Electric, magnetic, elastic and pressure-induced crystallographic phase transition properties of YbN using first-principle approach

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The structural, magnetic and elastic properties of the rare earth nitride YbN under hydrostatic pressure have been investigated using the Full Potential Non-orthogonal Local-Orbital minimum basis method (FPLO) using the Local Spin Density Approximation (LSDA) and Generalized Gradient Approximation (GGA). Three phase transitions are predicted from rock-salt (RS) to CsCl, zinc-blend (ZB) to CsCl, and ZB to RS at 220, 12, and-15 GPa, respectively. The half-metallic property was found only in the ZB phase, while the RS and CsCl phases show a metallic behaviour. The bulk moduli of YbN in RS, CsCl and ZB structures are calculated to be 172.8, 160, and 115.3 GPa, respectively.

1 Introduction

The high pressure structural phase transition in the rare earth compounds has attracted the interest of researchers in many fields, especially for their spintronics applications[1,2]. The rare earth nitrides have partially filled f-shell, which is highly delocalized under high pressure. The magnetic, structural and elastic properties of these compounds under high pressure have been studied by many researchers[3-8]. Possible structural phase transitions have been studied for almost all of these compounds, but with more emphasis on the RS to CsCl transition[7,9,10]. The phase transition from RS to CsCl in SmN has been predicted to take place at 8.6 GPa by Pagare *et al*[9]. using the first tight binding linear muffin tin orbital method. The zinc-blend phase of these compounds has only been studied for GdN by Abdelouhd *et al*[3]. using LSDA and GGA approximations and Shabara *et al*[7]. using LSDA approximation. The effect of these phase transitions on the magnetic properties and half-metallicity of YbN has been studied in the present paper. Szotek *et al*[11]. using the self-interaction corrected local spin density approximation (SIC-LSD) showed that YbN is metallic in both spin-channels, with a total magnetic moment of 0.94 μ_B. Li *et al*[12]. have reported a semi-metallic behaviour in YbN with a gap of 0.75 eV. Degiorgi *et al*[13]. claimed that YbN is a self-compensated semi-metal with the occupied f states about 6 eV below E_F and the empty f states about 0.2 eV above E_F.A theoretical study based on the density functional theory, predicted a phase transition[9] in YbN from RS to CsCl at 137 GPa. The RS to CsCl phase transition in YbN was reported to take place at a pressure of 133 GPa with volume change of 5.1% according to Rukmangad *et al*[10]. The bulk modulus of the RS phase of YbN was calculated to be 136 GPa by Winklur[14]. In the present study, the first-principles calculations of the electronic, magnetic and elastic properties and pressure-induced crystallographic phase transitions in YbN using the well known electronic structure[15,16] code FPLO.09, have been presented The relative stability under pressure of the three possible crystallographic phases of YbN, namely: the RS, ZB and CsCl structures has been investigated. The metallicity status of each phase has been checked by investigating the presence of half-metallicity by calculating the electronic structure in both spin directions.

2 Theory and Computation

The calculation are derived from first-principles study of YbN compounds in the ZB, CsCl and RS structures within the framework of density functional theory. The theoretical values of equilibrium lattice constant, magnetic moment, energy gap, bulk modulus and its pressure derivative are calculated from the electronic structure by the full-potential non-orthogonal local-orbital minimum basis[15,16] method (FPLO) using the LSDA approximation[17]. Several recent references were reported to use different forms

for the Equations of State e.g.Refs. (18, 190. The Birch-Murnghan equation of state has been used to calculate the bulk modulus and its pressure derivative[20-22]. We have used this equation in fitting volume versus energy data obtained from our *ab-intio* calculation:

$$E(V) = E_0 + \frac{9 B_0 V_0}{16} \left[\begin{array}{l} B_1 \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^3 \\ + \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\}^2 \left\{ 6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right\} \end{array} \right] \qquad \ldots(1)$$

where the pressure is given by:

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

where V_0 is equilibrium volume, E_0 is equilibrium energy, B_0 is bulk modulus and B_1 is the pressure first derivative of B_0. The parameters used in the calculation are: the k-mesh subdivision: 24×24×24, the accuracies of the density and total energy are 10^{-6} Å^{-3} and 10^{-8} Hartree, respectively. For the RS structure, the space group is (#225) and the atomic positions are (0, 0, 0) for Yb and (1/2, 1/2,1/2) for N. But for ZB structure, the space group is (#216) and the atomic positions are (0, 0, 0) for Yb and (1/4, 1/4, 1/4) for N. The atoms in the CsCl structure (space group #221) are located at (0, 0, 0) for Yb and (1/2, 1/2, 1/2) for N atoms.

3 Results and Discussion

The geometric optimization method is used, i.e. doing self-consistent calculation of the energy-volume dependence of the unit cell for different crystal structures; in order to find out the most energetically-favourable phase. The energy versus volume of YbN in its three possible phases (rock-salt, zinc-blend and cesium chloride) using the LSDA approximation is shown in Fig. 1. We found that RS structure is the most stable structure which agrees with the fact that the RS is the favourable and the most stable structure for most rare earth nitrides[6,23,24]. The theoretical lattice constant was obtained by minimization of energy for its different phases as shown in Table 1. There is a good agreement between our calculated lattice constant and that calculated by Duan *et al*[4]. for YbN in RS structure.

