Phonon Band Structures of Some FCC metals (Al, Ni) and some BCC metals (Na, Nb).

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Abstract

Progress has been made in the experimental determination of the phonon band structures of some materials, and further progress is expected. Therefore an accurate determination is clearly desirable.

In this paper, we studied the phonon band structures of some FCC metals (Al, Ni) and some BCC metals (Na, Nb) with the help of QUANTUM ESPRESSO package which is based on the density functional theory (DFT) within the local density approximation (LDA). The result obtained compare favorably to other works in literature.

The motivation is to assess the power of the code in the computation of phonons beginning with well-known materials, such as Al and Na.

1.0 Introduction

A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, such as solid and some liquids often referred to as quasi particles [1].

Phonons play a major role in many of the physical properties of solids, including thermal and electrical conductivity of materials. The study of phonons is an important part of solid state physics.

The phonon concept was introduced in 1932 by the Russian Physicist Igor Tamm. The name phonon comes from the Greek word φωνή (phonē), which translates as sound or voice because long-wavelength phonons give rise to sound [2].

The study of sound gives rise to acoustics which is an interdisciplinary science that deals with the study of all mechanical waves in gases, liquids and solids including vibration, sound, ultrasound and infrasound. The application of acoustics can be seen in almost all aspects of modern society with the most obvious being the audio and noise control industries. Phonons can be studied using a computational technique called QUANTUM ESPRESSO

In 1964, Hohenberg and Kohn [3] published a paper where they stated the fundamental theorem which gave birth to modern density functional theory (DFT), one of the approaches for dealing with many body problem in electronic structure theory. DFT is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many body systems, in particular atoms, molecules and the condensed phases .With the help of this theory, the properties of a many electron system can be determined by using a functional (function of another function). In this case the properties are determined as spatially dependent electron density and hence the name "density functional theory". DFT is the most popular and versatile method available in condensed matter physics and computational physics for the determination of electronic and other ground state properties of matter. The conceptual roots for DFT was laid by Thomas-Fermi model [4] but was put on firm footing by the Hohenberg-Kohn (H-K) theorems. The original H-K theorems held only for non-degenerate ground states in the absence of magnetic field, although they have since been generalized to encompass them. The first H-K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial co-ordinates which reduces our problem to 3 spatial co-ordinates from 3N spatial co-ordinates for N body problem because of the use of density functional. This theorem can be extended to the time dependent domain for the development of time dependent density functional theory. At first sight, it would seem that many ground state wave functions could yield the same density and therefore this statement seems unrealistic. But it can be shown that for a given ground state density $n(\vec{r})$, there is a unique one to one correspondence between the potential $V_s(\vec{r})$, the many body ground state wave function $\Psi(\vec{r}_1 \ldots \ldots \vec{r}_N)$ and the ground state charge density $n(\vec{r})$. The second H-K theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

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Density functional theory has become the work house in electronic structure calculations. Its success derives from the ability to produce accurate results with reasonable computational effort. The drawback of DFT is that it is bound to the ground state properties. However, the time dependent DFT extends its applicability to the excited states. DFT can be better understood with reference to the Kohn-Sham equations .Important insight into the properties of many particle systems can be obtained from the study of effective non-interacting particle models. With the

Kohn-Sham approach to DFT, the interacting system of particles in a static potential is replaced by a non-interacting system of particles in an effective potential. For a non-interacting particle system with Hamiltonian H, ground state density $n(\vec{r})$, external potential $V_s(\vec{r})$, the Schrodinger equation can be written as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

(1.1)

which yields the orbital's ϕ_i that reproduce the density $n(\vec{r})$ of the original many-body system, i.e

$$n(\vec{r}) \overset{\text{def}}{=} n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2 .$$

(1.2)

