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Theoretical Study of Phonon Spectra in Aluminium (Al) and Copper (Cu): Application of Density Functional Theory and Inter – Atomic Force Constant

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Abstract - Theoretical study were used to calculate the dynamical properties of Al and Cu 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 were compared with results obtained from analytical, quantum espresso and experimental data.

The results obtained show that the phonon spectra for Cu using analytical method which implements the inter – atomic force constant (IFCs) have been found to be closer to experimental results using 1st – 9th neighbour IFCs with a better percentage error when compared to 1st – 8th neighbour. For Al, LDA underestimates the lattice of about 2.4% while the GGA overestimates it by 0.3%.

Keywords: *Phonon, Quantum expresso, Eigen – value, Aluminium (Al), Copper (Cu)*

1.0 INTRODUCTION

The accurate description of *phonons* in a solid is one of the central research topics in the field of condensed matter physics and materials science for discussing phase stability (i.e., Gibbs-free energy), electron-phonon interaction, structural phase transitions of materials. *Ab initio* phonon calculations based on Density Functional Theory (DFT) have been successful for many compounds, but they often fail in strongly-correlated materials (Nakano *et al, 2020)*. Lattice dynamics in metals is determined by the interplay between the direct ion-ion and the indirect ion – electron – ion interactions (Ono and Kobayashi, 2020). Phonon dispersion relation in crystals is a materialization of the inter-atomic bonding forces; hence, they play a vital role in numerous physical effects and phenomena. It arises as a result of lattice vibration in crystals which is frequently described as harmonic travelling waves characterized in terms of their wavelength, angular frequency, amplitude and direction of travel . Efficient determination of these relations is important for the advancement of materials physics. Phonon dispersion relations are usually calculated from model interaction potential experimentally as well as theoretically. Several experimental techniques such as the inelastic neutron scattering and x-ray diffraction have been used to measure the frequency of phonon as a function of the wave vector in solid materials. Efforts have also been made to calculate the phonon dispersion relation theoretically using different models. The experimental results obtained provide a crucial test to the validity and accuracy of these theoretical models. However, the models which fail to reproduce the experimental phonons are inefficient even for thermal properties of metals (Sade *et al, 2017)*.

Born and Von Karman were the pioneers that worked on the theoretical computation of phonon frequencies in three dimensions using the force constant approach. Many other models that followed thereafter are basically upgraded versions of the model, with very few exceptions. The Born- von Karman model pictured a crystal as an assembly of atom linked together like springs which act to restore the atoms when displaced from their equilibrium positions. This theory does not work well for metals since it does not account for the effect of conduction electrons. The influence of conduction electrons, which form a mobile Fermi gas of electron in the dynamic lattice of metallic solids (especially those that crystallize in Simple Cubic (SC), face-centered cubic (FCC) and hexagonal closed packed (HCP) structures cannot be neglected without some costly consequences in the accuracy of the result. To cater to the effect of the conduction electrons in determining the crystal potential within which the vibrating ions are found in metals, the Born – Openheinmer (BO) or adiabatic approximation (Born and Oppenheimer, 1927), is imposed on the crystal. Following the BO approximation the total potential energy in the crystal can be split into three parts namely, the direct coulomb interaction between electrons and ions; the repulsive (Born – Mayer) core-core contribution and the electronic band structure contribution. The electronic band structure contribution may be represented as an indirect ion-ion interaction via the polarization of the conduction-electrons. The ion-ion electrostatic and exchange interaction give rise to central forces between the ions, while the free electrons give rise to volume-dependent forces which violate the Cauchy relation in the Born Von Karman theory (Fuchs, 1936). These observation led Bhatia (1955) to develop phenomenological models which accounted well foe the ion-electron interaction. However their models neglected the translational invariance of the lattice.

A further improvement was made on the initial phenomenological model by Krebs (1965). In his model, he took into account the remarks of the Lax and also the long-range interaction between ions by using screened Coulomb potential. The Krebs model efficiently reproduced the phonon dispersion curves of simple metals. However, it did not give a good fit to the phonon dispersion curves of noble and transition metals. This is because the outermost d-electron are not rigidly bound to it, hence there cannot be treated as free conduction electrons.

