Lattice Dynamics in Some FCC Metals: Application of Phonon Dispersions in Nickel (Ni) and Platinium (Pt)

Omamoke O. E. Enaroseha[1], Obed Oyibo,[2] Priscilla O. Osuhor[3], Ovie Oghenerhoro[4]*

[1,2&4]Department of Physics, Delta State University, Abraka - Nigeria.

[3]Department of Physics, University of Benin, Benin City, Nigeria.

*Corresponding author: enarosehaomamoke@gmail.com; eomamoke@delsu.edu.ng.

Tel: +2348036204434

Abstract– The computational theoretical investigation of lattice dynamics induced by phonon – electrons interactions were carried out in some FCC metals; Ni and Pt to described the results along the X, W, L points of the BZ which were compared with results obtained from analytical, quantum espresso and experimental data.

Frequency calculations of the 1- 9NN for Pt, and 1-6NN for Ni using inter – atomic force constant (IFCs) approach, the results obtained are reasonably close to experimental results which are available in the literature. We also observed smaller values of force constants for neighbours higher than the fourth neighbour. The computational lattice error of the LDA in Ni was – 2.7% and this was corrected to 0.2% using the GGA while the lattice constant of Pt was overestimated by 0.1% and this was also corrected to 2.1% by GGA. In Nickel the phonons of the IFCs predict well the experimental phonons than those from quantum espresso code.

We also employed the nineth (1-9NN) neighbour force constant to elucidate the nature of phonon diagrams of Pt while the first to sixth neighbour force constant has been employed to calculate the phonon diagrams of Ni analytically.

4640

1.0 INTRODUCTION

The theory of lattice dynamics which originated from the fundamental papers of Born. The first principle prediction of the dispersion curves of phonon of, FCC, BCC, noble and transition metals encounter challenges that lack adequate solution from the commonly used exchange correlation functions. To improve on the first principle calculation results, the density functional theory (DFT) was introduced, in recent years, and later, the phonon dispersion problem was tackled using the inter-atomic force constants (IFCs) technique as implemented in the Born-von Kármán model (Born and Oppenheimer, 1927), .

The dispersion curves of the following BCC metals, Cs, Cr, Fe, Mo, Nb, Na, Ta and W were calculated successfully using two techniques; The inter atomic force constants (IFCs) technique employing the Born – von Kármán model and the first principle technique based on DFT implemented by QUANTUM ESPRESSO. The different branches of the phonon band structure follow from the eigen values after diagonalizing the dynamical matrix. Calculations along the points of high symmetries ($\Gamma \rightarrow H$, $H \rightarrow P$ and $P \rightarrow \Gamma$) directions of the phonon frequencies in the first Brillouin zone (BZ) shows that, there are two dispersion branches (longitudinal and transverse).The two branches later split into three along the $\Gamma \rightarrow N$ direction with a degenerate of the transverse branch. The density of state (DOS) and thermodynamic properties from analytical and first principle were obtained and also compared with available experimental results.

IFCs calculations from some pilot papers and the extended force constants of this study are approximately the same with (MAE 0.0923THz, MARE 1.57%) and (MAE 0.1045THz, MARE

2.00%) respectively on the average. The first principle calculations show, the GGA (PBE) (MAE 0.8470THz, MARE 18.79%), PW91 (MAE 0.8568THz, MARE 14.60%), LDA (MAE 1.2079THz, MARE 28.74%) and GGA (PAW) (MAE 0.2236THz, MARE 6.23%) on the average. IFCs calculations gave better results compared to the first principle (QUANTUM ESPRESSO) calculations on the average and GGA (PAW) functional on an average is the best functional while LDA is the worst. The DOS agree reasonably well with experimental results andthe thermodynamic properties of the analytical results and the first principle results also agree reasonably well. In conclusion, the IFCs technique using Born – von Kármán model was found to be a bettertechnique in explaining the lattice dynamical properties of these metals compared to the first principle (QUANTUM ESPRESSO) method (Okocha, 2018).

These phonon frequencies, ω, are written as a function of wave-vectors q (Srivastava, 1990). The relationship between ω and q, ($\omega = \omega_j(q)$) is called phonon phase diagram and it is often times presented graphically as a plot of ω against q, known as phonon dispersion curves (PDCs). The j signifies the polarization branch and takes on three values in the case of the face-centered cubic crystals.