The effective single-particle potential can be written in more detail as

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{\text{XC}}[n_s(\vec{r})]$$

(1.3)

where the second term on the right-hand side of (1.3) denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term V_{XC} is called the exchange-correlation potential. Here, V_{XC} includes all the many-particle interactions. Since the Hartree term and V_{XC} depend on $n(\vec{r})$, which depends on ϕ_i, which in turn depend on V_s, the problem of solving the Kohn–Sham equation has to be done in a self-consistent way. Usually one starts with an initial guess for $n(\vec{r})$, then calculates the corresponding V_s and solves the Kohn-Sham equations for ϕ_i. From these, one calculates a new density and starts again. This procedure is then repeated until convergence is reached. A non-iterative approximate formulation called Harris functional DFT is an alternative approach to this time-dependent DFT.

If we apply the H-K theorem to this non interacting system, we find that there is at most one external potential $V_s(\vec{r})$ to within a constant which generates the density $n(\vec{r})$. Therefore for a given ground state density $n(\vec{r})$, all the properties of the system are determined. Thus one can write the total energy as a functional of charge density, in the following manner

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\ v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + V_H[\rho] + E_{\text{xc}}[\rho]$$

(1.4)

V_{ext} is the external potential acting on the interacting system while V_H is the Hartree (or Coulomb) energy, given by

$$V_H = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

(1.5)

and E_{xc} is the exchange-correlation energy. The Kohn–Sham equations are found by varying the total energy expression with respect to a set of orbital's to yield the Kohn–Sham potential as

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}.$$

(1.6)

where the last term in (1.6) is given by

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

(1.7)

It is this Kohn-Sham equation which is solved using the QUANTUM ESPRESSO Package in order to determine the properties of our system.
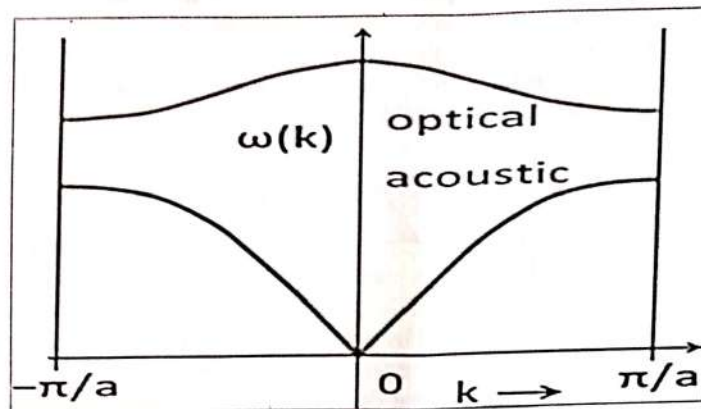
1.2   Acoustic and Optical Phonons

Fig. 1.1: Dispersion curves in linear diatomic chain [5].

Solids with more than one type of atom – either with different masses or bonding strengths – in the smallest unit cell, exhibit two types of phonons: acoustic phonons and optical phonons.

Acoustic phonons are coherent movements of atoms of the lattice out of their equilibrium positions. The displacement as a function of position can be given by $\cos(\omega x)$. If the displacement is in the direction of propagation, then in some areas the atoms will be closer and further apart in others, as in a sound wave in air (hence the name acoustic). Displacements perpendicular to the propagation direction is comparable to waves in water. If the wavelength of acoustic phonons goes to infinity, this corresponds to a simple displacement of the whole crystal, and this costs zero energy. Acoustic phonons exhibit a linear relationship between frequency and phonon wave vector for long wavelengths. The frequencies of acoustic phonons tend to zero with longer wavelength. Longitudinal and transverse acoustic phonons are often abbreviated as LA and TA phonons, respectively.