In this paper, we report phonon dispersion calculation of Aluminium (Al) and Copper (Cu) using Inter – atomic Force constant (IFCs) and Density Functional Theory (DFT) technique using quantum expresso code as implemented by Gionnozzi *et al* (2009), IFC approach up to at least 9th neighbour and compare phonons results with experimental data.

2.0 THEORETICAL CALCULATION AND CONSIDERATIONS

2.1 HARMONIC APPROXIMATION

In lattice dynamics, the potential energy of a crystal can be expressed as a series. For the purposes of calculations, it is usually truncated .the harmonic approximation involves keeping only the quadratic terms which is the basis for treating small oscillations (Maradudin *et al*, 1963; Bottger, 1983), Terms higher than the second are known as anharmonic.

Consider a Bravais lattice with one atom per atom unit cell defined by the basis vectors a_1, a_2, a_3. We denote the equilibrium position of the atoms in the lattice by the lattice translation vectors:

$$L = l_1 a_1 + l_2 a_2 + l_3 a_3 \tag{2.1}$$

Where l_1, l_2 and l_3 are any three integers which collectively we shall refer to as L. Assuming an atom L deviates from its thermal fluctuation, then the actual position of atom L (Cheng and Yang, 2007)

$$R_l = L + U(l) \tag{2.2}$$

For an atom of mass m, the kinetic energy of the lattice is given as

$$T = \sum_l p^2(l) \big/ 2m \tag{2.3}$$

Where $p(l) = m\frac{\partial(l)}{\partial t} = m\dot{u}(l)$ is the momentum of the l^{th} atom; thus we may write:

$$T \frac{1}{2} \sum_{l,\alpha} m\dot{u}_\alpha^2(l) = \frac{1}{2} \sum_{l,\alpha} m\dot{u}_\alpha(l)\, m\dot{u}_\alpha \tag{2.4}$$

$u_\alpha(l)$ is the α - Cartesian component of $u(l), \alpha = x.y, z.$

The total potential energy ϕ of the crystal is assumed to be some function of the instantaneous positions of all the atoms, i.e

$$v(R_1, R_2, R_3 \cdots R_N) = \sum_{l.l'} \phi\left(\left|R(l) - R(l')\right|\right) \tag{2.5}$$

Where $\phi\left(\left|R(l)-R(l')\right|\right)$ depends on the distance between the two atoms $l \; and \; l'$. Therefore, For small displacements of the atom, we can expand ϕ in Taylor's series of atomic displacements $u(l)$ which gives:

$$\phi = \phi_\circ + \sum_{l,\alpha}\left(\frac{\partial v}{\partial u_\alpha}(l)\right)_\circ u_\alpha(l) + \frac{1}{2}\sum_{l,l',\alpha,\beta}\left(\frac{\partial^2 v}{\partial u_\alpha}(l)\partial u_\beta(l)\right)_\circ u_\alpha(l)u_\beta(l) \qquad (2.6)$$

$$\phi = \phi_\circ + \sum_{l,\alpha}\phi_\alpha(l)u_\alpha(l) + \frac{1}{2}\sum_{l,l',\alpha,\beta}\phi_{\alpha,\beta}(l,l')u_\alpha(l)u_\beta(l) + \cdots \qquad (2.7)$$

Where $\phi_\alpha(l) = \left(\frac{\partial v}{\partial u_\alpha}(l)\right)_\circ$, $and \; \phi_{\alpha,\beta}(l,l') = \left(\frac{\partial^2 v}{\partial u_\alpha}(l)u_\beta(l)\right)$

Where subscript 0 means that the derivatives are evaluated in the equilibrium atomic positions, this being the configuration which atoms actually occupy, the lattice points. The first term in equation (2.7) is the fixed atoms, which is a constant. The second term is linear vanishes since the derivatives

$$\left(\frac{\partial v}{\partial u_\alpha}(l)\right) = 0 \qquad (2.8)$$

when $u_1 = u_2 \cdots = 0$

The only term left in the equation (2.8) is the quadratic (harmonic) term, hence we write

$$\phi = \frac{1}{2}\sum_{l,l',\alpha,\beta}\left(\frac{\partial^2 v}{\partial u_\alpha}(l)\partial u_\beta(l)\right)_\circ u_\alpha(l)u_\beta(l) \qquad (2.20)$$

