SIMULATION OF DISPERSION RELATION, DENSITY OF STATES AND HEAT CAPACITY OF SOME SELECTED FCC METAL CRYSTALS

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DECLARATION

I hereby declare that this work is the product of my research efforts undertaken under the supervision of Professor Garba Babaji and has not been presented anywhere for the award of a degree or certificate.

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CERTIFICATION

This is to certify that the research work for this dissertation and subsequent write-up (Yusra Abdullahi Sade SPS/13/MPY/00002) was carried out under our supervision.

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APPROVAL

This dissertation has been examined and approved for the award of Master of Science in Physics.

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Glory and thanks be to Almighty Allah most gracious most merciful for our lives and health without which all endeavor is not possible. Any struggle in the pursuit and attainment of certain objectives is a product of collective effort, this dissertation is no exception.

Special appreciation goes to my supervisor Professor Garba Babaji for his guidance and support throughout this research work. THANK YOU SIR and God bless.

Unreserved thanks to my dear husband for being there for me throughout this work. To my sisters and brothers THANK YOU ALL.

DEDICATION

This dissertation is dedicated to my beloved parents and my husband.

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ABSTRACT

The theoretical study of lattice dynamics of metals has been a challenging field of study for the past few decades. Several models for cubic metals have been developed with the aim of propounding a theory which can successfully reproduce the lattice dynamical properties with only a few free parameters. In this work, lattice dynamics of aluminum, copper and lead based on semi classical approach with nearest neighbor interaction have been investigated by using debye program from solid state simulation package. The calculated results of phonon dispersion relation along the three principal symmetry directions as well as the density of state and heat capacities were found to show reasonable agreements with the neutron scattering experimental result.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

Many properties of solids materials depend on the dynamics of the crystal lattice. Lattice dynamics is the study of the vibrations of the atoms in a crystal. Whilst we intuitively understand that atoms must be vibrating within crystals, it is the natural interpretation of temperature. Traditional crystallography often leads to the image of atoms being held in static positions through stiff chemical bonds. Yet crystallographic measurements tell us that atoms can be vibrating with amplitude that can be of order of 10% of an interatomic distance (Dove, 1993). Thus we need to understand lattice dynamics in order to have a complete picture of crystalline materials and indeed of amorphous materials too.

Understanding lattice dynamics is important for a number of key applications. The propagation of sound waves in crystals are a practical example of the role of lattice dynamics, as also is the interaction of materials with light. For example, the absorption of certain frequencies in the infra-red spectral region is directly due to the existence of speci□c lattice dynamics motions. It also gives us properties such as thermodynamics, superconductivity, phase transitions, thermal conductivity, and thermal expansion (Dove, 2011).

In the study of lattice dynamics, atomic motions are frequently found to be adequately described as harmonic travelling waves. Each wave can be fully characterized in terms of its wavelength, angular frequency, amplitude and direction of travel (Dove, 2003). The key approximation in the theory of lattice dynamics is the harmonic approximation which is illustrated by considering the potential energy between two atoms, it is effectively the only model for lattice dynamics that has an exact solution. Given the harmonic interatomic potential, a

plane wave harmonic (sinusoidal) solution to the equation of motion of the atom can be obtained. The sinusoidal time dependence is determined by the phonon frequency which is a function of the phonon wave vector (Silsbee & Draeger, 1997).

Phonon dispersion relations in crystalline materials are a manifestation of the interatomic bonding forces; as such, they play a fundamental role in many physical effects and phenomena (Xu *et al*., 2008). Efficient determination of these relations is important for the advancement of materials physics. Lattice dynamics offers two ways of finding the dispersion relation. One is the quantum mechanical approach where phonon dispersion relation can be obtained directly through finding the solution of the schrodinger equation for the lattice vibration. The other is the semi classical approach, which invokes one additional postulate taken from quantum mechanics that the energy of lattice vibration is quantized. The semiclassical models of metals are easy to handle physically and mathematically and contain only a few adjustable parameters to determine the lattice dynamics and thermal properties of the metals (Coelho & Shukla, 1996). The dispersion relation may be calculated if the interactions between the particles forming the crystal are known. Knowledge of the dispersion relation from experiment will provide a fairly direct test of the correctness of the theoretical interactions. The calculation can be reversed to some extent so that the force constants are deduced from the dispersion relation.

