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Structural, Magnetic And Electronic Properties Of NbN Polymorphs By Ab-Initio Study

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Abstract—The structural, electronic and magnetic properties of NbN are studied by ab-initio method by considering the four polymorphs {B1 (rock salt), B4 (wurtzite), B81 (NiAs) and Bh (WC-type)} of NbN. The results show that structurally, B81 is more stable since it has the least total energy per formula unit volume. The enthalpies of the polymorphs in relation to pressure increases from B81<B4<Bh<B1 respectively. It is also observed that the four structures have negative enthalpies; meaning they can be produced at ambient conditions. The calculated density of states and band structures indicate that the four polymorphs are metallic, while the magnetic moment implies that the four are non-magnetic.

Keywords—Polymorphs, Structural property, Electronic property, Magnetic property, Fermi level, Magnetic moment

I. INTRODUCTION

In recent years, there has been an increased attention of scientist, on NbN which is a hard material with excellent mechanical (Hardness, High Temperature stability, low compressibility), electronic and magnetic properties and also superconducts (Stampfl *et al.*, 2001), (Bull *et al.*, 2004), (Chen *et al.*, 2005), (Soignard *et al.*, 2007). Importantly, it is observed that superconducting and mechanical properties of a material largely depends on the electronic properties of the material (Meenaatci *et al.*, 2013), (Jhi *et al.*, 1999). Due to its ability to superconduct, it can be applied in Carbon nanotube junctions, Radio frequency superconducting accelerator cavities and hot electron photodetectors (Benvenuti *et al.*, 1993), (Lindgren *et al.*, 1998), (Kasumov *et al.*, 1999). Therefore, the knowledge on the physical properties of NbN is important for a variety of scientific and technological applications and electronic engineering. NbN exists in four polymorphs namely Rocksalt (B1), Wurtzite (B4), NiAs-Type (B81) and WC-Type (Bh) (Wang *et al.*, 2009), (Holec *et al.*, 2010). Some of the investigations that have been done on NbN include:

the effects of pressure on structural transition and thermodynamic transition of NbN in relationship to metallic bonding and its hardness (Wang *et al.*, 2011) whereas, (Zhao *et al.*, 2010), examined the structural, mechanical and electronic properties of 4d transition metal mononitrides, that is; from Yttrium to Palladium of which NbN is part. (Zou *et al.*, 2016) considered the hard hexagonal ϵ -NbN as a superconductor, Holec investigated structure and stability of phases within the NbN-AlN system particularly looking at B1, B4, BN anti-TIP and B81 structures (Holec *et al.*, 2010), whereas, (Zou *et al.*, 2015) singled out B81 (ϵ -NbN) and investigated its ultra- incompressibility, high shear rigidity as a possible high temperature superconducting material. In all these investigations, there has not been a consistent look at the four polymorphs of NbN (B1, B4, B81 and Bh) in terms of the structural, electronic and magnetic properties which this work examines via *ab-initio* method to give details on the structural, electronic and magnetic properties of the four polymorphs.

II. COMPUTATIONAL METHODS

The calculations were performed using plane-wave density functional theory as implemented within the QUANTUM ESPRESSO computer code (Giannozzi *et al.*, 2009). The electron-ion interactions were described using ultra-soft pseudopotentials (Vanderbilt, 1990). The local density approximation (LDA) was considered for the exchange-correlation energy functional as parameterized by Perdew and Zunger (Perdew *et al.*, 1981). A kinetic energy cut-off of 70 Ry and a charge density cut-off of 560 Ry were used for B1, B4, B81 and Bh, the cubic B1 (rocksalt or NaCl) has space group $Fm-3m$ with lattice parameters of $a=5.9489a.u.$, $b=5.9489a.u.$, $c=5.9489a.u.$ B4 which is hexagonal has space group $P63mc$ with lattice parameters of $a=6.0490a.u.$, $b=6.0452a.u.$, $c=11.4725a.u.$ B81 is also hexagonal in structure with space group of $P6_3/mmc$ (Holec *et al.*, 2010) with lattice parameters of $a=5.6672a.u.$, $b=5.6672a.u.$, $c=10.6165a.u.$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 120^\circ$ and lastly Bh has also hexagonal structure with space group of $P-6m2$

and lattice parameters: $a=5.6238\text{a.u.}$,
 $b=5.6238\text{a.u.}$, $c=5.4821\text{a.u.}$
 $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 120^\circ$ (Jain *et al.*, 2013).