Enaroseha *et al* (2021) using the Density Functional Theory (DFT) and Inter – atomic Force Constants (IFCs) studied theoretically the phonon dispersion spectra of Aluminium (Al) and Copper (Cu) and found good results that agree with experimental datas.

In this paper, We report lattice dynamics and phonon phase diagram in some FCC: Nickel (Ni) and Platinum (Pt) employing the Born Von Karman force constant model (Cowley,1973) from 1-2NN, 1-4NN, 1-6NN, 1-8NN and 1-9NN. The motivation of this work is to compare our

analytical calculation to the first principle calculation and also that of experiment in order to ascertain the nearest neighbors (NN) effects.

2.0 THEORETICAL CALCULATION AND CONSIDERATIONS
2.1 CONDUCTION ELECTRONS IN PHONON DISPERSION CURVE

Typical anomalies may be seen in dispersion curves (Smith, 1972) and are believed to arise from the influence of the conduction electrons. As early as 1936, Fuchs considered the role of conduction electrons in connection with the calculation of the elastic constants of alkali metals and of Cu with particular reference to the failure of Cauchy relations. Wigner and seitz previously employed a method for calculating the cohesive energy of the alkalis, Fuchs argued that one could divide the contributions to the potential energy of the crystal into two parts, one association with pair wise interactions between ions and the other associated with volume – dependent effects ascribable to the conduction electrons. This led him to deduce the relation $C_{11} - C_{12} = C_{12}^P - C_{12}^P$ which show that volume – dependent forces lead to the violation of cauchy relations. Fuchs further demonstrated that when a crystal is subjected to a uniform compression, forces due to both the pair potential and the volume – dependent potential are called into play in determining the bulk modulus, given by

$$K = \frac{C_{11}^p + C_{11}^v + 2C_{12}^p + 2C_{12}^v}{3} \qquad (2.1)$$

De Launay (1956) used ideas of Fuchs to incorporate phenomenologically the modification to the dispersion curve of simple cubic metals which arise from electron gas effects. He supposed that the conduction electron gas respond in phase to the longitudinal component of the lattice vibrational waves but is left unaffected by the transverse (Shear) components. The net result is now to modify the otherwise central force constants such that the deviation from the cauchy

4643

relation is equal to the bulk modulus of the electron gas. Bhatia (1955) later offered a slightly different effect. He argued that the force acting on an ion during its motion could be written as $(F_1 + F_2)$, where F_1 is due to the pair potentials of force constants. The part arising from volume – dependent forces is assumed to be given by

$$F_2 = -egrad\emptyset \qquad\qquad (2.2)$$

Where ϕ is the electrostatic potentials evaluated with the Thomas – Fermi description for screening effects. The effects on the elastic constants, dispersion curves and g (ω) were examined. Real understanding of the effects of conduction electrons began when the interplay of theory and experiment offered a detailed picture. The first step was taken by Toya (1964) when he calculated the dispersion curves for several alkalis, treating them as an array of positive ions immersed in a sea of conduction electrons. The modifications of the electronic wave functions consequent to ionic motion and their subsequent influence on normal – mode frequencies were handled by Hartee-fock theory. Tayo's work coincided with the period when rapid strides were being made in the understanding of many-body effects in electron gas systems. These considerations were widely applied to conduction electrons in metals especially Nearly Free – Electron (NFE) metals like the alkalis. In the case of simple cubic metals, motions corresponding to waves along the principal symmetry directions involve rigid displacement of atomic planes which are normal to q. The normal – mode, problem consequently is formally equivalent to a linear chain and may be analyzed in terms of interplaner force constants (Foreman and Lomer, 1957)

2.2 KOHN – SHAM ANSATZ

The Kohn – Sham (KS) approach Kohn and Sham, (1965) puts Hohenberg – Kohn theorem into practical used and making use of density functional theory (ΔFT) calculations. The popular application of DFT is as a result of the successes recorded using the Hohenberg – Kohn theorem.

Using auxiliary independent particles, the many – body systems is replaced by the KS approach provided their densities have similar ground state.

