

Investigation of high pressure phase transition and electronic properties of Lutetium Nitride

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Abstract. In the present manuscript we have investigated the structural, electronic and phase transition properties of the heaviest lanthanide lutetium nitride (LuN) compound using an *ab initio* calculations based on the density functional theory with Perdrew, Burke and Ernzerhof generalized gradient approximation (PBE-GGA) and Engel-Vosko(EV)-GGA as implemented in WIEN2k code. The basic ground state properties viz., lattice constants (a), bulk modulus (B_0) and its pressure derivative (B_0') and total energy (E_0) are calculated. The calculated values of lattice constant is 4.76 Å which is in good agreement with experimental value $a = 4.76$ Å and other theoretical value. The relative stabilities of LuN at high pressures in the NaCl (B1), CsCl (B2), zinc blende (B3) and body centred tetragonal (BCT) structures are analysed. At compressed volumes, this compound is found to favour the CsCl phase rather the body centred tetragonal phase and zinc blende as observed in other lanthanum pnictides, which has been predicted by the total energy minimization. Under compression LuN undergoes a transition from NaCl to CsCl type structure at around 250.81 GPa with a volume collapse of 3.75%. To see the effect of functional we have also computed the band structure in B1 and B2 structure. Obtained result on band structure shows that LuN are semimetal by GGA while depicts semiconducting behaviour by EV-GGA. It shows metallic nature in B2 phase.

1. Introduction

Lutetium (Lu) is the last and heaviest member of the lanthanide series with completely filled 4f subshells. Most of the lanthanide compounds crystallize in NaCl (B1) structure with space group $Fm-3m$ (no. 225) under ambient conditions [1,2]. Lutetium mono nitride (LuN) crystallize in B1 structure. Most attractive applications of lanthanide nitrides (LnNs) are as fire resistive materials as well as protective materials in reactor. Lutetium nitride (LuN) is one of the interesting compounds of LnNs family of materials and attracted attention of researchers due to their unusual structural and electronic properties. It is important to study the pressure and temperature behaviour and physical properties of. lutetium mono nitride (LuN). Because of the great applications and interesting electronic and elastic properties of the LuN has been investigated in the recent past with great interest [3-6]. The majority of these compounds undergo first order structural phase transition from the NaCl to CsCl structure at high pressure. Niwa et al. [2] have successfully synthesized Ln nitrides ($Ln = Ce, Pr, Gd, Lu$) at high pressure and high temperature using the diamond anvil cell and laser heating system.

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Larson et al. [3] have computed electronic structures of the LnNs in the B1 structure using the LSDA+U (local spin density approximation with Hubbard-U corrections) scheme within the density functional theory approach. Recently, Yang et al. [4] studied elastic properties and hardness of lanthanide nitrides using first principles. Painter et. al. [5] evaluated theoretical lattice constants and cohesive energy of LaN, GdN and LuN compound using the VASP package which are also good agreement with experiential value. Very recently, Yang et.al. [6] investigated the structural stability of LuN using first principles and predicted that it transform from B1 to B2 structure at 220 GPa.

2. Methodology of computations

The calculations were performed using an *ab-initio* full potential linear augmented plane wave plus local orbitals (FP-LAPW + lo) approach [7] within the framework of density functional theory (DFT) [8] as implanted in the WIEN2k package [9]. In this approach the GGA-PBE [10] and EV-GGA [11] is chosen for the exchange-correlation functional energy optimization for calculating the equilibrium properties. In this method, an orbital dependent potential is introduced for the chosen set of electron states which is present in 4f states of lanthanides. In this method the wave function charge density and potential are expanded by spherical harmonic function inside non overlapping spheres surrounding the atomic sites (muffin-tin (MT) spheres) and by a plane-wave (PW) basis set in the remaining space of the unit cell (interstitial region). The convergence parameter $R_{MT}K_{max}$, which controls the size of basis set in the calculations, was set to 7. The converged value of R_{MT} of Lu and N atoms are 1.51, 1.3 a.u in case of LuN. The valance wave functions inside MT spheres were expanded up to $l_{max}=10$, while the charge density was Fourier expanded up to $G_{max}=12$ a.u⁻¹. The integrals over the first Brillouin zone (BZ) are performed in mesh of $10 \times 10 \times 10$ for all phases in the irreducible BZ using the Monkhost-Pack special k-points approach [12]. Both the PW cut-off and the number of k-points were optimized to ensure total energy convergence. The self-consistent calculations are converged up to an accuracy of 10^{-4} Ry in the total energy of the system. The set of unit cell volume and total energy are fitted to the Murnaghan equation of state [13] to obtain equilibrium unit cell volume, optimized value of total energy, bulk modulus and pressure derivative of bulk modulus.