In this research lattice dynamics in harmonic approximation with nearest neighbor interaction will be considered. Experimentally determined macroscopic mechanical properties of some selected fcc crystals (Al, Cu and Pb) will be used to calculate the frequency of an elastic wave (or phonon) propagating with arbitrary wave vector. The frequencies are then used to obtain the dispersion relation and

knowledge of the normal mode frequencies allows the calculation of density of modes, internal energy and heat capacity of the crystals.

1.2 STATEMENT OF THE PROBLEM

The theoretical study of lattice dynamics of metals has been a challenging field of study for the past few decades. Before the advent of the thermal neutron scattering, the theoretical predictions were verified with the experimental findings in thermal properties. The introduction of neutron scattering techniques and the availability of the experimental phonon dispersion relations along the principal symmetry directions in metals afforded a crucial test of the validities of the theoretical models. Several models for cubic metals have been developed with the aim of propounding a theory which can successfully reproduce the lattice dynamical properties with only a few free parameters. The model which failed to predict well the experimental phonons were not trustworthy even for the thermal properties of metals. A close prediction of the experimental phonons by a theoretical model was only possible once the electron-ion interactions in metals were considered adequately.

This work uses the neutron scattering data to obtain the lattice dynamics properties of Aluminum, Copper and Lead and to test the validity of the theoretical model *debye*

1.3 AIM AND OBJECTIVES

The aim of this work is to simulate the lattice dynamics of fcc crystals (Cu, Al and Pb) and to obtain their dispersion relation and heat capacity.

The objectives of the work are to:

Compute phonon dispersion relation.

Calculate the density of states.

Compute the spectral density of internal energy.

Calculate the heat capacity.

Compare results obtained with Neutron scattering experimental results and Debye model.

1.4 SCOPE AND LIMITATIONS

In order to achieve these goals semi classical approach to lattice dynamics in the harmonic approximation with nearest neighbor interaction was considered on a phenomenological basis. The code *debye* written by Silsbee and Draeger was used to calculate the dispersion relation, density of states, internal energy and heat capacity of the following fcc metals: Aluminum, Copper and Lead. For each of these structures, neutron scattering experimental results was used to obtain the force parameter B which was used to compute the dispersion relation and from the dispersion relation the density of states, spectral density of internal energy and heat capacity were calculated using the *debye* lattice dynamics simulation and the Debye model.

This work is limited to harmonic approximation and takes into account only nearest-neighbor (N.N.) interactions.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The dynamics of crystals has been has been discussed at length. The basis of the theory of crystal dynamics is the use of the potential function. To drive such a potential function, an approximation known as the harmonic approximation was made considering only nearest neighbor interaction within the first Brillouin zone. This approximation is necessary in order to obtain a first solution to the equation of motion of the crystal, but is inconsistent with properties of the crystal like thermal expansion and heat conduction. Having obtained a first solution in terms of normal modes of vibration, the effects of the higher powers may be described by an interaction between the normal modes.

2.2 RECIPROCAL LATTICE AND BRILLOUIN ZONE

Many important physical, electrical and optical properties of metals can be understood by using the concept of reciprocal lattice. The reciprocal lattice is a geometrical construction which allows one to relate the crystal geometry directly to the electronic states and the symmetry properties of a crystal in the reciprocal space. For a perfect crystal, the lattice in reciprocal space consists of an infinite periodic three dimensional array of points whose spacing is inversely proportional to the distance between lattice planes of a bravais lattice (Li, 2012). Reciprocal lattice is an essential concept in the study of crystalline solids and their diffraction properties. The space generated by reciprocal lattice point is called the reciprocal space or q-space (Srivastava, 1990). It is convenient to describe the space surrounding each reciprocal lattice point using the formalism of the Brillouin zone.

The first Brillouin zone is the unit cell of the reciprocal lattice. It is the basic building block with the smallest volume in the reciprocal space, centered at one reciprocal lattice point, and bounded by a set of planes which bisects the reciprocal lattice vector connecting this reciprocal lattice point to all its neighboring reciprocal lattice points. In three dimensions, the first Brillouin zone is a volume of the reciprocal space centered at the origin and bounded by the perpendicular bisecting plane of the reciprocal lattice vector. It is also regarded as the locus of points closer to the origin than any other point in the reciprocal lattice. For a three dimensional crystal lattice, the first Brillouin zone can be constructed by drawing the reciprocal lattice vector from a chosen reciprocal lattice point to all its nearest neighboring points and then drawing the bisecting planes perpendicular to these reciprocal lattice vectors. The smallest volume enclosed by these bisecting planes is the first Brillouin zone of the reciprocal lattice. The importance of the first Brillouin zone is illustrated by considering the wave function of an electronic wave packet in a crystalline solid, which is described by the wave vector in reciprocal lattice space. It is also important in describing the excitation spectrum in periodic media. The phonon dispersion relation and the electronic states in a solid can be described by using the concept of reciprocal lattice and the first Brillouin zone (Li, 2012).