The auxiliary Hamiltonian is

$$H_{ks} = \frac{1}{2}\nabla^2 + V_{ks}, \tag{2.3}$$

Where the first term on the right of equation (2.3) is the kinetic energy term in atomic units

$$h = m_e = e = 4\frac{\pi}{\varepsilon} = 1.$$

For Schrodinger equation of the N single – electron, we have,

$$\left(\frac{1}{2}\nabla^2 + V_{ks}\right)\varphi_i(r) = \varepsilon_i\varphi_i(r) \tag{2.4}$$

For the single electron of the N orbitals $\varphi_i(r)$ having minimum eigen values ε_i, we can construct the density n(r):

$$n(r) = \sum_{i=1}^{N}|\varphi_i(r)|^2 \tag{2.5}$$

Assuming

$$\int n(r)dv = N \tag{2.6}$$

The un - perturbed kinetic energy T_s is given as

$$T_s\big(n(r)\big) = \frac{-1}{2} \sum_{i=1}^{N} \int \varphi_i(r) \nabla^2 \varphi_i(r) dr \tag{2.7}$$

Then the universal functional F[n(r)] takes the form

$$F[n(r)] = T_s[n(r)] + E_{xc}[n(r)] \tag{2.8}$$

Where $E_H[n(r)]$, is the classic electrostatic energy (Hatree) of the electrons is given by

$$E_H[n(r)] = \frac{1}{2} \iint \frac{n(r)n(r)}{|r-r|} dr dr \tag{2.9}$$

and $E_{xc}[n(r)]$ is the exchange correlation (XC) energy.

$$E_H[n(r)] = F[n(r)] + \int n(r) V_{ext}(r) dr, \tag{2.10}$$

$$\delta\{F[n(r)] + \int n(r) V_{ext}(r) dr - \mu(\int n(r) dr - N)\} = 0 \tag{2.11}$$

This leads to

$$\mu = \frac{\delta F[n(r)]}{\delta n(r)} + V_{ext}(r) \tag{2.12}$$

$$= \frac{\delta T_s[n(r)]}{\delta n(r)} + V_{KS}(r)$$

Where V_{KS} is the chemical potentials,

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r)$$

$$= V_{ext}(r) + \frac{\delta E_H[n(r)]}{\delta n(r)} + \frac{\delta E_{XC}[n(r)]}{\delta n(r)} \tag{2.13}$$

KS is one particle potential with the Hatree potential $V_H(r)$

$$V_H(r) = \frac{\delta E_H[n(r)]}{\delta n(r)}$$

$$= \int \frac{n(r')dr'}{|r - r'|} \tag{2.14}$$

And the XC potential $V_{xc}(r)$

$$Vxc(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \tag{2.15}$$

Equations (2.3),(2.4), and equations(2.13) together are the KS equations.

An implicit definition of $E_{XC}[n(r)]$ can be given as

$$E_{XC}[n(r)] = T[n(r)] - T_S[n(r)] + E_{int}[n(r)] - E_H[n(r)] \tag{2.16}$$

3.0 PRESENTATION OF RESULTS

The results of the lattice dynamics for Nickel (Ni) and Platinium (Pt) are presented in section 3.1 and 3.2 respectively using Density Functional Theory (DFT) and inter - atomic force constants (IFCs) approach with quantum espresso code.