Optical phonons are out of phase movement of the atoms in the lattice, one atom moving to the left, and its neighbour to the right. This occurs if the lattice is made of atoms of different charge or mass. They are called *optical* because in ionic crystals, such as sodium chloride, they are excited by infrared radiation. The electric field of the light will move every positive sodium ion in the direction of the field, and every negative chloride ion in the other direction, sending the crystal vibrating. Optical phonons have a non-zero frequency at the Brillouin zone center and show no dispersion near that long wavelength limit. This is because they correspond to a mode of vibration where positive and negative ions at adjacent lattice sites swing against each other, creating a time-varying electrical dipole moment. Optical phonons that interact in this way with light are called *infrared active*. Optical phonons that are *Raman active* can also interact indirectly with light, through Raman scattering. Optical phonons are often abbreviated as LO and TO phonons, for the longitudinal and transverse modes respectively.

When measuring optical phonon energy by experiment, optical phonon frequencies, ω are often given in units of cm^{-1}, which are the same units as the wave vector. This value corresponds to the inverse of the wavelength of a photon with the same energy as the measured phonon [5]. The cm^{-1} is a unit of energy used frequently in the dispersion relations of both acoustic and optical phonons.

1.3 Density functional theory

In recent physics literature, a large majority of the electronic structures and band plots are calculated using DFT. DFT calculated bands are in many cases found to be in agreement with experimentally measured bands, obtained, for example, by angle-resolved photoemission spectroscopy (ARPES). In particular, the band shape is typically well reproduced by DFT. But there are also systematic errors in DFT bands when compared to experiment results. In particular, DFT seems to systematically underestimate by about 30-40% the band gap in insulators and semiconductors. DFT is, in principle, an exact theory to reproduce and predict ground state properties (e.g., the total energy, the atomic structure, etc.). However, DFT is not a theory to address excited state properties, such as the band plot of a solid that represents the excitation energies of electrons injected or removed from the system [6]. What in the literature is quoted as a DFT band plot is a representation of the DFT Kohn-Sham energies, i.e., the energies of a non-interacting system, the Kohn-Sham system, which has no physical interpretation at all. The Kohn-Sham electronic structure must not be confused with the real, quasiparticle electronic structure of a system, and there is no Koopman's theorem holding for Kohn-Sham energies, as there is for Hartree-Fock energies, which can be truly considered as an approximation for quasiparticle energies.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces and some other strongly correlated systems; and in calculations of the band gap in semiconductors. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT in the treatment of systems which are dominated by dispersion or where dispersion competes significantly with other effects (e.g. in bio molecules) [6]. The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic [7].

2.0   Methodology

All computations have been performed using the Quantum Espresso 4.2.1 package [8]. This package does its calculation within the density functional perturbation theory (DFPT), using a plane wave basis set and pseudo potentials.

The code Pw.x is used to calculate the electronic and atomic structure. The phonon code ph.x calculates the normal modes at a given q-vector, starting from the data files produced by pw.x with a simple self consistent field (scf) calculation. The code q2r.x reads the D(q) dynamical matrices produced in the preceding steps and Fourier-transforms them, writing a file of interatomic force constants in real space, up to a distance that depends on the size of a grid of q-vectors. The program matdyn.x may be used to produce phonon modes and frequencies at any q using the interatomic force constant file as input. However, plotting of selected quantities are done mainly by post processing or plotband codes. This code reads the data files, extracts or calculates the selected quantity and then writes it into a format that is suitable for plotting. The output is written to a file in a simple format that can be directly read by plotting program plotband.x. Unpredictable plots may result if K-points are not in sequence along the lines.

3.0 Results and Discussion

For the self consistency field (scf) a kinetic cut off energy of 30Ry was used to generate the plane waves. The convergence tolerance for each of the calculations is 1.0E-10. A K-point mesh of 36 was sufficient to yield good convergence for all the calculations. This was done within the frame work of DFT, DFPT using LDA and undergo parametization [13].

It was found that the maximum deviation from the plot takes place in the vicinity of the first Brillouin zone [9]. This region lies nearly at half the distance of the first peak in the structure factor. The choice of the structure factor plays a major role in the study of phonon dispersion curve of metals.

