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Density Functional Theory Approach to the Study of the Structural Stability of Nitrides of Iron and Nickel

T. Atsue^{1,2}, O. E. Oyewande^{2,3}, I. B. Ogunniranye² and A. P. Aizebeokhai³

¹Department of Physics, Faculty of Physical Sciences, Federal University Dutsin-Ma, Katsina State-Nigeria

²Department of Physics, Faculty of Science, University of Ibadan, Ibadan-Nigeria

³Department of Physics, College of Science & Technology, Covenant University, Ota, Ogun State, Nigeria

tatsue@fudutsinma.edu.ng; oe.oyewande@ui.edu.ng; ib.ogunniranye@ui.edu.ng

Abstract. Nitrides of transition metals such as iron and nickel are known to possess excellent properties relevant for technological applications. Among these, FeN has been synthesized in zinc blende face centered cubic ($F4\bar{3}M$) crystal structure while NiN has not been synthesized yet. Literature search revealed that hexagonal close packed and primitive tetragonal structures of these compounds have not been investigated to ascertain their preference. Therefore, the structural stability of Zinc blende face centered cubic, hexagonal closed packed and primitive tetragonal crystal structures of the compounds were investigated in this study. Generalized gradient approximation of Perdew-Burke-Ernzerhof revised for solids (GGA-PBESol) as implemented in Quantum espresso package was used based on density functional theory for the computation. The results revealed that FeN and NiN compounds prefer Zinc blende face centered cubic crystal structure as their equilibrium lattice parameters occurred at the least equilibrium minimum energies in this structure. The lattice parameters of FeN and NiN compounds in the zinc blende FCC crystal structure were computed to be 4.232 Å and 4.324 Å respectively in agreement with experiment and previous computations. The preference of zinc blende FCC crystal structure by these compounds implies they may possess highly directional covalent bonds that prefer a tetrahedral arrangement of atoms, thus forming good binary semiconductor compounds. Therefore, these compounds have high possibility of being synthesized in zinc blende FCC crystal structure.

Keywords: structural stability, equilibrium minimum energy, lattice parameter, transition metals.

1. Introduction

Binary nitrides have gained research interests owing to its important properties relevant in semiconductor and micromechanical applications in technology. Production of these nitrides for commercial purpose has been hampered due to unstable formation and high cost of synthesis [1], [2]. Thin films of iron nitrides are grown by different methods which include surface sputtering, molecular beam epitaxy (MBE), physical vapor deposition as well as chemical vapor deposition and many others [1]. Surface sputtering treatment of materials at nanoscale has been studied by many researchers [3]–[6]. Theoretical computation is thus hoped on to be a major tool for accessing the excellent properties of these materials.

In particular, nitrides of transition metals have recently attracted research attention as they possess properties such as superconductivity, high hardness, optical, electronics, magnetism, high thermal stability, high melting points, resistance to corrosion among others [1],



[2], [7], [8]. These properties are responsible for the possible technological applications such as magnetic storage devices, sensors, superconductors, fuel cells etc. [2], [9].

Transition metal nitrides have been researched widely both in experiment and theory. Iron nitride (FeN) was synthesized in 1993 where its properties were studied and it was observed that the compound preferred zinc blende ($F4\bar{3}M$) crystal structure whose lattice constant is 4.307 \AA , exhibited good thermal stability at temperatures up to 593 K and at a temperature of 641 K, the compound decomposed into $\zeta\text{-Fe}_2\text{N}$ [10]. A recent study uncovered the stability of nitrides of iron in the form FeN_2 and FeN_4 [11] been novel structures of iron nitride. A study of the nickel nitride (NiN) compound using generalized gradient approximation (GGA) calculation in density functional theory indicated that the material possessed a non-magnetic ground state in the zinc blende structure while half-metallic ferromagnetic property was observed in its rocksalt structure when calculated with GGA plus Hubbard U correction [12]. Very few literature are available for nickel nitride compound.

Properties of a material in most cases depend on the crystal structure as can be observed in the case of the nickel nitride compound in reference [12] and FeN whose magnetic moment has been reported by different researchers [13]–[16] possessing non-zero magnetic moment in the rocksalt structure and zero or a very small magnetic moment in the zinc blende structure. Also for the purpose of material synthesis, compounds whose equilibrium lattice parameters occurred in the minimum equilibrium energy tend to be more stable and such crystal structure with the minimum equilibrium energy is preferred [17], [18]. Therefore, it is important to investigate the structural preference of a material before it is synthesized.