Crystals exhibits translational invariance which we may write:

$$\phi_{\alpha\beta} = (l,l') = \phi_{\alpha\beta}(l-l') = \phi_{\beta\alpha}(l,l') \qquad (2.9)$$

So that equation (2.10) becomes

$$\phi = \frac{1}{2}\sum_{l,l',\alpha,\beta}\phi_{\alpha\beta}(l-l')u_\alpha(l)u_\beta(l') \qquad (2.10)$$

Which is the expression respectively the harmonic approximation? Thus the total Hamiltonian, H is given as

$$H = T + V = \frac{1}{2}\sum_{l,\alpha} m\dot{u}_\alpha(l)\,\dot{u}_\alpha(l) + \frac{1}{2}\sum_{l,l',\alpha,\beta}\phi_{\alpha\beta}(l-l')u_\alpha(l)\,u_\beta(l') \tag{2.11}$$

For simplicity if we denote the Hamiltonian of the crystal by E, then, following arguments presented in Born and Huang (1954).

If a real solid is visualized as a classical model of vibrating lattices consisting of a number of atoms of point masses m, forming linear chains, then the second order coupling (force) constants are given as

$$\phi_{l,l'} = \frac{\partial^2 E}{\partial u(l)\partial u(l')} \tag{2.12}$$

Where E is the total energy of the system $u(l)$ and $u(l')$ are the displacements of atoms l *and* l' in the chain respectively.

2.2 LOCAL DENSITY APPROXIMATION (LDA) AND GENERALIZED GRADIENT APPROXIMATION (GGA)

The ground state properties and excitation spectrum of a many-electron system can be studied in two ways. First is to choose some model with one or more adjustable parameters to calculate some adjustable property, for example the spectrum and the fit the result to experimental data to determine the parameters of the model.

Secondly is to find the eigenfunction and eigenvalues of Hamiltonian in a parameter-free approximation (i.e the first principle approach).

The difficulty now is how to reconstruct and formulate the exchange-correlation functional for practical application. An approximation has to be made for this expression and the most famous one is the Local density approximation (LDA) which provides good results in a large number of systems. This approximation is still being used for first-principles calculations.

In the formalism of LDA, the functional for the exchange-correlation energy is chosen to have the same formal expression as the one of a uniform electron gas

$$\mathrm{E}_{XC}^{LDA}(p) = \int p(r)\, E_{XC}^{LDA}(p) d(r) \qquad (2.13)$$

Where E_{XC}^{LDA} is the exchange-correlation energy per particle of the uniform electron gas. It is well known that LDA often underestimates the theoretical results such as equilibrium volume and energy gap. A reasonable approximation for improving the LDA results is to include the gradient corrections, by making the functional to take account of the density gradient $|\nabla\rho|$ at the same co-ordinate. This is called the generalized gradient approximation (GGA) Nagy (1998). The exchange – correlation energy in the GGA method is given as

$$\mathrm{E}_{XC}^{GGA}(p) = \int \rho(r) \sum\nolimits_{XC}^{GGA} \langle\rho, |\nabla\rho\rangle \mathrm{dr} \qquad (2.14)$$

Where $\sum_{XC}^{GGA}$ is the exchange-correlation energy per particle of the uniform electron gas with inclusion of density gradient.

3.0 PRESENTATION OF RESULTS

The results of the phonon dispersion for Al are presented in section 3.1 while the results of the phonon dispersion relation for Cu from inter - atomic force constants (IFCs) approach and quantum espresso code are presented in section 3.2.