The Brillouin zone was sampled using a shifted $9 \times 9 \times 9$ k-mesh for the B1, an unshifted $5 \times 5 \times 5$ k-mesh for the B4 structure and an unshifted $9 \times 9 \times 9$ k-mesh for the B81 and Bh structures according to the Monkhorst-Pack Scheme (Monkhorst *et al.*, 1976).

The lattice parameters were obtained by fitting the total energy versus volume data on Murnaghan equation of state (Tyuterev *et al.*, 2005), (Murnaghan, 1944). Atomic positions were optimized by performing a relax calculation such that the component of force on each atom is less than 10^{-3} Ry. The optimized structures of the four polymorphs of NbN are as shown in Fig. 1 below.

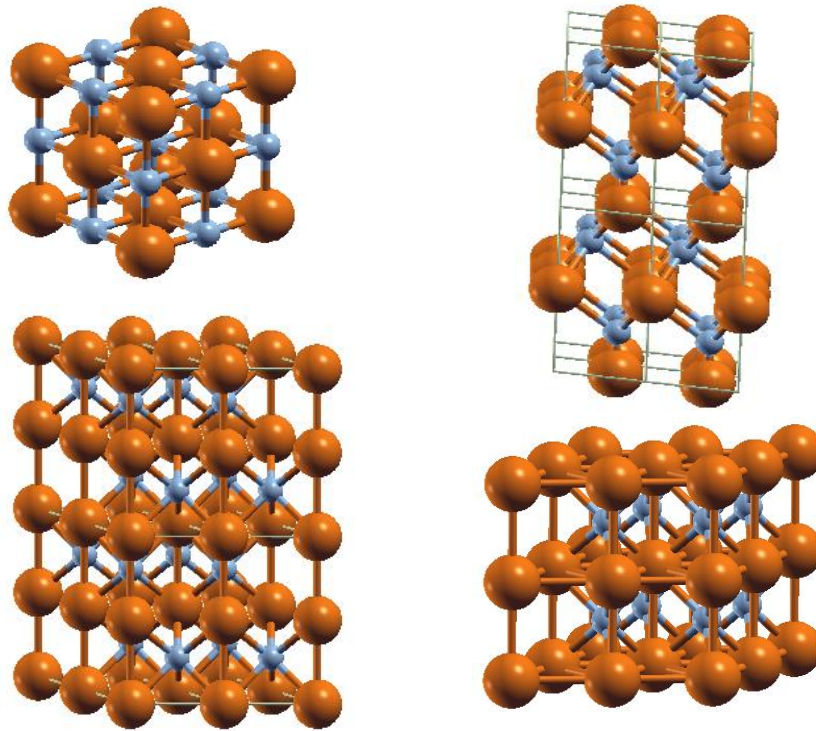


Fig.1.1 b1 unit **Fig. 1: Structures of B1, B4, B81 and Bh** cell (top left), $4 \times 2 \times 2$ supercell (top right), b81 $2 \times 2 \times 2$ supercell (bottom left) and bh

III. RESULTS AND DISCUSSION

A. Structural properties

The structural properties help in understanding the compound solid properties from the microscopic point of view. The optimized lattice parameters and cell volume for the four polymorphs are listed in table 1. It is clear from the table that there is a close agreement with the other theoretical and experimental values from (Zou *et al.*, 2016, Wang *et al.*, 2011, Holec *et al.*, 2010, Ivashchenko *et al.*, 2010, Stampfl *et al.*, 2001). The lattice parameters and the ratio of *c/a* were used to get the correct geometries of the four polymorphs.