3.1 LATTICE DYNAMICS AND PHONON PHASE DIAGRAMS IN NICKEL (Ni)
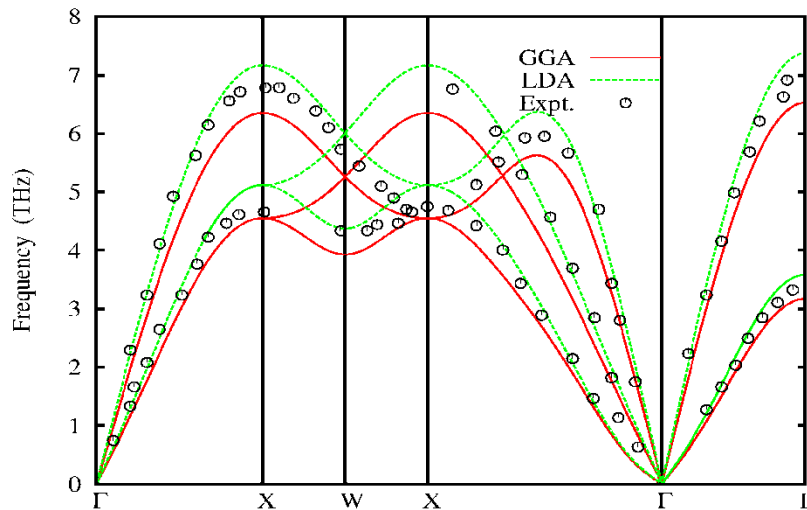

4647

Figure 3.1.1: Calculated phonon dispersions for FCC – Ni compared to inelastic neutron scattering data (black circles) Birgeneau *et al* (1964)

Table3.1.1: Frequencies calculated from quantum espresso at selected points of the BZ for Ni. All frequencies are in THz

Ni	a(a.u)	X_T	X_L	W_T	W_L	L_T	L_L
EXP (a)	6.65	6.26	8.54	6.20	7.49	4.23	8.89
LDA(b)	6.47	6.50	8.89	6.25	7.67	4.34	9.38
GGA(b)	6.66	6.46	8.61	6.30	7.51	4.60	8.88

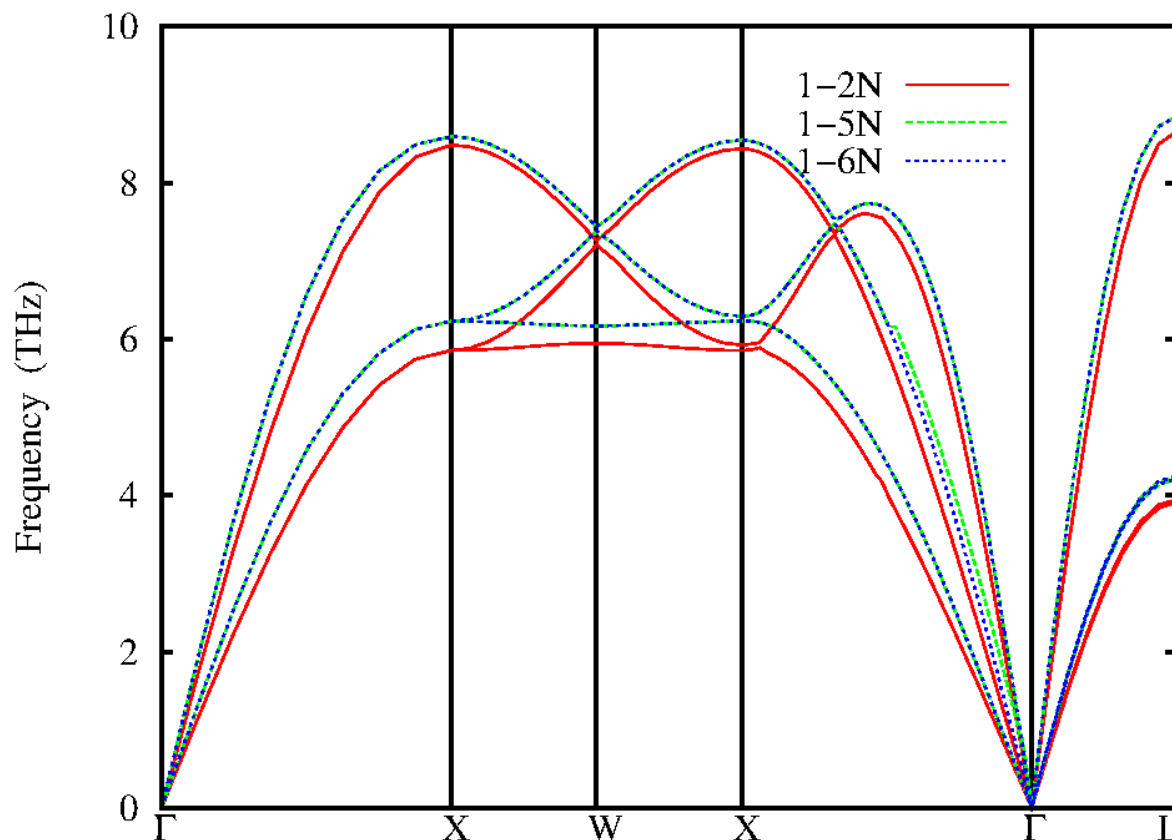   a   Birgeneau *et al* (1964)

    b   This work

Figure 3.1.2: Calculated phonon dispersions for FCC – Ni from analytical approach using IFCs up to 6th neighbour