3. Results and discussions

3.1 Structural and phase transition properties

To investigate the ground state properties of LuN we have first optimized the value of R_{MT} and k-points. The converged value of R_{MT} are for Lu (1.51 a.u.) and N (1.3 a.u.) in LuN. The optimized value of k-points are 1000. The equilibrium structural properties viz. lattice parameter (a), bulk modulus (B_0) and its first order pressure derivative (B_0') and total energy (E_0) are obtained by fitting the sets of the total energy and corresponding unit cell volume in the Murnaghan's equation of state. The energy vs. volume curves for LuN in four different phases have been shown in Figure 1. From figure 1 it is clear that (B1) phase is most stable phase with minimum energy $E_{min.} = -29271.97$ Ry for LuN corresponding to equilibrium volume $V_0 = 182.57$ a.u.³ for LuN. Calculated ground state lattice parameter (a), bulk modulus (B_0), its first order pressure derivative (B_0') obtained using GGA approximation are shown in Table 1 with other available data. From the Table 1 it is clear that the calculated equilibrium lattice constant $a = 4.76$ Å for LuN are very close to the experimental lattice parameters ($a = 4.766$ for LuN [1] and other theoretical reported results [3-5]).

The obtained values of B_0 is 161.10 for LuN. Our calculated lattice parameter, bulk modulus and its pressure derivatives for LuN are also in good agreement with the other theoretical and available experimental data [1-2]. From Figure 1, it is also evident that the optimization curve for B2 and BCT phase are very near to each other and optimization curve for B1 phase crosses these two phase curves at higher pressure points. This indicates that upon compression the B1 phase transforms into B2 phase. The pressure value for these transitions can be estimated by calculating the value of

enthalpy (H) as a function of the applied pressure as

$$H = E + PV \quad (1)$$

Here E is the total energy of the system at pressure (P) and volume (V). The enthalpy versus pressure curve for LuN is given in Figure 2. From Figure 2, the transition pressure for LuN is found to be 250.81 GPa. The calculated transition pressure for LuN is higher than the earlier reported in literature [6]. In order to confirm these structural transitions in LuN we have also analyzed the relative volume as a function of pressure and calculated the volume collapse for B1 to B2 transitions as 3.75% for LuN.

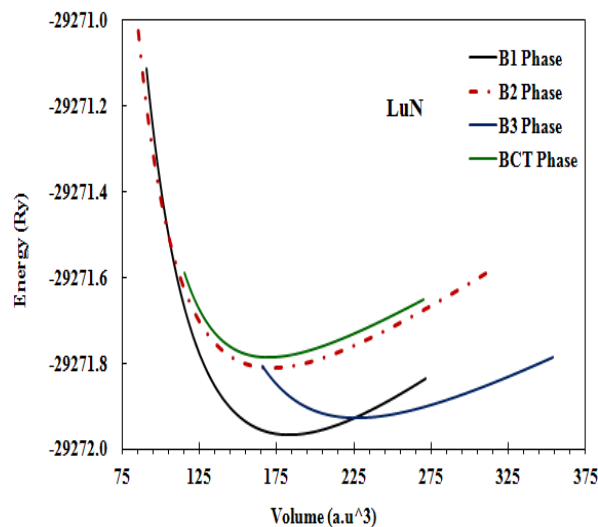


Figure 1. Energy versus volume curves of LuN.

