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INVESTIGATION OF STRUCTURAL PROPERTIES OF ALUMINUM NITRIDE USING FIRST PRINCIPLES CALCULATION

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ABSTRACT
Group-III nitrides have received extensive attention because of their outstanding properties leading to different technological application. It is therefore important to conduct an accurate and systematic theoretical study of the structural properties of one of the important member of these materials. In this work, we studied the structural properties which include the convergence test, convergence of a plane wave cutoff energy, convergence test result with respect to k-points and lattice structural parameter .Our calculations of the structural properties of Aluminum nitride (AlN) were studied using first principle theoretical investigation of the AlN based on density functional theory (DFT) calculation within the generalized gradient approximation (GGA) which was used in the exchange correlation functional as implemented in quantum espresso. Obtained results are discussed within the employed theoretical methods of calculations. Result suggests that, the structure was successfully converged at the cut off-energy of -48.36054179 Ry. Also 45.0 Ry was also found to be as the Kinetic energy cut-off of the plane wave basis set in this research. Furthermore, 4x4x2 k-point was used as the k-point obtained in this research based on Monkhost and pack method of selecting k-point as implemented in (DFT). The equilibrium value of the lattice parameter obtained at the point of minimum energy is about 3.95 Å which are in good agreement with experimental value which was 4.05Å. The deviation of result as shown in figure 4.5 from the experimental result is about 0.1Å of absolute error which is equivalent to 2.5% of relative error, this shows that, there is very negligible error in the calculation. The lattice parameter value that was determined in this work almost matches the experimental value. It can therefore be said that the equilibrium lattice parameters for various crystal structure can be evaluated using this method of energy minimization.

Keywords: DFT, GROUP-III NITRIDES, STRUCTURAL PARAMETER, GGA

INTRODUCTION

In recent decade, group-III nitrides have received extensive attention because of their outstanding properties (Baei M.and Bagheri Z., 2013). As an important member of group III-nitrides, Aluminum nitride is characterized by its unique properties such as superior mechanical strength, high thermal conductivity, high melting point, high resistance to chemicals, and very short bond lengths (Liu G et al, 2014). This makes them potential materials for electronics and optoelectronics industry (Lei T, Ludwig KF, Moustakas T, 1993). Therefore, they are potential materials for today's electronic industry (Zou C. et al, 2007). These materials are also used for constructing violet, quantum-point lasers, lasers that range from red to ultraviolet, green, and blue light-emitting devices and also high temperature transistors (V.N. Tondare, et al, 2002). AlN is one of the best materials, which is used to produce microelectronic and optoelectronic devices (M. Dvorak, 2013). More broadly, the AlN has different applications due to its greater piezoelectricity, which increases the chances of application on micro-transducers for ultrasound (P. Tsipas, 2013). AlN is an insoluble white to pale-yellow solid with a molar mass of 40.99g/mol and a density of 3.26g/cm^3(X. Zhang, 2007). The AlN crystallizes into a hexagonal wurtzite structure with a space group of C_{6v}^4-$P6_3mc$ and cubic zinc-blende structure with a space group of $F\bar{4}3m$(Paola, G, 2009). The wurtzite AlN is the only III-V semiconductor compound with a direct bandgap of approximately 3.5eV (M. Razeghi, 2006). The zincblende form has been theoretically reported to be metastable (Noei M. et al, 2013).

Despite this potential applications, there are few experimental and theoretical study of structural properties of AlN. Therefore, there is the need to conduct systematic and accurate theoretical description of the structural properties of aluminum nitride.

The aim of this research is to use Density Functional Theory (DFT) and study the structural properties of Aluminum nitride.

THEORETICAL FRAMEWORK

Many-Body Problem

The many-body problem refers to the problem of solving the Schrodinger equation for a system of atoms and electrons (I.V

Solovyev, 2008). Quantum mechanics is a mathematical tool for predicting the behaviors of microscopic particles. The results of quantum formalism cover wide range of phenomena. In fact, one of the advantages of quantum mechanical calculations is its ability to predict the total energy of a system of electrons and nuclei (M. Razeghi, 2006). The rules of calculating the energies of the complicated systems are the extension of those for simple one-atom systems. Having found the total energy of system, the instances are the equilibrium lattice constant that minimizes the total energy, or the fact that the surfaces and defects of solids adjust themselves in a way that minimize the related total energies. If total energies are calculated precisely, most of the physical properties can be estimated.