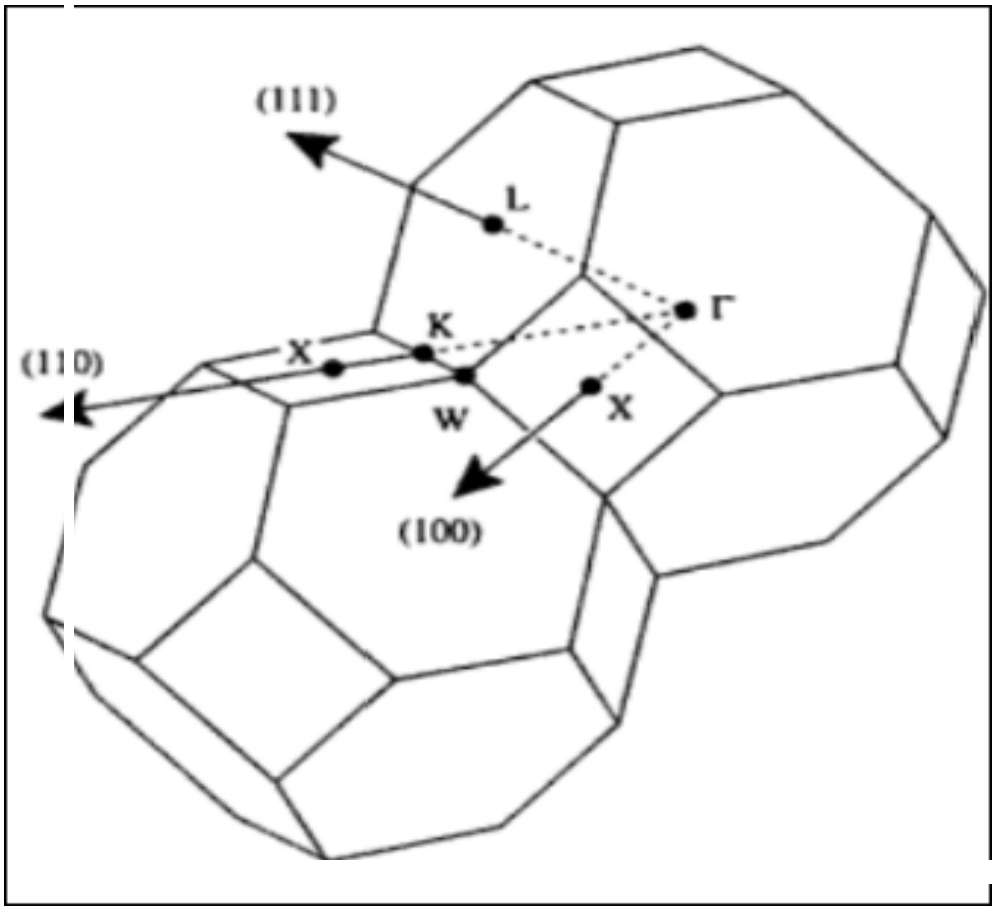


Plate 1.1: The first Brillouin zone and neighboring cell for fcc crystals

Plate 1.1 illustrates the first Brillouin zone for fcc crystals, along with one repeated image of it. The origin of reciprocal space is conventionally denoted as Γ, while X, L, K and W are assigned to various symmetry points on the surface of the zone. The Brillouin zone of the fcc lattice is highly symmetrical, it is unchanged by various rotation and is variant under reflection through certain plane containing the center of the cube (Yu & Cardona, 2010).

2.3 CONCEPT OF NORMAL MODES

The collective motion of atoms in crystalline solids form travelling waves called lattice vibrations. These vibrations which are called normal modes are

essentially non-interacting and harmonic in nature at low temperature. Two waves whose wave vectors differ by a reciprocal lattice vector have identical effect on real-space lattice point. As a result, the set of wave vectors contained within a single Brillouin zone are sufficient to describe the waves associated with lattice vibration and electronic wave functions (Dove, 2003). For crystalline solids, normal modes are propagating vibrational modes with wave vector **q**, determined by crystal geometry. A normal mode of vibration is expressed as a travelling wave $A\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]$, where **q** shows the direction of wave propagation, ω is the angular frequency of the wave and A is the amplitude of vibration (Sherwood, 1972). For each value of q, the frequencies are determined by diagonalizing the force-constant matrix, which is closely related to the interatomic potential.

