Chapter - 4

B1 → B10 → B2 Structural Transition Sequence in LaN under High Pressure

4.1 Introduction

The transition metal mononitrides are frequently used as refractory material as they exhibit unique mechanical properties such as high hardness, brittleness, elastic moduli and melting point [1-4]. These properties ensure an extensive and growing application of nitrides of d- and f- metals in modern technology, e.g., the basis for development of various corrosion and wear-resistant coatings (in cutting tools and magnetic storage devices). These materials also have unique combination of chemical characteristics with the above mentioned physical or mechanical properties; namely interesting optical, electronic, magnetic and vibrational properties [1-4]. A small deviation from the stoichiometry of these compounds can change the physical and chemical properties of these materials drastically. Several of these nitrides show superconducting behaviour with relatively high superconducting temperature. These properties of transition metal mononitrides make them suitable for various technological and scientific applications such as producing solid solution of improved physic-chemical properties, new composite materials. For example, nanocrystalline hard transition metal nitrides (TiN, VN, W2N, CrNx and others) can be embedded in amorphous Si3N4, BN to produce novel nanocomposite superhard materials [5]. The cubic δ-NbN has been found to posses high hardness (a Vickers hardness of 20 GPa) as well as superconducting behavior for possible applications at extreme conditions [2] and thus have attracted attention of scientific community.

LaN, a mononitride of 5d transition element La, possessing rocksalt type structure (B1) at ambient conditions, is one of the important transition metal nitrides, which has been studied by researchers in recent past [6-11], with the aim to determine the ground state properties and understand the structural stability under high pressure.
Some of the high pressure theoretical studies have concentrated mainly on B1 to B2 structural phase transition. For example, Vaitheeswaran et al. [7] through first principles total energy calculations predicted the rocksalt type to CsCl type (B2) structural phase transition in this material at ~ 26.9 GPa. The same transition has been predicted to occur at ~ 25 GPa by Ciftci et al. [8] on the basis of augmented plane wave pseudopotential calculations using VASP package. Stampfl et al. [6] have investigated ground state bulk properties of 3d, 4d and 5d transition metal mononitrides using full potential linearized augmented plane wave (FP-LAPW) method within both the local density approximation (LDA) and generalized gradient approximation (GGA). The main physical properties determined by these authors from their ab-initio calculations are lattice constants, bulk moduli, heat of formation, cohesive energy, band structure and density of states of these mononitrides in B1 phase. Based on the comparison of results obtained from GGA and LDA calculations, as expected, these authors reported that the GGA yields 1%–2% larger lattice constants, 10%–20% smaller bulk moduli, and 10%–30% lower heats of formation compared to the LDA. The structural and electronic properties of LaN have been investigated by Ghezail et al. [9] also using full potential linearized muffin tin (FP-LMTO) and FP-LAPW method within both the LDA and GGA. These authors report that the structure of the stable phase of LaN predicted using ab-initio calculations is sensitive to the kind of approximation used for treating exchange correlation interactions. Apart from these static lattice calculations, the lattice dynamic studies of LaN has also been reported in recent past [10].

In experimental front, recently, in a high pressure X-ray diffraction measurements carried out on LaN powder in diamond anvil cell (DAC), occurrence of a new phase at ~ 22.8 GPa has been reported by Schneider et al. [10]. This high pressure phase has been identified as a primitive tetragonal structure with space group P4/nmm and is named as HP-LaN [11] phase by the authors. In the present thesis, following the literature, we have named this structure as B10 phase. This experimental finding is in contrast with the earlier theoretical predictions [7-8].
The material with rocksalt type structure at the ambient condition transforms generally to the CsCl type structure. There are large numbers of compounds showing this transition sequence under pressure. For example, alkali halides (except CsCl, CsBr and CsI), thorium chalcogenides and pnictides ThX (X=S, Se, P, As, and Sb) [12], barium chalcogenides and pnictides BaX (X= S, Se and Te) [13] follows this phase transition sequence. Thus the occurrence of high pressure B10 structure in LaN is rather unusual in nature. However, Iron monoxide (FeO) exists in the B1 structure under ambient conditions and transforms to the nickel arsenide-type (B8) structure under high pressure [14-15]; but above 3850 K temperature B1 to B2 transition is observed [16]. As the existence of high pressure B10 phase is bit unusual, we attempted to investigate the reason behind its stability by performing the detailed analysis of the electronic band structure.

