

# Half Metallic Ferromagnetism in Alkali Metal Nitrides XN (X= Li, Na): A First Principles Study

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**Abstract** – The structural, electronic and elastic properties of two alkali metal nitrides (XN: X= Li, Na) are investigated by the first principles calculations based on density functional theory as implemented in Vienna *ab-initio* simulation package. At ambient pressure both nitrides are stable in the ferromagnetic state with NaCl structure. The calculated lattice parameters are in good agreement with the available results. The electronic structure reveals that these materials are half metallic ferromagnets at normal pressure. A pressure-induced structural phase transition from NaCl to ZB phase is observed in LiN and NaN. Half metallicity and ferromagnetism are maintained in both nitrides at all pressures.

**Keywords** – Ab-initio calculations; Structural phase transition; Electronic structure; Elastic properties;

## 1 INTRODUCTION

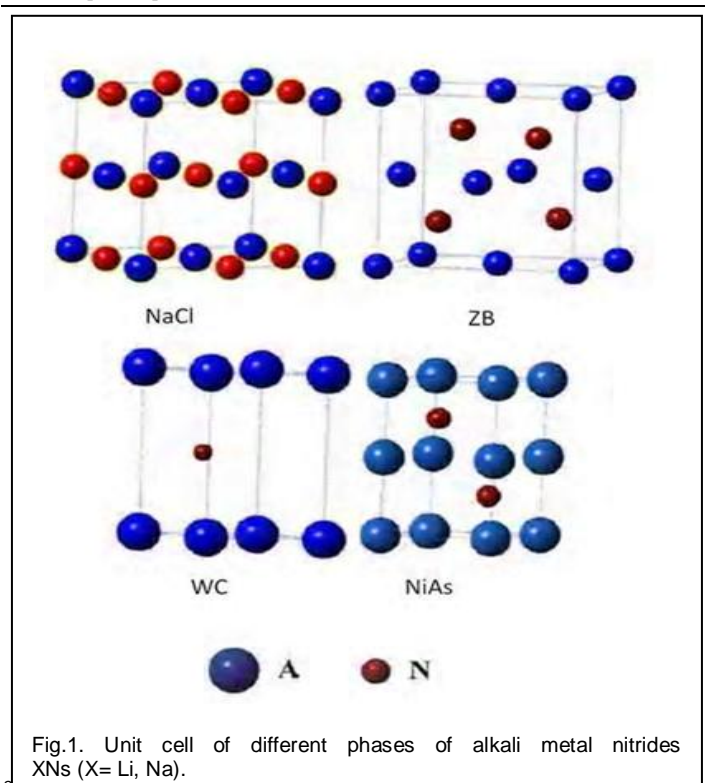
IN recent years, spin based electronics or spintronics have been studied actively. They have the possibility to bring new ideas to create a new generation of multifunctional devices combining traditional charge based microelectronics with spin dependent effects [1]. Half metallic ferromagnetic materials are a class of materials that have metallic behaviour for one type of electron spin ( $\uparrow$ ) and insulating or semiconducting behaviour for the other spin ( $\downarrow$ ), which leads to complete (100%) spin polarization at the Fermi level. The conductivity of these materials occurs with only one spin channel. In 1983, de Groot et al. [2] predicted the half metallic (HM) ferromagnetism in NiMnSb, rare earth nitrides [3], and alkali nitrides such as RbN and CsN [4-5]. The mechanism of ferromagnetism in these materials is different from both the double exchange and the p-d exchange that are important in magnetic 3d compounds. This motivated us to investigate the structural stability, electronic, elastic and magnetic properties of alkali nitrides XNs (X: Li, Na). More over to the best of our knowledge the structural phase transition and elastic properties for the normal and high pressure phases of LiN, NaN have not been reported yet.

In the present work, electronic structure calculations at ambient and high pressures are performed. The structural, elastic and magnetic properties of lithium nitride (LiN) and sodium nitride (NaN) are investigated.