This work deals with the computation of the phonon dispersion curves of some metals, viz Na, Ni, Nb and Al with the aim to explore their K-points and pseudo potentials of their structure factor, i.e BCC and FCC structures.

The constants and parameters used in the computation are obtained by following the calculation procedures. The computed phonon dispersion curve and structure factor are also shown for Na, Al, Nb and Ni in Figs. 3.1, 3.3, 3.5, and 3.7 respectively.

Fig. 3.1 shows the phonon dispersion for Sodium (Na) plotted along points of high symmetry in the first or irreducible Brillouin zone. There are three Acoustic Band which correspond to the single Atom in the unit cell. They are, Two Transverse Acoustics (TA1,TA2) and One Longitudinal Acoustic (LA). The first two (2) lines from the bottom are the Transverse, while the single line on top is the Longitudinal. From Γ - X bands TA1, TA2 and LA degenerated till about half way to X bands. In Γ - K direction no degeneracy occurred as the lines were seen separated at K, but at Γ - L direction TA1, TA2 degenerated and all the waves converged at L-bands.

In Fig. 3.3, the Aluminum(Al) phonon dispersion shows that TA1 and TA2 degenerated but cross LA wave half way to Γ - W band and Γ - L band, a band softening was observed at about 300cm^{-1} on L-bands, W-bands and X-bands.

Fig. 3.5 shows the Niobium (Nb) dispersion curve. At Γ - H direction degeneracy occurred for TA1 and TA2 wave on both sides, but at about 230cm^{-1} both TA1, TA2 and LA wave degenerated. Softening was observed on LA wave at about 350cm^{-1}. At Γ - N band on both sides degeneracy only took place between TA1 and TA2 waves.

Fig. 3.7 witness a similar acoustic behavior for a Nickel (Ni) phonon dispersion, were at Γ - X bands direction TA1 and TA2 waves degenerated and crosses the X band at about 360cm^{-1}. In the Γ - K direction no degeneracy occurred at all as the three waves were seen separated.