Table3.1.2: Frequencies calculated analytically using ifcs up to 6th neighbour at selected points of the BZ for Ni. All frequencies are in THz

Ni	X_T	X_L	W_T	W_L	L_T	L_L

EXP (a)	6.26	8.54	6.20	7.49	4.23	8.89
1-2N (c)	5.85	8.48	5.95	7.26	3.94	8.66
1-5N (b)	6.23	8.58	6.17	7.43	4.24	8.85
1-6N (c)	6.24	8.59	6.18	7.44	4.25	8.86

a   Birgeneau *et al* (1964)

b   Dutton et al (1972)

c. This work

3.2   LATTICE DYNAMICS AND PHONON PHASE DIAGRAMS IN PLATINIUM(Pt)
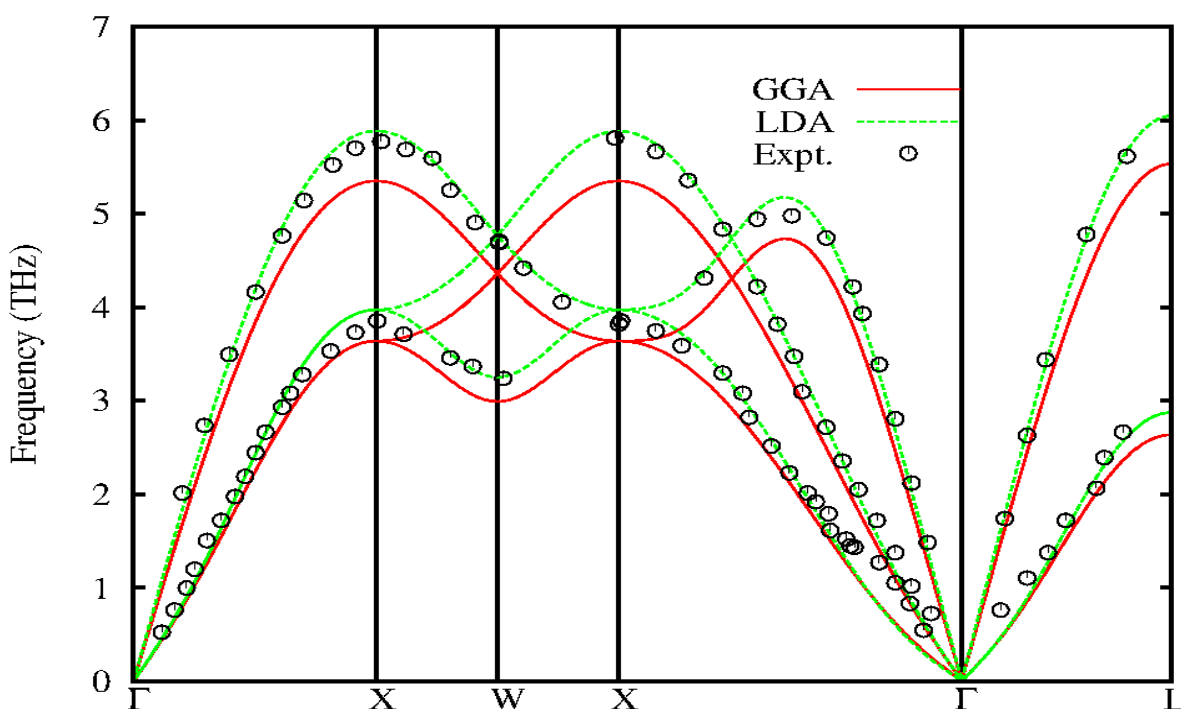

Figure 3.2.1: Calculated phonon dispersions for FCC – Pt compared to inelastic neutron scattering data (black circles) Dutton *et al* (1972)