## 2 THEORETICAL FRAMEWORK

The total energy calculations are performed in the frame work of density functional theory as implemented in the VASP [6-8] code. The generalized gradient approximation parameterised by Perdew, Burke and Ernzerhof (GGA-PBE) [9-11] are used for the exchange and correlation. 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. 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 electronic configurations of Li, Na and N atoms are  $[1s^2] 2s^1$  (Z= 3),  $[\text{Ne}] 3s^1$  (Z=11) and  $[\text{He}] 2s^2 2p^3$  (Z=7) respectively. The valence electron configurations are Li  $2s^1$ , Na  $3s^1$  and N  $2s^2 2p^3$  atoms. The unit cell of the proposed structures of alkali metal nitrides is shown in Fig.1. The ground state properties like lattice constant a, c (Å), cell volume  $V_0$  (Å<sup>3</sup>), valence electron density  $\rho$  (electrons/ Å<sup>3</sup>) and cohesive energies at ambient pressure for NaCl, ZB, WC and NiAs phases of LiN and NaN are listed in Table 1. The calculated lattice constants are in agreement with the other theoretical results [12,13].



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**TABLE 1**  
CALCULATED LATTICE PARAMETERS (Å), EQUILIBRIUM VOLUME  $V_0$  (Å<sup>3</sup>), COHESIVE ENERGY  $E_{\text{coh}}$  (eV) AND VALENCE ELECTRON DENSITY (ELECTRONS/Å<sup>3</sup>) FOR LiN AND NaN FOR CONSIDERED STRUCTURES

Compounds	a	c	$V_0$	$E_{\text{coh}}$	$\rho$	
NaCl	4.059	-	16.72	5.83	0.359	
	4.33 <sup>a</sup>					
LiN	ZB	4.557	-	23.66	5.58	0.253
	WC	2.171	3.605	14.73	5.51	0.407
	NiAs	2.174	3.769	14.77	5.47	0.406
NaCl	4.872	-	28.91	5.46	0.208	
	5.29 <sup>b</sup>					
NaN	ZB	5.514	-	41.91	5.09	0.143
	5.81 <sup>b</sup>					
	WC	2.842	4.021	21.45	4.66	0.279
	NiAs	2.502	4.028	21.84	4.61	0.274

<sup>a</sup>Ref [12]

<sup>b</sup>Ref [13]

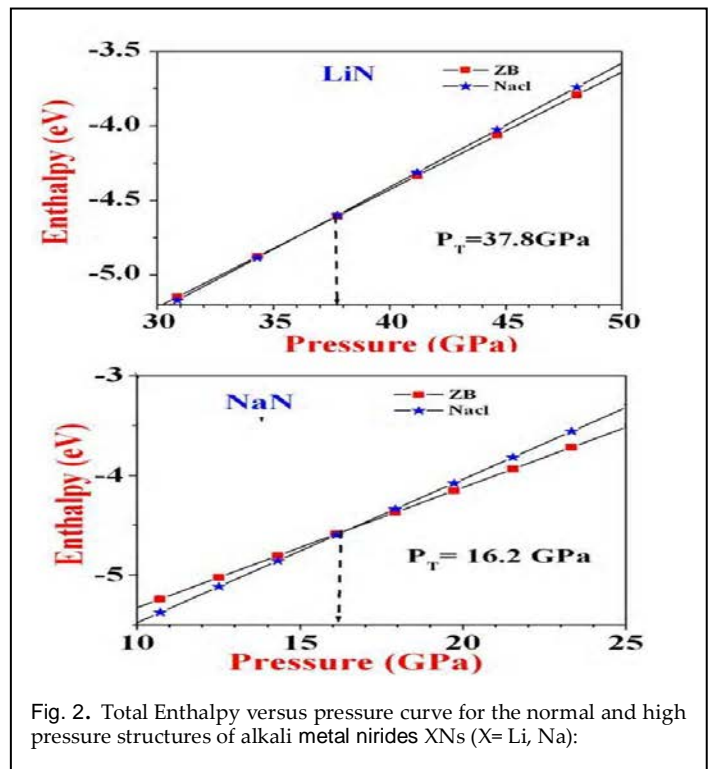


Fig. 2. Total Enthalpy versus pressure curve for the normal and high pressure structures of alkali metal nitrides XNs (X= Li, Na):

