THE FIRST PRINCIPLE CALCULATION OF THE PROPERTIES OF ALUMINIUM AND GALLIUM USING DENSITY FUNCTIONAL THEORY.

Omamoke O. E. Enaroseha[1*], Obed Oyibo[2],Oghenevovwero E. Esi[3], Edward O. Tuggen[4], and Jennifer A. Nomuoja[5]

[1*]Department of Physics, Delta State University, Abraka, Nigeria, Email: enarosehaomamoke@gmail.com
[2]Department of Physics, Delta State University of Science and Technology, Ozoro, Nigeria.
[3]Department of Physics, Dennis Osadebay Univeristy, Asaba, Delta State, Nigeria
[4&5]Department of Mathematics, Dennis Osadebay Univeristy, Asaba, Delta State, Nigeria

***Corresponding Author:** Omamoke O. E. Enaroseha
*Department of Physics, Delta State University, Abraka, Nigeria, Email: enarosehaomamoke@gmail.com

Abstract
The theoretical calculations for the structural, thermodynamic, electrical and mechanical characteristics of aluminum and gallium were studied using ab initio principles. The Density Functional Theory (DFT) was used as the methodology, and it provides solutions to the Kohn – Sham equation.

The elemental structures were obtained using Xcryden software, and the exchange correlation functions within the Perdew–Burke–Ernzerhof (PBE) functional were treated using the PAW pseudo–potentials and Generalized Gradient Approximation (GGA).

The results obtained from the ab initio calculations engulfthat the structural properties of a(A), B(GPa), B'(GPa) and E(eV) for both elements studied. The parameters obtained for the mechanical properties C11, C12 and C44 were calculated for both metals. The elastic properties; G, B/G, E, μ, A and H were also calculated for both elements. The results obtained for aluminum shows the values of B, C', C11, C12 and C44 are 45, 3.9, 50.20, 47.6 and 31 respectively. For gallium we obtained 47, 4.03, 52.373, 44.313 and 29.0 corresponding to B, C', C11, C12 and C44 respectively.

keywords: Aluminum, gallium, structural, mechanical, thermodynamic

DOI: - 10.31838/ecb/2023.12.si5.034

1.0 INTRODCTION

Metals are crystalline solids. They typically have a fairly straightforward crystal structure that is characterized by dense atom packing and a high level of symmetry. Metal atoms often have fewer than half of their total number of electrons in their outermost shell. This property makes metals less likely to combine to form compounds. However, non – metals (such as oxygen and sulfur), which typically contain more than half the maximum amount of valence electrons, interact with them more easily. The chemical reactivity of different metals varies greatly.Aluminum is strong and lightweight, and is used in many applications ranging from construction to cookware. Aluminum is often alloyed with other metals to improve its strength and mechanical properties. One particularly useful alloy is duralumin, an alloy of aluminum with about 4% copper, and small amounts of magnesium, manganese, iron, and silicon. Aluminum and its alloys are used in aircraft and automobile frames, rockets, window frames, doors, siding, kitchenware, packaging (aluminum cans, aluminum foil), electrical wiring (although aluminum has a higher resistance than copper, it is cheaper), as a silvering agent in paints (usually in powdered form), in heat sinks, and many other uses [1].

Gallium is a soft, silvery-white metal with a low melting point (29.8ºC); unlike most metals, it expands when cooled. It is found in the Earth's crust at a concentration of 18 ppm, making it the 34th most abundant element. It is found in trace amounts in bauxite, coal, diaspore, germanite, and sphalerite[2]. The existence of gallium was predicted by Dimitri Mendeleev in 1869 from a blank space in his periodic table beneath aluminum.

The theory of quantum mechanics is arguably one of the greatest discoveries of physics; it revolutionized our understanding of molecules, atoms, radiation, and the world of the sub-atomic particles[3]. The study of matter and its interactions with energy on the scale of atomic and subatomic particles is known as quantum mechanics. Classical physics, on the other hand, only explains matter and energy on a scale familiar to human experience, including the behavior of astronomical bodies such as the moon. Much of modern science and technology is still based on classical physics. Toward the end of the nineteenth century, however, scientists discovered phenomena in both the large (macro) and small (micro) worlds that classical physics could not explain. The basic equation that was develop to suit the purpose of understanding the atomic scale of particles wave mechanics was the Schrödinger wave equation[4].