The plane wave lattice vibrations in the long wave length ($q \rightarrow 0$) are of two types. The first type of lattice vibration is such that the displacements of neighboring ions are identical; these modes are called acoustic branches. The second kind of lattice vibration corresponds to the displacement of oppositely charged neighboring ions in opposite directions and their magnitudes are such that the centre of mass remains stationary. These modes are called optical branches. The optical vibration frequencies approach finite limits while the acoustic frequencies tend to zero as the wave vector q tend to zero.

The displacement corresponding to the acoustical as well as the optical lattice vibrations can be further resolved into three components, one parallel to the wave vector **q** (longitudinal motion) and the other being mutually perpendicular to the wave vector **q** (transverse motion). In certain special directions the normal vibrations will be strictly transverse and/or longitudinal because of symmetry, since the vibrations involve restriction of the motion of particle to a plane. For a face-centered cubic crystal, the (100), (110), and (111) planes correspond to one

longitudinal and two transverse modes, and the dispersion relation calculated as three separate linear lattice problems. The two transverse optical modes will be degenerate, but the longitudinal optical mode will occur at higher frequency at q=0 because such vibrations are associated with a finite macroscopic electrostatic field (Sherwood, 1972).

2.4 THE HARMONIC APPROXIMATION

The harmonic model gives many features of lattice dynamic, such as dependence of frequency on wave vector, and features that are not explained by the harmonic model can be incorporated in to a model that looks like a harmonic model. Thus the harmonic approximation does more than simply providing a model that can be solved. It provides the whole frame work for the study of lattice dynamics in which improvements can be made (Dove, 2003). Harmonic approximation is the key approximation in the study of lattice dynamics which is illustrated by considering the potential between two atoms. It involves neglecting all terms of power higher than two.

In the classical picture within the harmonic approximation, the atoms of a crystal are visualized as joined by harmonic springs and the crystal dynamics is analyzed in terms of a linear combination of 3N normal modes of vibration (Sherwood, 1972). In this approximation, it is assumed that each atom undergoes a simple harmonic motion about its equilibrium position, which remains fixed (Putnis, 1992). The harmonic approximation which fixes the equilibrium interatomic distance does not directly include the effects of temperature and therefore does not predict some properties of the lattice. Since the effect of temperature on thermodynamic properties is of interest, a way of incorporating temperature must be included in the lattice dynamical calculation.

2.5 LATTICE DYNAMICS PROPERTIES

There are many properties associated with the study of lattice dynamics of material. This research focuses on the dispersion relation, density of states and heat capacity.

2.5.1 Dispersion Relation

Phonon dispersion relations are defined as the wave vector **q** dependence of of normal modes for all branches and selected directions in the crystals. The number of phonon branches is equal to the number of degrees of freedom in the primitive unit cell. Each point on the dispersion curve gives the frequency of a phonon. Conventionally, phonon dispersion relations are drawn along crystal high-□□(□)

2.5.2 Density of States

□is the number of phonon modes per unit frequency interval (Razeighi, 2009). It □□(□) in a given frequency interval, if the density of wave vectors **q** in the Brillouin zone is homogeneously distributed. The phonon density of states spreads from zero to the maximal phonon frequency existing in a given crystal.

2.5.3 Heat Capacity

The heat capacity of materials is a measure of the ability with which a substance can store heat energy. The greater the heat capacity of a material, the more the energy added to change its temperature (Razeghi, 2009). The total thermal energy of a crystal is the integral over all frequencies of the internal energy

density. The heat capacity of a crystal per unit volume is the temperature derivative of internal energy (Silsbee & Draeger, 1997).

2.6 THEORY OF LATTICE DYNAMICS MODEL

The harmonic approximation is the starting point for all theories of lattice dynamics (except, perhaps, in solid helium) (Ashcroft and Mermin, 1987). Lattice dynamics model of this work is based on a harmonic interaction with one free parameter, the force constant of the nearest neighbor interaction. The starting point is an fcc crystal in which every atoms under goes small oscillation about its equilibrium position. Given a harmonic interatomic potential, we seek plane wave harmonic (sinusoidal) solutions to the equation of motion of the atoms. The sinusoidal time dependence is determined by the phonon frequency, ω which is a function of phonon wave vector, **q**. As we will see below the phonon frequency, ω of each mode is closely related to the eigen values of the dynamical matrix, D(**q**), which in turns depends on the atomic arrangement of the dynamical matrix and the interatomic potential.

