

First-Principles Study on Electronic, Magnetic and Elastic Properties of CeN and PmN.

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We have used the Full Potential Nonorthogonal Local-Orbital minimum basis method (FPLO) in the Local Spin Density Approximation (LSDA) to calculate the electronic, magnetic and elastic properties of CeN and PmN. We predicted a phase transition from Rock Salt structure (RS) to Cesium Chloride (CsCl) structure in both CeN and PmN compounds at pressures of 40.7 and 42 GPa respectively. The half-metallic property was found only in the RS phase of PmN. The CeN compound, however, shows a metallic behavior in the two structures. The calculated bulk modulus of CeN and PmN in RS structure are 170.02 GPa and 154.6 GPa respectively. For PmN the energy gap and the total magnetic moment are 0.56 eV and $4 \mu_B$ respectively.

1. Introduction

The rare-earth nitrides RENs offer interesting magnetic properties in the field of spintronics applications [1-5]. The unfilled and highly localized f-orbital atoms are responsible for the interesting structural and magnetic properties of these compounds. All RENs exhibit strong magnetic ordering because of the interaction between the partially filled rare earth 4f orbital, the 5p valance on the N and 5d conduction band. All RENs undergo structural transformations when pressure is applied, and many compounds transform to the CsCl structure under high pressure. The reason is that the reduction of the lattice dimensions, upon applying pressure, causes the interionic coulomb interaction to favor the CsCl structure over the rock salt structure. In general, compounds with high ionicity values are expected to have low transition pressures. The magnetic structure of the rare earth nitrides is not always known. Szotek et al [6] have performed first- principles calculations using SIC-LSD method for all rare earth nitrides in the ferromagnetic ordering. They predicted that most of light rare earth nitrides are half-metallic, and only CeN is a metallic compound. TbN, DyN and HoN compounds have an insulating character with a narrow gap. GdN is the most studied compound of the rare earth nitrides, where it has a half-filled Gd 4f shell and the highest Curie temperature among these compounds.

Almost all of the rare earth nitrides undergo phase transitions under different pressures. Both of SmN and EuN undergo transition from NaCl structure to CsCl structure at high pressure. Pagare et al [7] calculated a phase transition pressure of 8.5 GPa and 14.6 GPa for SmN and EuN (with 17.5% and 14.9 % volume collapse respectively) using the Self-Consistent Tight-Binding Linear Muffin Tin Orbital method (TBLMTO) based on the density functional theory [8,9]. The RS to CsCl phase transitions in YbN and LaN were reported to take place at pressures of 133 GPa and 100 GPa with volume change of 5.1 % and 2.6% respectively according to Rukmangad et al [10] by using two-body interionic potential theory. The transition pressure of CeN was found to be 62 GPa by Svane et al [11]. Also PmN transform into CsCl structure from NaCl structure at 3.4 GPa with a volume collapse of 20% [12]. Srivastava et al [13] using the Tight-Binding Linear Muffin Tin Orbital (TBLMTO) method within the local density approximation predicted a phase transition in GdN from NaCl structure to CsCl structure at 30.4 GPa with $V/V_0=0.845$ for NaCl and 0.696 for CsCl. Another theoretical study by Shabara et al [14], based on DFT using the Local Spin Density Approximation (LSDA) [15,16] and the Generalized Gradient Approximation (GGA) [17,18] approximations, have found the phase transition pressure in GdN from RS into CsCl structure to be 93 GPa and 113 GPa respectively. The phase transition from RS to CsCl in SmN was predicted to take place at 8.6GPa by Pagare et al [7] using the first tight binding linear muffin tin orbital method. Huleil et al [19] using the Full Potential Nonorthogonal Local-Orbital minimum basis method (FPLO), within the LSDA and GGA approximations, predicted a phase transition in SmN from RS to CsCl at pressure of 49 GPa.

In this study, we present first-principles calculations of the electronic, magnetic and elastic properties of PmN and CeN using the electronic structure code FPLO.09. In addition, we predicted pressure induced phase transition in both compounds. The density of states and energy band are calculated for PmN and CeN compounds.

