

PAPER • OPEN ACCESS

Prediction of Lattice Constants of some Transition Metal Nitrides using Different Functionals and Pseudo-potentials

To cite this article: O. E. Oyewande *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **655** 012045

View the [article online](#) for updates and enhancements.

You may also like

- [Predicted pressure-induced spin and electronic transition in double perovskite \$R_2\text{CoMnO}_6\$ \(\$R = \text{rare-earth ion}\$ \)](#)
Hong Jian Zhao, Haiyang Zhou, Xiang Ming Chen et al.
- [First principles study of hydrogen in lead zirconate titanate](#)
Manura Liyanage, Ronald Miller and RKND Rajapakse
- [First-principle study of Sr-doping effect in \$\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3\$](#)
Fenglin Deng, Peiheng Jiang, Yi Lu et al.



The Electrochemical Society
Advancing solid state & electrochemical science & technology

242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Extended abstract submission deadline: April 22, 2022

Connect. Engage. Champion. Empower. Accelerate.

MOVE SCIENCE FORWARD



Submit your abstract



Prediction of Lattice Constants of some Transition Metal Nitrides using Different Functionals and Pseudo-potentials

O. E. Oyewande¹, T. Atsue^{1,2*}, I. B. Ogunniranye¹ and M. Usikalu³

¹Department of Physics, Faculty of Science, University of Ibadan, Ibadan-Nigeria

²Department of Physics, Faculty of Physical Sciences, Federal University Dutsin-Ma, Katsina State-Nigeria

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

*Corresponding Author's e-mail: tatsue@fudutsinma.edu.ng

Abstract. Properties of materials are best analyzed when lattice parameters of such compounds of materials are predicted accurately. In density functional theory prediction of lattice parameters, density functionals play important role in obtaining accurate values. In this study, density functional theory was used to investigate accurate prediction of lattice parameters of some transition metal nitrides. Local Density Approximation (LDA) and Generalized Gradient Approximation of Perdew-Burke-Ernzerhof revised for solids (GGA-PBEsol) functionals combined with ultrasoft and projector augmented wave (PAW) pseudo-potentials were used for the investigation. The results indicated that GGA-PBEsol functional with PAW pseudo-potential performed better in predicting lattice parameters of these compounds. For FeN compound, the calculated lattice parameter with GGA-PBEsol functional and PAW pseudo-potential was 4.232 Å compared with the experimental values of 4.307 Å and 4.296 Å corresponding to a little underestimation of about 1.74% and 1.49% respectively. Ultrasoft pseudo-potential of GGA-PBEsol functional and LDA functional with the two pseudo-potentials overestimated the lattice parameters for over 5%. It was concluded that, for the functionals and pseudo-potentials considered, GGA-PBEsol with PAW pseudo-potential may be a very good choice for prediction of lattice parameters of binary compounds with transition metals.

Keywords: Binary compounds, overestimation, projector augmented wave, local density approximation.

1. Introduction

In materials science applications, accurate information on the lattice constants of compounds of materials is very useful for accurate determination of their various properties. Crystalline structures are completely described by their lattice constants, together with their atomic positions and site occupancy. Materials are fully characterized and identified having knowledge of its accurate lattice parameters [1], [2]. Thus, obtaining accurate lattice parameters of materials' compounds is of utmost interest in the present day's research.

Lattice parameters are determined by both experimental and theoretical methods. Common experimental methods include X-Ray Diffraction (XRD) [2], electron diffraction [3], combined X-Ray and optical interferometer [4] among others. The popular experimental method been XRD has been researched extensively by many researchers [2], [5]–[9]. Due to the complexity of experimental techniques in predicting lattice parameters of materials'



compounds, computational tools are the hope for providing reasonable insight into lattice parameter prediction.

Density Functional Theory (DFT) has over the years become a powerful computational tool for the calculation of electronic properties. It is based on Kohn Sham method [10], [11] and it is capable of computing several properties of molecules, surfaces and solids [12]. It is efficient and computationally less expensive and thus can compute systems of several atoms up to thousands. This simplicity is due to the ability of DFT to recast a system of interacting electrons of many body Schrodinger equation into a fictitious system of non-interacting electrons that is easy to compute [13]. Thus, the exchange correlation energy between the electrons has to be represented by an approximate functional. The choice of this exchange correlation functional in many calculations determines the accuracy of calculations [12], [13].

