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Structural, electronic, mechanical and magnetic properties of rare-earth nitrides REN (RE=Ce, Pr, Nd): A first principles study

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ABSTRACT

The structural stability of rare earth nitrides REN (RE=Ce,Pr,Nd) is investigated among three cubic structures, namely, NaCl (B1), CsCl(B2) and zinc blende (B3). It is found that NaCl structure is the most stable structure for all the three nitrides. On increasing the pressure, structural phase transition from NaCl (B1) to CsCl (B2) phase is predicted in CeN and NdN at the pressures of 88 GPa and 36.5 GPa while NaCl (B1) to zinc blende (B3) phase transition is observed in PrN at the pressure of 68 GPa. At normal pressure, all the three nitrides are stable in the ferromagnetic state (FM) with cubic NaCl (B1) structure. The calculated lattice parameters and bulk modulus values are in good agreement with experimental and other theoretical values. Electronic structure reveals that PrN and NdN are half metallic while CeN is metallic at normal pressure. Ferromagnetism is quenched in CeN and PrN at the pressures of 152 GPa and 121 GPa respectively. The positive values of elastic constants indicate that all the three nitrides are mechanically stable in NaCl Phase. It is found that all these nitrides are ductile and anisotropic in nature.

1. Introduction

The rare-earth mononitrides have received renewed attention due to their peculiar electronic and magnetic properties and potential application in spintronics [1–4]. The rare-earth mononitrides (RENs) are family of NaCl type structure compounds [5,6]. The rare-earth nitrides are narrow band gap semiconductors and they are also known as refractory materials [6,7]. One of the promising material is CeN, because it has different properties like smaller lattice constants and susceptibility, when compared to other rare-earth nitrides [8,9]. Recently, the rare-earth mononitrides and their properties were reviewed by Natali et al. [10]. Imamura et al. [11] synthesized the rare-earth nitrides and characterization of rare-earth nitrides were performed by using X-ray diffraction study. The lattice parameters of the cubic (NaCl type) compounds LaN, CeN, NdN and ErN were determined by Olcese [12] experimentally. Zhang et al. [13] analysed the structural stability of cerium mononitride by using first principles calculations. They have predicted NaCl (B1) to CsCl (B2) phase transition in CeN in the pressure range of 62–88 GPa. The electronic structure, structural stability and lattice dynamics of cerium mononitride were investigated by Kanchana et al. [14]. They have predicted that CeN exhibits semi metallic nature. Cynn et al. [15] analysed high pressure crystal structure of PrN experimentally and they reported that PrN crystallizes in tetragonal structure and high pressure crystal structure was predicted as CsCl structure. The electronic and magnetic properties of CeN were studied by Min et al. [16] using first principles calculations. They found that CeN is half-metallic and the magnetic moment of CeN is $0.99\mu_B$. Hao et al. [17] investigated the physical properties of NdN under various pressures by using first principles calculations and NaCl(B1) to CsCl(B2) phase transition was observed at a pressure of 52.7 GPa. Kocak et al. [18] analysed structural, elastic, electronic and thermodynamic properties of PrN with various crystal structures by using first principles study. They have reported that NaCl structure is the most stable one among the various structures. Larson et al. [3] have studied the electronic structure of rare-earth nitrides using density functional theory calculations within the local spin density approximation with Hubbard-U correction (LSDA+U) approach in the NaCl structure. Yang et al. [19] investigated the elastic and hardness properties of rare-earth nitrides in NaCl structure using first principles study. Sclar [20] has predicted that CeN is a semiconductor with a band gap of 1.8 eV. Xiao and Takai [21] reported that CeN is a p-type semiconductor with a optical band gap of 1.76 eV. Experimentally Lee et al. [22] determined that CeN is a metal. So the controversy about the electronic structure of CeN leads to the analysis of electronic structure in the present work. Despite of these studies, high pressure behavior of structural and mechanical properties of CeN, PrN and NdN are still unknown. This motivated us to analyse the structural, electronic and magnetic

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properties of CeN, PrN and NdN.

In this work, the electronic structure calculations have been performed at normal pressure. The structural and magnetic stabilities of CeN, PrN and NdN are analyzed. The elastic constants are calculated using energy strain method. The charge density distribution is also reported for these nitrides.