The total harmonic potential of a three-dimentional crystal can be written (Silsbee and Draeger, 1997) in terms of the displacement vector, **u** of each atom from its equilibrium position, **R** as

□□□□□=*12*□□□□□□□.□(□−□′).u(□′) (2.1)

. The quadratic matrix, D(**R-R'**) can be specified in terms of the interatomic pair □′).

Force as a function of the potential is given as,

□□□□□ =−□□□□□□□□□ 2.2

From Newton's second law of motion, force is given as,

□(□) 2.3

From equations 2.2 and 2.3, it then follows that the motion of atom of mass M is determined by

□(□)=−□′□□−□′.□□′. 2.4

The equation of motion has solutions of the form

□□□□/□.□−□□□□] 2.5

□□(**q**) is the phonon frequency associated with polarization p and wave vector **q**. As it turns out, the polarization vectors and their associated phonon frequencies can be determined from the dynamical matrix, D(**q**),

□D(□)e−i□.□ 2.6

□□are the real three eigen vectors of D(**q**) and the angular frequency □□(□) is given □□ as

□□(□)=□□(□)/□ 2.7

contributes to the sum in equation (1) only for nearest neighbors then equation (4) reduces to a sum over 12 nearest neighbors **R** in an fcc crystal,

□□□2(12□.□)□□ 2.8

where □□ is the dyadic (the outer product) $(□□)_{ij} = □_i□_j$ of the unit vectors □=**R**/R. The *2*) for an fcc crystal.

The thermal contribution to the internal energy per unit frequency interval of a crystal is given by

□□□(□,□)=□□ħ□1□ħ□/□□−1 2.9

□□□,□ is obtained from the average energy associated with a normal mode of in equilibrium with a heat bath of temperature, T given by;

$$1□ħ□/□□□−1+12)≡□□□,□+12ħ□ \quad 2.10$$

,T)

$$0∞□□□(□,□) \quad 2.11$$

□□then follows from the temperature derivative of the internal energy U(T).

$$□□(□)=1□□□□□□□□ħ□□ħ□/□□−1 \quad 2.12$$

2.7 CRYSTAL SYMMETRY DIRECTIONS

Symmetry plays an important role in crystallography. The ways in which atoms and molecules are arranged within a unit cell and unit cells repetition within a crystal are governed by symmetry rules. There are three types of symmetry in crystallography. The simplest is the set of translation operations needed to fill a two-dimensional infinite plane or three-dimensional infinite space (Dreele, 1990). The symmetry of the crystal determines some features of the normal modes. The phonon dispersion relation shows the full symmetry of the crystal.

Directions in a lattice have similar symbols, they are given by three integers in square brackets [UVW]. In cubic system, the first direction is given along the axis which is either a 2-fold or 4-fold axis and/or a plane perpendicular to them. The second direction gives 3-fold symmetry along the body diagonal and the third gives symmetry along the face diagonal (Massa, 2000). The three high symmetry directions in the Brillouin zone of fcc lattice are [100], [110] and [111]. Different symmetry directions can be symmetrically equivalent, for example, the three fourfold axes parallel to the edges of a cube. In crystals sometimes there are up to three classes of symmetrically equivalent directions of non-trivial symmetry (Muller, 2013). Directions having the same indices regardless of order or sign are

equivalent in cubic crystal system and they are called a family of directions. The directions [100], [010] and [001] are equivalent and they are represented by <100> similarly in the case of [110].

For a given direction of propagation, the displacement vectors are neither parallel (purely longitudinal waves) nor perpendicular (purely transverse waves) to the vector **q** (Planes and Manosa, 2001). Purely longitudinal and purely transverse waves can propagate along some crystallographic directions. In cubic crystals, a purely longitudinal and two purely transverse waves can propagate along [110] direction.

2.8 REVIEW OF RELATED PREVIOUS WORK

The lattice dynamics properties of materials such as the dispersion relation, internal energy and heat capacity have been investigated by several researchers using different methods. Most of the results obtained were in good agreement with the experimental data as reviewed below.

Xu *et al*. (2008) developed a new method of mapping phonon dispersion relations based on momentum-resolved x-ray calorimetry. X-ray scattering intensities were measured at selected points in reciprocal space with suitably chosen polarization con□gurations; the thermal part of the scattering intensity is extracted by scanning the temperature of the sample. The intensity variations, governed by the phonon populations, are analyzed to yield the energies of the phonons. This method is applied to copper. With high-order effects under control, the results were in excellent agreement with the known phonon dispersion relations.