Comparing these works with the experimental results from references [10], [11] and [12] we observe that they follow the same pattern and trend.
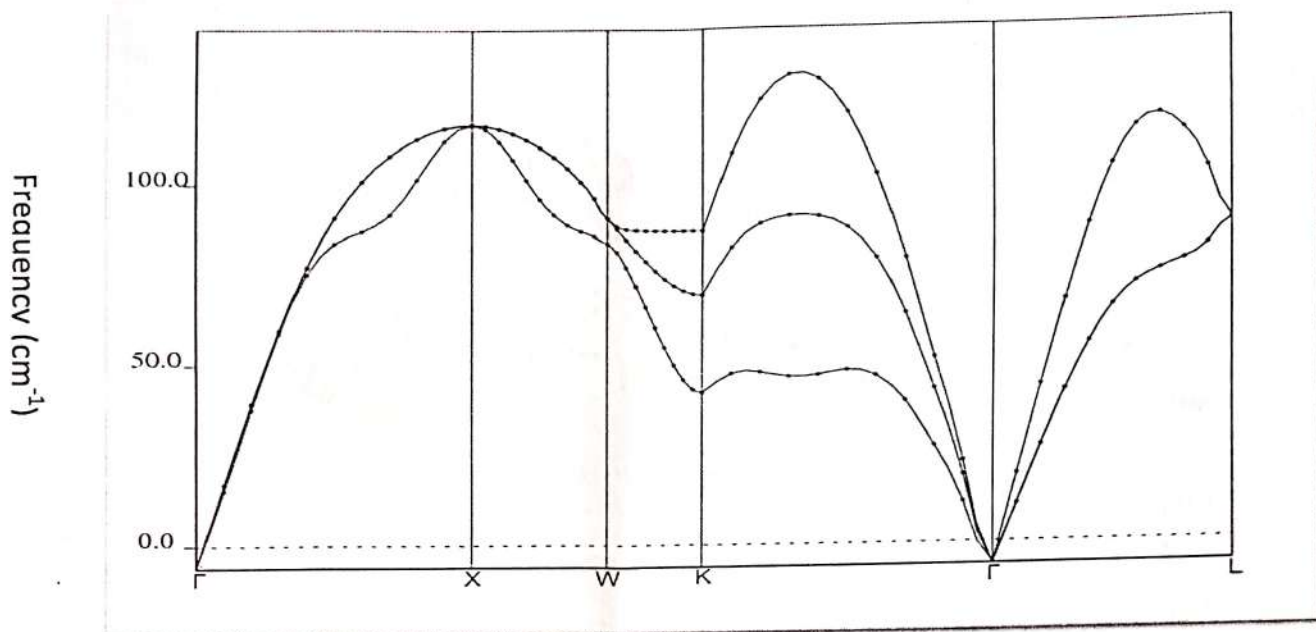
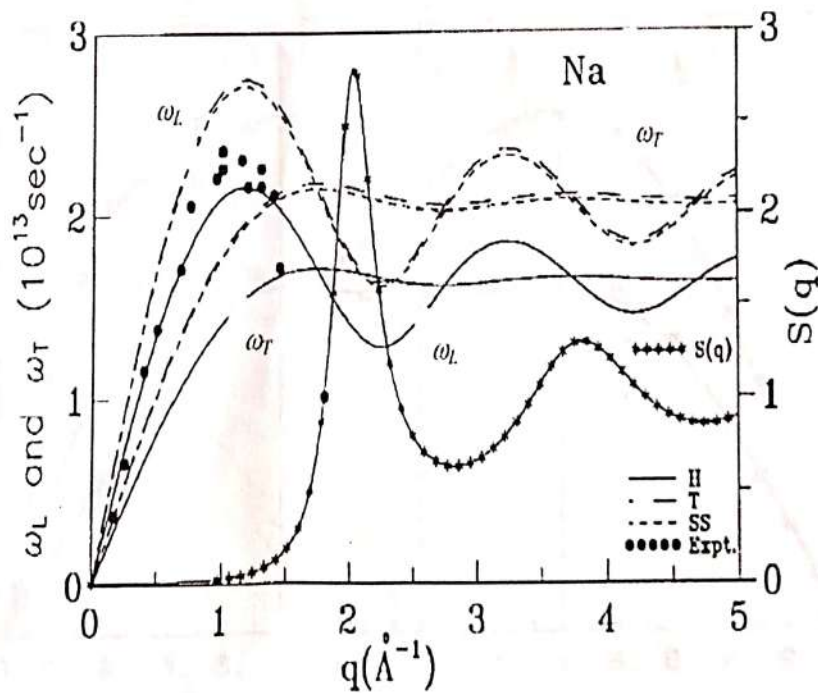Fig. 3.1: Na Phonon Structure (this work)
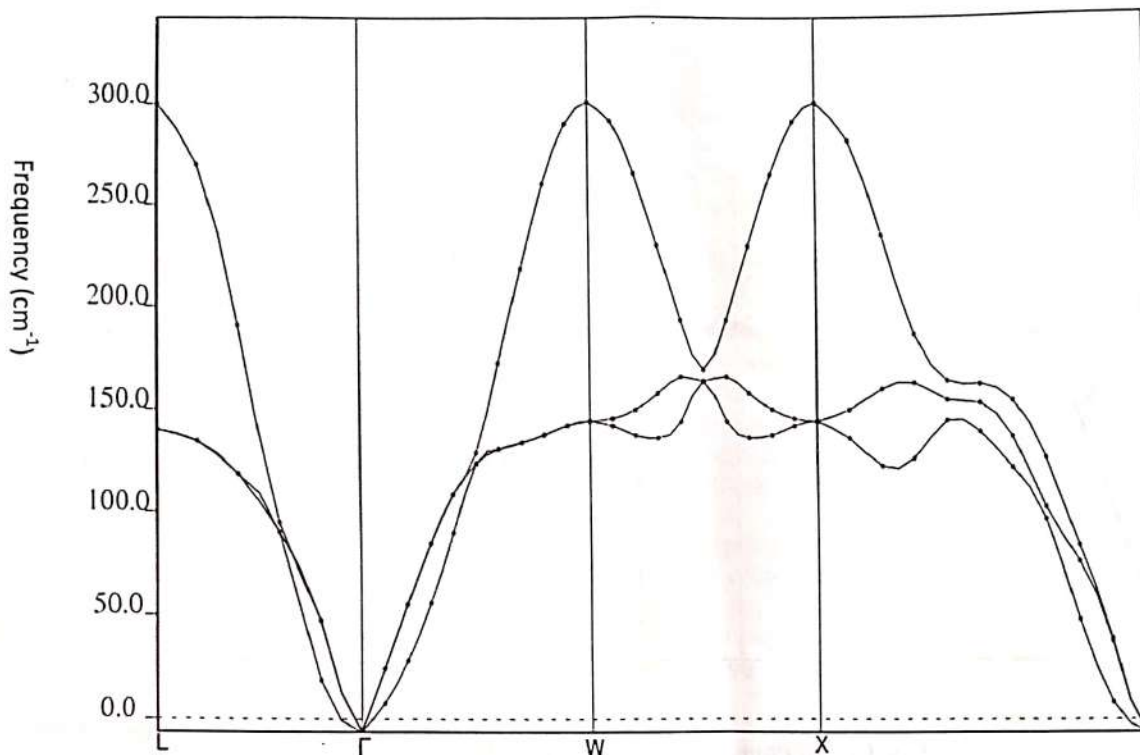