Table I: The optimized lattice parameters (a, c) and cell volume

NbN phase		a (a.u)	c (a.u)	c/a	Cell Volume (a.u ³)
B1 (NaCl-type)	Present work	8.2596			140.869
	Expt	8.2751			5
	Theory	8.3337			
B4 (wurtzite)	Present work	6.226	10.209	1.6397	342.706
	Theory	6.047	11.440	1.8858	5
B81 (NiAs-type)	Present work	5.823	10.517	1.8061	308.808
	Theory	5.6219	10.486	1.8652	1
					287.026
Bh (WC-type)	Present work	5.444	5.448	1.0007	139.826
	Theory	5.582	5.431	0.97297	3
					146.551

Among the four polymorphs (B1, Bh, B4 and B81), B81 was found to be more stable than the other three polymorphs, because it had the lowest total energy per formula unit according to the graph of total energy versus volume as shown in Fig. 2. It is also clear; wurtzite B4 (hexagonal) has the highest energy per formula unit. Similarly, the energies of the rocksalt B1 (cubic) and WC-type, Bh (hexagonal) were closer to that of NiAs-type, B81 (hexagonal), a finding also confirmed by (Wang *et al.*, 2010). These results may not differ much from the experimental results, since the optimization is carried out at ground state and the polymorphs being solids, their atoms are held by strong cohesive forces meaning that a small change in temperature may not affect the structure of the solids.

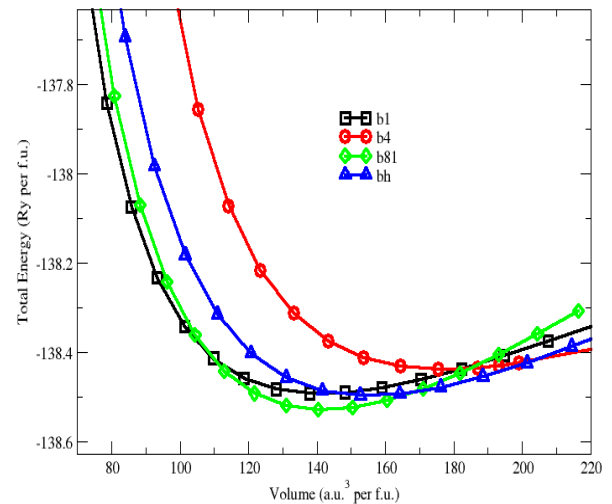


Fig 2: Total energy vs volume for the NbN polymorphs

According to (Wang *et al.*, 2010) who investigated pressure induced structural transition of NbN, specifically looking at B1, B81 and Bh, indicated a phase transition between B1 to Bh at 200.64GPa using Cambridge Serial Total Energy Package(CASTEP) with Perdew-Berke-Ernzerhof (PBE) as the exchange correlation functional. This investigation got Pressure-induced structural phase transition for Bh to B1 at -1.51961 GPa and B81 to B4 at -21.7402 GPa using QUANTUM ESPRESSO code and Local Density Approximation (LDA) exchange correlation functional.