The properties of a many-body quantum system are formulated in many-body Schrodinger equation. The simplest form of time-independent Schrodinger equation is:

$$\hat{H}\Psi_I(\vec{x}_1, \vec{x}_2, \ldots., \vec{x}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) = E\Psi(\vec{x}_1, \vec{x}_2, \ldots., \vec{x}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) \ldots\ldots\ldots (1)$$

The Hamiltonian of a system of electrons and nuclei is given by:

$$\hat{H} = \frac{-\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i,I}\frac{-Z_i e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_i^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \qquad (2)$$

Where $\hbar$ is the reduced Plant constant, e is the electron charge, Z is the nuclei charge and electron and nuclei properties are shown by lower case and upper case respectively. The first term is the electronic kinetic energy, the second term is electron-nuclei Coulomb attraction, the third term is the electron-electron repulsion, the fourth term is the nuclear kinetic energy and the last term is nuclei-nuclei repulsion. In the presence of external electric or magnetic fields, Hamiltonian may contain even more terms (Richard M, 2004).

Solving quantum mechanics quantitatively requires several approximations, of which the most widely used is independent-electron approximation. Within this approximation each electron move independently of the others, except that the electrons obey the exclusion principle and each move is some average effective potential which may be determined by the other electrons.

STRUCTURAL PROPERTIES

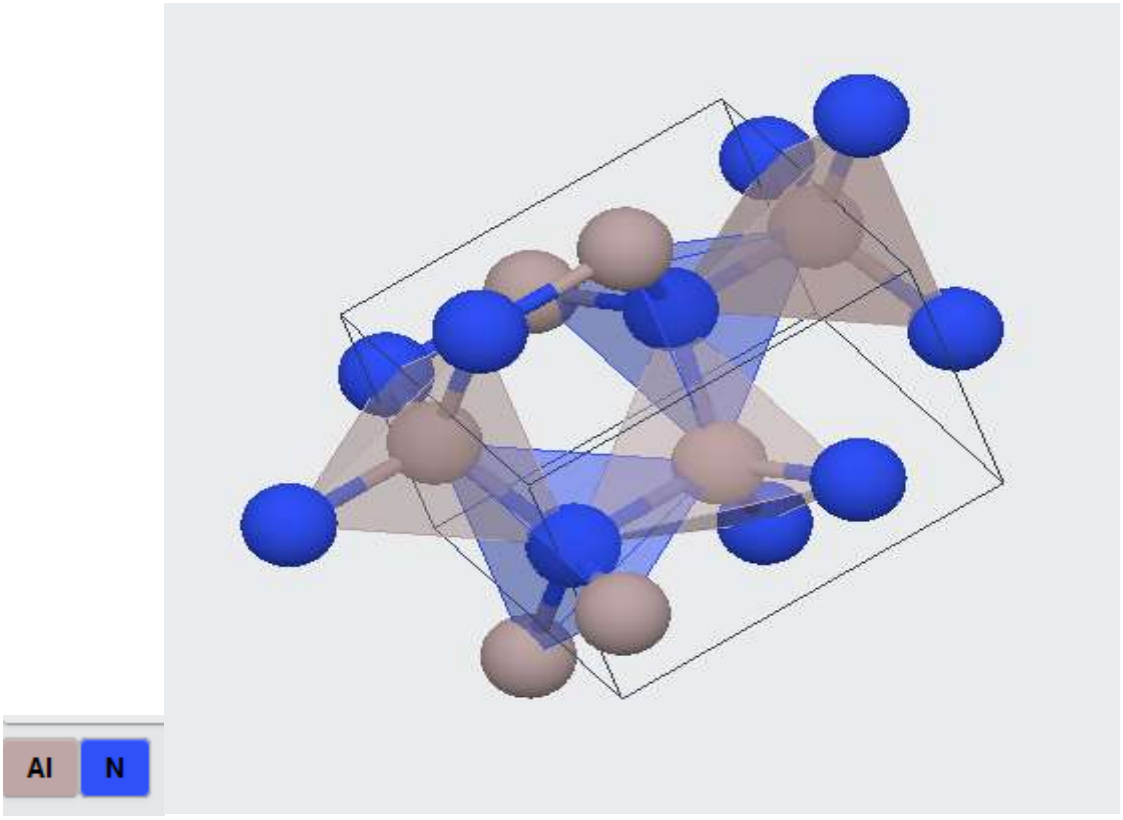

Plate 1: Crystal structure of Aluminum nitride

The primitive unit cell was adopted in this work. Aluminum nitride is Wurtzite structured and crystallizes in the hexagonal. The structure is three-dimensional. Al^{3+} is bonded to four equivalent N^{3-} atoms to form corner-sharing AlN4 coordinate geometry of tetrahedral. The hexagonal crystal structure corresponds to conventional unit cell (Feneberg M, et al 2010).