Table 3.2.1: Frequencies calculated from quantum espresso at selected points of the BZ for Pt. all frequencies are in THz

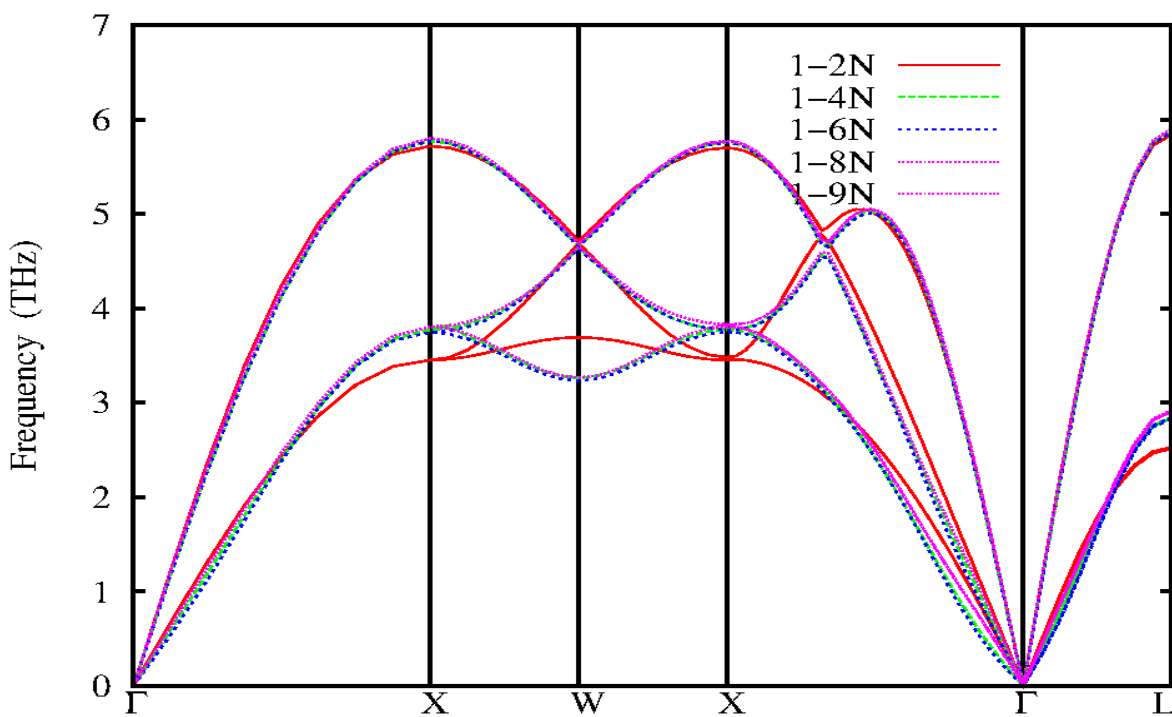| Pt	a(a.u)	X_T	X_L	W_T	W_L	L_T	L_L
EXP (a)	7.40	3.84	5.79	3.24	4.65	2.91	5.85
LDA(b)	7.39	3.97	5.89	5.02	3.25	2.87	6.05
GGA(b)	7.56	3.64	5.35	4.36	2.99	2.64	5.53

a   Dutton *et al* (1972)

b   This work

Figure 3.2.2: Calculated phonon dispersions for FCC – Pt from analytical approach using IFCs up to 9th neighbour

Table3.2.2: Frequencies calculated analytically using IFCs up to 9th neighbour at selected points of the BZ for Pt. all frequencies are in THz

Pt	X_T	X_L	W_T	W_L	L_T	L_L
EXP (a)	3.84	5.79	3.24	4.65	2.91	5.85
1-2N (c)	3.45	5.72	3.69	4.71	2.52	5.84
1-4N (c)	3.78	5.77	3.26	4.65	2.84	5.89
1-6N (c)	3.75	5.77	3.23	4.65	2.84	5.87
1-8N (b)	3.80	5.80	3.27	4.68	2.91	5.90
1-9N (c)	3.82	5.82	3.28	4.69	2.93	5.92

a   Dutton et al (1972)

b   Dutton et al (1972)

c   This work

4.0 DISCUSSION OF RESULTS

The lattice dynamics and Phonon phase diagrams of some FCC metals; Ni, and Pt, have been calculated using the Born-von Karman model with different numbers of interacting neighbours and exchange functions and the calculated values compared with experimental results.