Schrodinger wave equation is a mathematical expression describing the energy and position of the electron in space and time, taking into account the matter wave nature of the electron inside an atom. It is based on three considerations. They are;Classical plane wave equation,Broglie's Hypothesis of matter-wave, andConservation of Energy.

Schrödinger equation can be used to determine the trajectory, location, and energy of these systems. The time-dependent Schrödinger equation in three dimensions (for a non-relativistic particle) is:
the basic form of Schrödinger's wave equation is as follows:

$$E\Psi(r,t) = H\Psi(r,t) \quad (2)$$

The Schrödinger equation, or Schrödinger's wave equation, is a partial differential equation that utilizes the wave function to describe the behavior of quantum mechanical systems[5]. The

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r,t)\right]\Psi(r,t) \quad (1)$$

Ψ is called a *wave function*; *H*, with, hat, on top is known as the Hamiltonian operator; and *E* is the binding energy of the electron. Solving Schrödinger's equation yields multiple wave functions as solutions, each with an allowed value for *E*. The Schrodinger equation serves the same function in classical mechanics as Newton's laws and the conservation of energy, i.e., it forecasts how a dynamic system will behave in the future. In terms of the wave function, it is a wave equation that precisely and analytically forecasts the likelihood of events or outcomes. The precise result is not predetermined, but the Schrodinger equation may forecast the distribution of outcomes given a large number of events. The Hamiltonian, which works on the wave function to cause the wave function to evolve in time and space, is created by transforming the kinetic and potential energies. The Schrödinger equation provides the system's quantized energies as well as the wave function's shape, allowing other parameters to be determined.

The Schrödinger wave equation and its wave mechanics that encompassed the subject of the first

principle application of quantum mechanics can be applied to both single particles and many particle systems[6]. The study of systems of particles at the atomic scale is called the many body system.

2.0 METHODOLOGY AND COMPUTATIONAL PROCEDURES

The experimental cell parameter or cell dimension, energy cutt off frequency (ecut), and kpoint for each of the elements were accepted and used in this study. The experimental work was acquired from the materials project website (). The command/q-e-qe-6.7.0/bin/pw.xSc.scf.in>Al.scf.out> on the terminal of the Ubuntu environment was used to optimize this cell dimension. The following is an example of the script for optimizing this cell dimension:

```
&control
calculation ='scf',
prefix='Al'
pseudo_dir='/home/nathaniel/pseudo/',
outdir='./',
/
&system
ibrav=2,
celldm(1)=10.689,
nat=1, ntyp=1, occupations='smearing', smearing='mv', degauss=0.01
ecutwfc=38.22
/
&electrons
mixing_beta = 0.7
diagonalization='david'
/
ATOMIC_SPECIES
Sc 72.64 Ge.pbe-kjpaw.UPF
ATOMIC_POSITIONS
Sc 0.50  0.50  0.50
K_POINTS (automatic)
8 8 8 0 0 0
```

Following that, we optimized the ecut and kpoint using the improved cell dimension. In order to acquire the alatnm utilizing the optimized cell dimension, ecut, and kpoint, the ev.x (/q-e-qe-6.7.0/bin/ev.x) program is then immediately executed on the terminal.

First principle computations were carried out using the solution of the Kosh-Sham equations within the DFT as implemented in the Quantum Espresso Code[7]. The interaction between core ions and valence electrons was studied using the Projected-Augumented Wave (PAW) and pseudopotentials[8]. We treated the exchange-correlation function in the Perdew-Burke-Ernzerhof (PBE) functional with the accuracy of the PAW pseudopotentials and GGA [9, 10].

3.0RESULTS AND DISCUSSIONS.

In sections 3.1 to 3.4, the computed results using the PBE generalized gradient approximation approach as applied in quantum espresso, utilizing density functional theory, the first principle consideration of two transition elements—Aluminum and Gallium—are presented and analyzed.