Fig. 3.2: Phonon dispersion curve for Na [10]

Fig. 3.3: Al Phonon Structure (this work)
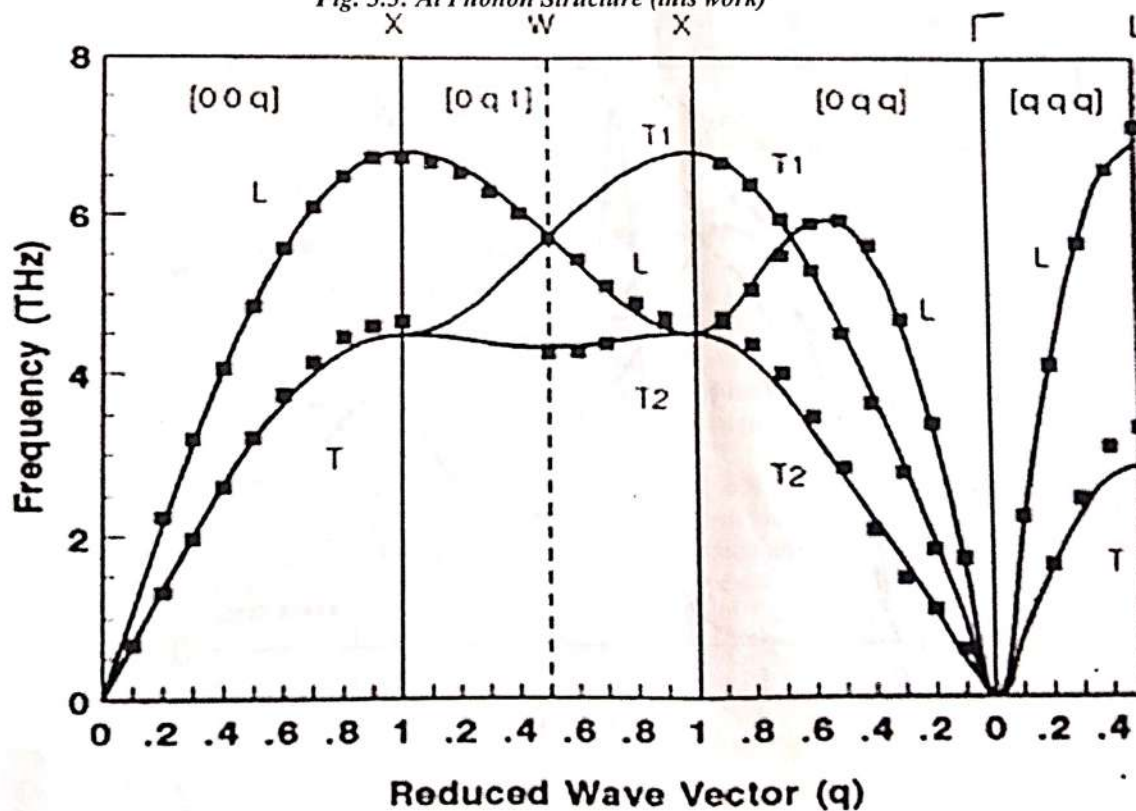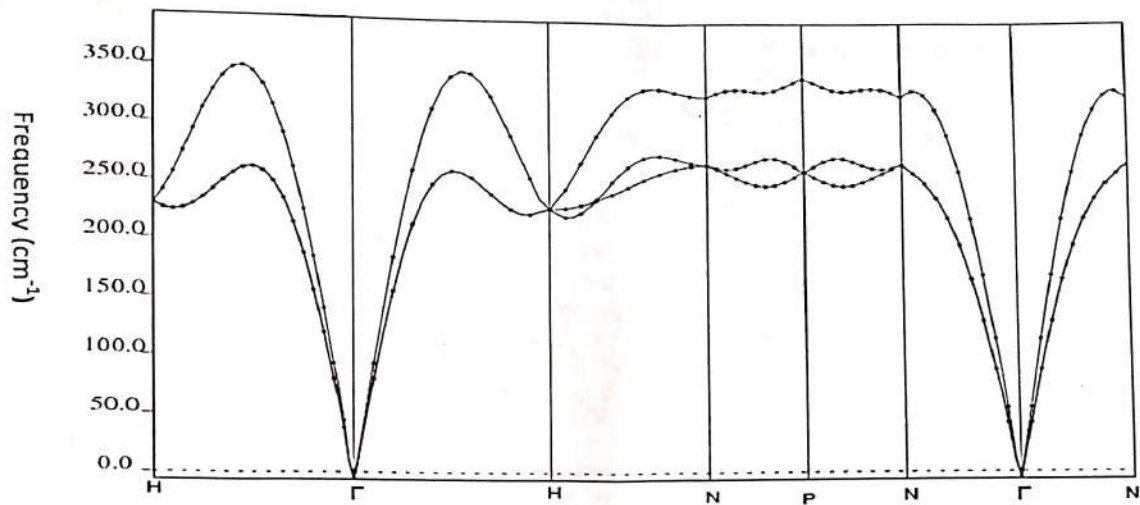

Reduced Wave Vector (q)

Fig. 3.4: Phonon dispersion curve for Al [10]

Fig. 3.5 Nb Phonon Structures (this work)
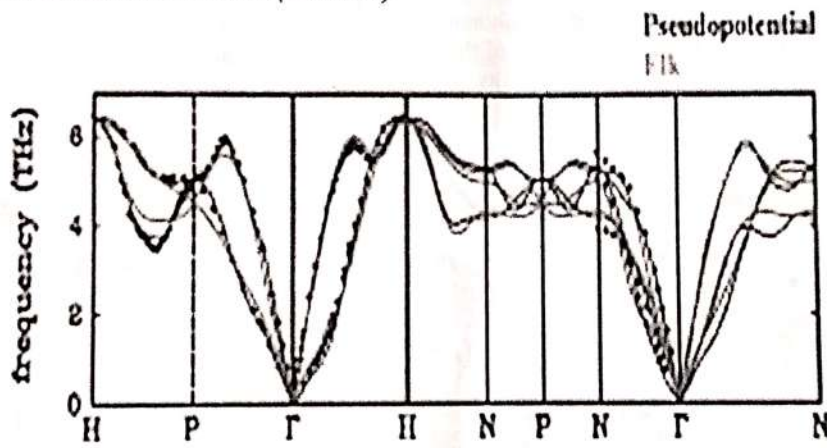