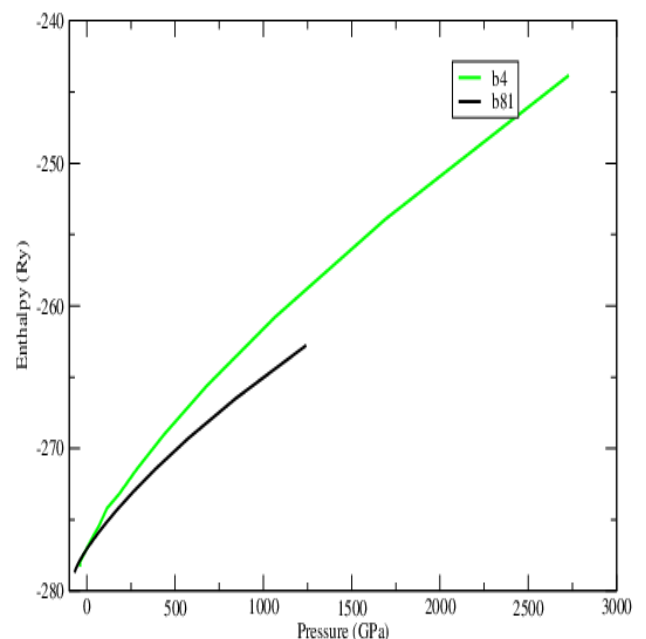


Fig. 3A: Enthalpy as a function of pressure for B4 and B81 at T=0K

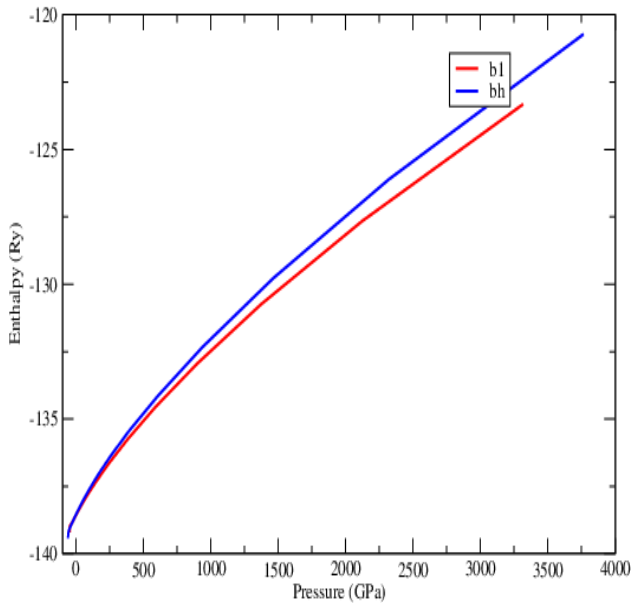


Fig 3B: Enthalpy as a function of pressure for B1 and Bh at T=0K.

The four polymorphs are observed to have negative enthalpy with B81 having the lowest followed B4, B1 and Bh at -278.908 Ry, -278.277 Ry, -139.419 Ry and -139.244 Ry respectively. This represents their relative stability energetically and the possibility of their synthesis. The Corresponding pressure values to phase transition for B1 to Bh is -1.51961 GPa and B81 to B4 is observed at -21.7402GPa. Moreover, the enthalpy of Bh and B1 considerably overlap after transition point then slightly diverges with increase in pressure and enthalpy. For B4 and B81, after the transition point B4 diverges off with increase in pressure and enthalpy. At zero pressure, the enthalpies of B81 and B4 is -277 Ry while B1 and Bh is -138 Ry respectively

B. Electronic Properties

The valence configuration of NbN compound in orbitals is $4d^4$, $5s^1$ for Niobium and $2s^2$, $2p^3$ is for Nitrogen. The atomic numbers for Niobium (Nb) and Nitrogen (N) are 41 and 7 respectively. Usually, the $2s^2$ orbitals for Nitrogen are localized; that is, they lie at approximately or lower than 1Ry energy level (low energy bands) making it impossible for them to participate in bonding (Holec *et al.*, 2010). The d - p orbitals that are at high energy level; that is, N p and Nb- d for Nitrogen and Niobium are the ones that strongly interact and cause bonding and anti-bonding, similar to the early d -block transition metal carbides (Levy *et al.*, 1973). The bonding between Nb and N is covalent like bonding with partial ionicity due to hybridization caused by presence of a pseudogap and metallic contribution (Wang *et al.*, 2010).

Figures 4A-4D clearly shows the calculated density of states and band structures for B1, B4, B81 and Bh. The four graphs of DOS confirm the separation of N-s states from the other states. For B1, the N-s states lie at approximately (-15 - -18) eV, while, B4 is at (-15 - -16) eV, B81 (-12 - -13) eV and Bh is at (-12 - -13) eV, with their width differing approximately by 1.0eV. The peak of N-s state in B4 is highest compared to the other three polymorphs. These states (N-s) do not participate in bonding because they are strongly held by the core of the atom. The other states, mainly, N-p and Nb-d occupy (-9-5) eV for B1, (-5- -7) eV and (- 2- 11) eV for B4, (-9 - 12) eV for B81 and (- 9 - 12) eV for Bh. The Fermi level for B1, B4, B81 and Bh is 20.85 eV, 16.33 eV, 18.03 eV, 19.97eV respectively. There is a sharp depression (pseudogap) above the Fermi level of B1, B4, B81 and Bh. The pseudo gap separates the valence band on the left and conduction band on the right. The valence band represents occupied electronic states, while the conduction band is the unoccupied electronic states. This means the electrons occupying the level above the Fermi level (valence band) are delocalized, whereas, the unoccupied conduction band on the right has zero electrons. Therefore, the polymorphs are all metals and good conductors of electric current due to the free electrons in the valence band. Finally, it's good to note that, all the four polymorphs have high density of unoccupied states above the Fermi level with B4 exhibiting the highest among the four followed by B81 then Bh and lastly B1.