The common and most popular approximation to the exchange correlation energy are the Local Density Approximation (LDA) [14], [15] and the Generalized Gradient Approximation (GGA) [16]–[18]. Under GGA, there exist PW91 functional (Perdew Wang) [15], Perdew Burke Ernzerhof (PBE) functional [17], [18] and Perdew Burke Ernzerhof revised for solid (PBEsol) [19]. These functionals are believed to be sufficient for lattice parameter calculations for most compounds but have limited performance in calculation of some other properties like cohesive energies and also determination of band gaps of compounds [12], [20]. Thus meta-GGA [21] and hybrid functionals [22] which are more computationally expensive have been in existence for the improvement of other properties.

In this study, lattice parameters of iron nitride (FeN) and nickel nitride (NiN) in their zinc blende crystal structure have been considered. Two pseudo-potentials of LDA and PBEsol functional of GGA were chosen to compare the accuracy of lattice parameters based on these functionals and pseudo-potentials. FeN and NiN are binary solids that found applications in surface nanotechnologies [23]–[25], magnetic storage devices [26], [27] among others. Surface treatment of materials at nanoscale for nanotechnology application has been studied comprehensively [28]–[30]. As the accuracy of many properties of compounds depend on the accuracy of the lattice parameters, it becomes imperative to consider functionals and pseudo-potentials that produce results comparable to experiments.

2. Materials and Methods

Quantum Espresso [31]–[33], an open source code was used to implement Density Functional Theory (DFT) for investigation of the lattice parameters of the zinc blende crystal structure of FeN and NiN compounds. Local density approximation (LDA) [14], [15] and Generalized gradient approximation of Perdew-Burke-Ernzerhof revised for solids (GGA-PBEsol) [19] were used for the exchange correlation functional. Ultrasoft [34] and Projector augmented wave (PAW) [35] pseudo-potentials were 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 PAW pseudo-potentials of PBEsol whereas for other pseudo-potentials, kinetic energy cutoff of 50 Rydberg was used. Brillouin zone (BZ) sampling was done using k-point meshes of $10 \times 10 \times 10$ on the Monkhorst Pack grid [36]

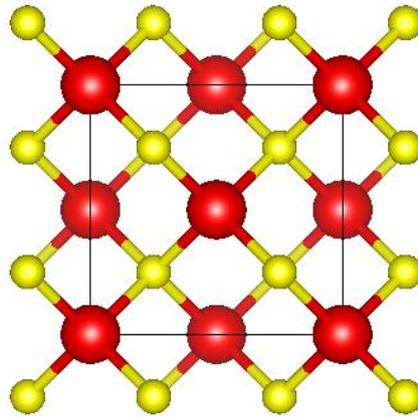


Figure 1: Crystal structures of XN in zinc blende lattices

Figure 1 shows the crystal structure of the transition metal nitrides considered in this study. The structure is the zinc blende face centered cubic lattice with space group $F\bar{4}3M$. The balls in red represent the atoms of the transition metal (X) whereas the ones in yellow represent the atoms of nitrogen (N). The atoms are arranged in the crystal in such a way that the X atom are coordinated tetrahedrally by the N atoms. This arrangement of atoms forms an XN_4 corner sheared tetrahedrons.

3. Results and Discussion.

In this study, iron nitride (FeN) and nickel nitride (NiN) were chosen to investigate the accuracy of their lattice parameters calculated with two different pseudo-potentials of LDA and GGA-PBEsol functionals. The pseudo-potentials were Ultrasoft (USPP) and projector augmented wave (PAW) pseudo-potentials. The lattice parameters were varied around the experimental value and computation was performed on each lattice parameter to obtain minimum energy of each of them respectively. The results for each pseudo-potential and the two compounds were recorded and presented graphically as shown in Figure 2.

