Study of electronic and structural properties of half metallic rare earth mononitrides

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Abstract. In the present work we investigated theoretically the electronic, magnetic and structural properties of two rare-earth nitrides (REN: RE= Sm, Eu) by using self-consistent tight-binding linear muffin tin orbital (TBLMTO) method. Magnetically, both the rare earth nitrides (RENs) are stable in ferromagnetic (FM) state, while its ambient structure is found to be stable in NaCl-type (B₁) structure. From the present study we predict the pressure induced structural phase transition in both RENs from the relatively open NaCl-type structure into more dense CsCl-type structure at 8.6 GPa and 14.6 GPa respectively. They form a new class of half-metallic magnets with high magnetic moments and are strong candidates for applications in spintronics and spinfiltering devices. We have therefore, calculated electronic band structures, equilibrium lattice constants, cohesive energies, bulk moduli and magnetic moments for REN compounds in both B₁ and B₂ phases.

1. Introduction

In recent years, the mono-pnictides of rare earth (RE) compounds have drawn considerable interest of material scientist, due to the intricate structural, transport, magnetic and electronic properties [1-5]. An accurate description of the electronic structure of RE compounds is a very challenging problem because of their partially filled 4f shells [6]. These partially filled 4f shells are responsible for many of the interesting properties in the rare earth pnictides. The class of the rare earth nitrides (RENs), which belong to mono-pnictide family, have a broad range of behavior, from metallic or semi-metallic to semi-conducting. The ambient structure of both rare earth nitrides (REN: RE= Sm, Eu) is NaCl structure [7]. The RENs lie on the boundary between metals and insulators. These materials have high magnetic moment and form a wide range of magnetic structures. There has been speculation in the literature that RENs may form half-metallic ferro magnets [8-9]. According to Aerts et al [10], both SmN and EuN show half-metallic behaviour. Because of this property, these materials became strong candidates for applications in spintronic and spin-filtering devices and provide new interest in these...
materials. The HM behaviour regarding the electronic, magnetic and transport properties of these compounds is also discussed by Duan et al [11].

In the present investigations, we are interested in the pressure induced phase transition in SmN and EuN. The knowledge of the pressure behavior of these compounds is important in developing, comparing and understanding the systematic of the lanthanide and actinide mono-pnictides. Our interest in these materials is motivated by the fact that the rare earth elements show anomalous behaviour due to partially filled f-electron orbital and there is no information of structural changes under pressure and the variation in magnetic moment under pressure in literature. Both spin and non-spin polarized electronic band structure calculations are performed by us by using first principals tight binding linear muffin tin orbital (TB- LMTO) method at ambient as well as at high pressure. These RENs crystallize in NaCl structure and we predict a NaCl to CsCl structural phase transition at high pressure. We further report the lattice constant, band structures (BS), band gap, bulk modulus and magnetic moment.

2. Method of calculation

Both the rare earth nitrides SmN and EuN considered in the present work crystallize in the NaCl structure with space group symmetry Fm3m. The rare earth atom is positioned at (0, 0, 0) and nitrogen at (1/2, 1/2, 1/2). The high-pressure phase predicted in these compounds is of CsCl structure with the space group symmetry Im3m in which the nitrogen atom is positioned at (1/2, 1/2, 1/2). The electronic band structures are calculated using the self-consistent TB-LMTO method [12-13] within the local density approximation (LDA) [14]. Von-Barth and Hedin [15] parameterization scheme has been used for the exchange correlation potential. Combined correction terms, which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere so as to minimize the errors in the LMTO method are included. Wigner-seitz sphere radii are chosen in such a way that sphere boundary potential is minimum and the charge flows between the atoms are according to the electro negativity criteria. The s, p, d, and f partial waves are included. The tetrahedron method [16] of the Brillion zone integration is used to obtain the total and partial density of states. E and K convergence is also checked. For loosely packed structures, empty spheres are introduced in the appropriate interstices in B1 phase without breaking the crystal symmetry. To study the phase stability of RENs the electronics structure and total energies are calculated at different cell volumes ranging from 1.05V0 to 0.65V0 in a manner similar to our earlier works [17] where V0 is the equilibrium cell volume. The calculated total energy is fitted to Birch equation of state [18] to obtain the pressure-volume relation. The pressure is obtained by taking volume derivative of the total energy. The bulk modulus B= -V0dP/dV is also calculated from P-V relation. It is well known that the LMTO method gives accurate results for closely packed structures. Since the structures under consideration are loosely packed, empty spheres are introduced to make them densely packed without breaking the crystal symmetry.