Motivated with this experimental study, we have attempted to theoretically investigate the pressure induced B1 to B10 structural phase in LaN. For this purpose, we have performed first principles electronic band structure calculations on B1, B10 and B2 phase of LaN using FP-LAPW method implemented in the WIEN2K package [17-18]. The theoretical study presented in this chapter includes the analysis of the relative stability of these phases of LaN as a function of hydrostatic compression and the possible mechanism behind the occurrence of low symmetry phase B10 under high pressure before the B2 phase gets stabilized at still higher pressures.

### 4.2 Theoretical Method

The structural stability and equation of state of LaN has been determined from first principles total energy calculations using FP-LAPW method [17-18]. To analyze the structural stability we have considered three plausible phases of LaN namely B1, B10 and B2 structures. For the total energy calculations, the unit cell of these structures is divided into two regions, the one consisting of non overlapping atomic spheres centered at the atomic site and the other an interstitial region as discussed in the first chapter. The muffin tin radius for atomic sphere of La was chosen to be 2.2 a.u. while the same for nitrogen was kept to be 1.5 a.u. The parameter \( R_{MTKMAX} \) that
determines the number of basis functions (size of matrices) is chosen to be 7; here $R_{MT}$ is muffin tin radius and $K_{MAX}$ is the magnitude of the largest $K$ vector (reciprocal lattice vector) used in plane wave expansion. The dimension of $K^2_{max}$ is that of energy. The magnitude of the largest vector ($G_{max}$) used in charge density Fourier expansion was set to be 12. A grid of 5000 k-points was used for sampling of the Brillouin zone. The exchange correlation interaction was treated within generalized gradient approximation (GGA) [19] for all the calculations. For B10 and B2 phases the calculations have been performed on the tetragonal cell as described in chapter 2.

The HP-LaN or B10 structure, which, has been found to occur in LaN under high pressure has also been reported to exist in BaO at high pressures [20]. The atomic species La and N of the two units of LaN contained in the tetragonal cell of the B10 structure were located at 2c (0 $\frac{1}{2}$ $z$, $\frac{1}{2}$ 0 $-z$) and 2a (0 0 0, $\frac{1}{2}$ $\frac{1}{2}$ 0) sites (international table of Crystallography, Vol. 2). The value of $z$ determined experimentally at 39 GPa is 0.3450, which increases to 0.3586 at ~ 60 GPa [11]. At 39 GPa, the experimentally measured c/a ratio of B10 phase is reported to be 0.75412, which shows a slight variation with pressure and reaches to ~ 0.7415 at ~ 60 GPa [11]. As already discussed in chapter 2, the B10 structure becomes identical to B2 phase for c/a = $1/\sqrt{2}$ and $z = \frac{1}{2}$. In our calculations we have optimized both the c/a ratio and the $z$ for B10 structure for all volumes. For this purpose, at each volume, we have chosen several c/a ratios ranging from 0.76 to 0.69 (which include the c/a corresponding to B2 structure also) and optimized the value of $z$ for each c/a. The optimum c/a and z at a given volume is the one for which the total energy is minimum. This procedure was repeated at various volumes and optimum c/a and z as a function of volume has been obtained. The structural stability as a function of hydrostatic compression has been analyzed by comparing the total energies of B1, B10 and B2 phases as a function of volume.

The 0 K pressure-volume ($P$-$V$) data for LaN have been determined by finding the negative volume derivative of total energy calculated at various unit cell volumes. The 300 K isotherm is derived by adding the thermal contributions to the 0 K isotherm. The zero pressure bulk modulus ($B_0$) and its pressure derivative at zero
pressure \( (B_0') \) were obtained by fitting the isotherm to the third order Birch-Murnaghan equation of state [21] as described in section 2.2.1. Further, the elastic constants of B1 phase of LaN have also been determined as a function of hydrostatic compression following the procedure described in the chapter 2.

4.3 Results and Discussions

4.3.1 Structural Phase Transition Sequence and the EOS

![Diagram](image.png)

**Figure 4.1:** The optimized c/a and fractional coordinate z as a function of volume for tetragonal structure. The regions marked as B1, B10 and B2 represent the regime of stability of B1, B10 and B2 structures, respectively. It may be noted that the tetragonal structure with \( 0.707 < \text{c/a} \leq 0.7597 \) and \( 0.3271 \leq \text{z} < 0.5 \) represents the B10 phase, however, the c/a = 0.707 and z = 0.5 corresponds to B2 phase.