3.1 PHONON DISPERSIONS OF ALUMINIUM(Al)

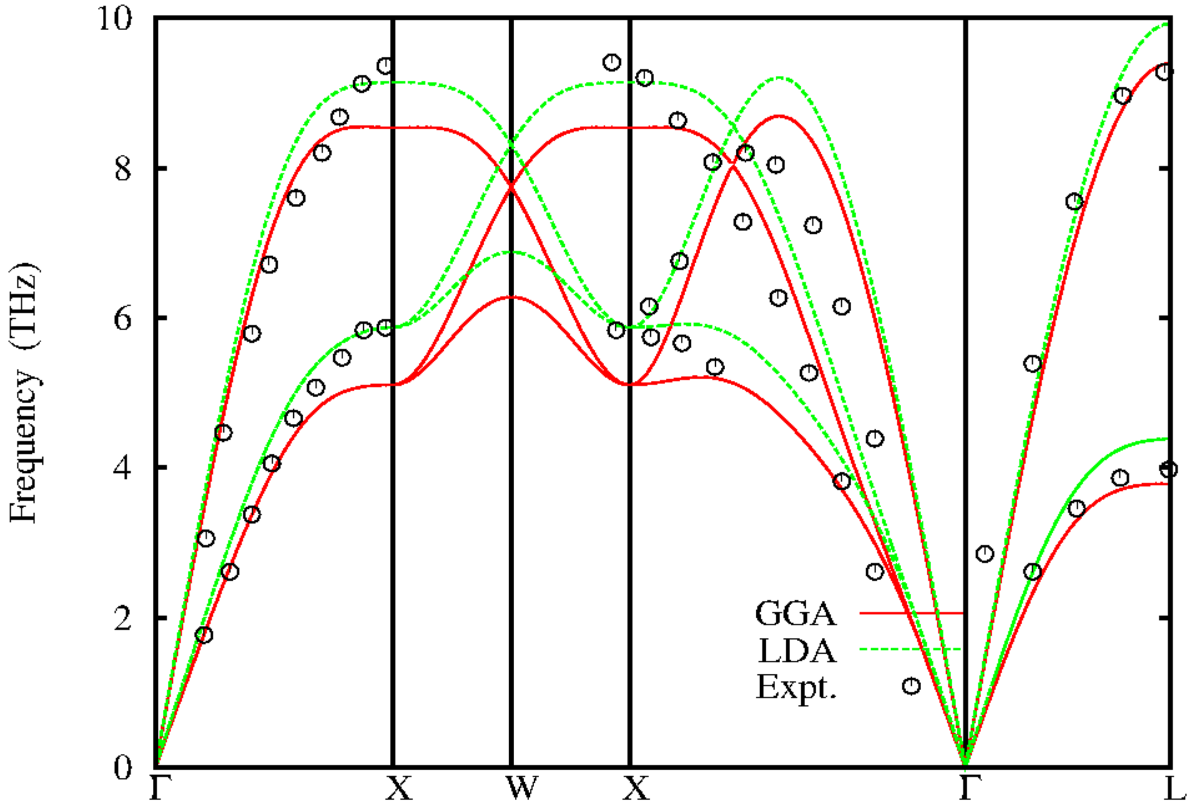

Figure 3.1.1: Calculated phonon dispersions for FCC – Al compared to inelastic neutron scattering data (black circles) Chulkov and sklyadneva (1994)

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

Al	**a(a.u)**	**X_T**	**X_L**	**W_T**	**W_L**	**L_T**	**L_L**
EXP (a)	7.65	5.87	9.36	-	-	3.49	9.65
LDA(b)	7.47	5.87	9.14	6.88	8.31	4.38	9.92
GGA(b)	7.67	5.10	8.53	6.28	7.74	3.78	9.40

a Chulkov and sklyadneva (1994)