4.1   LATTICE DYNAMICS AND PHONON PHASE DIAGRAMS OF NICKEL (Ni)

The phonon dispersion of Ni calculated from quantum Espresso code (Gionnozzi, *et al*, 2009) and inter atomic force constant (IFCs) compared with experimental results of Birgeneau *et al*, 1964, these are shown in figure 3.1.1 and 3.1.2. The experimental results of Birgeneau *et al*, 1964 are shown as blue squares, the red lines are the dispersions calculated by GGA while the LDA diagram are indicated with green lines, in density functional theory (DFT) calculations carried out for Ni the electron – ion was treated by using ultra – soft and norm – conserving Ab initio pseudo – potential, within the applied self – consistent method.

Perdew and Zunger (1981) using LDA and Perdew *et al* (1986) investigated the exchange and correlation energy using quantum espresso code. The pseudo – wavefunction are expanded in plane waves with a kinetic energy cut off of 35Ryd for both LDA and GGA. The integration over Brillouin zone were performed in the reciprocal space with uniform K – point meshes of 8 x 8 x 8 points for both LDA and GGA. The iteration of the different energies of the self – consistent calculations converge at 1.0×10^{-3} Ryd.

In Nickel the LDA and GGA dispersions calculated at theoretical equilibrium lattice constant do not agree with experiment. In this work, the LDA and GGA overestimates frequencies, giving their frequencies higher than experimental results. The overestimation of the frequencies by GGA functional show discrepancies with other studies. The computational lattice error of the LDA in Ni was – 2.7% and this was corrected to 0.2% using the GGA.

The analytical calculated phonon dispersions of Ni using IFCs approach of the 1-2NN, 1-5NN and 1-6NN are shown in figure 3.1.2. The red, green and blue line represents the nearest neighbours respectively. The calculated phonon dispersions of the 1-2NN are lower than experiment while that of 1-5NN and 1-6NN are in good agreement with experiment. Therefore, in Nickel the phonons of the IFCs predict well the experimental phonons than those from quantum espresso code.

4.2 LATTICE DYNAMICS AND PHONON PHASE DIAGRAMS OF PLATINIUM (Pt)

The phonon dispersion of Platinium (Pt) calculated from Quantum Espresso code and inter-atomic force constants (IFCs) compared with experimental data of Dutton *et al*, (1972) are shown in figures 3.2.1 and 3.2.2. The experimental results of Dutton *et al*, (1972 are shown as black circles, the red lines are the dispersions calculated by GGA while the green lines are the LDA dispersions. In density functional theory (DFT) calculations carried out for Pt, the electron-ion was treated by using ultra soft Ab initio pseudo –potential within the applied self-consistent method. The pseudo-wave – function is expanded in plane waves with a kinetic energy cut-off of 40Ryd and 60Ryd for LDA and GGA respectively. The integration over the Brillouin zone was performed in the reciprocal space with uniform k-point meshes of 12 x 12 x 12 for both LDA and GGA.. In the phonon calculations of previous papers (Grabowski and Neugebauer, 2007; Dal Corso,2013) it has been found that the LDA phonon dispersions of Pt agree with experiment which correlates with our LDA result in this work, although some details of the dispersions depend on technical details of the calculation. For instance, Grabowski and Neugebauer found a significant error of the LDA at the W point. The GGA dispersions give results close to experiment except at the transverse acoustic (T) branch about the w point where the frequency is

4652

slightly lower. The LDA underestimates the lattice constant by 0.1% and GGA overestimates it by 2.1%.