Coelho and Shukla (1996) modified the original model of Sarkar *et al.* (1977) for cubic metals in extending the ion-ion interaction, ion-electron

interaction and the introduction of crystal equilibrium condition. They applied their scheme to alkali metals. They studied the lattice dynamics of noble metals by calculating phonon dispersion relations along the three principal symmetry directions, and the thermal properties of three noble metals: copper, silver and gold. They obtained reasonable agreement with the experimental findings.

Scharoch *et al.* (2000) used direct method and ab initio force constants to calculate phonon dispersion curves and phonon density in Al. They determined the force constants from the Hellmann—Feynman forces induced by the displacement of an atom in the 2 x 2 x 2 fcc crystallographic supercell. This size of the supercell gives exact phonon frequencies at Γ, X, L, W points of the Brillouin zone. The calculated phonon dispersion curves are in good agreement with the experimental data.

Scharoch *et al.* (2007) also calculated the phonon dispersion relations in fcc Al crystal from first principles using density functional perturbation theory, as implemented in ABINIT code. Their results were compared with experimental data as well as with the results of previously done ab initio calculations based on the direct method and a slightly better agreement of density functional perturbation theory phonons with experiment was observed.

Jun (2013) used the Born–von K´arm´an theory of lattice dynamics and the modified analytic embedded atom method to reproduce experimental results of the phonon dispersion in fcc metal (Cu) at zero pressure along three high symmetry directions and four off-symmetry directions, and then simulated the phonon dispersion curves of Cu at high pressures of 50, 100, and 150 GPa. The results show that the shapes of dispersion curves at high pressures are very similar to that at zero pressure.

CHAPTER THREE

METHODOLOGY

3.1 INTRODUCTION

This research is computational and is based on semi classical approach. The program *debye* from Solid State Simulation package by Silsbee and Draeger was used to simulate the lattice dynamics of fcc crystals. The essential materials for the research are: a laptop, windows 8 system and the code *debye.*

3.2 THE *debye* CODE

The program *debye* computes the phonon dispersion relation, the phonon density of states, heat capacity and the spectral density of internal energy for fcc crystals. The model underlying the algorithm can be chosen to be either lattice dynamics model or the Debye model.

3.2.1 Lattice dynamics simulation algorithm

The (normalized) phonon density of states, g(ω) is proportional to the (unnormalized) number N(ω) of phonon frequencies ω in the frequency interval ω defined below.To calculate N(ω) we have to sample all of reciprocal space evenly, determine the dynamical matrix D in Eq. 2.8 for each of the sampled wave vectors **q**, and then compute the three phonon frequencies ω_p (**q**) from the three □□ of the dynamical matrix, *D*(**q**), for any phonon wave vector **q,** *debye* computes the characteristic polynomial of D(**q**)and finds its three real roots.

Instead of sampling all of reciprocal space, *debye* chooses the positive octant ($0 < q_x q_y, q_z < 2\pi r/a$) of a bcc cubic unit cell centered at the origin. Sampling **q** in the positive octant is equivalent to sampling it in all of reciprocal space: it suffices to pick a unit cell because of translational symmetry. Because of the cubic symmetry of the bcc reciprocal lattice, only one octant of the unit cell is needed. The remaining octants have dispersion relations which can be inferred from those of the chosen octant using the cubic symmetry, and thus have the same phonon spectrum associated with them.

A simple Monte-Carlo (MC) method is then used to compute the (unnormalized) number of phonon frequencies N(ω) in a given frequency interval. The computation of N(ω) can be broadly classified in to three steps as follows;

Step 1: To determine the frequency range 0-ω_{max}, *debye* samples 100 random **q-**vectors in the positive octant of the unit cell centered at the origin, computes for each **q** the three associated phonon frequencies ω_p, and finds from these 300 values the maximum, max(ω_p). The frequency ω_{max} = 1.25 max(ω_p) is then used as an estimate for an upper limit of the frequency range. Any frequency above ω_{max} is disregarded in the simulation described in step 3.

Step 2: *debye* then divides the frequency range 0-ω_{max} into NUMBER OF BINSbins of size $D\omega = \omega_{max}$/NUMBER OF BINS

Step 3: *debye* samples a new set of NUMBER OF MC POINTS *(NMC)* random**q-**vectors in the positive octant of the unit cell, computes the associated phonon frequencies ω_p, and sorts these phonon frequencies into the appropriate bins. The number of phonon frequencies in each bin, N(ω), corresponds to the number of phonon frequencies in the interval ω to ω + Δω. Any *ω* larger than $\boldsymbol{\omega_{max}}$is disregarded.