b This work

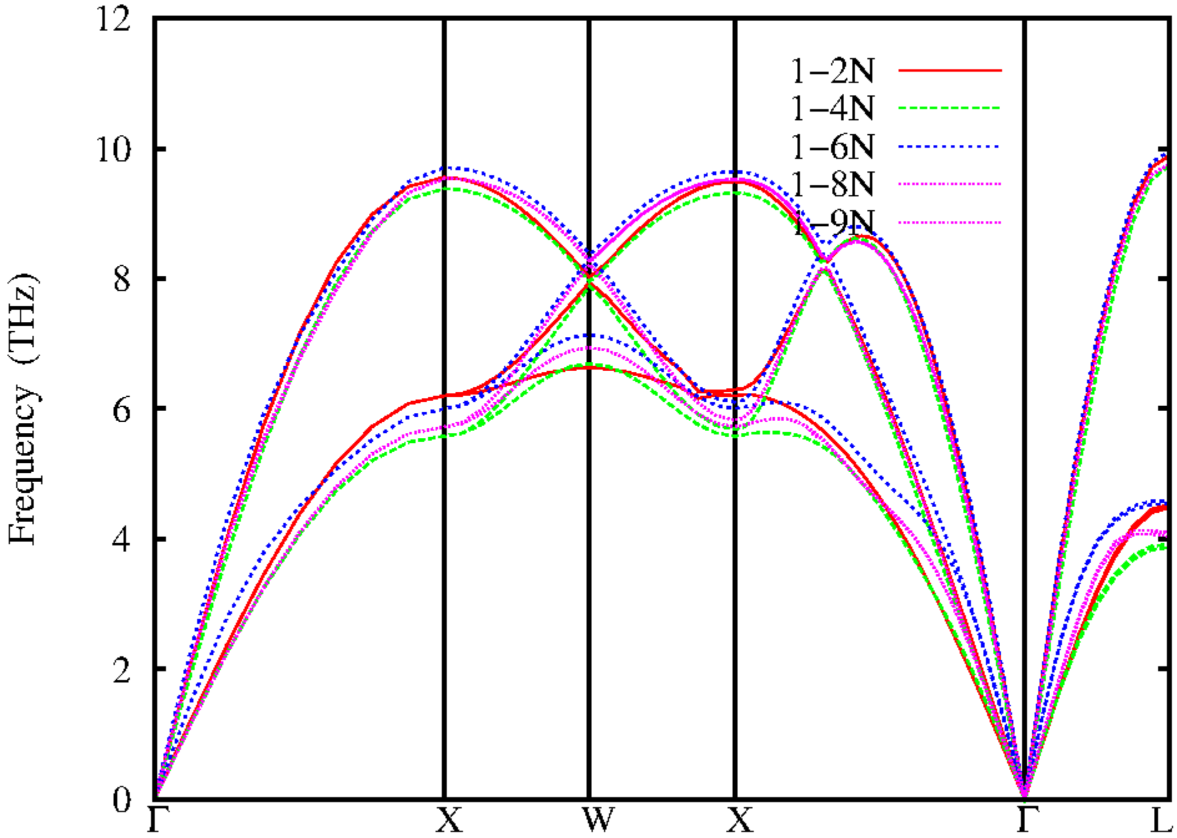

Figure 3.1.2: Calculated phonon dispersions for FCC – Al from analytical approach using IFCs up to 9th neighbour

Table3.1.2: Frequencies calculated analytically using IFCs up to 9th neighbour at selected points of the BZ for Al. All frequencies are in THz

Al	**X_T**	**X_L**	**W_T**	**W_L**	**L_T**	**L_L**
EXP (a)	5.87	9.36	-	-	3.49	9.65
1-2N (c)	6.20	9.56	6.63	8.02	4.53	9.90
1-4N (c)	5.58	9.38	6.69	7.96	3.93	9.74
1-6N (c)	6.00	9.71	7.14	8.38	4.59	9.96
1-8N (b)	5.72	9.55	6.94	8.26	4.09	9.77
1-9N (c)	5.72	9.56	6.95	8.28	4.10	9.79