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Structural Phase transition Under Pressure

The total energy calculations are carried out as a function of volume in four different phases: NaCl, Zinc blende (ZB), WC and NiAs and their plots are given in Fig.2. It is observed that these nitrides are stable in the NaCl phase at ambient pressure. On further reducing the volume, they undergo a structural phase transition from NaCl to ZB phase.

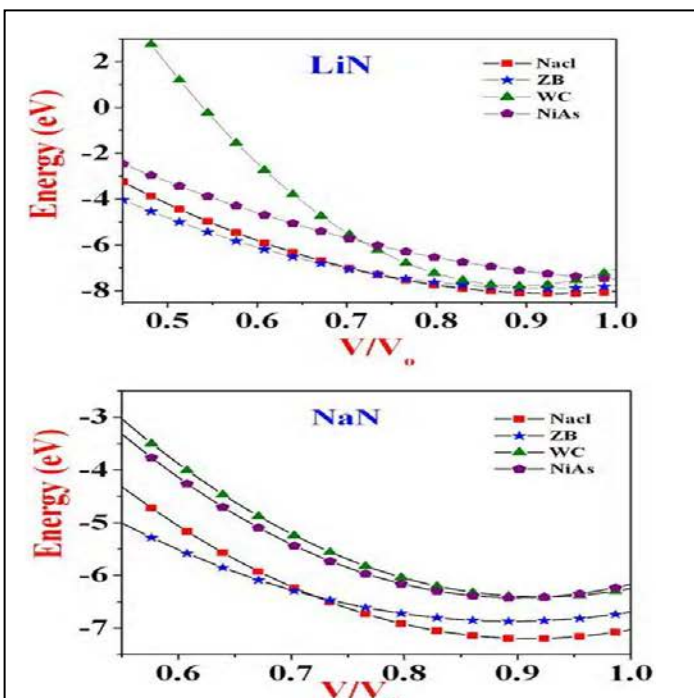


Fig. 2. Total energy (in eV) versus reduced volume for the normal and high pressure structures of alkali metal nitrides XNs (X= Li, Na):.

In order to observe these transitions in a more accurate manner, the enthalpy is calculated using the formula

$$H = E + PV \quad (1)$$

The transition pressure value is determined from the intersection of enthalpy versus pressure curve (Fig. 2). It is found that the transition pressures are 37.8 GPa, 16.2 GPa for LiN, NaN respectively.

#### 3.2 Electronic Structure

In order to understand the electronic structure of LiN and NaN with rock salt structure, the spin dependant total and partial density of states (DOS) of alkali metal nitrides XN (X: Li, Na) at normal pressure are computed and are given in Fig 3 (a,b), Fig 4 (a,b). It is found that, the minority-spin (spin-down) state exhibit metallic behaviour whereas the majority spin (spin-up) channel exhibits non-metallic behaviour. The energy gap for majority spin (spin-up) channel is found to be 9.4 eV, 1.6eV for LiN, NaN respectively. From the total DOS, it is also observed that the peak due to 2s state electrons of the nitrogen atom lies at an energy range of ~-10eV. For the spin up case, the top of the valence state is formed due to N-2p states electrons along with a small contribution from Li-2s state electrons. The metallic behaviour in the minority spin channel is mainly due to the contribution from N-2p state electrons at the Fermi level. The both alkali metal nitrides XNs (X: Li, Na) exhibit half metallic behaviour at normal and high pressures.

