk modulus of LnNi’s compounds (Ln=Ce, Pr and Nd) at T=0K and T=300K.
Figure 4.7  Effect of temperature at high pressure on thermal properties of CeNi
(a) Thermal expansion coefficient $\alpha$,
(b) Specific Heats $C_v$ and $C_p$, and
(c) Debye temperature $\theta_D$. 

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Figure 4.8  Variation of entropy ($S$) and Gruneisen parameter of CeNi with temperature at high pressures.
Figure 4.9  Effect of temperature at high pressure on thermal properties of PrNi  
(a) Thermal expansion coefficient $\alpha$,  
(b) Specific Heats $C_v$ and $C_p$, and  
(c) Debye temperature $\theta_D$.  

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Figure 4.10  Variation of entropy (S) and Gruneisen parameter of PrNi with temperature at high pressures.
Figure 4.11  Effect of temperature at high pressure on thermal properties of NdNi

(a) Thermal expansion coefficient $\alpha$,  
(b) Specific Heats $C_v$ and $C_p$, and  
(c) Debye temperature $\theta_D$.
Figure 4.12  Variation of entropy (S) and Gruneisen parameter of NdNi with temperature at high pressures.