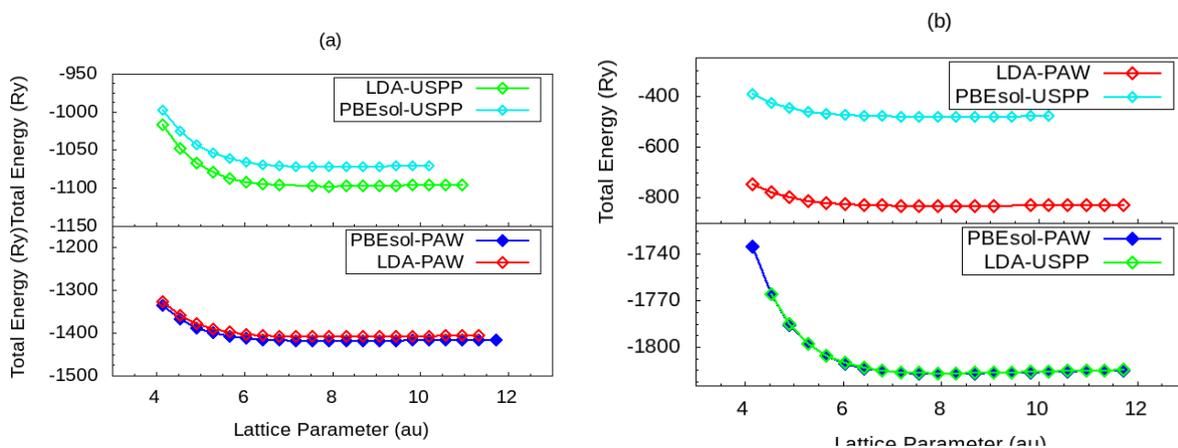


Figure 2: Minimum energy as function of lattice parameter for (a) FeN and (b) NiN

In the result presented on the graphs, it was observed that PBEsol functional of GGA with PAW pseudo-potential produced lattice parameters whose minimum energy is the least for the two compounds.

In order to obtain accurate lattice parameters comparable with experimental results, Murnaghan equation of state[37] was used to fit the energy-lattice parameter data which is presented in table 1. The Murnaghan equation of state is expressed as

$$E = \frac{Kv}{K'} \left[\frac{1}{K' - 1} \left(\frac{v_0}{v} \right)^{K'} + 1 \right] + E_0 \quad (1)$$

The least – square method determinestheparameters v_0 , K , K' and E_0 which represent the equilibrium unit cell volume, bulk modulus, pressure derivative of bulk modulus and the equilibrium minimum energy respectively.

The table presents calculated lattice parameters compared with experiment and percentage difference as error. Bulk modulus, its pressure derivative, equilibrium minimum energy and equilibrium unit cell volume. The results revealed that, GGA-PBEsol functional with PAW pseudo-potential produced result that is by far better than the other results as it showed a little underestimation of about 1.74% and 1.49% respectively for the compared experimental values. GGA-PBEsol functional with USPP and LDA functional with PAW and USPP both overestimatethe lattice parameter for over 5% of the compared experimental results.

The trend of the lattice parameter of FeN compound is such that it increases with increasing equilibrium minimum energy and is near the experimental value when the equilibrium minimum energy was least. This trend was not observed in the lattice parameter of NiN compound, however the least calculated equilibrium lattice parameter corresponding to the GGA-PBEsol functional with PAW pseudo-potential occurred at the least equilibrium minimum energy. This is an indication that lattice parameters of these compounds are best predicted with the GGA-PBEsol using PAW pseudo-potentials.

Table 1: Lattice Parameter, Bulk modulus and other equilibrium parameters.

Compound	Functional	Pseudo-potential	Lattice Const. (Å)		Error (%)	Bulk Modulus (GPa)	Derivative of Bulk Modulus	Equil. Min. Energy (Ry)	Equil. Min. Volume (Å ³)
			Calc.	Expt.					
FeN	GGA-PBEsol	PAW	4.232	4.307[9]	-1.74	983.0	3.71	-1419.00	75.7944
				4.296 [38]	-1.49				
	USPP	PAW	4.532	4.307[9]	+5.22	513.7	3.08	-1071.74	93.1124
				4.296 [38]	+5.49				
	LDA	PAW	4.527	4.307[9]	+5.11	491.6	3.18	-1408.17	92.7831
				4.296 [38]	+5.38				
	USPP	PAW	4.529	4.307[9]	+5.15	498.6	3.17	-1097.10	92.8969
				4.296 [38]	+5.42				
	GGA-	PAW	4.324			810.4	3.67	-1817.31	80.8227

NiN	PBEsol	USPP	4.552	513.0	3.19	-481.64	94.3225
	LDA	PAW	4.536	490.6	3.21	-832.01	93.3123
		USPP	4.572	530.6	3.14	-1816.90	95.5907

The bulk moduli of the computation of the compounds are quite high. This is responsible for high hardness of transition metal nitrides. No experimental values were found in literature for comparison, though we understand that LDA and GGA functionals overestimate bulk modulus.

4. Conclusion

In this study, we have investigated the accuracy of lattice parameter calculations of FeN and NiN compounds in the zinc blende crystal structure through first principles studies. LDA and GGA-PBEsol functionals with ultrasoft and PAW pseudo-potentials were used in both cases.