COMPUTATIONAL METHODOLOGY

In this particular work, the calculations are performed on the primitive cell of AlN using first principle calculation, based on DFT as implemented in the QUANTUM ESPRESSO simulation package. Quantum ESPRESSO is an integrated software suite for atomistic simulation based on electronic structure, using DFT a plane wave (PW) basis set and pseudopotentials (PP) (norm-conserving, ultra-soft and projector-augmented wave) (Paola, G, 2009).

For the Aluminum nitride, the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) scheme has been employed in approximating the exchange-correlation potential(Perdew, J.P.,Burke, K., and Ernzerhof, M, 1996). The plane wave basis sets with the maximum kinetic energy has been used to expand the wave functions. The electron-ion core interaction is treated by ultra-soft pseudopotentials for AlN valence orbitals as all in the pseudopotential files. For integrals, smearing has been adopted and to be specific Maxfessel-Paxton smearing method with small Gaussian spreading has been used. The brillouin zone integration is performed using Monkhorst-Pack scheme with k-points grids (Monkhorst and Pack, 1976).

COMPUTATIONAL STEPS

The computational steps followed in this research work can be explained as follows:

a) Obtaining the crystal parameters and atomic positions of the Aluminum nitride: the crystal parameters and atomic positions for the Aluminum nitride used in this work were obtained from two main sources, the material project site (Jain A, et al 2013) and AFLOW.ORG (Curtarolo S.,et al, 2012).

b) Optimizing the crystal parameters and atomic positions: The second step is optimizing the obtained crystal parameters and the atomic positions (of the AlN) by relaxation or convergence calculation using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm which is an iterative method for solving unconstrained nonlinear optimization problems. In a structural optimization, the minimum of the potential energy surface (PES) that is closest to the starting configuration is looked for. So, in practice we search for the ionic configuration where the forces are zero.

c) Self-Consistent Field (SCF) calculation: The SCF calculation was performed with the optimized structure. This is the step were the Kohn-Sham equation was solved iteratively. But, before performing the final SCF calculation, convergence test calculations were done in order to find the exact and actual kinetic energy cut-off and k-points to be used in the calculation. To this regards, two convergence tests were performed, the kinetic energy cut-off and k-points convergence tests. So, the final SCF calculation was done with the converged k-points and kinetic energy cut-off.

RESULTS AND DISCUSSION

CONVERGENCE TEST RESULTS AND DISCUSSION

In any DFT calculations, it is of paramount importance to perform some convergence test calculations before commencing the actual calculation. That is why, in order to get a well-converged total energy, there is need to test for all other parameters relatively on a convergence scale to ensure that convergence is achieved consistently. The results presented below represent the energy convergence of SCF, the convergence test with respect to plane wave kinetic energy cut-off and k-points mesh for Aluminum nitride.