a Chulkov and sklyadneva (1994)
b Gilat and Nicklow (1966)
c This work

3.2 PHONON DISPERSIONS OF COPPER(Cu)

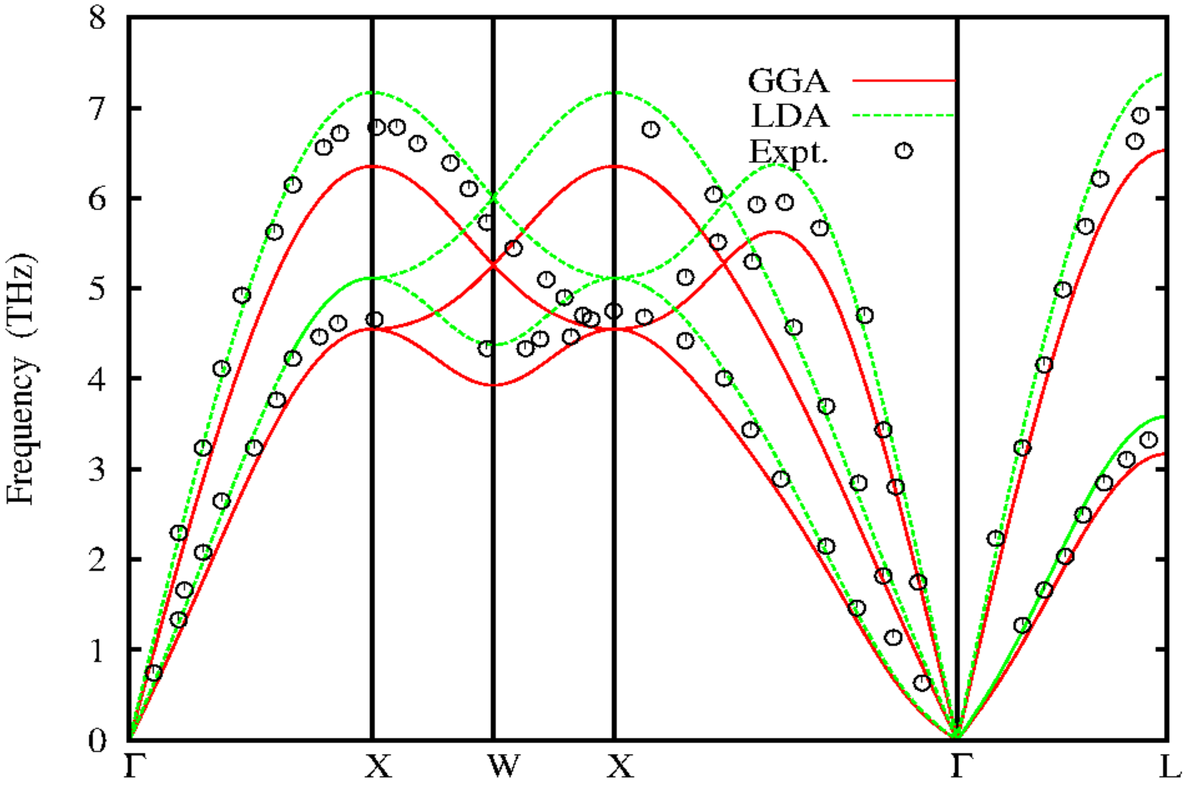

Figure 3.2.1: Calculated phonon dispersions for fcc-Cu compared to inelastic neutron scattering data (black circles) Svensson *et al* (1967)

Table3.2.1: Frequencies calculated from quantum espresso at selected points of the BZ for Cu. All frequencies are in THz

Cu	**a(a.u)**	**X_T**	**X_L**	**W_T**	**W_L**	**L_T**	**L_L**
EXP (a)	6.83	5.07	7.19	4.89	6.09	3.36	7.40
LDA(b)	6.72	5.31	7.77	5.02	6.51	3.60	7.99
GGA(b)	6.96	4.73	6.96	4.36	5.77	2.94	3.12