It is found that only the ZB structure exhibits half-metallicity, in contrast to the RS and CsCl structures. The effect of a hydrostatic pressure on the magnetic moment and energy gap of YbN in the half-metallic ZB phase has been investigated. A strong pressure dependence of the partial and total magnetic moments
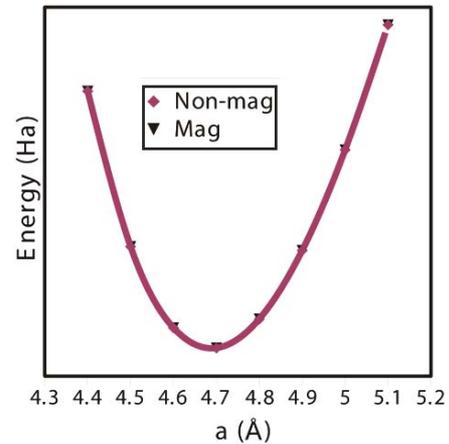
Fig. 1 — Total energy dependence on the unit cell volume for ZB, RS, and CsCl phases of YbN

Table 1 — Calculated lattice constant, magnetic moment, and energy gap using both LSDA and GGA approximations

Approximation method Structure	LSDA			GGA		
	a (Å)	m (μ_B)	Energy Gap (eV)	a (Å)	m (μ_B)	Energy Gap (eV)
RS	4.68 4.78[13] 4.79[25]	0.00 0.94[9,24]	0.00 0.75[12] 0.00[25]	4.8	0	0
CsCl	2.89	0.44	0.00	2.97	0.7	0
ZB	5.05	1.00	2.43	5.2	1.00	2.43

of the ZB phase has been predicted. We have found three possible phase transitions from ZB to RS, RS to CsCl and ZB to CsCl. The results of Table 1 show that half-metallicity appears only in the ZB structure whose total magnetic moment and energy gap in the spin-up channel are, 2.43 eV and 1 μ_B, respectively, as shown in the density of states and energy band structure of YbN (Fig. 2). Figure 2 shows the band structure of minority spin crosses the Fermi level, while there is a band gap in the majority spin band. On the other hand, the RS and CsCl structures of YbN show a metallic behaviour which is evident from the absence of any energy gap as shown in Fig. 3 for RS structure.

The electronic structure and structural phase transitions of YbN under hydrostatic pressure have been investigated in the present paper. Three phase transitions were predicted by inspection of the enthalpy versus pressure as shown in Fig. 4. We have predicted the following phase transitions: from RS to CsCl at P = 220 GPa, from ZB to CsCl at P= 12 GPa, and from ZB to RS at P =−15 GPa.

It is evident that YbN undergoes a structural phase transition at a high pressure of 220 GPa, from RS structure to CsCl structure as shown in Fig. 5(a, b). On contrast, under lower pressure, the rock-salt structure expands to larger volume and transforms to zinc blend structure at transition pressure-15 GPa. There is a doubt around the negative pressure and if we can reach this transition. This transition was predicted in GdN by Abdelouahed et al[3]. They show that under tensile stress there would be a transition to zinc blend GdN, so, it is nonetheless of interest as a hypothetical compound.

The magnetic properties and the energy gap of YbN under hydrostatic pressure have been investigated for the half-metallic ZB phase. The

dependence of the total, partial magnetic moments and energy gap for the ZB phase are shown in Fig. 6. The total magnetic moment decreases from ~1 μ_B for pressures up to 15 GPa to a vanishing value at ~ 90 GPa. At ambient pressure, there is an energy gap of 2.43 eV with E_f located in the middle of it. By increasing the pressure, the hybridization of d-state in Yb and p-state in N increases and the lower energy
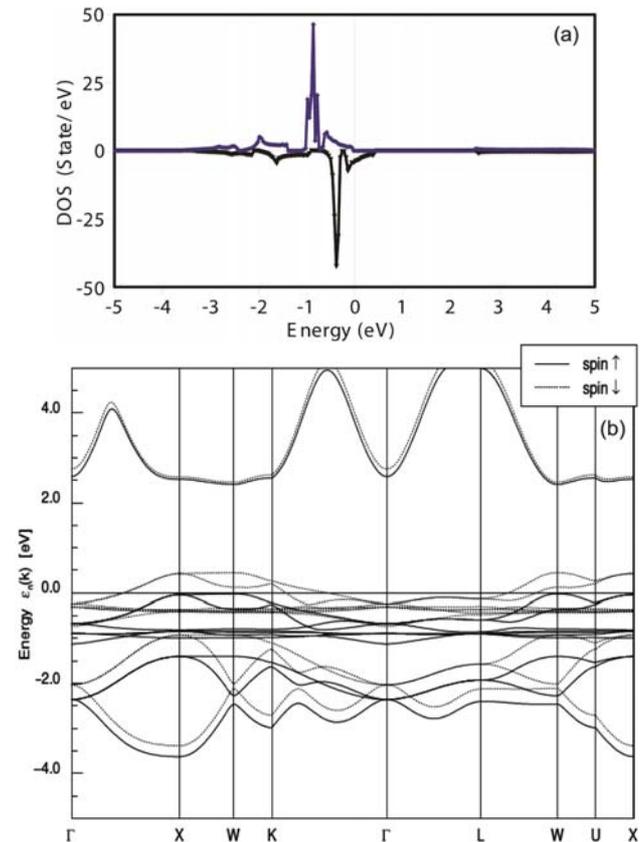
Fig. 3 — DOS of the RS structure