2. Theory and Computation

Our study is a first- principles based calculation of the elastic and magnetic properties of PmN and CeN compounds in the two crystallographic structures; CsCl and RS, within the framework of density functional theory (DFT). The theoretical values of equilibrium lattice constant, magnetic moment, energy gap ,density of states (DOS) and band structures are calculated from the electronic structure by the full-potential local-orbital minimum-basis code (FPLO), to solve the Kohn-Sham equations on a regular lattice using the local spin density approximation (LSDA). The bulk modulus and its pressure derivative have been computed using the modified Birch-Murnghan equation of state [20-22]. We have used equation (1) for fitting volume vs. energy data obtained from our ab-initio calculation:

$$E(V) = E_0 + \frac{9B_0V_0}{16} \left[B_1 \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^3 + \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^2 \left\{ 6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right\} \right] \quad (1)$$

and the pressure is given by

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (B_1 - 4) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right] \quad (2)$$

where V_0 is the equilibrium volume, E_0 the equilibrium energy, B_0 the bulk modulus, and B_1 the first derivative of B_0 with respect to pressure.

The parameters used in FPLO run are: the k-mesh subdivision: $24 \times 24 \times 24$, the accuracies of the density and total energy are 10^{-6} \AA^{-3} and 10^{-8} Hartree respectively. For the RS structure, the space group is (#225) and the atomic positions are (0, 0, 0) for Pm (Ce) and (1/2, 1/2, 1/2) for N. The atoms in the CsCl structure are located at (0, 0, 0) for Pm (Ce) and (1/2, 1/2, 1/2) for N atom with space group (#221).

3. Results and Discussion

The dependence of the total energy on the unit cell volume of the two rare earth nitrides are investigated in the magnetic state in the two possible phases (RS, CsCl), using the LSDA approximation. We found that RS structure is the most stable and the favorable structure of these compounds by minimization of energy as shown in Figs.(1 and 2). In agreement with the fact, that RS structure is the most stable and favorable structure of the rare earth nitrides compounds. Table (1), displays the calculated lattice constant of both compounds in the two structures. The equilibrium cell volume of PmN and CeN in the RS structure are 121.287 \AA^3 and 123.506 \AA^3 respectively. In the present study, the magnetic phase of PmN in RS and CsCl structure is ferromagnetic. The calculated magnetic moments of PmN in RS and CsCl are $4 \mu_B$ and $3.98 \mu_B$ respectively. Only in the RS structure of PmN, we have found an energy gap of 0.56 eV in the spin-down channel. The integer value of magnetic moment and the presence of the gap indicate that PmN is a half-metal compound in the RS phase. In contrast, the CsCl structure has zero energy gap, in both spin channels, which confirms the metallic behavior of this structure. Pandit et al [13] have checked out the presence of half-metallicity in CsCl structure of PmN, and found a small crossover of the d-band in the spin down channel at one point(G). (However PmN is a semiconducting in all directions except this point in the spin-down channel). Olsen et al [23] have found the experimental lattice constant of CeN to be 5.021 \AA using the energy-dispersive X-ray diffraction and synchrotron radiation using a diamond anvil cell at a maximum pressure of 77 GPa. They also used the full-potential linear muffin-tin orbital method within the GGA approximation to calculate the lattice constant and found it to be 5.024 \AA . Our calculated lattice constant agrees well with both

experimental and theoretical results of Olsen et al [23]. There are many authors who have calculated the lattice constant of CeN experimentally e.g. Landelli et al [24] and Schlegel et al [25] who reported lattice constants of 5.021 Å and 5.019Å respectively.