3. Result and discussion

The structural properties of half-metallic ferromagnetic (HMF) RENs (RE: Sm, Eu) will be discussed at ambient and high pressure in this section. Both spin and non- spin- polarized electronic band structure calculations are performed for Ferro-magnetic and Non-magnetic states and it is found that two RENs are stable in FM state under ambient conditions. The total energy was plotted against different compressions, as shown in figure 1 for both the compounds. The minimum of the curves defines the equilibrium volume V0. In this phase the calculated equilibrium lattice parameter ‘a’ is 9.43 and 9.41 a. u. for SmN and EuN, respectively, which can be compared with the available experimental values of 9.51 and 9.48 a.u. for both the compounds [11, 19]. The B1 to B2 phase transition in various RE chalcogenides and pnictides have been observed and predicted both theoretically [20] and experimentally [21]. We have studied RENs under pressure. The high-pressure phase is considered to be B2 phase. The total energies for both B1 and B2 phases in FM state are calculated. The calculated total energies are fitted to the Birch equation of state [18] in order to obtain the pressure-volume (P-V) relation. The equations of states are presented in figure 2 for both the compounds. It is found that B1 phase is more stable than B2 phase at ambient pressure.
From figure 2 one can easily observe that SmN and EuN undergo a structural phase transition from B$_1$ to B$_2$ phase at 8.6 and 14.1 GPa with 17.5 and 14.9% volume collapse, respectively. The reason of such a large volume collapse may be understood as some of the RE compounds like chalcogenides of Eu, Sm and Yb show valence fluctuation under ambient and high pressure due to partially filled f-states. Under the application of pressure these states show delocalization of f-electrons. The delocalization of f-states during structural phase transition could be the reason of large volume collapse in the two nitrides of Eu and Sm. Due to the unavailability of the experimental results, we could not compare the present results with them. At phase transition pressure, the lattice parameter ‘a’ varies from 9.43 a.u. to 5.44 a.u. as the structure goes from NaCl to CsCl phase for SmN. Similarly for EuN ‘a’ varies from 9.41 to 5.43 a.u. at phase transition pressure. The calculated values of bulk modulus ($B_0$) at ambient pressure are found to be 157.97 and 164.95 GPa for SmN and EuN, respectively. They are compared with the measured results in the literature [19]. The bulk modulus for B$_2$ phase is found to be 111.88 GPa for SmN and 154.4 GPa for EuN, which is yet to be confirmed experimentally.

At ambient pressure the net magnetic moment (MM) is calculated to be 5.0 $\mu_B$/Sm and 6.0 $\mu_B$/Eu, which is in excellent agreement with the other theoretical values reported by Aerts et al [22]. We have also estimated total magnetic moment under pressure and it is found that the magnetic moment decreases with increase in pressure, which is quite natural in this kind of magnetic materials.

The band structures (BS) in B$_1$ and B$_2$ phases at ambient conditions are calculated and shown in figure 3 and 4 for SmN and EuN respectively. In the band structure for SmN, the solid lines represents majority spins, while minority spins shown by dotted lines. It is clear from the figure that the band structures of majority spin crosses the fermi level $E_F$, whereas the band structures of minority spin have a gap. As can be seen form figure 3(a), the lowest lying bands are due to s-like states of nitrogen stay around -0.8 Ry, while the bands near $E_F$ at around -0.22 Ry, arise due to the mixing of d-states of RE with p-states of nitrogen showing its metallic nature, while the gap between N-p like and RE-d like states showing its semi-conducting nature and overall resulting them as half-metallic. Similar analysis
is done for EuN. Since both the compounds are half-metallic, we have calculated the band gap for both the compounds in B\(_1\) phase. It is 0.096 Ry. (1.305 eV) for SmN and 0.104 Ry. (1.414 eV) for EuN. Our results on electronic properties are in good agreement with the experiment [22].