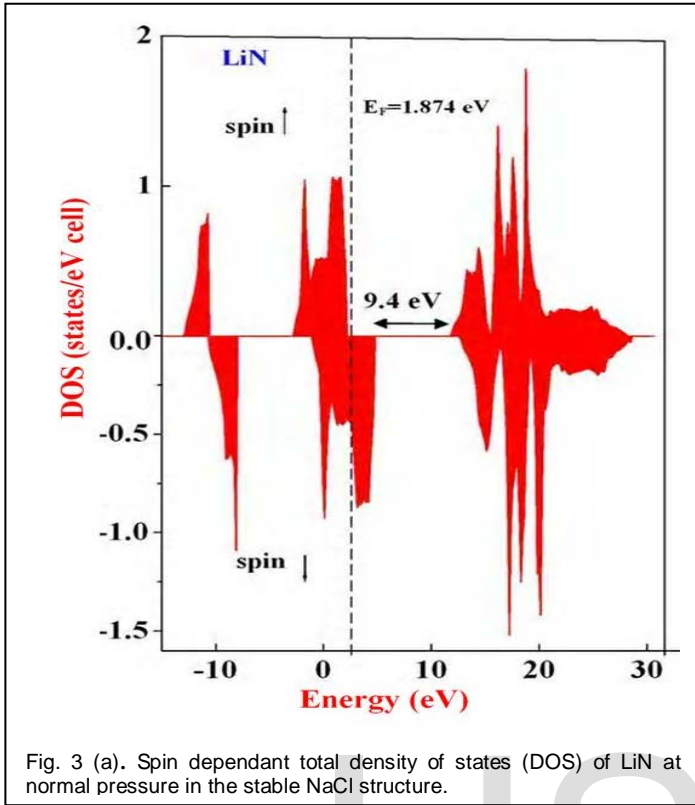


Fig. 3 (a). Spin dependant total density of states (DOS) of LiN at normal pressure in the stable NaCl structure.

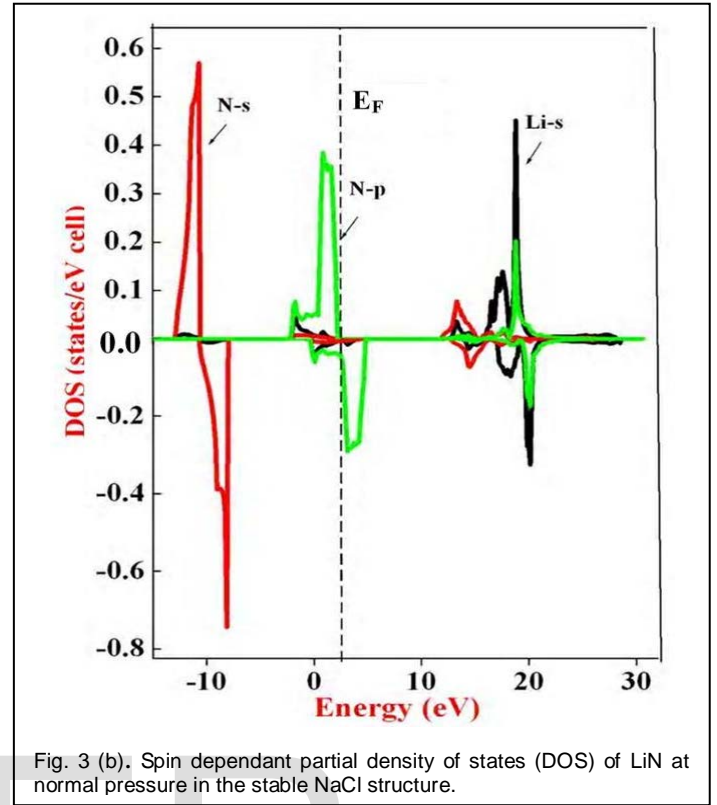


Fig. 3 (b). Spin dependant partial density of states (DOS) of LiN at normal pressure in the stable NaCl structure.