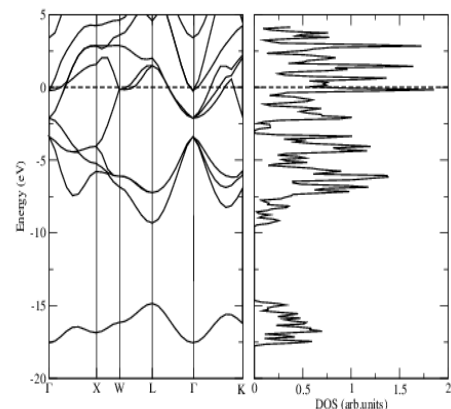


Fig. 4A: Band structures and DOS for B1

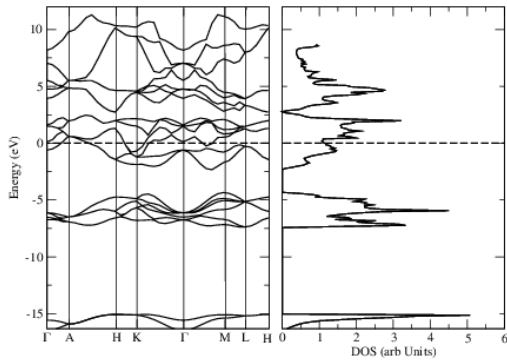


Fig. 4B: Band structures and DOS of B4

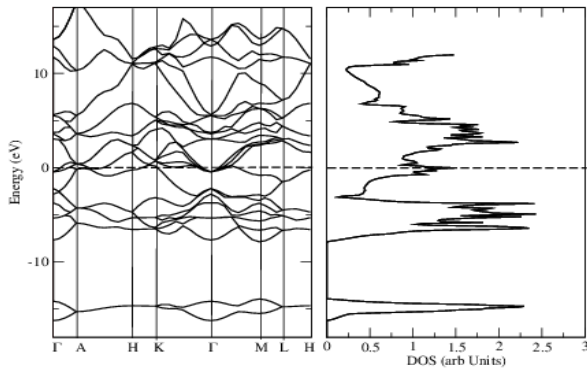


Fig. 4C: Band structures and DOS for B81

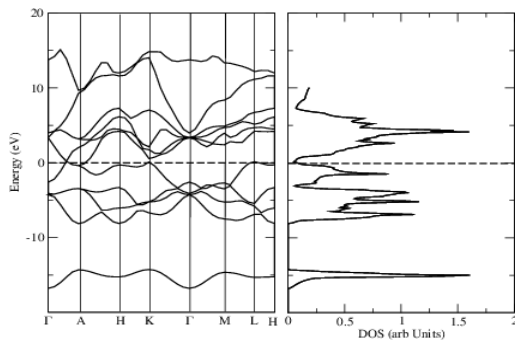


Fig.4D: Band structures and DOS for Bh

The calculated band structures for B1, B4, B81 and Bh above, indicate that the four polymorphs are metallic with charge densities overlapping at the Fermi level agreeing with DOS. B81 has the highest density of charges at the Fermi level followed by B4, Bh then B1.