Similarly we have plotted the band structure along the high symmetry directions for majority (solid lines) and minority spin (dotted lines) in figure 4 for CsCl structure for both the compounds. It is found from the figure 4 that all the states seen very similar to the NaCl structure. As we increase the pressure the hybridization of RE-'d' and N-'p' like states increases and the lower energy bands are shifted to higher energy side. In the minority spin, the gap between the N-p and RE -d states reduces, while RE-f states shifts to higher energy side. On the other hand, in case of majority-spin the metallic property increases and resulting it as half-metallic in CsCl structure.

4. Conclusion
The electronic band-structure calculations are obtained for both the B\(_1\) and B\(_2\) phases of RENs using the TB-LMTO method. Both RENs are stable in ferro-magnetic state and there is no non-magnetic to ferro-magnetic or ferro-magnetic to non-magnetic transition. At ambient pressure they also show half metallicity with total magnetic moment of 4.99 and 6.00\(\mu_B\) for SmN and EuN, respectively. From the energy-volume relation we found that both RENs are stable in the B\(_1\) phase as compare to B\(_2\) phase at ambient pressure and we predict a phase transition from the B\(_1\) to B\(_2\) phase at around 8.6 GPa for SmN and 14.6 GPa for EuN. High-pressure experimental studies are indeed needed to verify our structural and magnetic properties of RENs.

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References
[1] Bendict U & Holzapfel W B 1993 Handbook of physics & chemistry of rare earths Edited by Gschneidnet K A, Eyring L Jr, Lander G H & Choppin G R, North Holland, Amsterdam, 17 245
[2] Pagare G, Soni P, Srivastava V and Sanyal P Sankar 2009 J. Phys. Chem. Solids 70 650
[3] Vaitheeswaran G, Petit L, Svane A, Kanchana V and Rajagopalan M 2004 J. Phys. Condens. Matter 16 4429
[4] Shirotani I, Hayashi J, Yamanashi K, Hirano K, Adachi T, Ishimatsu N, Shimomura O, and Kikegawa T, 2003 Physica B 334 167
[5] Jha P K and Sanyal P Sankar 1994 Indian J. Pure App. Phys. 32 824
[6] Yakovkin I N, Komesu T & Dowben P A 2002 Phys. Rev. B 66 035406
[7] Hullinger F 1978 Hand Book of the Physics and Chemistry of the Rare Earths Edited by Gschneidner K A, Eyring L Jr North Holland Amsterdam 4 153
[8] Birgeneau R J, Bucher E, Passell L & Turber-field K C 1971 Phys. Rev. B, 4 718
[9] Kaldis E, Schulthess G V & Wachter P 1975 Solid State Comms. 17 1401
[10] Aerts C M et al. e-print arXiv:cond-mat/0308354
[11] Duan C G, Sabirianov R F, Mei W N, Dowben P A, Jaswal S S & Tsymbal E Y 2007 J. Phys.: Cond. Matter 19 315220
[12] Andersen O K 1975 Phys. Rev. B 12 3060
[13] Andersen O K & Jepsen O 1984 Phys. Rev. Lett. 53 2571
[14] Kohn W & Sham L J 1965 Phys. Rev. A 140 1133
[15] Von Barth U & Hedin L 1972 J. Phys. C 5 1629
[16] Jepsen O, Andersen O K 1971 Solid State Commun. 9 1763
[17] Srivastava V, Rajagopalan M & Sanyal S P 2008 Eur. Phys. J. B 61 131
[18] Birch F 1978 J. Geophys. Res. 83 1257
[19] Larson P & Lambrecht W R L 2007 Phys. Rev B 75 045114
[20] Srivastava V, Sanyal Sankar P and Rajagopalan M 2009 J. Mag. Mag. Mat. 321 607
[21] Leger J M 1993 Physica B 190 84
[22] Aerts C M, Strange P, Horne M, Temmerman W, Szotek Z & Svane A 2004 Phys. Rev. B 69 045115