3.1. Structural properties

Table 3.1: The structural Properties of Aluminum and Gallium

`Properties		Al	Ga
a(A^o)	Present work	3.51	3.62
	Experiment and other calculations	3.434	3.852
B(GPa)	Present work	45.00	47.00
	Experiment and other calculations	45.90	50.20
B'(GPa)	Present work	267	76
	Experiment and other calculations	276	79
E_f(eV)	Present work	515	510
	Experiment and other calculations	521	513

We looked at the transition elements Aluminium (Al) and Gallium(Ga). They crystallize in the Fm3m structure with space group F432 as previously stated, as seen in Figs. 3.1 and Fig 3.2 below. To create the structure of the elements, the input file for each of these elements was uploaded into the Xcryden package. The constructions are depicted as follows.

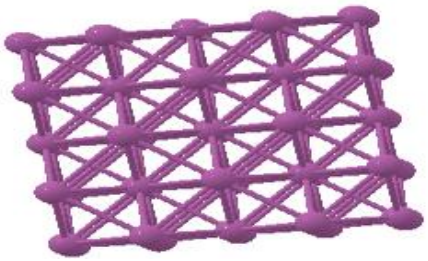


Fig 3.1: Structure of Aluminum

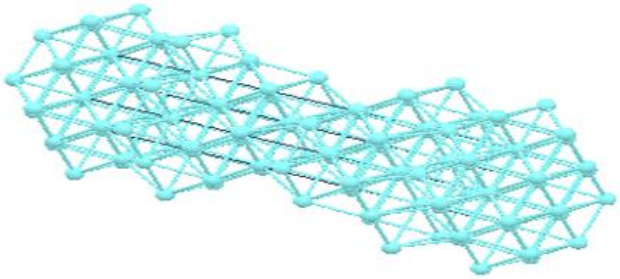


Fig 3.2: Structure of Gallium

Table 3.1 displays the results for the lattice parameter, bulk modulus, and pressure derivatives that were determined from the convergence of the lattice constant by fitting the computed results for a range of lattice parameters (-o.3 x + 0.3) in steps of 0.1 (where x is an experimental lattice parameter value), fitted to the third order Birch-Murnaghan equation of state as given in the form[11].

$$E_v = E_0 + \frac{9BV_o}{16}\left\{\left[\left(\frac{v_o}{v}\right)^{\frac{2}{3}} - 1\right]^3 B' + \left[\left(\frac{v_o}{v}\right)^{\frac{2}{3}} - 1\right]^2 \times \left[6 - 4\left(\frac{v_o}{v}\right)^{2/3}\right]\right\}$$

In line with the pattern shown in[12], an increase in the molar mass of the 4d electron was found to increase the lattice constant of the compound. However, as all 4d electrons had the same atomic radius of 135 pm, this was not the case for the atomic radii. The lattice parameter result, which differs by around 1.5% for Al and 1.8% for Ga from experimental and theoretical values. Both parts are consistent with earlier findings, it may be claimed. The bulk moduli also add up experimental data and other published findings.

3.2. Electronic properties

Table 3.2: The band Gap of Aluminium and Gallium

	Aluminium	Gallium
Band Gap	0.0000	0.0000

Using the quantum espresso code and the cell dimension derived from the ferromagnetic state of the elements, the band structure and density of states were created. These substances are in fact metals with conductivity, as indicated by the zero band gap. The structure of their band is as follows. A peak over the Fermi level may be seen in the corresponding density of state, suggesting that the covalent band has engulfed the valence band.

The energy of production must be negative, or the compound must be more stable than its component parts at absolute zero, for half – Heusler alloys to be thermodynamically stable in their ground state. The equation below may be used to determine the formation energy for each alloy:

$$E_{formation} = E_{Mn} + E_Q + E_{Sb}$$

The fact that they have a negative energy of formation suggests that they are both easily synthesized in a laboratory and thermally stable.