Once the number N(ω) of frequencies in the interval ω to ω + Δω is computed, the Density of states is given by

□*(*□*)*□□□□□□□□□□ 3.1

Where *a* is the lattice constant of the fcc crystal whose atomic density, $n = N/V$ with four atoms per cubic unit cell is given by $n = 4/a^3$.

3.2.2 *Debye model*

Instead of calculating the density of states with the lattice dynamics simulation described above, we can make a crude approximation (known as the Debye model) by assuming the same linear dispersion relation for each of the three $(q) = v_s q$. Here v_s is the Debye velocity of sound. This approximation results in a particularly simple density of states,

□□□= □□□□□□□□□□ □□□<□□□ □□□□□□□□□ 3.2

where the factor of 3 arises from the three directions of polarization. Normalization requires that the number of modes in a crystal with *N* atoms is 3N,

0□□□□□□*(*□*)*= 3N 3.3

□□. In an fcc crystal with density $n = N/V = 4/a^3$ we thus find

□□=*324*□*2*□□/□ 3.4

,T) and the heat capacity for both the lattice dynamics simulation and the Debye

□ is taken either from Eq. 3.1 or from Eq. 3.2.

3.2.3 The *debye* code panel

The left hand display in *debye* shows the dispersion relation either along the symmetry directions [100], [110], and [111], or along an arbitrary direction which can be specified on the panel. The right hand display offers the choice of the density of states, the spectral density of the internal energy, or the heat capacity. Quantities computed from the lattice dynamics simulation are displayed in blue, quantities computed from the Debye model are displayed in red, and experimental neutron diffraction data as a series of points. The wave vector for the experimental data is scaled to whatever lattice constant happens to be chosen in the panel: i.e., */a* rather than 1/**Å**.