FeN has been synthesized in zinc blende face centered cubic ($F4\bar{3}M$) crystal structure while NiN has not been synthesized yet. Literature search revealed that hexagonal close packed and primitive tetragonal structures of these compounds have not been investigated to ascertain their preference. Therefore the present study investigates the preferred crystal structure of nitrides of transition metals (FeN and NiN) in terms of energy minimization by considering zinc blende face centered cubic ($F4\bar{3}M$), hexagonal close packed ($P6_3/mmc$) and primitive tetragonal ($P4_2/mmc$) structures.

2. Computational Methods

Density functional theory (DFT) as implemented in quantum espresso [19]–[21], an open source code is used to investigate the structural stability of FeN and NiN compounds based on energy minimization. Generalized gradient approximation of Perdew-Burke-Ernzerhof revised for solids (GGA-PBEsol) [22] was used for the exchange correlation functional. Projector augmented wave (PAW) pseudopotential method [23] was used to describe the interactions between ions and electrons. Optimize kinetic energy cutoff of 80 and 90 Rydberg were used for plane wave basis set expansion for FeN and NiN compounds respectively for the three crystal structures considered. Atomic positions were optimized fully using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [24], [25] via variable cell optimization until the force and energy on the atomic positions were less than 10^{-4} Ry/Bohr and $4 \times 10^{-5} \text{ Ry}$ respectively. Brillouin zone (BZ) sampling was done using K-point meshes of $10 \times 10 \times 10$, $18 \times 18 \times 9$ and $13 \times 13 \times$

9 for Zinc blende face centered cubic (FCC), hexagonal closed packed (HCP) and primitive tetragonal structures respectively. The three structural phases considered are shown in figure 1.

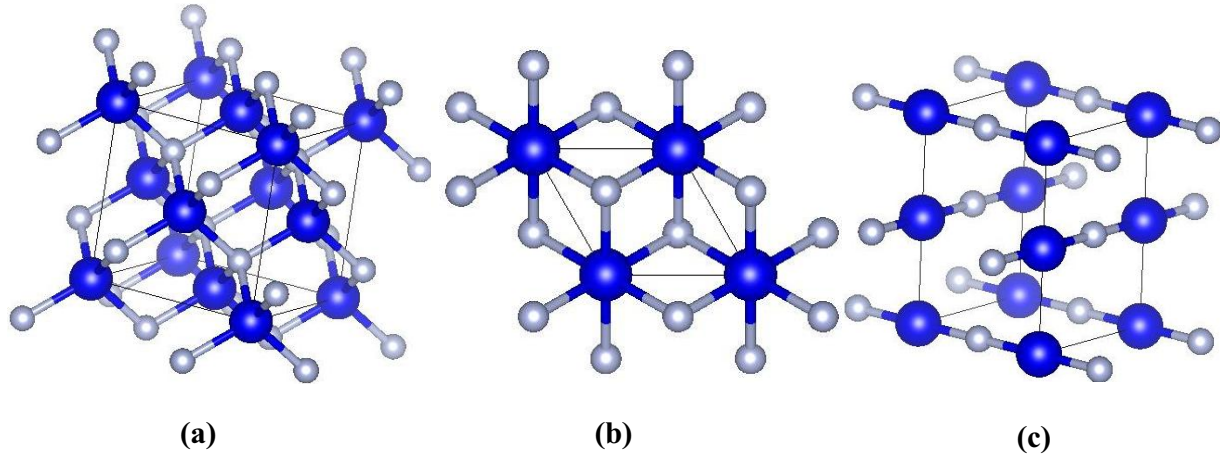


Fig. 1: Crystal structures of XN in (a) zinc blende (b) hexagonal and (c) tetragonal

The zinc blende and tetragonal structures with space groups $F4\bar{3}M$ and $P4_2/mmc$ respectively are presented in Fig. 1a and c. The metal atoms X are shown in blue colour while the nitrogen atoms N are in grey colour. The X atom can be seen to be tetrahedrally coordinated by the N atoms forming XN_4 corner sheared tetrahedrons. The hexagonal close packed structure with space group $P6_3/mmc$ presented in Fig. 1b showed that the X atom is octahedrally coordinated by N atoms thereby forming corner sheared XN_6 octahedrons.

3. Results and Discussion.

To obtain the equilibrium lattice parameters of the zinc blende FCC structure of the FeN and NiN compounds, lattice parameters around the experimental value were varied until equilibrium minimum energies were obtained for each compound. The results were then fitted using Murnaghan equation of state [26] to extract the equilibrium lattice parameter at the equilibrium minimum energy. The obtained results presented in table 1 are in accordance with experimental value [10] and other calculated values [14]–[16], [27]. This shows that the computation can be trusted.

Table 1: Calculated lattice parameters and magnetic moments of FeN and NiN for the three crystal structures.