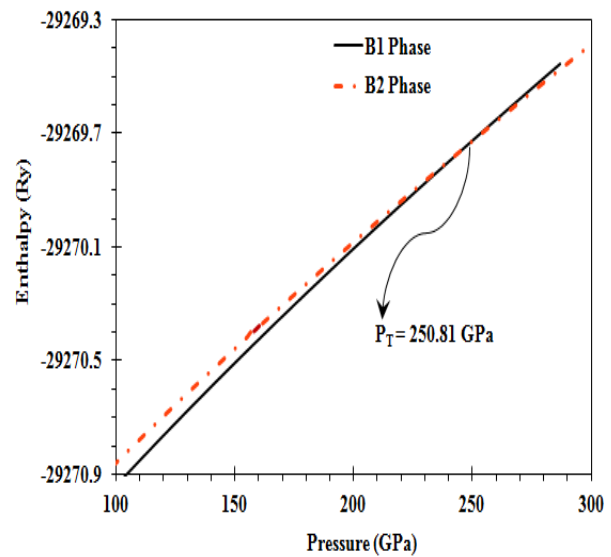


Figure 2. Enthalpy versus pressure curves for LuN.

TABLE 1. Lattice parameter (a in Å), bulk modulus (B_0 in GPa) and its pressure derivative (B_0'), phase transition pressure (P_T in GPa), the % volume collapse at P_T ($\Delta V(P_T)/V(0)$) for LuN.

| Material | Phase | Space Group | a | B_0 | B_0' | E_0 | Reference |
|----------|--------------------|---------------|------|--------|--------|-----------|------------|
| LuN | B1 <i>Fm-3m</i> | | 4.76 | 161.10 | 3.73 | -29271.97 | Present |
| | | | 4.76 | - | - | - | Expt.[1] |
| | | | 4.74 | - | - | - | Expt.[2] |
| | | | 4.87 | 170 | - | - | Others [3] |
| | | | 4.83 | 183.0 | | | Others [4] |
| | | | 4.76 | | | | Others [5] |
| | B2 | <i>Pm-3m</i> | 2.94 | 142.68 | 4.02 | -29271.81 | Present |
| | B3 | <i>F-43m</i> | 5.12 | 120.52 | 4.32 | -29271.93 | Present |
| Material | Phase | Space Group | c/a | B_0 | B_0' | E_0 | Reference |
| LuN | BCT | <i>P4/mmm</i> | 0.88 | 169.72 | 4.73 | -29271.79 | Present |

3.2 Electronic properties of LuN

The GGA and EV-GGA approach has been used to compute the electronic structure in B1 phase at the equilibrium lattice constant which are presented in figure 3 and at high pressure B2 phase in figure 4 respectively. It can be seen from Figure 3 that there is no band gap at the Fermi level. Top of the valence band is matched to zero of the Fermi level (E_F). It is observed that top three bands in valence band region are from N p orbitals lying up to -3.28 eV while all fourteen completely occupied Lu $4f$ energy bands hybridized with N p , s bands. One of the empty band from conduction bands dips slightly at X point, as a result, LuN exhibit a semi metallic character by GGA approach while EV-GGA approach LuN shows Γ -X indirect energy band gap of 0.14 eV, Γ - Γ direct band gap is 3.4 eV which confirms the semiconducting behaviour at ambient conditions. This result is consistent with other theoretical works [3].