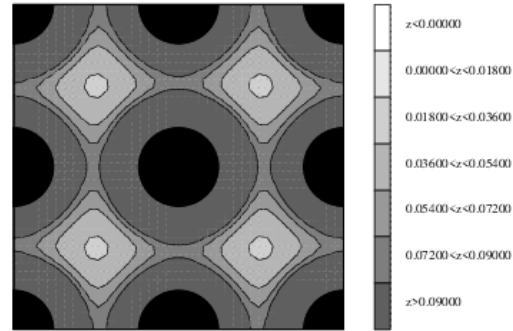


Fig. 5A: Charge density for B1

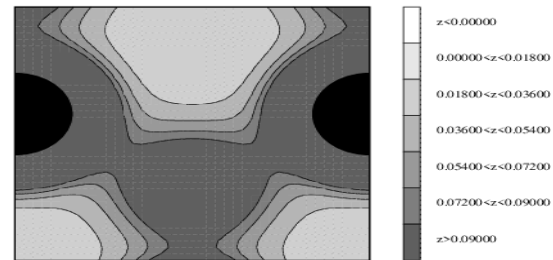


Fig. 5B: Charge density for B4

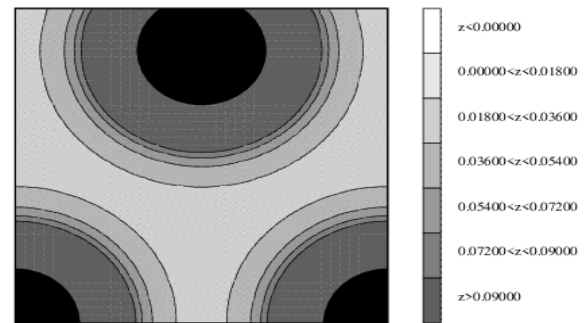


Fig. 5C: Charge density for B81

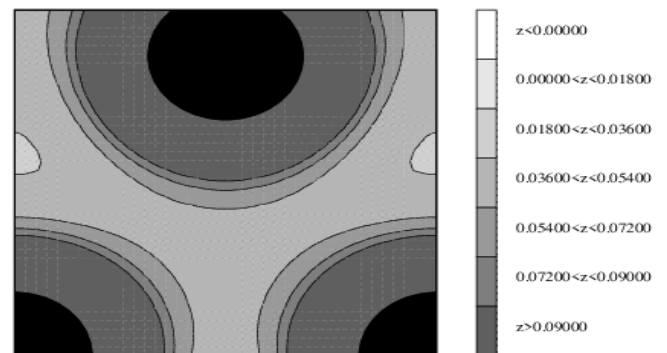


Fig. 5D: Charge density for Bh

The above charge density maps corresponds to NbN polymorphs; B1 rocksalt, B4 wurtzite, B81 NiAs and Bh WC-type. Looking at the individual elements that

make up NbN, we have Nb which has a valence of 13 and N 5. Therefore Nb has more charge density states than N. This is clearly seen from the maps with Nb atoms having more contours around them than N. For B1 and B4 that have 2 atoms per unit cell, their maps present a dark spot (N atom) that is surrounded by bright patches with many contours (Nb atom) directed towards N vacancy sites (Ethridge *et al.*, 1995), indicating Nb-N bonding in the cubic and hexagonal structures is (covalent bonds). On the other hand, B81 and Bh with 4 atoms per unit cell present dark contoured patch (Nb atom) with two or no bright spot (N atom). In this case the maps present Nb-Nb metallic bonds indicating hexagonal hybridization where more d states involve in bonding lowering the total energy (Holec *et al.*, 2010). Where bright spots are seen, one of the Nb pulls the N forming covalent bond Nb-N. The bonding in the last two is affected by the minimum that is seen at the Fermi level in B81 and Bh separating bonding and anti-bonding states.

C. Magnetic property

Magnetism of a material is a result of the spin of electrons. The average electron spin per atom is magnetic moment which is used to characterize the magnetism of a material. In a case where the total electron spin per state is zero (there are two electrons per state having spin up and down and therefore couple) then the material is said to be diamagnetic. Where, the electrons don't pair (there is one electron per state) and are oriented in the same direction the material has a magnetic moment of one and therefore its referred to us ferromagnetic. Anti-ferromagnetic is a material with electrons spins alternating in direction and its magnetic moment summing to zero (Sholl *et al.*, 2009). In this case the magnetic moment of all the polymorphs are found to be zero, since the sum of spin up and spin down of electrons in there states is zero indicating the material is non-magnetic.