The structural stability of B1, B10 and B2 phases has been examined as a function of hydrostatic compression. As one can go from B10 structure to B2 structure by changing the c/a ratio to \( 1/\sqrt{2} \) and the z value to 0.5, for these two
structures the calculations have been performed in primitive tetragonal cell only and at each volume the c/a ratio and z value is optimized. In Fig. 4.1, we have plotted the optimum c/a and z value as a function of volumes/formula unit of tetragonal cell. The optimum value of c/a ratio and z at the zero pressure equilibrium volume of tetragonal cell \( V_{0t} = 35.87 \, \text{Å}^3/\text{formula unit} \) is \( \sim 0.7687 \) and \( \sim 0.2791 \), respectively. The c/a ratio decreases monotonically with increasing compression and approaches a constant value of \( \sim \frac{1}{\sqrt{2}} \) at \( V/V_{0t} \sim 0.542 \) with corresponding pressure \( \sim 169 \, \text{GPa} \), whereas, the z parameter increases with increasing compression and reaches a constant value of \( \sim 0.5 \) at above mentioned compression. This indicates that beyond 169 GPa the B2 structure becomes lower in energy than the B10 Phase. Further, in Fig. 4.2, we have compared the theoretically determined optimum lattice parameters of B10 structure with the experimental values of Schneider et al. [11] at various pressures. The theoretical lattice parameters are found to agree with the experimental values within \( \sim 2.5\% \).

The total energies of B1 and optimized primitive tetragonal cell are compared in Fig. 4.3 as a function volume. Also, for sake of clarity, the optimum c/a and z values for tetragonal cell are also plotted. It is clear from the figure that the B1 phase which is a stable structure at ambient conditions transforms to a tetragonal structure (B10) at \( V = 32.01 \, \text{Å}^3/\text{formula unit} \) with \( V/V_{0t} \sim 0.852 \) and corresponding pressure of \( \sim 25.83 \, \text{GPa} \). This is in agreement with the experimental findings of Schneider et al [11], where authors have reported this transition to occur at \( \sim 22.8 \, \text{GPa} \). Further, the c/a ratio of \( \sim 0.7541 \) and \( z \sim 0.3416 \), determined theoretically for B10 phase at \( \sim 40 \, \text{GPa} \) (\( V \sim 27.01 \, \text{Å}^3/\text{formula unit} \)) are in good agreement with the experimental values of 0.7522 and 0.3450, respectively. Similarly, at \( \sim 60 \, \text{GPa} \) the theoretical c/a and z are found to be \( \sim 0.7500 \) and \( \sim 0.3583 \) as compared to the experimental values of 0.7415 and 0.3586, respectively [11]. Additionally, present calculations predict that upon further compression the B10 phase will transform to B2 structure at \( V \sim 19.44 \, \text{Å}^3/\text{formula unit} \) with corresponding pressure of \( \sim 169 \, \text{GPa} \).
Further, using calculated total energies and pressures, we have determined the enthalpy of B1, B10 and B2 structures at various pressures. The Fig. 4.4 displays the enthalpies of these structures relative to that of B2 phase. As is clear from the figure, the comparison of enthalpies puts the B1 to B10 transition pressure at ~19 GPa as compared to 25.8 GPa obtained from the comparison of total energy. This is expected as this transition is of first order in nature (as a volume discontinuity occurs at the transition pressure). The B10 to B2 transition is of second order in nature (as no volume discontinuity is associated with this transformation) and thus, the transition pressure determined from the enthalpy comparison is identical to that obtained from the total energy comparison i.e. ~ 169 GPa. Table 4.1 compares the theoretically determined transition pressures with available experimental data [11].
Table 4.1: The comparison of theoretically determined phase transition pressures with experimental data.

