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 (rocksalt), 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 superconductors (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 cavites 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 mononitrdes, 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 P6_3mc 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 P63/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: $a=5.6238\text{a.u}$, $b=5.6238\text{a.u}$, $c=5.4821\text{a.u}$, $\alpha = 90^0$, $\beta = 90^0$ and $\gamma = 120^0$ (Jain et al., 2013).

The Brillouin zone was sampled using a shifted 9x9x9 k-mesh for the B1, an unshifted 5x5x5 k-mesh for the B4 structure and an unshifted 9x9x9 k-mesh for the B81 and Bh structures according to the Monkhorst-Pack Scheme (Monkhost 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.
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>
<thead>
<tr>
<th>NbN phase</th>
<th>a (a.u)</th>
<th>c (a.u)</th>
<th>c/a</th>
<th>Cell Volume (a.u^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 (NaCl-type)</td>
<td>Present</td>
<td>8.2596</td>
<td>140.869</td>
<td></td>
</tr>
<tr>
<td></td>
<td>work</td>
<td>8.2751</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>8.3337</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4 (wurtzite)</td>
<td>Present</td>
<td>6.226</td>
<td>342.706</td>
<td></td>
</tr>
<tr>
<td></td>
<td>work</td>
<td>6.047</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>11.440</td>
<td>1.6397</td>
<td></td>
</tr>
<tr>
<td>B81(NiAs-type)</td>
<td>Present</td>
<td>5.823</td>
<td>308.808</td>
<td></td>
</tr>
<tr>
<td></td>
<td>work</td>
<td>5.6219</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>10.486</td>
<td>1.8061</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.8652</td>
<td>287.026</td>
<td></td>
</tr>
<tr>
<td>Bh (WC-type)</td>
<td>Present</td>
<td>5.444</td>
<td>139.826</td>
<td></td>
</tr>
<tr>
<td></td>
<td>work</td>
<td>5.582</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>5.448</td>
<td>146.551</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.97297</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

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 2: Total energy vs volume for the NbN polymorphs](image)

![Fig 3A: Enthalpy as a function of pressure for B4 and B81 at T=0K](image)
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 -21.7402 GPa. 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 4d⁴, 5s¹ for Niobium and 2s², 2p³ is for Nitrogen. The atomic numbers for Niobium (Nb) and Nitrogen (N) are 41 and 7 respectively. Usually, the 2s² orbitals for Nitrogen are localized; that is, they lie at approximately or lower than 1 Ry 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).
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.

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.

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

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