Compound	Space Group	E_0 (Ry)	Equilibrium Properties			
			Lattice Parameter (Å)			
			Calculated		Experimental	
			a_0	c_0	a_0	c_0
FCC FeN	$F4\bar{3}M$	-1419.00278	4.232		4.307[10]	
			4.348[14]			
			4.200[27]			
			4.232[16]			
HCP FeN	$P6_3/mmc$	-709.43431	2.619	4.484		
Tetragonal FeN	$P4_2/mmc$	-709.12096	3.395	4.486		
FCC NiN	$F4\bar{3}M$	-1817.30876	4.324			
			4.241[15]			
HCP NiN	$P6_3/mmc$	-908.65778	2.851	4.777		
Tetragonal NiN	$P4_2/mmc$	-908.46813	3.345	4.634		

The variable cell optimization was performed to obtain the lattice parameters of the hexagonal closed packed (HCP) and the primitive tetragonal structures of the compounds. The lattice parameter (c) of these compounds was then fixed and the lattice parameter (a) was varied so that total energy (ground state energy) for each lattice parameter (a) was obtained. The plotted results are presented in Figure 2. The HCP and the primitive tetragonal structures of these compounds have no available results in literature for comparison.

The ground state total energy as a function of lattice parameter is presented graphically in Figure 2a and b for all the crystal structures of the compounds.

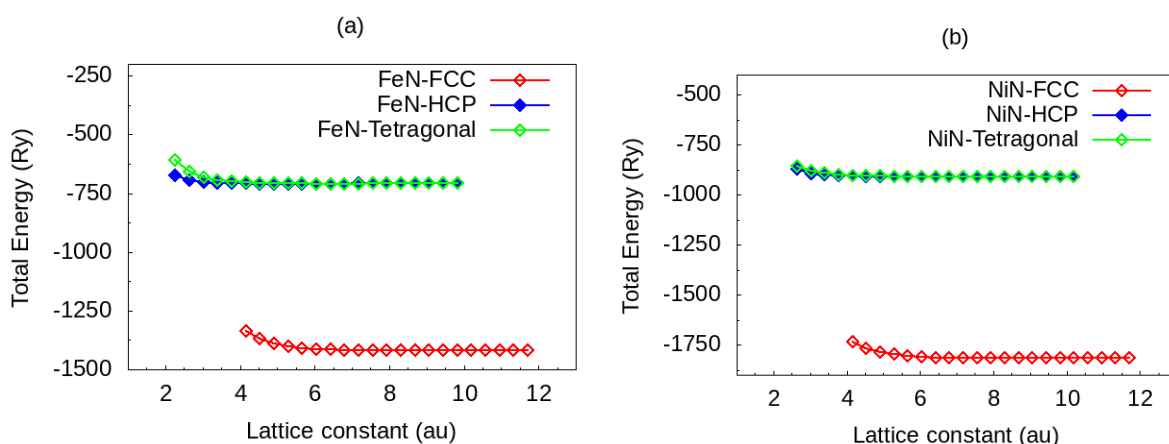


Fig. 2: Total energy as a function of lattice parameter for (a) FeN and (b) NiN compounds

The results indicate that, both FeN and NiN compounds have their equilibrium lattice parameters at the equilibrium minimum energies of -1419.00278 and -1817.30876 Rydberg respectively corresponding to the zinc blende FCC crystal structure. This suggests that, the compounds may possess highly directional covalent bonds which usually prefer a tetrahedral arrangement of atoms. It is also an indication that they may form good binary semiconductor compounds. The equilibrium lattice parameters of the compounds for HCP and primitive tetragonal crystal structures occurred at much higher equilibrium minimum energies as can be observed from the curves of figure 2. These values are listed in table 1. The results therefore indicate that, the compounds energetically prefer the zinc blende FCC crystal structure. This is in agreement with experimental result of previous studies [10].

4. Conclusion

In this study, investigation of structural stability of nitrides of iron (Fe) and nickel (Ni) transition metals was performed using density functional theory approach. The zinc blende FCC, hexagonal closed packed and primitive tetragonal crystal structures were considered. The results obtained showed that both FeN and NiN compounds prefer zinc blende FCC crystal structure as their equilibrium lattice parameters occurred at the least equilibrium minimum energies in this structure. Equilibrium lattice parameters of the compounds in the HCP and primitive tetragonal crystal structures occurred at equilibrium minimum energies much higher than this. The lattice parameters of FeN and NiN compounds in the zinc blende FCC crystal structure were computed to be 4.232 Å and 4.324 Å respectively in agreement with experiment [10] and previous computations [14]–[16], [27] as presented in Table 1. The fact that these compounds prefer zinc blende FCC crystal structure suggest they may possess highly directional covalent bonds that prefer a tetrahedral arrangement of atoms, thus forming good binary semiconductor compounds. Therefore, these compounds have high possibility of been synthesized in zinc blende FCC crystal structure.

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