<table>
<thead>
<tr>
<th>Phase transition (GPa)</th>
<th>Theory (Present work)</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From total energy</td>
<td>From enthalpy</td>
</tr>
<tr>
<td>B1→B10</td>
<td>25.8</td>
<td>19</td>
</tr>
<tr>
<td>B10→B2</td>
<td>169</td>
<td>169</td>
</tr>
</tbody>
</table>

Figure 4.3: The total energy of B1 phase and tetragonal structure. The total energy at each volume for tetragonal structure is plotted for optimum c/a and z. For clarity, the optimized c/a and fractional coordinate z of tetragonal structure as a function of volume is also plotted. It may be noted that for $V \leq 19.44$ $\text{(Å}^3/\text{formula unit})$, i.e., pressure $\geq 169$ GPa, the optimum c/a and z of tetragonal structure saturate at a value of $\sim 0.707$ and 0.5, respectively, indicating the transition of B10 phase to B2 structure.
The theoretical isotherm along with experimental data [11] is displayed in Fig. 4.5. As far as B1 phase is concerned, the agreement of theoretical isotherm is good with the experimental data [11], whereas, for B10 phase the theoretical isotherm is underestimated systematically as compared to the experimental data with maximum deviation of ~ 16% at experimental pressure of 60GPa (the maximum pressure in the experiment). The volume discontinuity determined theoretically at the B1 $\rightarrow$ B10 transition point is ~ 9% as compared to the experimental value of 11%. Theoretical isotherm shows no volume discontinuity at B10 $\rightarrow$ B2 phase transition indicating that this transition will be of second order in nature. Further, in Table 4.2, we have compared equilibrium volume, bulk modulus and its pressure derivative determined theoretically at ambient conditions with the available experimental data [11] and theoretical values reported in literature [6-9, 22]. The equilibrium volume shows excellent agreement with the experimental value, however, the bulk modulus and its pressure derivative agree with the experimental data within ~ 9% and ~ 32%,
respectively. Further using $B'_0$ in the Slater’s definition [23], we have determined the value of Gruneisen parameter ($\gamma$) to be 1.52 (listed in Table 4.2).

![Figure 4.5: Pressure versus volume curve of LaN. The solid curves display the theoretical isotherm and the symbols correspond to the experimental data [11].](image)

**Table 4.2:** Various physical quantities for B1 phase of LaN at zero pressure.

<table>
<thead>
<tr>
<th></th>
<th>Theory Present work</th>
<th>Experimental</th>
<th>Theory (other sources)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0 (A^0)^3$/formula unit</td>
<td>37.53</td>
<td>37.32[11]</td>
<td>37.64[6], 34.3[7], 37.36[8], 36.85[9], 37.37[22]</td>
</tr>
<tr>
<td>$B_0$(GPa)</td>
<td>123.2</td>
<td>135.5[11]</td>
<td>148[6], 152[7], 117[8], 124.4[9], 152[22]</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>3.38</td>
<td>5[11]</td>
<td>3.65[8], 4.48[9], 4.16[22]</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>208</td>
<td></td>
<td>213[8], 201[10], 221[22]</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>81</td>
<td></td>
<td>84 [8], 65[10], 118[22]</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>69</td>
<td></td>
<td>71[8], 49[10], 71[22]</td>
</tr>
<tr>
<td>$\theta_D$(K)</td>
<td>318.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.52</td>
<td></td>
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4.3.2 Stability of B10 phase: Symmetry Breaking Mechanism