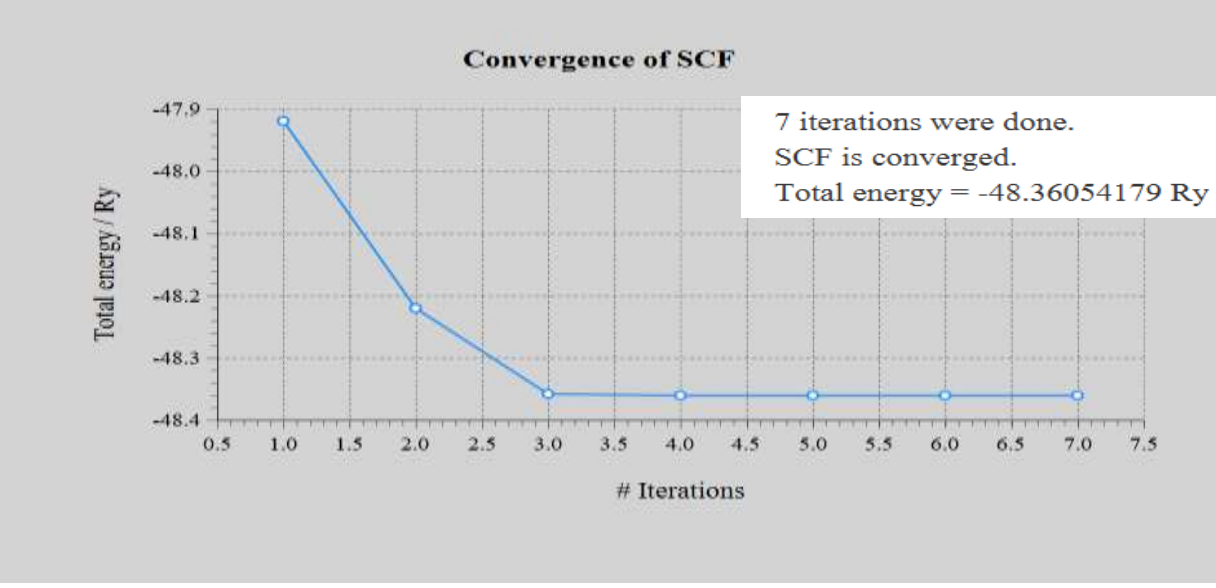

Figure 3.1: Energy Convergence of SCF

The structure was successfully relaxed or converges at the cut off-energy of -48.36054179 Ry as produce by the output footage of Quantum Espresso which was shown in fig. 3.1. which indicate that, the total energy remains constant with any further increase of iteration from 3.0. Seven iterations were done, the system were able to achieved convergence since from the third iterations.

CONVERGENCE OF PLANE WAVE CUTOFF-ENERGY

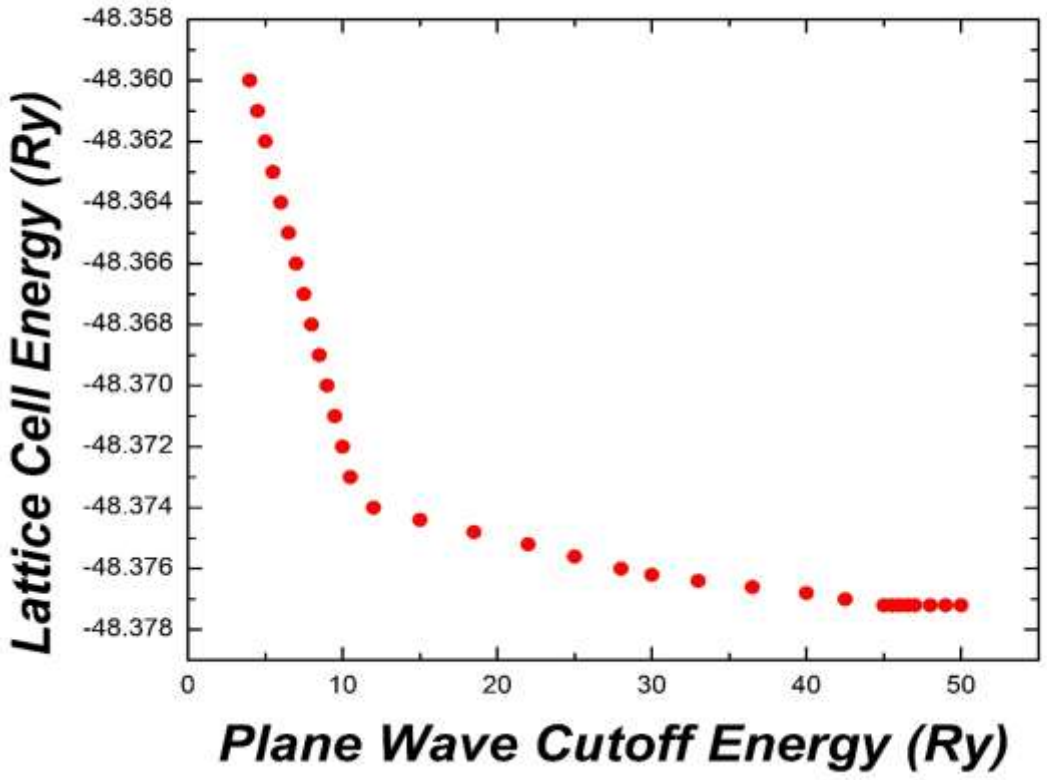

Figure 3.2: Lattice Cell Energy Vs. Plane Wave Cut off Energy for Aluminum nitride

It can be seen from figures 3.2 that the lattice cell energy changes considerably with the plane wave energy cut-off, until at some energy cut-off where it becomes almost stable. In this case, as the lattice cell energy decreases, the plane wave cut off increases from 4Ry to 50Ry and becomes stable at 45Ry. That is to say, the total energy remains constant with any further increases in the plane wave energy cut-off from 45Ry. This indicates a well-converged energy cut-off. That is why 45Ry was used as the kinetic energy cut-off of the plane wave basis set for this case.