2. Computational method

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA) [23–25] as implemented

in the VASP code [26–29]. Ground-state geometries are determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV Å^{-1}. Brillouin-zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. The cutoff energy for plane waves in our calculation is 600 eV. The valence electronic configurations of Ce, Pr, Nd and N atoms are $4f^7$ $5d^1$ $6s^2$, $4f^{10}$ $6s^2$, $4f^{11}$ $6s^2$ and $2s^2 2p^3$ respectively. Brillouin-zone integrations are performed on the Monkhorst-Pack K-point mesh [30] with a grid size of $12 \times 12 \times 12$ for structural optimization and total energy calculation. Iterative relaxation of atomic positions is stopped when the change in total energy between successive steps is less than 1 meV/cell. The rare earth nitrides CeN, PrN and NdN considered in the present work crystallize in the NaCl structure with space group symmetry Fm3m at normal pressure. In the unit cell of these nitrides, the rare earth atom is positioned at (0, 0, 0) and nitrogen atom at (1/2, 1/2, 1/2). The unit cell structures of the three cubic phases are shown in Fig. 1. In order to get more accurate value of the band gap energy for the rock salt (B1) phase, we have used GGA plus on-site coulomb self- interaction correction potential (U^{SIC}). The GGA+U^{SIC} scheme is more appropriate for systems having strongly correlated d or f electrons. In the GGA+U^{SIC} method, the strong correlation between localized d or f electrons is explicitly taken into account through the screened effective electron–electron interaction parameter ($U^{eff}=U^{SIC}-J$), where U^{SIC} and J denote the coulomb and exchange integrals respectively. To obtain the best agreement with experiment, the present results are obtained with the $U^{SIC}=4.0$ eV, 2.6 eV and 3.5 eV and $J=1.2$, 1.21 and 1.25 for CeN, PrN and NdN respectively.

3. Results and discussions

3.1. Structural properties

The stability of rare earth nitrides RENs (RE=Ce, Pr, Nd) is analyzed by calculating the total energy. The total energies of the rare earth nitrides RENs (RE=Ce, Pr, Nd) for various volumes are fitted to the universal second order Birch-Murnaghan equation of state [31] to determine the bulk modulus B_0 and its first derivative $B_{0'}$ at normal pressure. 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 the super hard materials. The calculated ground state properties like lattice constants a (Å), cell volume V_0(Å3), valence electron density ρ(electrons/Å^3), cohesive energy Ecoh (eV), bulk modulus B_0 (GPa) and its derivative $B_{0'}$ and magnetic moment (μ_B) for the normal structures of CeN, PrN and NdN are listed in Table 1 and are compared with the available experimental and previous theoretical results [3,12–14,17–19,32–34]. From Table 1, it is found that the calculated bulk modulus value of NaCl- CeN (152 GPa) is in close agreement with the experimental results of Olsena et al. (153 GPa) [33]. The bulk modulus values are computed as 120 Gpa and 194 GPa for PrN and NdN in B1phase. These values are in agreement with the results of Yang et al. (121 GPa) [19] and Larson et al. (197 GPa) [3]. The calculated lattice constant (5.132 Å) of NaCl- NdN is in good agreement with the experimental (5.132 Å) value [12]. From Table 1, it is observed that, valence electron density value is high for CsCl- NdN, which indicates that NdN is relatively hard in CsCl phase. The cohesive energies for rare earth metals (REs) and their nitrides (RENs) are given in Fig. 2. It is also observed that, NdN owing to its highest cohesive energy is the most stable one among the considered nitrides.

The total energies of CeN, PrN and NdN are plotted as a function of reduced volume in Fig. 3. It is observed that all the three rare earth nitrides are stable in the NaCl phase at normal pressure. On further reducing the volume, CeN and NdN undergo structural phase transition from NaCl (B1) to CsCl (B2) phase and PrN undergoes structural phase transition from NaCl (B1) to zinc blende (B3) phase.In order to observe these transitions in a more accurate manner, the enthalpy is calculated using the formula

$$H = E + PV \tag{1}$$

where E is the total energy in eV and P represents the pressure (GPa) corresponding to a particular volume V (Å^3). The transition pressure value is determined by the intersection of enthalpy versus pressure curve (Fig. 4). It is observed that B1 to B2 phase transition occurs at a pressure of 88 GPa in CeN and 36.5 Gpa in NdN. In PrN, B1 to B3 phase transition is predicted at a pressure of 68 GPa. The calculated transition pressure value for CeN is close to the result (62–88 GPa) of Zhang et al. [13].

3.2. Electronic properties

The total and partial density of states (DOS) of CeN, PrN and NdN for both spin up and spin down states are given in Figs. 5–7(a and b) respectively. From the total DOS, it is observed that the peak due to 2s state electrons of the nitrogen atom is present around an energy of −8 eV. In the majority spin channel, the highest spike at the Fermi level is due to the 4 f state electrons of the rare earth atom. The spikes, just below the Fermi level are

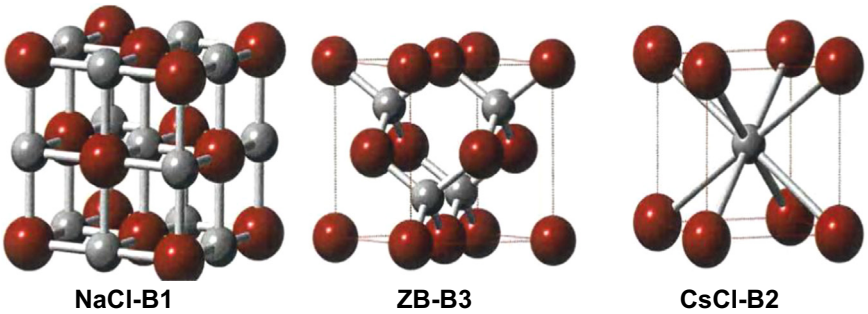

Fig. 1. Unit cell of different phases of rare earth nitrides RENs (RE=Ce, Pr, Nd).