The calculated results of the lattice parameters were compared with the experimental results. It was confirmed that GGA-PBEsol functional with PAW pseudo-potential performed better in predicting lattice parameters of these compounds. Observations showed that for FeN compound, the calculated lattice parameter with GGA-PBEsol functional and PAW pseudo-potential was 4.232 Å compared with the experimental values of 4.307 Å and 4.296 Å corresponding to a little underestimation of about 1.74% and 1.49% respectively. Ultrasoft pseudo-potential of GGA-PBEsol functional and LDA functional with the two pseudo-potentials overestimated the lattice parameters for over 5%.

The bulk moduli of the compounds computed with both functionals and pseudo-potentials were high, which is typical of compounds with transition metals. It is the reason for high hardness of nitrides of transition metals.

It can be concluded that for the considered functionals and pseudo-potentials, GGA-PBEsol with PAW pseudo-potential may be a very good choice for prediction of lattice parameters of binary compounds with transition metals.

Acknowledgement

The authors wish to acknowledge The Postgraduate College of the University of Ibadan, Ibadan, Nigeria for the computational access to the High Performance Computing (HPC) resources. All the computational tasks were performed with these resources.

References

- [1] I. O. Alade, I. A. Olumegbon, and A. Bagudu, "Lattice constant prediction of A₂XY₆ cubic crystals (A = K, Cs, Rb, TI; X = tetravalent cation; Y = F, Cl, Br, I) using computational intelligence approach," *J. Appl. Phys.*, vol. 127, no. 1, 2020.
- [2] E. S. K. Menon, A. G. Fox, and R. Mahapatra, "Accurate determination of the lattice parameters of γ -TiAl alloys," *J. Mater. Sci. Lett.*, vol. 15, no. 14, pp. 1231–1233, 1996.
- [3] J. C. Lodder and K. G. v. d. Berg, "A method for accurately determining lattice parameters using electron diffraction in a commercial electron microscope," *J. Microsc.*, vol. 100, no. 1, pp. 93–98, 1974.

- [4] E. Massa, G. Mana, U. Kuetgens, and L. Ferroglio, "Measurement of the lattice parameter of a silicon crystal," *New J. Phys.*, vol. 11, 2009.
- [5] S. Wang, M. Jiang, L. Gao, Z. Ma, and F. Wang, "Theoretical and experimental studies on the crystal structure, electronic structure and optical properties of SmTaO₄," *Materials (Basel)*, vol. 9, no. 1, 2016.
- [6] M. Frentrup, N. Hatui, T. Wernicke, J. Stellmach, A. Bhattacharya, and M. Kneissl, "Determination of lattice parameters, strain state and composition in semipolar III-nitrides using high resolution X-ray diffraction," *J. Appl. Phys.*, vol. 114, no. 21, 2013.
- [7] B. Lavina, P. Dera, and R. T. Downs, "Modern X-ray diffraction methods in mineralogy and geosciences," *Rev. Mineral. Geochemistry*, vol. 78, pp. 1–31, 2014.
- [8] Z. Moore, "Application of X-ray Diffraction Methods and Molecular Mechanics Simulations to Structure Determination and Cotton Fiber Analysis," p. 155, 2008.
- [9] K. Suzuki, H. Morita, T. Kaneko, H. Yoshida, and H. Fujimori, "Crystal structure and magnetic properties of the compound FeN," *J. Alloys Compd.*, 1993.
- [10] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, vol. 136, no. 3B, p. B 864, 1964.
- [11] W. Kohn and L. J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects*," 1965.
- [12] P. Haas, F. Tran, and P. Blaha, "Calculation of the lattice constant of solids with semilocal functionals," no. February, pp. 1–10, 2009.
- [13] A. E. Mattsson, P. A. Schultz, and M. P. Desjarlais, "Designing meaningful density functional theory calculations in materials science — a primer," vol. 1, 2005.
- [14] P. A. M. Dirac, "Note on Exchange Phenomena in the Thomas Atom," vol. 24, no. May 1930, pp. 376–385, 2019.
- [15] J. P. Perdew and Y. Wang, "Accurate and simple analytic representation of the electron-gas correlation energy," vol. 45, no. 23, pp. 244–249, 1992.
- [16] J. P. Perdew, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," vol. 46, no. 11, 1992.
- [17] J. P. Perdew, K. Burke, and M. Ernzerhof, "Perdew, Burke, Ernzerhof - 1997 - Generalized Gradient Approximation Made Simple(2)," no. 3, pp. 3865–3868, 1996.
- [18] M. Ernzerhof and G. E. Scuseria, "Assessment of the Perdew–Burke–Ernzerhof exchange–correlation functional," *J. Chem. Phys.*, vol. 5029, 1999.
- [19] J. P. Perdew *et al.*, "Restoring the density-gradient expansion for exchange in solids and surfaces," *Phys. Rev. Lett.*, vol. 100, no. 13, pp. 1–4, 2008.
- [20] O. O. Johnson, P. E. Olutuase, and O. E. Oyewande, "First principles calculations of the optoelectronic properties of magnesium substitutes in Lead based ABX₃ compounds," *J. Phys. Conf. Ser.*, vol. 1299, no. 1, 2019.
- [21] J. P. Perdew, S. Kurth, and P. Blaha, "Accurate Density Functional with Correct Formal Properties : A Step Beyond the Generalized Gradient Approximation," vol. 82, no. 12, pp. 2544–2547, 1999.
- [22] A. D. Becke, "Density-functional thermochemistry . III . The role of exact exchange," vol. 5648, no. August 1998, 2001.
- [23] E. O. Yewande, A. K. Hartmann, and R. Kree, "Propagation of ripples in Monte Carlo models of sputter-induced surface morphology," *Phys. Rev. B*, vol. 71, no. May 2004, pp. 1–8, 2005.
- [24] E. O. Yewande, R. Kree, and A. K. Hartmann, "Morphological regions and oblique-

