A DFT Approach to Structural, Electronic, and Thermodynamic Properties of Binary Rare-earth Nitrides REN (RE = Pr & Nd)

Suparn Kumar Barmase[1,a], Hansraj Dhadse[1,b], Purnima Singh[1,c], Shubha Dubey[2,d], and Jagdeesh Pataiya[3,e]

[1] *Department of Physics, Govt. Motilal Vigyan Mahavidyalaya, Bhopal – 462008, M.P., India.*
[2] *Department of Physics, Barkatullah University, Bhopal, 462026, M.P., India.*
[3] *Department of Physics, Dr. Bhimrao Ambedkar Government College, Amla, Betul, 460551, M.P., India.*

[a] suparn404880@gmail.com
[b] hrdhadse2050@gmail.com
[c] purnimasep@gmail.com
[d] shubha.dubey4@gmail.com
[e] jagdeesh8115@gmail.com

Abstract

In the present work, we apply density functional theory (DFT) with the PBE (Perdew–Burke–Ernzerhof) and WC (Wu–Cohen) exchange-correlation functionals using the generalized gradient approximation to investigate the structural, electronic, and thermodynamic properties of binary rare-earth nitrides REN (RE = Pr and Nd) compounds. Our computed structural parameters, such as equilibrium lattice constants, bond angles, and bond lengths, show excellent agreement with both experimental and previous theoretical results. The electronic properties of praseodymium and neodymium nitrides are examined through electronic band structure and density of states analyses. Additionally, we compute thermodynamic properties using the quasi-harmonic Debye model. This study provides a valuable basis for further experimental and theoretical exploration of the potential applications of these materials.

Keywords: Density of States; Structural Parameters; Metallicity; Rare-Earth.
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*** Address of correspondence**
Suparn Kumar Barmase
Department of Physics, Govt. Motilal Vigyan Mahavidyalaya, Bhopal – 462008, M.P., India

Email: suparn404880@gmail.com

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Introduction

Rare-earth nitrides (RENs) exhibit an exceptional range of electrical and magnetic properties, making them highly versatile materials for advanced technological applications. Their unique characteristics arise from the interplay between their electronic structure and the localized nature of the 4f orbitals [1]. These materials demonstrate behaviours spanning metallic, semi metallic, and semiconducting regimes. NdN and PrN, in particular, stand out as remarkable magnetic narrow-gap semiconductors, ideally suited for devices requiring simultaneous magnetic and semiconducting functionalities. Beyond their potential in spintronics, NdN and PrN provide a valuable platform for exploring fundamental physical phenomena [2]. Their stable magnetic ordering and narrow electronic band gaps make them ideal for studying magneto-optical effects, magneto-transport phenomena, and the interplay between spin, charge, and lattice dynamics. These materials are also excellent candidates for both experimental and computational research into correlated electron systems. Computational techniques such as density functional theory (DFT) using Wien2k can offer detailed insights into their electronic, thermodynamic, and structural properties.

DFT studies have provided valuable insights into their lattice constants, bulk moduli, and cohesive energies, demonstrating good agreement with experimental data [3]. Investigations on NdN and PrN have revealed their stable magnetic ordering and magnetoresistance effects, further validating their potential for device applications [4]. Additionally, thermodynamic studies employing the quasi-harmonic Debye model have explored their heat capacity, thermal expansion, and Debye temperature variations under high-pressure and high-temperature conditions, highlighting their stability in extreme environments [5].

Recent advancements in experimental techniques such as high-resolution X-ray diffraction (XRD) and neutron scattering have significantly improved structural characterizations, while computational methodologies incorporating Hubbard U corrections and many-body perturbation theory (GW) calculations have enhanced the accuracy of electronic structure predictions [6]. These developments emphasize the importance of RENs in fundamental research and technological applications, particularly in the fields of high-performance electronics and spintronic devices.

Computational Details

Calculations are performed using the Wien2k software with the FP-LAPW method for DFT-based ground-state energy calculations [7]. The exchange-correlation potential is described by PBE-GGA, with an energy convergence parameter, R_{MT}Kmax, set to 7.0. The Gmax parameter is set to 12 a.u.$^{-1}$, and self-consistency is achieved when total energy stabilizes within 10^{-4} Ry. The Monkhorst-Pack method with 1000 k-points is used for Brillouin zone integration, and a cut-off energy of -6.0 Ry is applied to separate valence and core states, with a charge convergence threshold of 0.0001e. The Monkhorst-Pack method [8] is a systematic approach for generating k-points in the Brillouin zone of a crystal for numerical integration in electronic structure calculations, particularly in density functional theory (DFT).

Results & Discussion

The structural characterization of REN (RE = Pr and Nd) was executed by assigning the RE atoms to the Wyckoff position corresponding to the fractional coordinates (1/2, 0, 0) and the nitrogen atoms to the (0, 0, 0) position. The resultant optimized conventional unit cell, as depicted in Fig. 1, manifests a cubic crystal structure with the Fm-3m space group.