Fig 3.3: Band Structure and density of state of aluminum

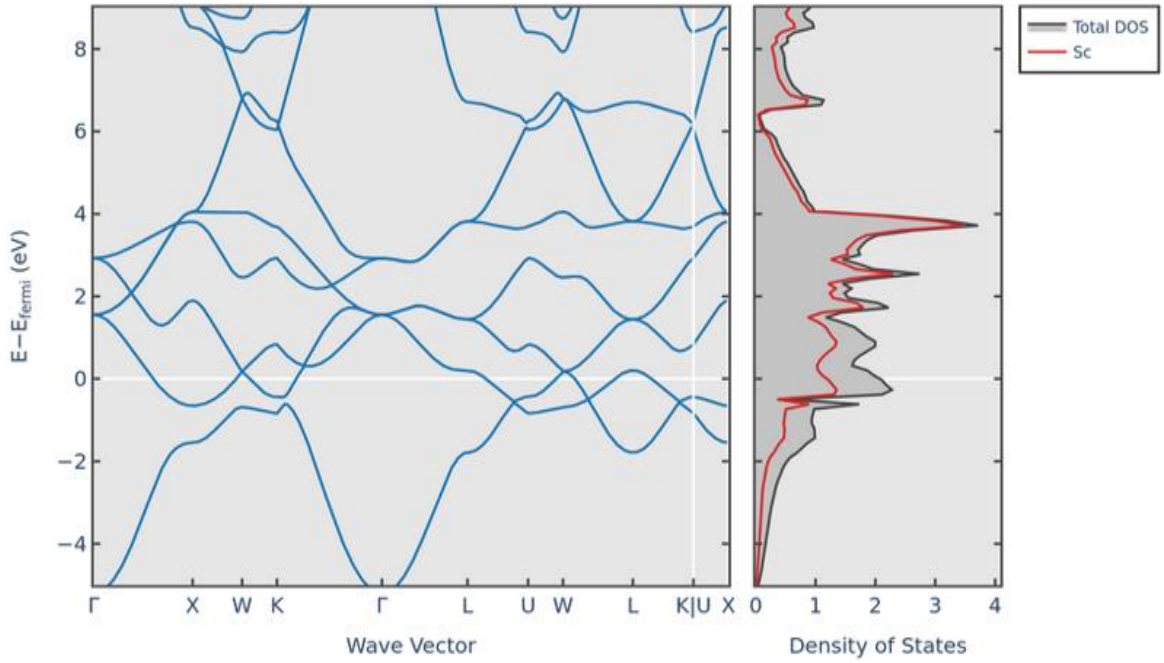
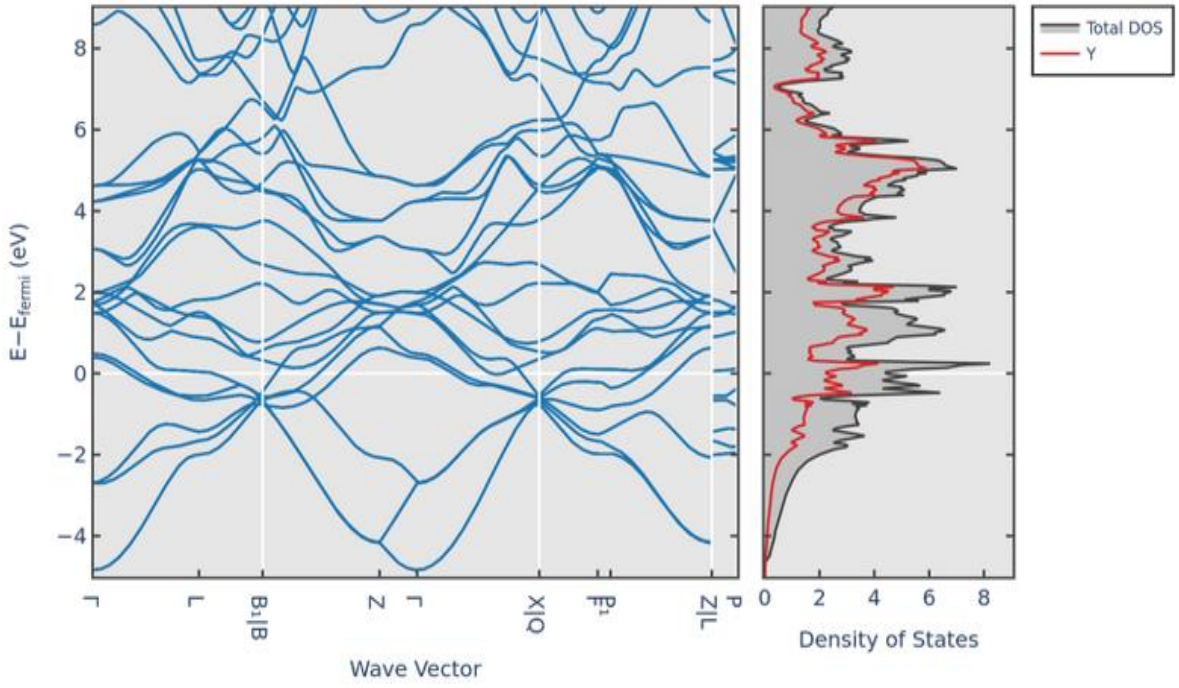