In an attempt to understand the occurrence of low symmetry B10 structure before the stabilization of high symmetry B2 phase, we have analyzed the electronic band structure and DOS of B10 and B2 structure. To have a proper comparison, the B2 structure is also represented in tetragonal geometry and band structure and density of states are calculated in the tetragonal unit cell for both the B2 and B10 structure. Fig. 4.6 displays the band structure and corresponding DOS for B10 and B2 structure in the pressure regime where the B10 phase is stable. Along with the total DOS, the projected density of states is also plotted. The band structure plot displays that the band gap opens at Fermi energy for both the B10 and B2 structure. However, in B10 phase the opening is extended in all Brillouin zone directions, whereas the same is limited to only Z-R-A-M-X directions for B2 structure. Moreover, the amount of depression in energy bands is large for B10 structure as compared to that for the B2 structure. The total density of states plot displays that for B10 phase there are no states around the Fermi energy, however, that for B2 structure shows a density of ~0.5 states/eV at Fermi energy. These results suggest that relatively extended opening of the band gap and large depression of electronic bands near the Fermi energy in B10 as compared to that in B2 structure might have lowered the total energy low symmetry B10 phase and led the stabilization of this structure at lower pressures. The B2 phase due to its higher symmetry has high density of degenerate states (which are composed of $d$ states of La and, $s$ and $p$ states of N hybridized near Fermi energy) near the Fermi energy. The energy of such a high symmetry structure can be lowered by lowering its symmetry as this lifts the degeneracy and pushes some of the states down in energy. It may be possible that the energy lowering caused by this symmetry breaking mechanism in the lower pressure region, is large enough to win over the high symmetry structure supporting Madelung energy term, leading to stabilization of B10 structure, which actually is a distortion of B2 structure. This kind of symmetry breaking mechanism also known Peierls distortion has been found to be even more pronounced in group IV d-electron metals Ti, Zr and Hf, where at lower pressure the low symmetry $\omega$ phase, which actually is a distortion of bcc structure occurs before the high symmetry bcc phase stabilizes at higher pressures [24-25]. Similarly, in light actinides the occurrence of low symmetry distorted structures even at ambient conditions has been associated to the lowering of total energy due to Peierls distortion.
[26]. It has been argued that in case of group IV d-electron systems it is the narrow d bands pinned near Fermi level play a significant role in stabilizing the lower symmetry \( \omega \) structure [24, 27], whereas in light actinide series the 5f bands are responsible for stabilizing distorted structures [28].

Additionally, the band structure and distribution of DOS indicates that the HP-LaN structure must be an insulator or semiconductor with a direct band gap of \(~ 0.2\) eV; however, the B2 phase must be a weakly metallic in character.

### 4.3.3 Elastic constants as a function of pressure

Further, we have examined the elastic stability of B1 phase under hydrostatic compression. For this purpose, we have calculated the elastic constants of B1 phase as a function of hydrostatic compression. To our knowledge, there are no experimental measurements available on elastic constants of this material. In Table 4.2, we compare the elastic constant of B1 phase at zero pressure calculated in the present work with those reported by other theoretical works [8, 10]. Values reported in the present work show very good agreement with those reported by Ciftci et al. [8].

Using these elastic constants, we have determined the zero pressure Debye temperature (\( \theta_D \)) of LaN by following the procedure provided in Ref. (28-30). As listed in the Table 4.2, the value of \( \theta_D \) is calculated to be 318.1 K. In Fig. 4.7, we have plotted the variation elastic moduli as a function of pressure. The bulk modulus and shear modulus \( C' \) increases monotonically with increasing pressure, however, the shear modulus \( C_{44} \) shows opposite trend with increasing pressure. It gets soften with pressure and vanishes at \(~ 107\) GPa i.e. much beyond the B1 \( \rightarrow \) B10 phase transition pressure.
Figure 4.6: The electronic band structure and density of states of LaN in B10 and B2 structure at ~ 30 GPa i.e. in the regime of stability of B10 phase.
4.4 Summary

First principles electronic band structure calculations have been performed on LaN using FP-LAPW method with the aim to explore the possibility of existence of low symmetry B10 phase in the low pressure regime before the stabilization of high symmetry B2 phase at higher pressures. Present analysis predicts that the B1 phase of LaN will transform to this B10 primitive tetragonal structure (space group symmetry P4/nmm) at ~ 25.8 GPa as compared to the experimental value of 22.8 GPa [11]. Additionally, it has also been predicted that this structure will transform to B2 phase at higher pressure of ~ 169 GPa. Present analysis of band structure of B10 and B2 phases suggests that the occurrence of B10, which is a distortion of B2 structure, could be due to the Peierls distortion. The examination of elastic moduli as a function of pressure shows that the shear stability of B1 phase reduces monotonically due to decreasing $C_{44}$ modulus. However, the B1 to B10 transition does not seem to be

Figure 4.7: Theoretically determined elastic moduli of B1 phase of LaN as a function of pressure.
driven by shear instability. Finally, various physical quantities such as $V_0$, $B_0$, $B_0'$ have been derived from present theoretical calculations and compared with the available theoretical and experimental data. The agreement of these quantities with experiment is reasonably good. The elastic constants could not be compared with the experimental data as, to our knowledge; there are no experimental measurements available on elastic constants. However, our theoretical values show good agreement with those of Ciftci et al. [8].
References

18. P. Blaha, K. Schwarz and J. Luitz, WIEN2K (Technical University of Vienna).