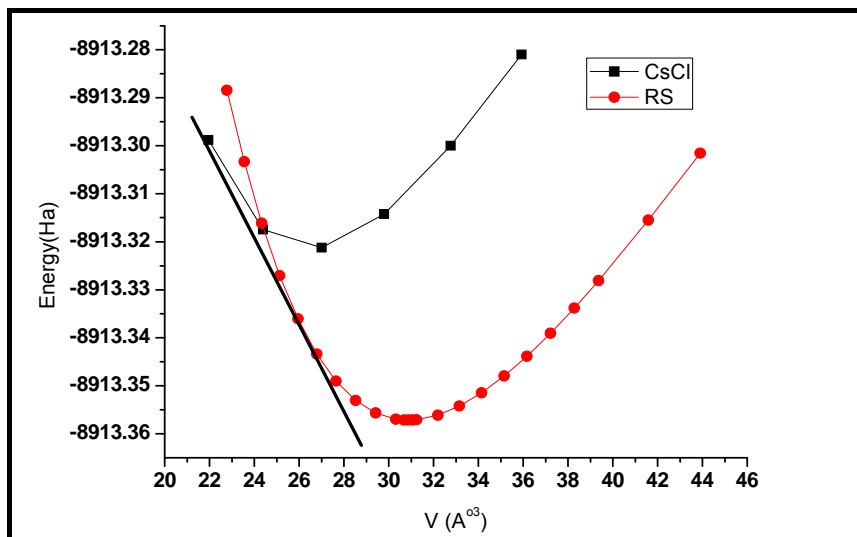


Fig.(1): The total energy dependence on the unit cell volume for magnetic CeN.

We have calculated the density of states and band structure of both PmN and CeN compounds in the RS and CsCl structures as shown in Figs.(3-5). We predicted from these Figures that:

- 1- The presence of an energy gap in the spin-down channel of PmN in the RS structure (Figs.3) confirms its half-metallic property.
- 2- PmN in CsCl structure and CeN in both RS and CsCl structures show a metallic behavior.

Table (1): The calculated lattice constant, magnetic moment, energy gap, and electronic state using LSDA approximation.

Compound	CeN		PmN	
	RS	CsCl	RS	CsCl
a(Å)	4.98 5.021 ^[23] 4.9 ^[23]	3	4.95 4.984 ^[12] 5.08 ^[25]	2.95 2.857 ^[12]
m(μ _B)	0.00 0.00 ^[23]	0.00	4 3.999 ^[12]	3.98 3.976 ^[12]
Energy Gap(eV)	0.00	0.00	0.56	0.00
Electronic state	M	M	H.M	M

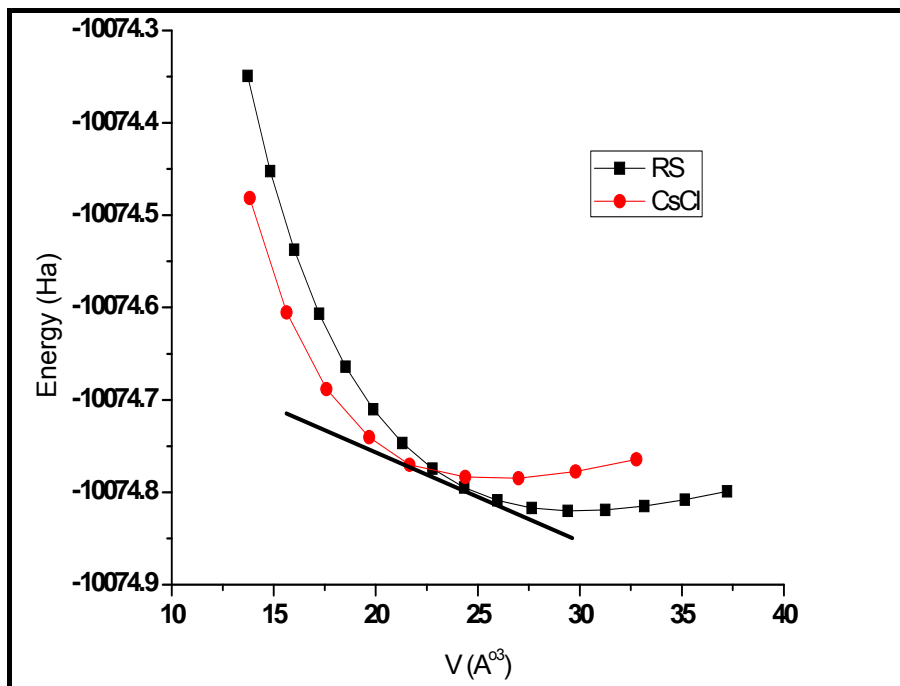


Fig.(2): The total energy dependence on the unit cell volume for magnetic PmN.

The bulk modulus and its pressure derivative are displayed in Table.(2). The bulk modulus of CeN compound is higher than the bulk modulus of PmN compound. The bulk modulus of PmN in RS and CsCl structures are 154.6 GPa and 113.96 GPa respectively in good agreement with results of Pandit at al [12].

Table (2): The bulk modulus and its pressure derivative and phase transition pressure from RS to CsCl structure.