Fig 3.4: Band Structure and Density of state of gallium



3.3. Mechanical properties

Table 3.3: The mechanical properties of Aluminum and Gallium

`Properties		Aluminum	Gallium
C’		3.90	4.03
C_{11}	Present work	50.20	52.37
	Experiment and other calculations	56.33[13]	50.44[14]
C_{12}	Present work	47.60	44.31
	Experiment and other calculations	44.86[13]	39.2[15]
C_{44}	Present work	31.00	29.00
	Experiment and other calculations	37.00[13]	32.00[15]
$C_{11} – C_{12}$		2.60	8.06
$2C_{11} + 2C_{12}$		195.6	193.36

The mechanical and dynamical behaviors of a crystal are connected by the solids' elastic constants, which also provide important details about the nature of forces in solids[16]. Elastic constants may be used to describe how materials flex when subjected to any tiny stresses. the impact of strain on a material's electrical characteristics. Three distinct elastic constants—C11, C12, and C44—apply to cubic crystals. In order to determine the mechanical stability of the alloys under investigation, the elastic constants of the materials were examined, and the results are shown in table 3.3. These elastic constants provide the criterion for the mechanical stability of the alloy. An alloy must have positive strain in order for it to be mechanically stable. This implies that the elastic constants must satisfy each of the three Born criteria [17].

$C11 - C12 > 0$,
$C44 > 0$ and
$C11 + 2C12 > 0$

The findings of this investigation suggest that the examined elements are mechanically stable, which is in excellent accord with the literature. The bands' three-fold, two-fold degenerate, and non-degenerate levels are represented by the parameters C44, C11-C12, and 2C11+2C12.

3.4. Elastic properties

Table 3.4: The elastic properties of Aluminium and Gallium

`Properties		Aluminium	Gallium
G_v		20.16	19.01
G_R		27.45	26.99
G	Present work	23.815	23.002
	Experiment and other calculations	22.991 [14]	23.241 [14]
B/G	Present work	1.890	2.043
	Experiment and other calculations	1.344 [14]	2.102 [14]
E	Present work	60.731	59.325
	Experiment and other calculations	58.207 [14]	59.22 [14]
μ	Present work	0.108	0.123
A	Present work	23.85	7.196
	Experiment and other calculations	22.32 [15]	6.78 [15]
H	Present work	0.128	0.123

3.5. Elastic parameters

The elastic properties of materials arise from Hooke's law and include the Shear Modulus, Anisotropy, Young's modulus, Poisson's ratio, and Hardness. The Voigt and Reuss approximation, G_v and G_R of the shear modulus were also presented accordingly. The young's modulus E is the ratio of tensile stress to tensile strain and it measures the stiffness of the material. The values obtained for E in all alloys depicts high level of stiffness and these values are a close proximity to experimental data. Sc is therefore stiffer and also harder.