Fig. 3.6 Phonon dispersion curve for Nb [11]
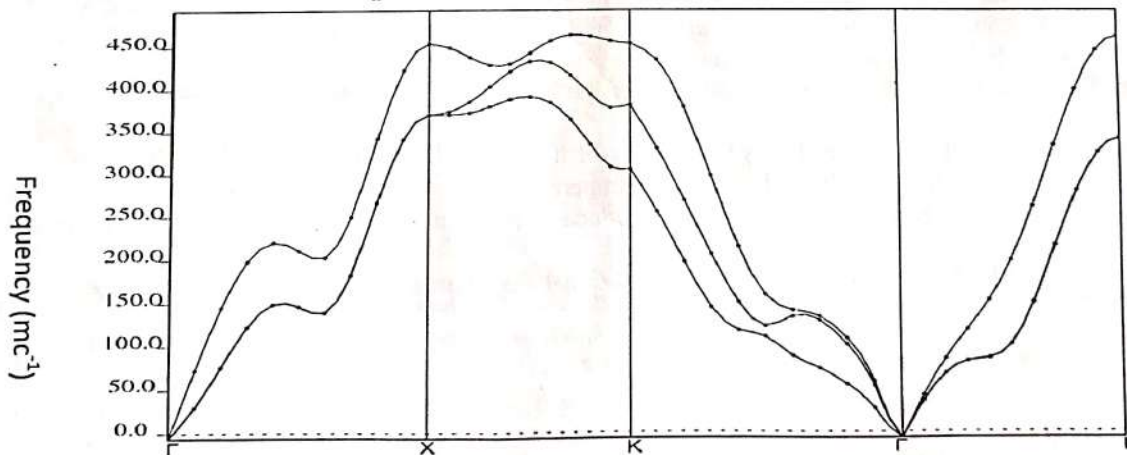

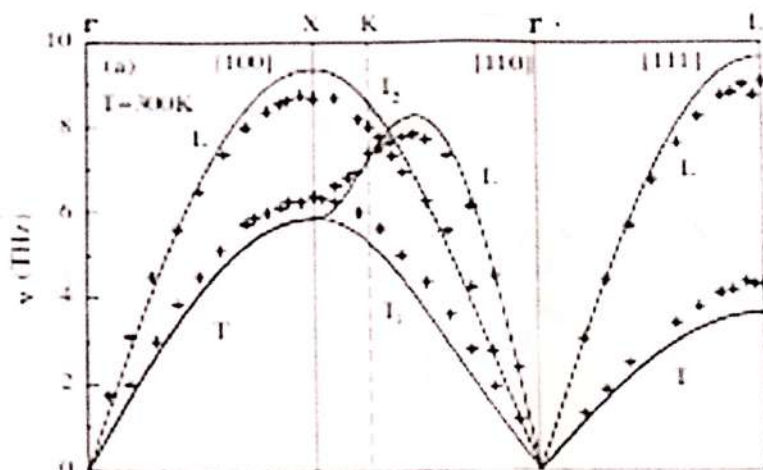**Fig. 3.7 Ni Phonon Structure (this work)**

Fig. 3.8 Phonon dispersion curve for Ni [12]

4.0   Conclusion

It was observed from this work that the dispersion of the phonons in Na, Ni, Nb and Al, exhibit acoustic behavior extending to a large wave vector transfer region. The comparison of the results from this work with that of the work of [10] indicate good agreement. Thus, in the absence of experimental results, such calculations may be considered as reliable guides for further theoretical or experimental investigation.

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