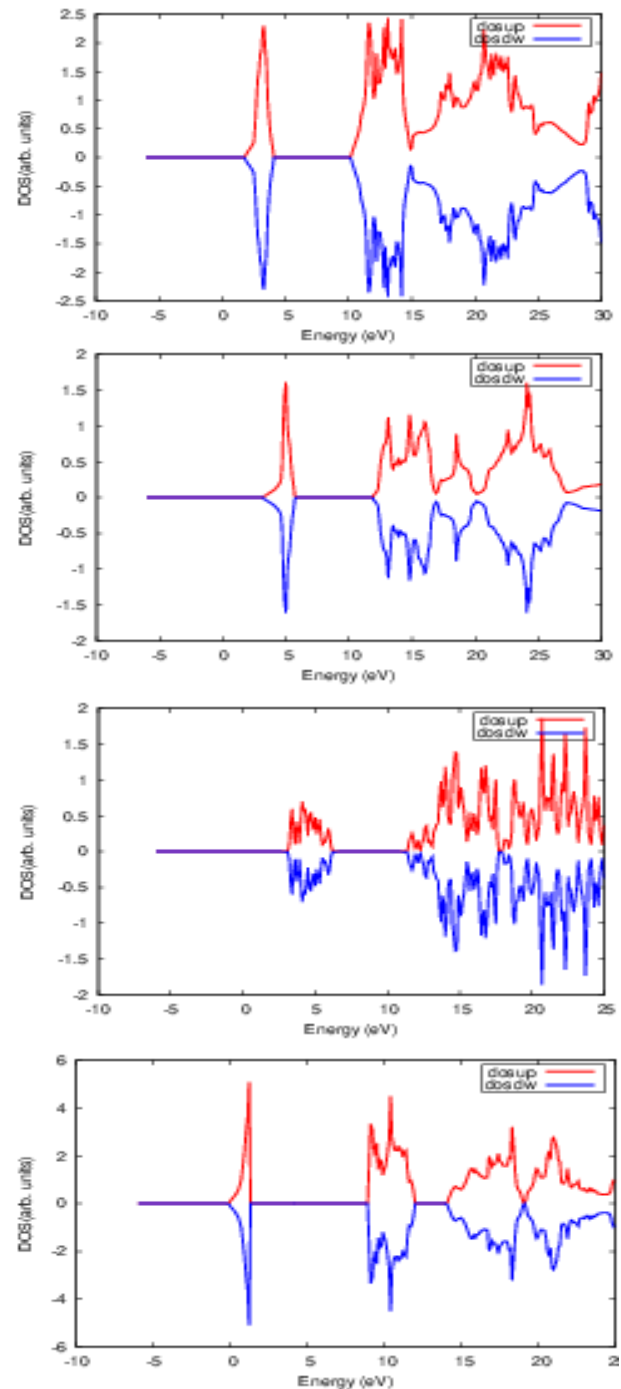


Fig. 6: Spin up and spin down of electrons in their states in B1, B4 B81 and Bh respectively.

IV. CONCLUSION

In this study, NbN, a 4d transition metal nitride was investigated using density functional theory. Its four polymorphs that were considered are B1 (rock salt or NaCl), B4 (Wurtzite), B81 (NiAs-type) and Bh (WC-type). The four were investigated in consideration of their structural, electronic and magnetic properties. The results from a plot of total energy per formula unit as a function of volume per formula unit, showed B81 to be the most stable phase followed by B1, Bh and B4. The outcome of the plot between enthalpy

and pressure confirmed a phase transition between B81 to B4 and B1 to Bh. The least enthalpy was recorded in B81 followed by B4, Bh and B1. The enthalpies of the four phases were negative meaning the structures could be synthesized at ambient conditions. The optimized density of states and band structures indicated the four polymorphs to be metallic. Charge density maps showed the dominance of covalent bonds in B1 and B4, and a mixture of metallic and covalent bonds in B81 and Bh. Magnetically the four are non-magnetic since their magnetic moment is zero.

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