Other elastic parameters presented also include; the ratio of the bulk modulu B (which characterizes the ability of a material to resist fracture) to shear modulus G (which defines the resistance of the material to plastic deformations), B/G. hence the ratio is also called the Pugh's ratio and it determines the ductile/brittle behavior of the material. Ductile/brittle behavior of the materials plays a key role during manufacturing of materials. As reported by Bhardwaj and Singh (2016), B/G is critical at 1.75. If B/G > 1.75, the material is ductile, otherwise it is brittle. The calculated values of B/G from Table 3.4 implies that Both elements are ductile.

The poisson's ratio which suggests the possible bonding of the atoms in the compound supports ionic bonding for both Sc and Yt since $\mu > 0.26$. the Cauchy pressure defined by C12 – C14 for Sc suggests a directional covalent bonding since it is negative. Isotropic materials have their properties direction – independent, while anisotropic materials are direction dependent. In other words, a deviation direction from unity in a material renders it anisotropic. Results shows that Sc is more anisotropic compared to Al and likely to change its property with the direction of its covalent bonding. Also we can say that it will endure cracking when undergoing experimental growth compared to Al since its anisotropy extensively deviate from unity than the other. This is of course true as it is also harder and stiffer.

4.0CONCLUSION

In order to use Al and Ga effectively in technological progress, it is crucial to understand their qualities. As a result, several researchers have conducted a number of studies to determine their

structural, thermodynamic, electrical, optical, and mechanical characteristics. In order to improve production, hybridization, and doping (when necessary) with other elements in the periodic table, the first principle calculation was used in this work to determine the properties of these elements in the periodic table and checkmate the result with already known experimental properties of these elements. For the structural properties of these elements, the result for the lattice parameter shows that both elements can be said consistent with previous reports. The bulk moduli B also tally experiments and other reported results.

Additionally, the cell dimension derived from the ferromagnetic state of the elements was used to construct the band structure and density of states for its electrical structure using the quantum espresso code. These substances are in fact metals with conductivity, as indicated by the zero band gap. The structure of their band is as follows. A peak across the fermi level may be seen in the corresponding density of states, suggesting that the covalent band has engulfed the valence band.
The findings from this work suggest that the examined elements are mechanically stable in addition to their mechanical qualities, which is in excellent agreement with the literature. The bands' three-fold, two-fold degenerate, and non-degenerate levels are represented by the parameters C44, C11-C12, and 2C11+2C12.

The results also indicate that Al is more anisotropic than Ga in terms of its elastic characteristics and is more prone to modify its properties depending on the direction of its covalent bonding. Additionally, we may say that it will withstand breaking during experimental development compared to Ga because of its anisotropy's greater deviation from unity. Of course, this is accurate given that it is also stiffer and tougher. Some interesting results on Al has been extensively studied in our paper[9] and process of many body interaction explained[18, 19, 20].

REFERENCES

[1] Tim S. and Jeanna B. (2022). Periodic table of elements. Retrieved from https://www.livescience.com/25300-periodic-table.html.

[2] John E. (2001). Nature's Building Blocks: An A-Z Guide to the Elements. Oxford: Oxford University Press,.

[2] Gerald H. (2018). Time, the arrow of time and quantum mechanics. Frontiers in physics. Retrieved from arXiv:1804 – 01383.

[4] Enaroseha O. E. Omamoke, Priscilla O. Osuhor and Obed Oyibo (2021) Phonon Dispersion Relation of Lead (Pb) and Palladium (Pd) The Journal of Applied Sciences Research, 8 (1): 1 – 14.

[5]Brown, LeMay, Busten, Murphy, and Woodward (2022). Chemistry of nonmetals. https://chem.libretexts.org/Courses/University_of_Missouri/MU%3A__1330H_(Keller)/22%3A_Chemistry_of_the_Nonmetals.Retrieved March 16, 2023

[6] Xie, F., Zhang, T.A., Dresinger, D. and Doyle, F. (2009) A critical review on solvent extraction of rare earths from aqueous solutions. Miner. Eng., 56: 10–28.