Structure	RS		CsCl		Pt(RS→CsCl) (GPa)
	B_0 (GPa)	B_1	B_0 (GPa)	B_1	
CeN	170.02 210 ^[23]	4.39	180.33	1.087	40.7 62 ^[11]
PmN	154.6 150,165.6 ^[12]	5.93	113.96 90.83 ^[12]	4.98	42 3.4 ^[12]

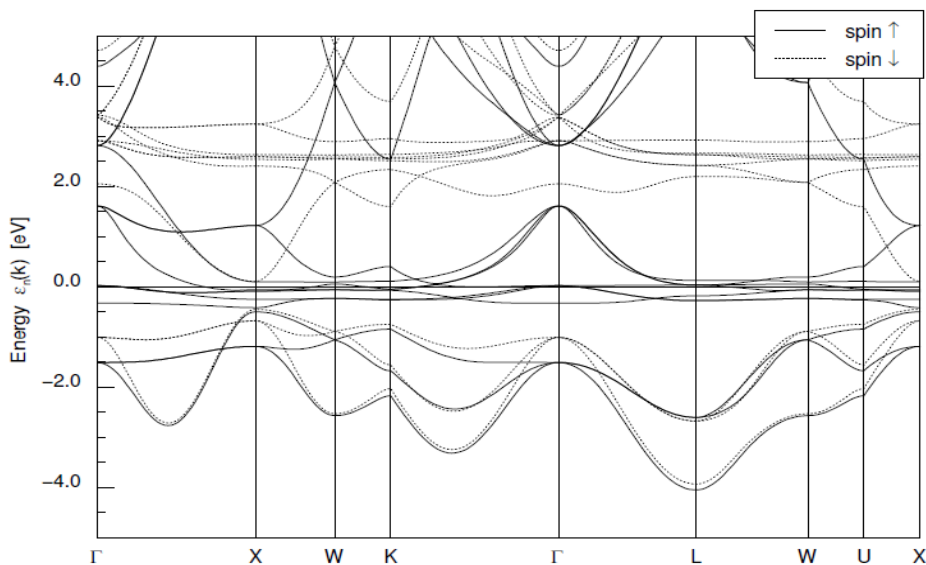


Fig.(3a): The band structure of PmN in the RS structure

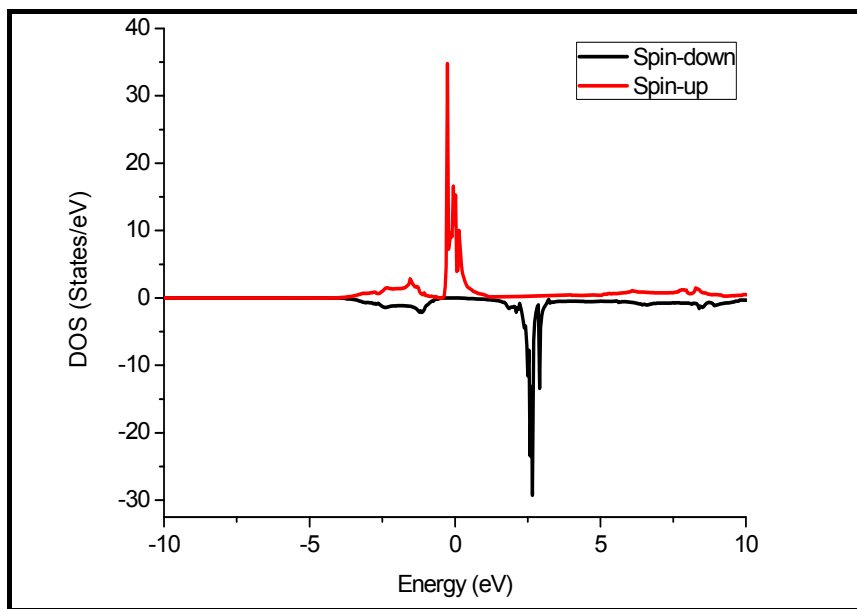


Fig.(3b): The DOS of PmN in the RS structure

We have investigated the structural phase transitions of PmN and CeN under hydrostatic pressure. A phase transition from RS into CsCl structure was predicted in both compounds at transition pressure of 42 GPa and 40.7 GPa respectively. This phase transition is predicted using the unit cell volume vs. pressure relationship as shown in Figs. (6 and 7) for CeN and PmN respectively.