- incidence dot formation in a model of surface sputtering,” *Phys. Rev. B*, vol. 73, no. December 2005, pp. 1–8, 2006.
- [25] E. O. Yewande, R. Kree, and A. K. Hartmann, “Numerical analysis of quantum dots on off-normal incidence ion sputtered surfaces,” *Phys. Rev. B*, vol. 75, no. November 2006, pp. 14–16, 2007.
- [26] B. Eck, R. Dronskowski, M. Takahashi, and S. Kikkawa, “Properties of Binary 3D Transition Metal Nitrides,” *J. Mater. Chem.*, vol. 9, pp. 1527–1537, 1999.
- [27] N. S. Gajbhiye, R. S. Ningthoujam, and J. Weissmüller, “Synthesis and magnetic studies of nanocrystalline nickel nitride material,” *Phys. Status Solidi Appl. Res.*, vol. 189, no. 3, pp. 691–695, 2002.
- [28] A. Akinpelu *et al.*, “Analytical Form of Sputtering in Relation to Surface Binding Energy for Different Types of Perovskites,” *J. Phys. Conf. Ser.*, vol. 1299, no. 1, 2019.
- [29] O. E. Oyewande and A. Akinpelu, “An ion-beam surface sputtering approach to the quest for lead-free metal halide perovskite for solar cells,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 434, no. August, pp. 102–108, 2018.
- [30] O. E. Oyewande, I. B. Babalola, and M. Usikalu, “Effect of surface diffusion algorithm on nanostructure formation in a semi-empirical Monte Carlo model of sputter erosion of materials,” *J. Phys. Conf. Ser.*, vol. 1299, no. 1, 2019.
- [31] Giannozzi *et al.*, “QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials,” *J. Phys. Condens. Matter*, vol. 21, no. 39, 2009.
- [32] P. Giannozzi *et al.*, “Advanced capabilities for materials modelling with Quantum ESPRESSO,” *J. Phys. Condens. Matter*, vol. 29, no. 46, p. 465901, Nov. 2017.
- [33] <https://www.quantum-espresso.org>, “QUANTUM ESPRESSO - QUANTUM ESPRESSO.” [Online]. Available: <https://www.quantum-espresso.org/>. [Accessed: 03-Aug-2019].
- [34] D. Vanderbilt, “Soft self-consistent pseudopotentials in a generalized eigenvalue formalism,” *Phys. Rev. B*, vol. 41, no. 11, pp. 7892–7895, 1990.
- [35] P. E. Blöchl, “Projector augmented-wave method,” *Phys. Rev. B*, vol. 50, no. 24, pp. 17953–17979, Dec. 1994.
- [36] J. D. Pack and H. J. Monkhorst, “Specials points for Brillouin-zone integration,” *J. Chem. Inf. Model.*, vol. 53, pp. 1689–1699, 2013.
- [37] F. D. Murnaghan, “The volume changes of five gases under high pressures,” *J. Franklin Inst.*, vol. 197, no. 1, p. 98, 1924.
- [38] D. Laniel, A. Dewaele, S. Anzellini, and N. Guignot, “Study of the iron nitride FeN into the megabar regime,” *J. Alloys Compd.*, 2017.