The analytical calculated phonon dispersions of Pt using inter atomic force constants (IFCs) approach of the second (1-2NN), fourth(1-4NN), sixth(1-6NN), eighth(1-8NN), and ninth(1-9NN) nearest neighbour are shown in Figures 3.2.2 with the red lines, green lines, blue lines, purple lines and pink lines representing the 1-2NN, 1-4NN, 1-6NN, 1-8NN, and 1-9NN respectively. The phonon dispersions of the fourth (1-4NN), sixth (1-6NN), eight (1-8NN) and ninth (1-9 NN) nearest neighbours are found to be in good agreement with experiment while at the X and L of the transverse acoustic (L) the second(1-2NN) is found to give lower frequencies compared to others. Therefore, the phonon dispersions of the IFCs predict well the experimental phonons than those of Quantum espresso.

5.0   CONCLUSION

We have calculated and plotted the dynamical phases of Ni and Pt in the FCC structure by using analytical and density functional theory (DFT) within LDA and GGA functional. We calculated phonon frequency and described the results along the X, W, L points of the BZ which we compared with results obtained from analytical, quantum espresso and experiment. The calculated frequencies of the 1-9NN Pt and 1-6NN for Ni are from inter-atomic force constant IFCS approach are reasonably close to experimental results which are available in the literature. We also observed that the force constant for neighbor more distant than the fourth neighbor has distinctly smaller values.

The nineth (1-9NN) neighbour force constant has been employed to elucidate the nature of phonon diagrams of Pt while the first to sixth neighbour force constant has been employed to calculate the phonon diagram of Ni analytically. We also extend our calculation from first to

ninth neighbour for Pt and first to sixth neighbour of Ni where there is an improvement in the

phonon dispersion curve when compared with first to eight and first to fifth neighbours IFCs in

the literature.

REFERENCES

[1]   Born M., and Oppenheimer, J. K. (1927). On the quantum theory of molecules. Ann. Physik

     84, 457

[2]   Bhatia, A, B. (1955) Vibration spectra and Specific Heat of Cubic Metals: Theory and

     Application of Sodium. *Phys. Rev.* **97***, 363.*

[3]   Birgeneau R.J., Cordes J., Dolling G. and Woods A.D.B.(1964). Normal modes of vibration

     in Nickel. Phys. Rev. 136, A1359.

[4]   Cowley E. R. (1973). A Born-Von Karman Model for Lead. Solid State Comm, vol. 14, pp.

     587-589

[5]   Dal corso, A. (2013) Ab initio phono dispersions of Transition and Noble Metals: Effects of

     exchange and Correllation Function. J. Phys.: Cond. Matter 215, 145401

[6]   De Launay(1956). Solid State Physics. Ed. F. Seitz and D. Turnbull Academics Press Inc,

     NY. Vol. 2, 255

[7]   Dutton, D. H., Brockhouse, B. N., and Miller, A. P. (1972). Crystal Dynamics of Platinum
     by Inelastic Neutron Scattering. Can. J. of Phys. 50, 2915

[8]   Enaroseha, O. O. E., Oyibo O., Osuhor, P. O. and Ojegu, E, O. (2021). Theoretical study of

     Phonon Spectra in Aluminium (Al) and Copper (Cu): Application of Density Functional

     Theory and inter – Atomic Force Constants. *Solid State Technology* 64, Issue 2, 1984 –

     1999.

[9]   Foreman, A. J. E. and Lomer, W. M. (1957). Lattice Vibrations and Harmonic Forces in

     solids. Proc. Phys. Soc. B 70, 1143

[10] 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

[11] Grabowski G., Hickel T., and Neugebauer J.,(2007). Ab initio study of the thermodynamic properties of non-magnetic elementary fcc metals. Exchange-correlation-related error bars and chemical trends. Phys. Rev. B. 76 024309.

[12] Kohn W. and Sham L.J. (1965). Self-consistent correlation Effects. Phys. Rev. 140, A1133 - A1138.

[13] Okocha, G. O. (2018). Phonon Dispersion of Some Bcc Metals. *PhD Thesis submittd to the University of Benin, Nigeria*

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

[15] Perdew J.P., Burke, K., and Ernzerhof M.,(1996). Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865

[16] Smith, H. G. (1972) Superconductivity in the d and f band metals. Ed. By Douglas D. H.. AIP Conf. Proc. 4, 321, NY

[17] Srivastava G. P (1990). The Physics of Phonons, Hilger, Bristol

[18] Toya, T (1964). Lattice Dynamics. Ed. By R. Wallis, Oxford University Press, pp 91 – 95.
.