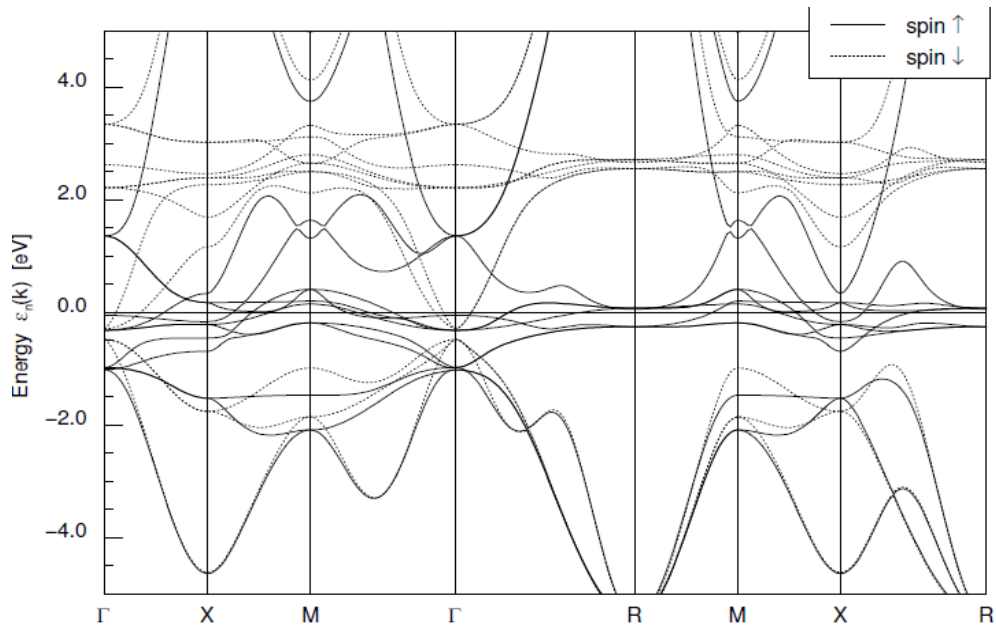


Fig.(4a): The band structure of PmN in the CsCl structure.