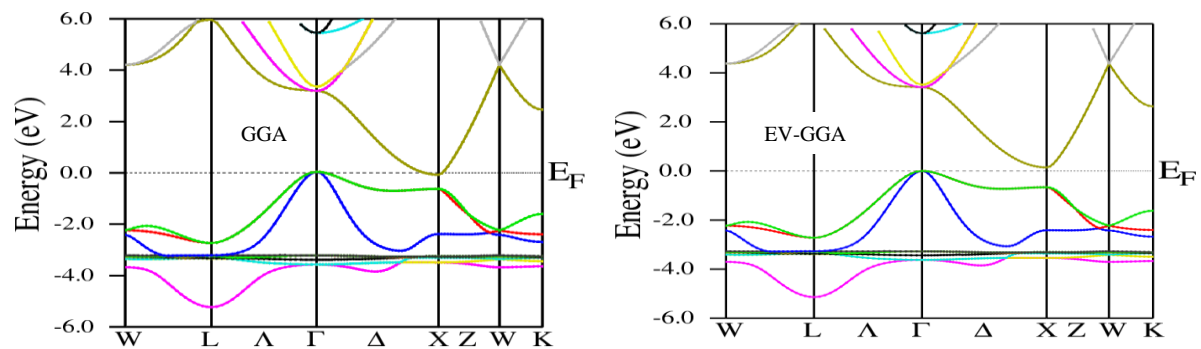


Figure 3. Band structure of LuN in B1 phase with GGA and EV-GGA.

To understand change in the nature of bands, high-pressure band structure of LuN in the B2 phase at their corresponding metallization pressures (or reduced volume) is given in Figure 4. In Lu, all the f -states are occupied and are present 3-4 eV below the Fermi energy and thus make up the valence band. The conduction band states are instead constituted from the anion states and the Lu d -states. The upper valence bands which lie above this band are mainly due to 'p'-like states of the N-atom with the top occurring at the Γ point. It is clear from figure 4 that at the Γ point, the top of the valence band crosses Fermi level and at the Γ point the bottom of the conduction band lies down near the Fermi level. Hence, it is metallic in nature.

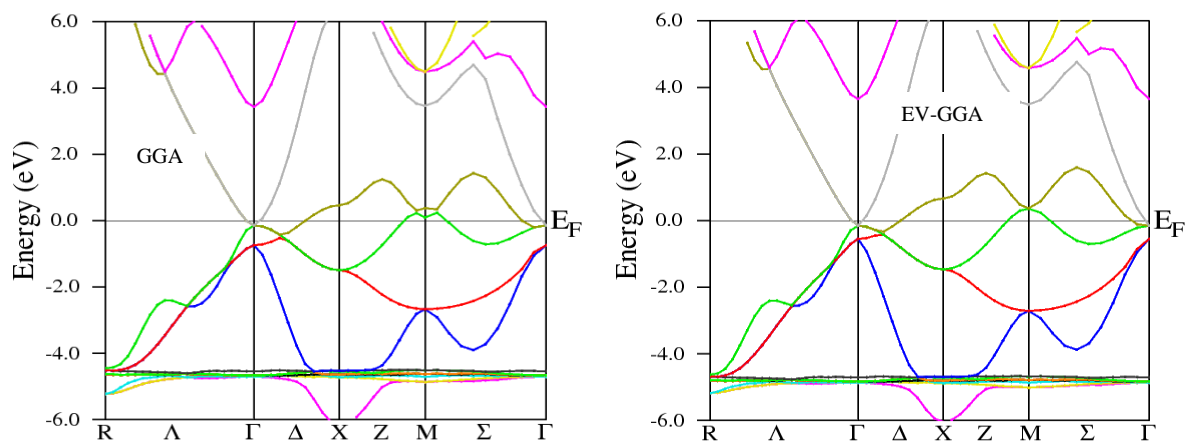


Figure 4. Band structure of LuN in B2 phase with GGA and EV-GGA.

4. Conclusions

The present paper deals with the computations of structural and phase transition properties of LuN compound GGA approach. The computed values are explained well and show good agreement with experimental data. LuN shows first-order phase transition from B1 to B2 phase under compression. The electronic structure has been computed in B1 and B2 phases which predict semi-metallic nature using GGA while small band gap semiconductor.

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