To ascertain the most energetically favourable configuration and magnetic ordering, total energy calculations were performed as a function of volume for both non-spin-polarized (NM) and ferromagnetic (FM) states. The energy in the NM state was consistently lower than that in the FM state across all volumes, thereby corroborating the thermodynamic stability of the NM configuration. Structural parameters, including lattice constant and bulk modulus, were derived using the Birch-Murnaghan equation of state. The optimized lattice constants, presented in Table 1, elucidate the most stable structural configuration for REN (RE = Pr and Nd). The results exhibit a commendable agreement with available theoretical values from alternative research groups, with the minor discrepancies ascribed to variances in computational methodologies employed.

Table 1: Optimized Structural parameters of REN (RE=Pr & Nd).

Parameters	PrN	NdN
a (Å)	4.9842	4.9541
V (Å^3)	208.8890	205.1310
B (GPa)	153.6173	149.4908
B´	4.5624	4.8269
E_0	-18595.272902	-19369.749887

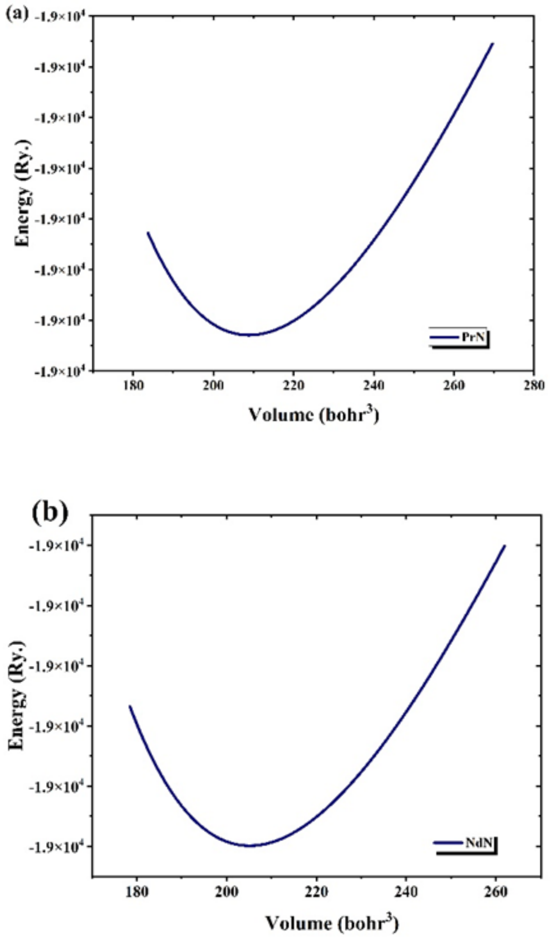

Figure 1: Energy versus Volume curve for REN (RE= Pr & Nd).

The figure 2 illustrates the Density of States (DOS) and electronic band structures for Praseodymium Nitride (PrN) and Neodymium Nitride (NdN), highlighting their electronic properties. The DOS plots, centered around the Fermi level (E_f=0), reveal sharp peaks near the Fermi level for both materials, indicative of a high density of electronic states. This suggests metallic behavior, as partially filled bands enable free electron movement [10]. For PrN, the DOS (panel a) shows pronounced features at both occupied and unoccupied energy levels, while the inset band structure (panel b) confirms the metallic nature through band crossings at the Fermi level along high-symmetry directions (W, L, Γ, X, and K). Similarly, the DOS for NdN (Figure 2c) also exhibits a sharp peak near the Fermi level, with its band structure (Figure 2d) showing comparable metallic behavior due to similar band crossings. Differences in band dispersion and DOS features between the two compounds

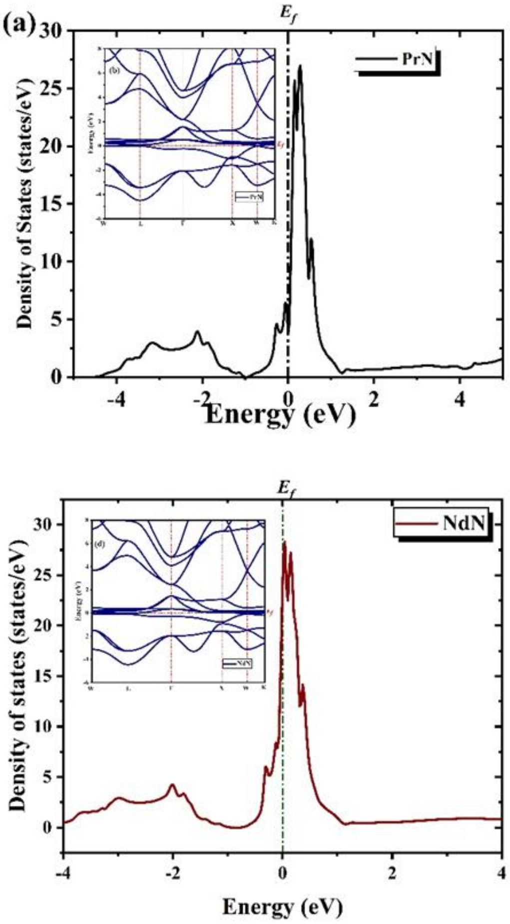

Figure 2: Total density of states TDOS and Band structure BS for REN (RE= Pr & Nd).