Fig. 2 — DOS and band structure of the ZB structure
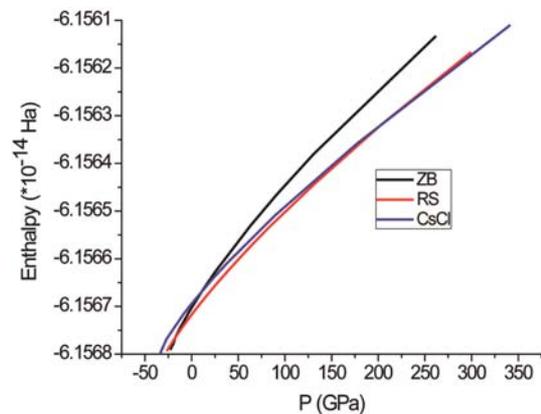
Fig. 4 — Enthalpy versus pressure for the three crystal structures
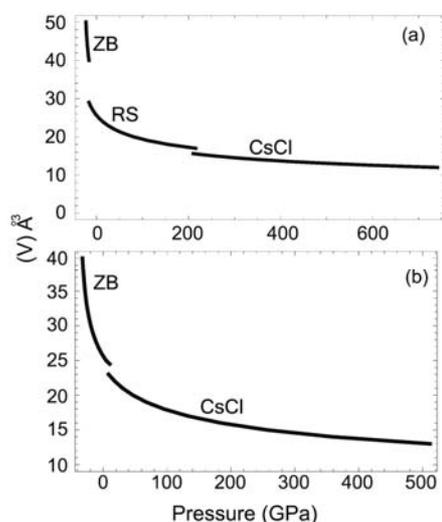
Fig. 5 — (a) Pressure versus unit cell volume relationship showing the phase transition from (a) ZB to RS and RS to CsCl and (b) ZB to CsCl
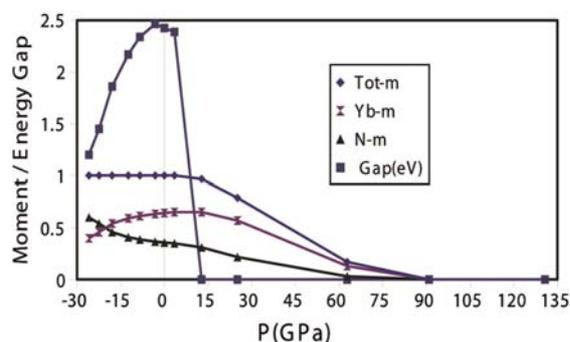
Fig. 6 — Pressure dependence of total and partial magnetic moment and energy gap for the ZB structure

Table 2 — Bulk modulus and its pressure derivative of the three structures of YbN

Structure	B_0 (GPa)	B_1
RS	1.72.756 136[10] 190[25]	4.687
CaCl	160.015	4.374
ZB	115.293	4.27

even in the rare-earth nitrides. The exchange splitting must be large enough to form a gap between the unoccupied and occupied states in one spin channel and at the same time the other spin channel should be partially occupied. It is concluded that half-metallicity strongly depends on the magnitude of exchange splitting as well as on the details of the electronic structure. The exchange splitting in YbN at ambient pressure is not enough to form a gap, while by transformation into ZB structure, the exchange splitting increases to form a half-metallic compound. At zero pressure, the partial magnetic moment of Yb atom is larger than partial moment of N atom by nearly 0.4 μ_B. By increasing the pressure, both Yb and N moments vanish at pressure of nearly 90 and 65 GPa, respectively.

4 Conclusions

The rare earth nitride YbN has the half-metallic state in one zinc blend (ZB) phase and is metallic in the other two phases. Geometric optimization has indicated that the RS phase is energetically favourable in this compound. Three phase transitions have been predicted in the present work from RS to CsCl at $P = 220$ GPa, from ZB to CsCl at $P = 12$ GPa, and from ZB to RS at $P = -15$ GPa. The total and partial magnetic moments of YbN are pressure dependent and vanish at nearly 90 GPa.

bands are shifted to higher energy level which results in gap vanishing and the half-metallicity disappears as transition from ZB into RS phase. To discuss the origin of the half-metallicity in the ZB phase of YbN, half-metallicity will not occur if there is no exchange splitting according to band calculation. While an exchange splitting is a necessary condition for half-metallicity, exchange splitting alone is not enough,

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