[7] Gionnozzi P., Baroni S., Bonini N., Calandra M., Car R., Cavazzoni C.,Ceresol D., Chiarotti G., Cococcioni M., Dabo I., Corso A., de Goroncoli S., Fabris S.,Gebauer R., Gerstmann U., Gougoussis C., Kokalj A., Lazzeri M ., Martin-samos L., Marzari N., Mauri F., Mazzarello R., Paolini S., Pasquarello A., Paulatto L., Sbraccia C., Scandolo S., Sclauzero G., Seitsonen A P., Smogunov A., Umari P., Wentzcovitch R.M.,(2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys. Cond. Matter 21(39): 395502

[8] Perdew J. P and Zunger A., (1981). Self-Interaction Correction to density-functional approximation for many-electron systems. Phys. Rev. B 23, 5048

[9] Enaroseha O. E. Omamoke, P. O. Osuhor, Obed Oyibo and Ernest O. Ojegu (2021). Theoretical Study of Phonon Spectra in Aluminium(Al) and Copper(Cu): Application of Density Functional Theory and Inter – Atomic Force Constant. Solid States Technology. Vol. 64, Number 2: 1984 – 1999.

[10] Kresse G and Furthmuller J (1996) Efficiency of ab – initio total energy calculations for metals and semiconductors using plane – wave basis set. Computational Material science, 6(1) 15 – 50.

[11] Hao J, Simon W. K., Adams J.P., and Krishna P. Y. (2019). Computational Investigation of Transition Metals and their Structural Properties. Computational Material science, 79, 703 – 709.

[12] Srikrisna Kandand Sbradhip P. (2018). Experimentation of First Principle Calculations of some metals and non metals. Journal of Physics Series: Conference Series, 1531, 012047

[13] Miao, J., Chai, C., Zhang, W., Song, Y., & Yang, Y. (2020). First-Principles Study on

Structural, Mechanical, Anisotropic, Electronic and Thermal Properties of III – Phosphides: XP (X = Al,Ga, or In) in the $P6_422$ Phase. Materials,13(3),686.https://doi.org/10.3390/ma1303068 6

[14] Xu, B., Zhu, C., He, X., Zang, Y., Lin, S., Li L. and Lei, Q. (2018). First-Principles Calculations on Atomic and Electronic Properties of Ge/4H-SiC Heterojunction. Advances in Condensed Matter Physics, 2018, 1–9. doi:10.1155/2018/8010351.

[15] Khuili, M., El Hallani, G., Fazouan, N., El Makarim, H. A., and Atmani, E. H. (2019). First - Principles calculation of (Al,Ga) Co – doped ZnO. Computational Condense Matter, e00426.doi: 10.1016/j.cocom.2019.e00426

[16] Randeria, M. (2017). Introduction to Many-Body Physics. Piers Coleman, Cambridge University Press, 810. ISBN 978-0-521-86488-6. Physics Today, 70(5), 59–60. doi:10.1063/pt.3.3558

[17] Born M. and Huang K. (1955). Dynamical Theory of Crystal Lattice. Americal Journal of Physics 23, 474. http://doi.1119/1.1934059

[18] Enaroseha O. E. Omamoke, Obed Oyibo, P. O. Osuhor, O. Oghenerhoro (2021). Lattice Dynamics in Some FCC Metals: Application of Phonon Dispersions in Nickel (Ni) and Platinium (Pt). Solid State Technology Volume: 64 Issue: 2, 4640 - 4685

[19] Enaroseha O. E. Omamoke, Obed Oyibo and A. O. Nwabuoku (2022) Many Body Interaction With Spin Localization Of The Periodic Andeson Model. NeuroQuantOlogy, Vol. 20(14), 638 – 643. Doi: 10.4704/nq.2022.20.14.NQ88090

[20] Enaroseha O. E. Omamoke, Isioma M. Ezeh and Obed Oyibo(2022) Generation of Localized Magnetic Order using 4-Electrons nn a 2x2 Square Lattice (2-D): Application of the Periodic Anderson Model. International Journal of Mechanical Engineering, Vol. 7 (2)554 - 558