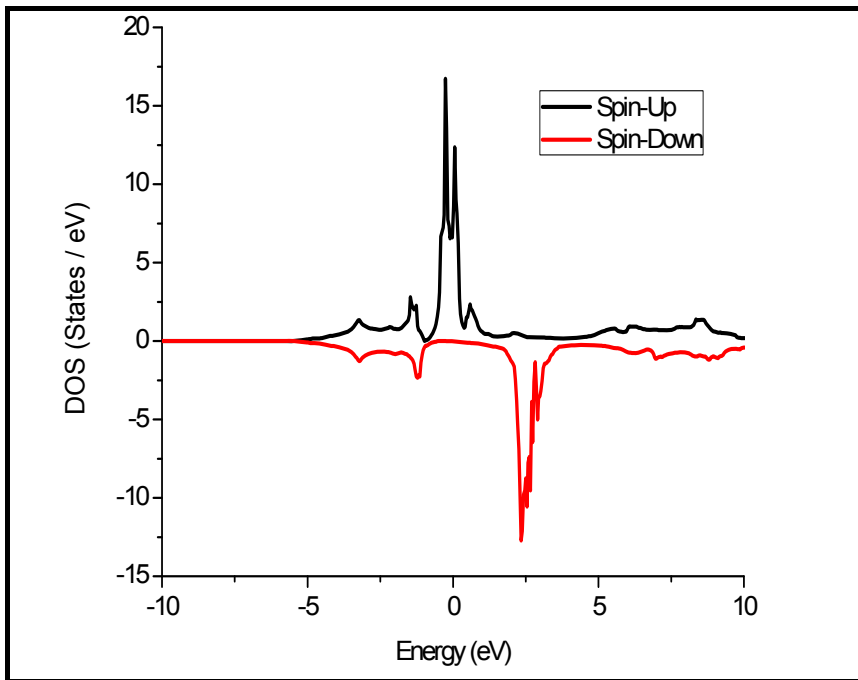


Fig.(4b): The DOS of PmN in the CsCl

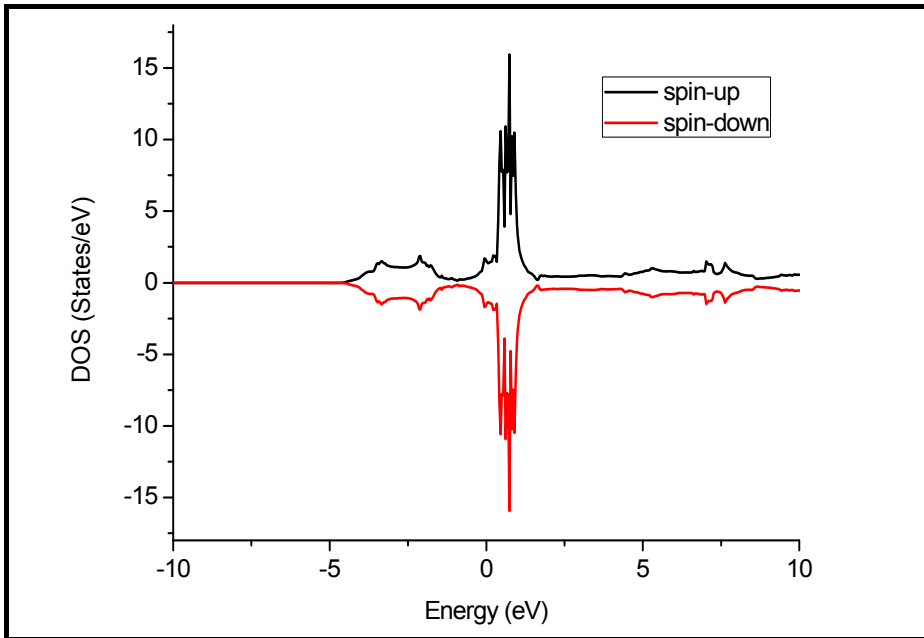


Fig.(5a): The DOS of CeN in RS

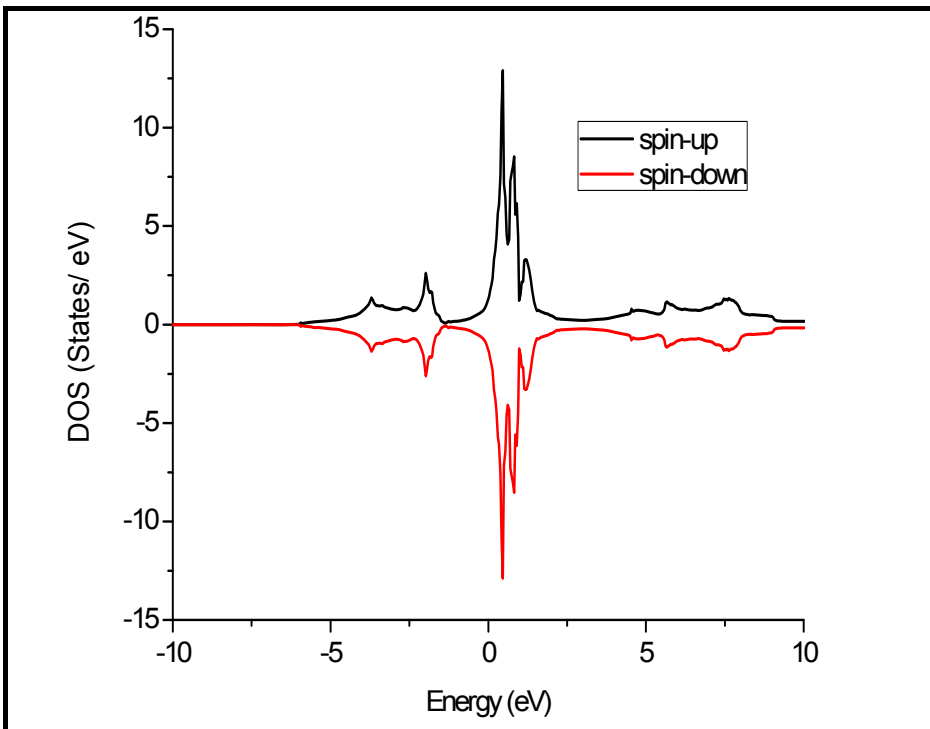


Fig.(5b): The DOS of CeN in CsCl

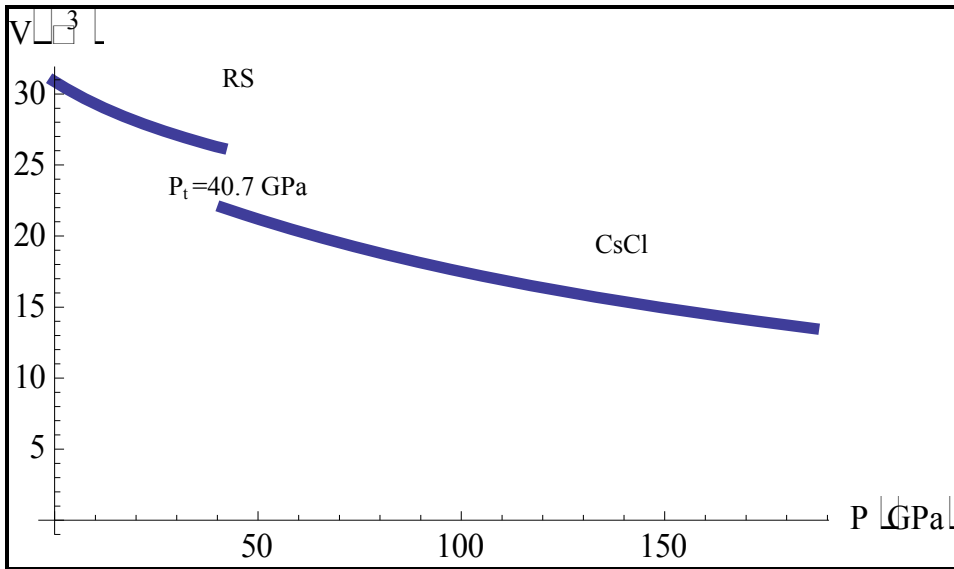


Fig.(6): The pressure vs. unit cell volume relationship showing the phase transitions from RS to CsCl structure in CeN compound.

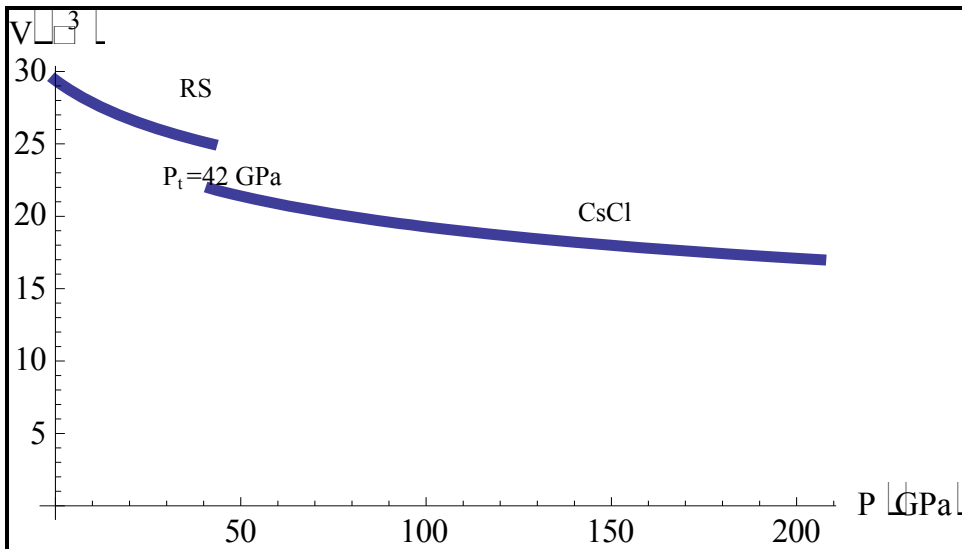


Fig.(7): The pressure vs. unit cell volume relationship showing the phase transitions from RS to CsCl structure in PmN compound.

4. Conclusions

Geometric optimization has indicated that the RS phase is energetically favorable in PmN and CeN compounds. We have studied PmN and CeN compounds in both RS and CsCl structures, and found that half metallicity appears only in the RS structure of PmN compound but the CsCl structure of PmN

is metallic, and also CeN compound is metallic in both RS and CsCl structures. A phase transition was predicted in CeN and PmN from RS to CsCl at $P= 40.7\text{GPa}$ and 42 GPa respectively. The bulk modulus and its pressure derivative for both compounds were calculated in the two structures.

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