CONVERGENCE TEST RESULTS WITH RESPECT TO K-POINTS

The convergence test results with respect to the kinetic energy cut-off and k-points for the Aluminum nitride are presented below.

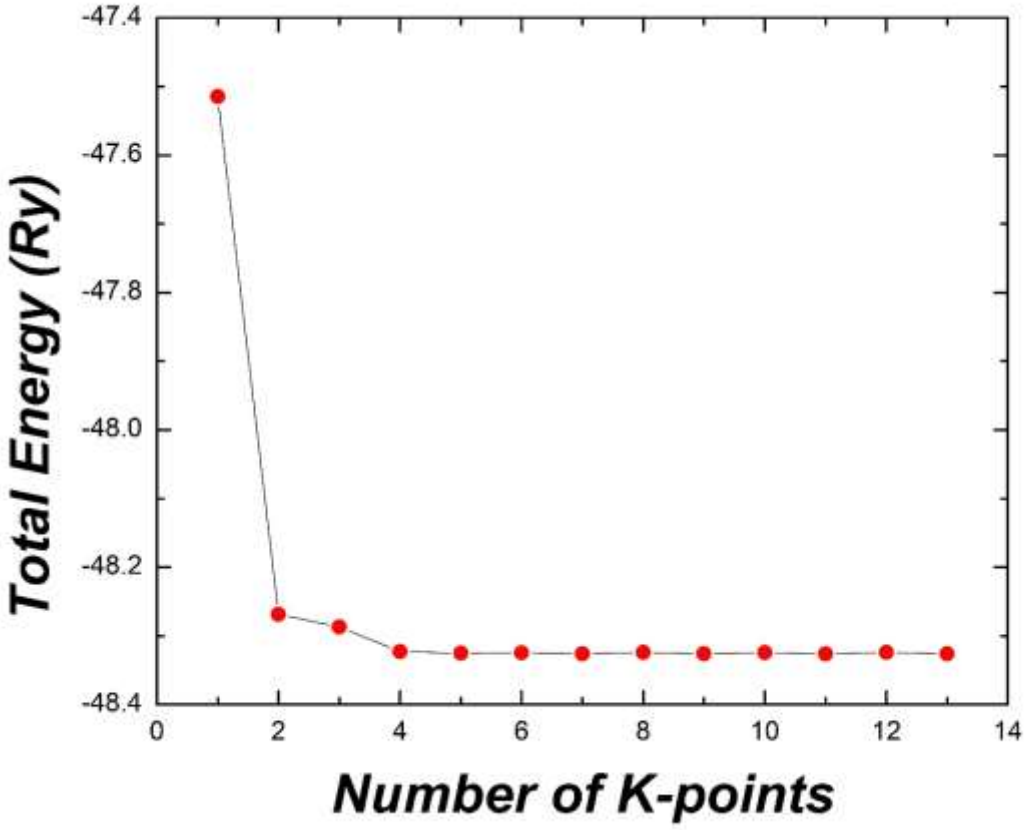

Figure 3.3: Total Energy Vs K-Point

Figure 3.3 shows the variations of the total energy with respect to the k-points grids. The total energy becomes independent of the number of k-points at a certain points. The total energy keeps changing from 1×1×0 to 4×4×1 k-point grids and then it almost becomes stable from 4×4×2 k-points grid which shows a well converged value at -48.32274125 Ry. As such, 4×4×2 k-points grids which correspond to the total energy of -48.32274125 Ry have been adopted for this case based on Monkhorst and Pack method of selecting k-points as implemented in DFT calculations (Monkhorst and Pack, 1976). Most of the DFT codes provide ways of choosing k-points using Monkhorst and Pack method. So, one of the basic idea adopted in the method is to specify the number of k-points that are to be used in each direction in reciprocal space.