a Svensson *et al* (1967)
b This work

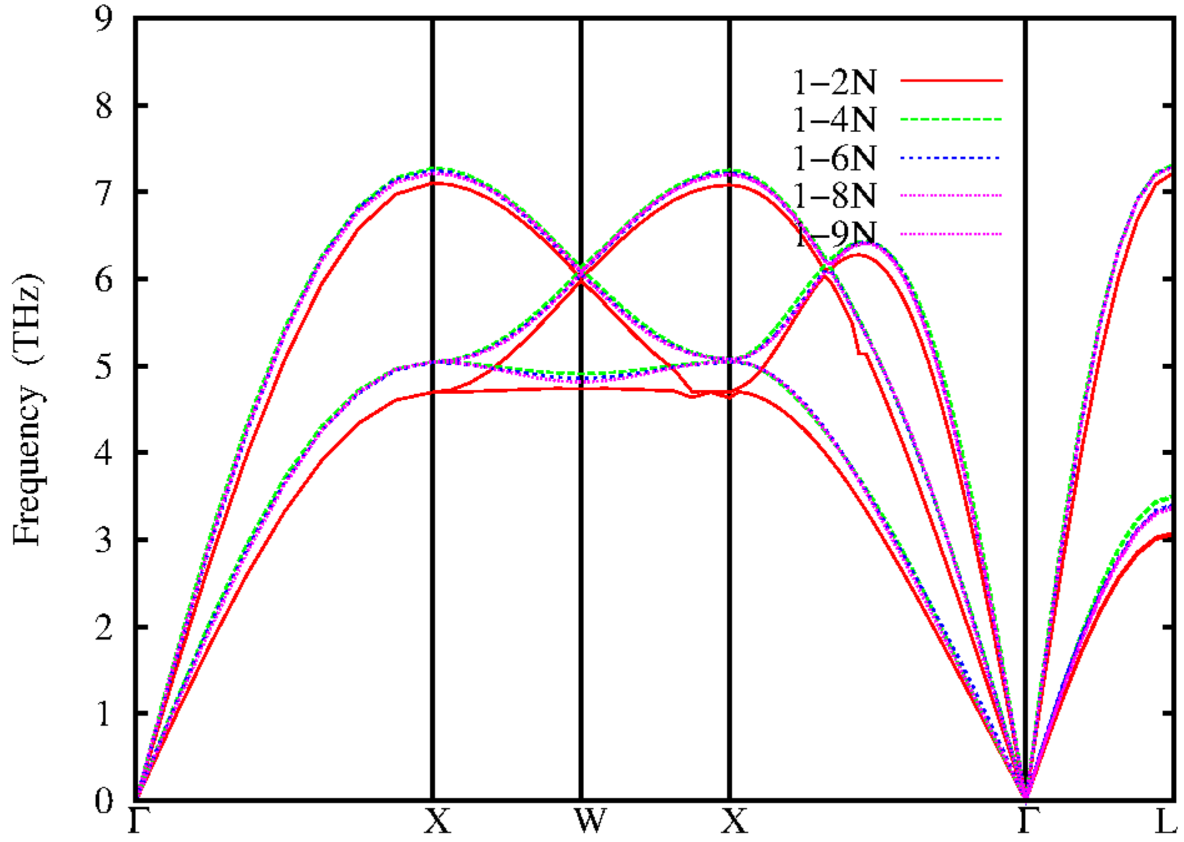

Figure 3.2.2: Calculated phonon dispersions for fcc-Cu from analytical approach using IFCs up to 6th neighbour

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

Cu	**X_T**	**X_L**	**W_T**	**W_L**	**L_T**	**L_L**
EXP (a)	5.07	7.19	4.89	6.09	3.36	7.40
1-2N (c)	4.70	7.11	4.74	6.01	3.08	7.23
1-4N (c)	5.04	7.28	4.91	6.14	3.49	7.32
1-6N (c)	5.04	7.25	4.85	6.08	3.39	7.30
1-8N (b)	5.05	7.23	4.82	6.09	3.38	7.29
1-9N (c)	5.04	7.22	4.82	6.08	3.36	7.30

a. Svensson *et al* (1967)
b. Dutton *et al* (1972)
c. This work

4.0 DISCUSSION OF RESULTS

The phonon spectra of the FCC metals; Al, and Cu, have been calculated using the Born-von Karman model with different numbers of interacting neighbours and exchange functional and the calculated values compared with experimental results. The different branches of the phonon band structure follow from the Eigen values after diagonalizing the dynamical matrix. The phonon frequencies in the first Brillouin zone were calculated along some high symmetry points and the current calculations show that from the gamma points, along the high symmetries $R \rightarrow X$ and $R \rightarrow L$ directions there are two branches of dispersion (Transverse and Longitudinal) which later split into three branches along the $X \rightarrow W$ direction. By differentiating the phonon frequencies into two modes via acoustic longitudinal (LA) and Acoustic transverse (TA) at the Brillouin zone boundary, it is possible to characterize the high symmetry directions and identify which split corresponds to any of the modes.