likely arise from variations in the electronic configurations and atomic interactions of Pr and Nd. These results emphasize the influence of localized f-electron states on the electronic structures of these nitrides, contributing to their characteristic peaks near the Fermi level. The calculated temperature dependent thermodynamic properties of REN's are calculated, including the variation of heat capacity at constant volume as a function of pressure range from 0 to 20 GPa within the temperature ranging from 0 to 1000 K, where the quasi-harmonic model remains valid [9]. The heat capacity at constant volume (C_v) for PrN and NdN exhibits (as shown in Figure 3) a typical temperature dependence, increasing sharply at low temperatures (<100K) due to phonon contributions and gradually saturating toward the Dulong-Petit limit (~50 J/mol·K) at higher temperatures (>300K).

The effect of pressure on C_v is minimal, with only slight variations observed as pressure increases from 0 to 20 GPa, indicating that phonon softening or stiffening effects are weak in both compounds. A comparison between PrN and NdN reveals similar overall trends, though NdN shows slightly lower C_v values at low temperatures, likely due to differences in phonon density of states arising from atomic mass variations. However, at higher temperatures, the C_v values for both compounds converge, reflecting dominant lattice contributions. This behaviour suggests that the thermodynamic properties of PrN and NdN are primarily governed by their photonic structure, with pressure exerting only a minor influence.

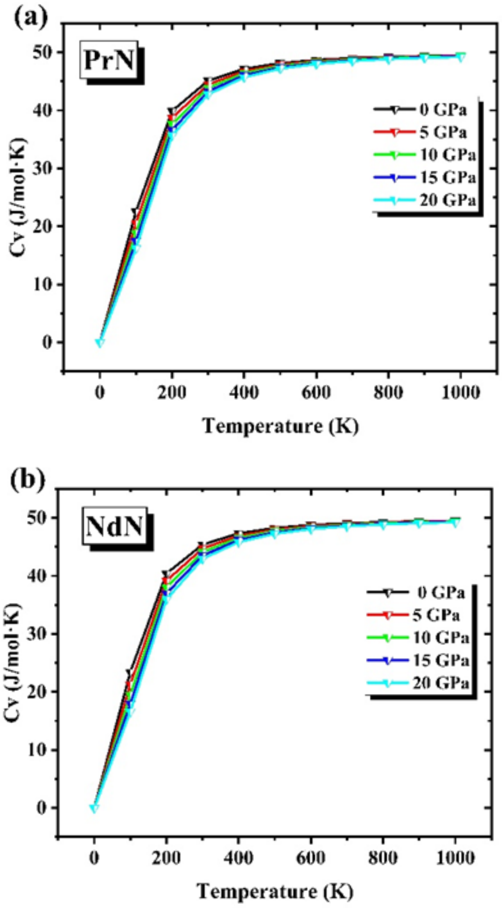

Figure 3: heat capacity at constant volume of REN (RE= Pr & Nd).

Conclusion and Future Prospective

We have conducted a detailed investigation into the structural, electronic, and thermodynamic properties of rare-earth nitrides REN (RE = Pr and Nd). Structural analysis reveals that REN exhibits non-magnetic behavior in the ground state, with the calculated equilibrium volume and lattice parameters provided. Electronic structure analysis shows that both REN compounds display metallic characteristics under the PBE-GGA exchange correlation. Additionally, high-temperature and high-pressure dependent thermodynamic parameter suggest that REN is a promising candidate for technological applications under extreme conditions.

References

1. P. Larson et al., Phys. Rev. B, 75, 4511 (2007).
2. T. A. Yamamoto et al., J. Alloys Compd., 376, 17 (2004).
3. M. G. Smith et al., J. Appl. Phys., 104, 093905

(2008).
4. S. R. Banerjee et al., J. Phys.: Condens. Matter, 21, 025501 (2009).
5. H. M. Wang et al., J. Phys. Chem. C, 124, 5436 (2020).
6. G. K. H. Madsen et al., J. Chem. Phys., 152, 7 (2020).
7. Blaha, P., Schwarz, K., Tran, F., Laskowski, R., Madsen, G. K. H., & Marks, L. D. Journal of Chemical Physics, 152(7), 2020.
8. H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
9. Jain, E., Pagare, G., & Dubey, S. AIP Conference Proceedings, 2100, 2019.
10. Singh, D. J., & Nordström, L. Springer, Vol. 2, 2nd ed., (2006).