LATTICE PARAMETER

By going through the process of total energy minimization per unit cell for the material under investigation whose crystal structure is known, the equilibrium lattice parameters can be evaluated. An SCF program in Quantum Espresso is used to determine the lattice parameter for which the energy is a minimum. In this work the process was only done for Aluminum nitride to demonstrate how the lattice parameters are obtained using the principle of energy minimization. To get a particular value, a series of values are going to be plotted and at each point the energy is noted.

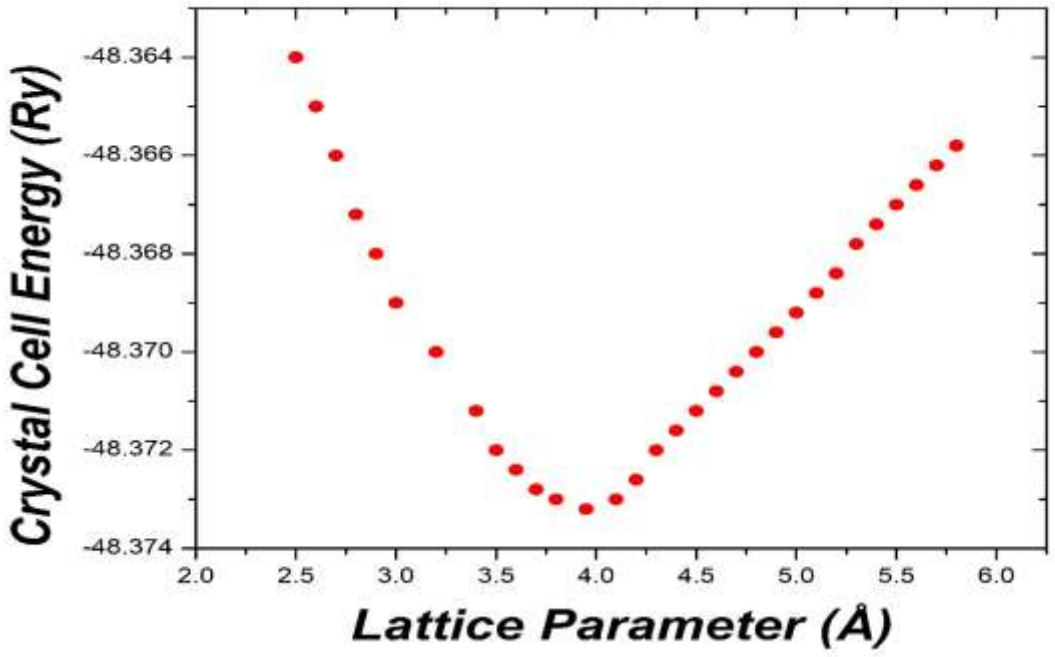

Figure 3.4: Lattice parameter, *a*, for Aluminum nitride

The equilibrium value of the lattice parameter *a* obtained at the point of minimum energy is about 3.95 Å. which are in good agreement with previously reported values. The experimental result often used in literature is 4.05Å (S. K. Yadav, 2014).

The deviation of the result as shown in figure 3.4 from the experimental result is about 0.1Å of absolute error which is equivalent to 2.5% of relative error, this shows that, there is very negligible error in the Calculation. The lattice parameter value that is determined in this work almost matches the experimental value. It can therefore be said that the equilibrium lattice parameters for various crystal structures can be evaluated using this method of energy minimization.

CONCLUSIONS

In this work, we studied the structural properties of Aluminum nitride through a first-principles density functional theory scheme with generalized gradient approximation (GGA) as implemented in Quantum Espresso to approximate the exchange and correlation energies. The structure is Aluminum nitride three-dimensional. Al3+ is bonded to four equivalent N3- atoms to form corner-sharing AlN4 coordinate geometry of tetrahedral, the structure was successfully relaxed or converge at the cut off-energy of -48.36054179 Ry. Our result shows that, the lattice cell energy decreases while the plane wave cut off increases from 4Ry to 50Ry and becomes stable at 45Ry. The total energy becomes independent of the number of k-points at a certain point, showing a well-converged value at -48.32274125 Ry. The equilibrium value of the lattice parameter *a* obtained at the point of minimum energy is about 3.95 Å. which are in good agreement with previously reported values. More importantly, further research is highly needed in order to put up an experimental application of this work. Finally, another computational method should also be employed to carry out the same investigation for better results.

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