4.1 PHONON DISPERSION OF ALUMINIUM (Al)

The phonon dispersion of Aluminium (Al) calculated from quantum espresso code and interatomic force constant (IFCs) compared with experimental in elastic neutron scattering data (Chulkov and Sklyadneva, 1994) are shown in Figures 3.1.1 and 3.1.2. The experimental inelastic neutron scattering data are shown as black circles, the red line are the dispersions calculated by GGA functional while the green lines are the LDA dispersions. In the density functional theory calculations carried out for Al, The electron – ion was treated using norm-conserving ab initio pseudopotential, within the applied self – consistent method. The calculations are carried out within the local density approximation (LDA) (Perdew and Zunger, 1981) and generalized gradient approximation GGA (Perdew *et al*, 1996) for the exchanged and correlation energy using Quantum espresso code. The pseudo-wave function is expanded in plane waves with a kinetic cut-off of 45Ryd and 25Ryd for LDA and GGA functional respectively. The integration over the Brillouin zone were performed in the reciprocal space with uniform K-point meshes of 10 x 10 x 10 for both LDA and GGA respectively. The self – consistency calculation was assumed to have converged when the difference in energy between subsequent iteration was 1.0×10^{-3} Ryds. In the phonon dispersion calculated, the LDA functional at the transverse acoustic (T) branch about the X point agrees with experiment while GGA functional slightly under estimates it. At the longitudinal acoustic (L) about the X point the LDA and GGA slightly underestimates and overestimates the experiment respectively. While at the T branch about the L point GGA and LDA overestimates experiment. Also at the T branch about the L point LDA frequencies are higher than experiment while GGA gives frequencies slightly lower than experiment. The LDA underestimates the lattice of about 2.4% while the GGA overestimates it by 0.3%

The analytical calculated phonon dispersions of Al using IFCS approach of the 1-2NN, 1-4NN, 1-6NN, 1-8NN and 1-9NN (NN means Nearest Neighbour) are shown in figure 3.1.2 with red lines, green lines, blue lines, purple lines and pink lines representing the nearest neighbours respectively. The results obtained analytically using IFCs are found to be slightly closer than experiment. The analytical results predict the experimental results better than Quantum espresso.

4.2 PHONON DISPERSION OF COPPER (Cu)

The phonon dispersion of Copper (Cu) calculated from quantum espresso code and interatomic force constant (IFCs) compared with experimental in elastic neutron scattering data (Svensson *et al*, 1967) are shown in Figures 3.2.1 and 3.2.2. The experimental inelastic neutron scattering data are shown as blue squares, the red line are the dispersions calculated by GGA functional while the green lines are the LDA dispersions. In the density functional theory calculations carried out for Cu, The electron-ion was treated using norm-conserving ab initio Pseupotential, within the applied self-consistent method. The calculations are carried out within the local density approximation (LDA) (Perdew and Zunger, 1981) and generalized gradient approximation GGA (Perdew *et al*, 1996) for the exchanged and correlation energy using Quantum espresso code. The pseudo-wave function are expanded in plane waves with a kinetic cut-off of 30Ryd and for both LDA and GGA functional respectively. The integration over the Brillouin zone were performed in the reciprocal space with uniform K-point meshes of 8 x 8 x 8 for both LDA and GGA respectively. The self – consistency calculation was assumed to have converged when the difference in energy between subsequent iteration was 1.0 x 10^{-3}Ryd in the copper at the equilibrium geometry the LDA gives phonon dispersions higher than experiment and the GGA functional gives low frequencies (Favot and Dal, 1999; Grabowski *et al*, 2007) an error that is correlated with the overestimation of the lattice constant. The LDA gives lattice constant 1.6% lower than experiment while GGA lattice constant is 1.9% higher. The analytical calculated phonon dispersions of copper using IFCs approach of the 1-2NN, 1-4NN, 1-6NN, 1-8NN and 1-9NN are shown in Fig 3.2.2 with the red lines, green lines, blue lines, purple lines and pink lines representing the nearest neighbours respectively. The analytical phonon dispersion curve of copper shows that the second neighbour forces (1-2NN) underestimates the experimental except at the longitudinal acoustic branch about the W point where the frequencies of the 1-4NN, 1-6NN, 1-9NN gives a better prediction of the experimental phonon dispersion than those of the LDA and GGA functional from Quantum espresso.

5.0 CONCLUSION

We have calculated the dynamical and thermodynamic properties of Al and Cu 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 phonon dispersion curve for Cu using analytical method which implements the the inter – atomic force constant (IFCs) have been found to be closer to experimental results using 1st – 9th neighbour IFCs with a better percentage error when compared to 1st – 8th neighbour.

For Al, LDA underestimates the lattice of about 2.4% while the GGA overestimates it by 0.3%

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