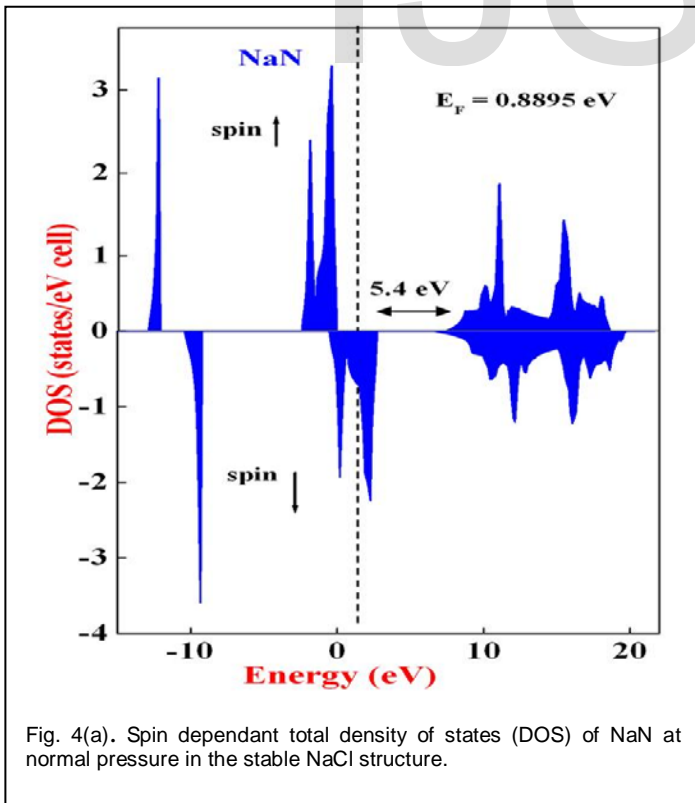


Fig. 4(a). Spin dependant total density of states (DOS) of NaN at normal pressure in the stable NaCl structure.

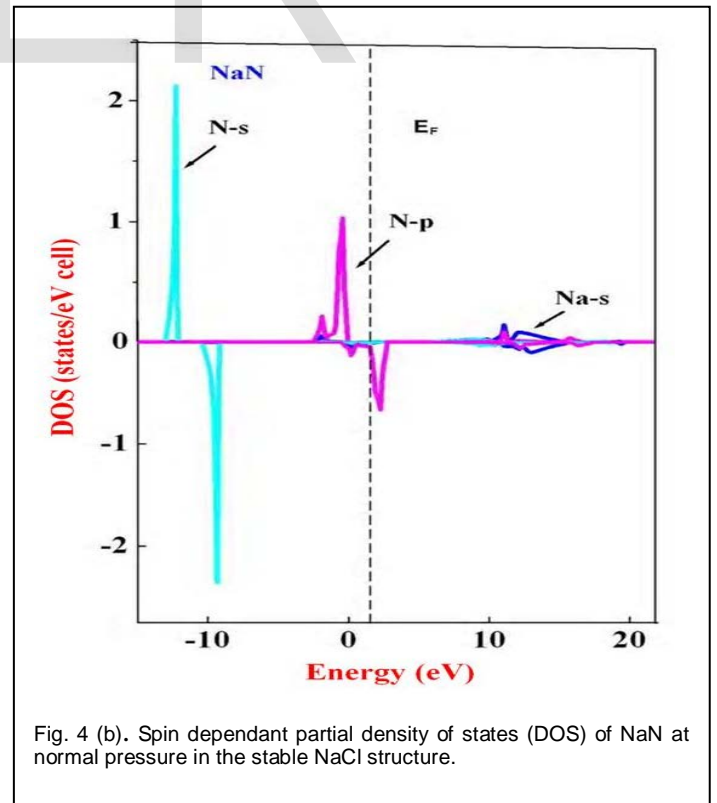


Fig. 4 (b). Spin dependant partial density of states (DOS) of NaN at normal pressure in the stable NaCl structure.

### 3.3 Elastic Properties

The mechanical stability is analysed by computing the elastic constants. The elastic constants  $C_{ij}$  are calculated within the total-energy method, where the unit cell is subjected to a number of finite-size strains along several strain directions. Cubic lattices have three independent elastic constants, namely,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . The bulk and shear moduli are calculated using the relations

$$B = 1/3 (C_{11} + 2 C_{12}) \quad (2)$$

$$G = 1/2 (C_{11} - C_{12}) \quad (3)$$

The obtained elastic stiffness constants are given in table 2. For a stable cubic structure, the independent elastic constants should satisfy the well-known Born-Huang criterion [14], given by:  $C_{44} > 0$ ,  $C_{11} > |C_{12}|$ ,  $C_{11} + 2 C_{12} > 0$ . It can be seen that the XNs are mechanically stable.

Young's modulus and Poisson's ratio can be calculated using the relations:

$$E = \frac{9BG}{(3B + G)} \quad (4)$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \quad (5)$$

For cubic phase, the anisotropy factor is defined as

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (6)$$

The value of  $A=1$ , represents completely elastic isotropy, while values smaller or larger than one measure the degree of elastic anisotropy. From Table 2, it is seen that LiN and NaN are elastically anisotropic.

TABLE 2

Calculated elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  (GPa), Young's modulus  $E$  (GPa), shear modulus  $G$  (GPa), elastic isotropy  $A$ , Bulk modulus  $B_0$  (GPa) and Poisson's ratio  $\nu$  at normal NaCl and high pressure ZB phase.

	LiN		NaN	
	NaCl	ZB	NaCl	ZB
$C_{11}$	158.87	280.20	78.39	158.39
$C_{12}$	63.41	37.73	27.67	16.63
$C_{44}$	13.61	60.57	14.39	58.66
$E$	74.65	205.49	49.39	143.22
$G$	25.26	84.83	18.78	63.15
$\nu$	0.369	0.211	0.315	0.134
$B_0$	95.23	118	44.57	65.22
$B/G$	3.77	1.39	2.37	1.03
$A$	0.285	0.499	0.567	0.839

### 3.4 Magnetic Properties

Non-spin and spin polarized calculations are performed to obtain total energies of stable phase of XNs (X: Li, Na). The magnetic moment for cubic NaCl phase of XNs (X: Li, Na) is found to be  $2\mu_B$  per formula unit. This integer value comes out because, for the majority spin direction, the Fermi level ( $E_F$ ) is

situated within a gap, which means that the bands below are occupied by an integer number of spin-up electrons. Since the total number of electrons is an integer as well, a resulting magnetic moment has to be an integer, too. The magnitude of the magnetic moment can be determined by the  $|8-n|$  rule, where  $n$  denotes the total number of valence electrons per formula unit. In other words, the rather localized anion  $p$  band is completely filled with the exception of one hole, which is responsible for the magnetic moment of  $2\mu_B$ . The calculated magnetic moments are in good agreement with results obtained by Gao and Yan et.al [12, 13]. It is observed that the considered alkali metal nitrides are ferromagnetic at normal and high pressures.

## 4 CONCLUSION

In conclusion, first principles calculations have been performed using VASP code with GGA-PBE exchange correlation to investigate the structural, electronic, elastic and magnetic properties of LiN and NaN. The calculated ground state properties are in good agreement with the available results. Our results suggest that cubic NaCl structure is the most stable structure at ambient pressure. A structural phase transition from NaCl to ZB phase is predicted in LiN and NaN under pressure. The electronic structure reveals that cubic NaCl-LiN and NaN are half-metallic ferromagnets. The elastic constants obey the necessary mechanical stability conditions suggesting that both nitrides are mechanically stable.

### Acknowledgment

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