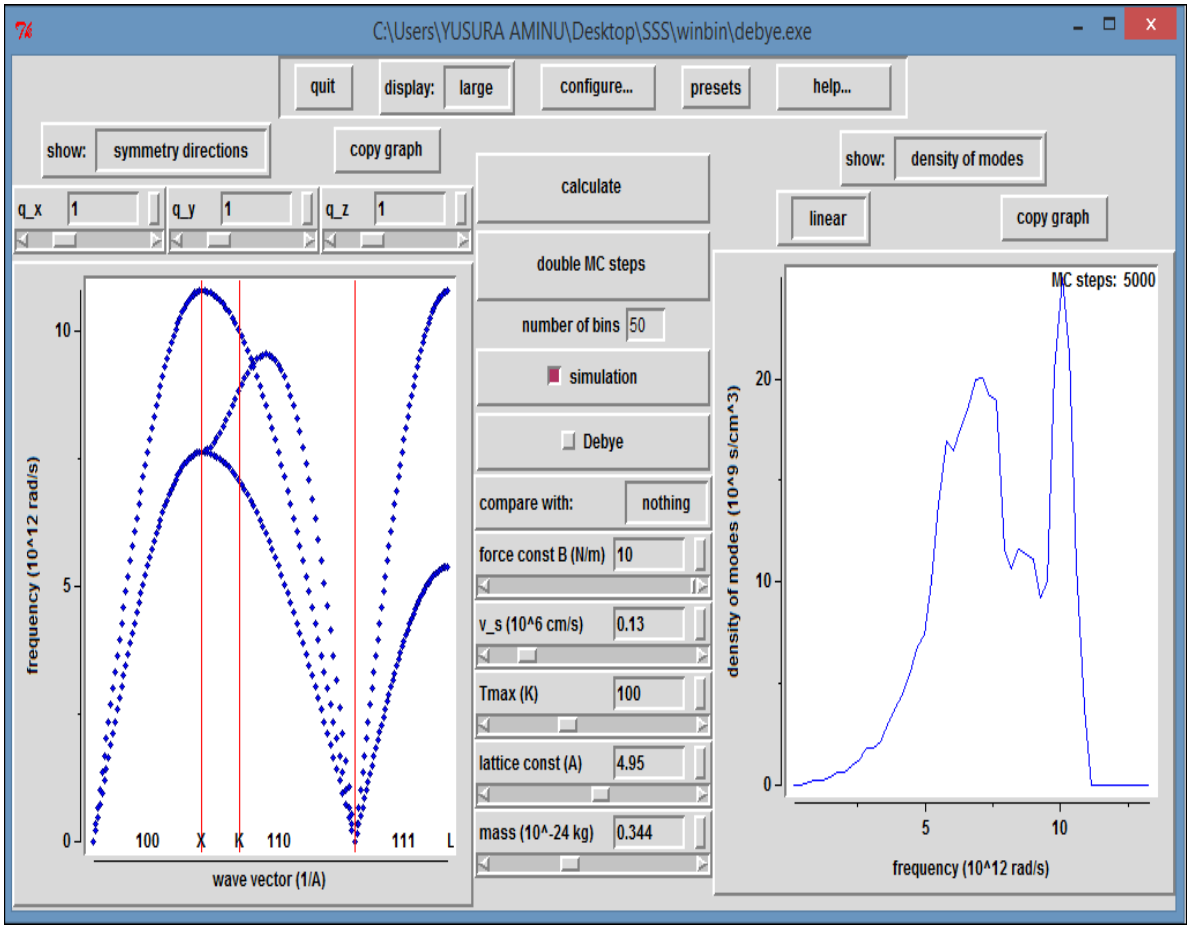


Plate 3.1: The *debye* code panel

Sliders

Force const B: Twice the force constant, in N/m, of the springs connecting nearest neighbors of the fcc structure.

v_s: The velocity of sound in units of 10^6 cm/s, used in the Debye model. It is specified independently of the force constant, lattice constant and mass and need not to be consistent with them (Restricted to be positive).

Tmax: Sets the maximum, in Kelvin, of the temperature range displayed in the heat capacity and internal energy plots. The ten internal energy curves plotted are spaced in T at equal intervals namely Tmax/10 (Restricted to values greater than 10).

Lattice constant: The lattice constant in angstroms, of the fcc (Restricted to be positive).

Mass: The atomic mass, in units of $10^{(-24)}$ kg, of the atoms (restricted to be positive).

qx:,qy:, and qz: Define the miller indices for the arbitrary direction in q –space along which the dispersion relations are plotted (restricted to integers).

Menus

Compare with; allows comparison of the model calculation with experimental results both for the dispersion relations along any or all of the three symmetry directions and for the heat capacities.

= nothing: No comparisons shown.

=lead: Experimental data for lead.

= copper: Data for copper

= aluminum: data for aluminum

Show (left): The dispersion relations may be plotted in two different ways: either

= symmetry directions: along the symmetry directions (100), (110), and (111), as well as along the X-K line in reciprocal space; or

= arbitrary direction: along an arbitrary line in reciprocal space defined by the miller indices (qx qy qz) which may be entered as integers in the sliders beneath the left hand graph.

Show (right): offers several choices for the plot in the right hand graph:

= density of modes: The density of modes (or density of phonon states),in units of 10^{9} s/cm^{3} versus angular frequency in units of 10^{12}rads/s.

= heat capacity: The heat capacity, in units of J/Kcm^{3}, versus temperature in Kelvin.

=internal energy: The internal energy spectral density, in units of 10^{-14} Js/cm^{3}, versus angular frequency in units of 10^{12} rad/s.

Toggles

Simulation: Turns on and off, in the right hand graph, the display (in blue) of the results from the simulations.

Debye: Turns on and off, in the right hand graph, the display (in red) of results from the Debye model.

Linear/log (above the right hand graph) allows choice of linear or log-log plots in the right hand graph.

Buttons

Calculate: initiates the calculation of the density of modes, the heat capacity and the internal energy which are to be displayed in the right hand graph.

Double MC steps: Doubles the size of the data set used to construct the density of modes histogram, by calculating additional mode frequencies and adding to the existing results. The total accumulated number of q-samples is displayed as MC steps in the right hand graph.

Presets: Takes you to a tear off menu with which you may select the presets.

Configure:

= number of MC points: sets the number of q space which are sampled by calculate to develop the density of modes.(restricted to positive.)

= revert: updates the listed configure parameters to the current values (which may have been changed by a preset command).

Help: opens the help system

Quit: terminates *debye*

Entry boxes

Number of bins: The number of bins assigned to develop the histogram for the density modes plot (Restricted to positive integer).

Displays

in rad/s and q in units of 1/**Å**, along either the symmetry directions in q space or

else along an arbitrary directions specified by the miller indices (qx qy qz) below the graph.

Right side: Displays the density of modes, heat capacity or spectral density of the internal energy, as described for the right hand show graph menu.

Readouts

MC steps: Gives, in the corner of the right hand, the accumulated number of q points sampled to generated the histogram for the density of modes plot. This will change to RED if any parameter relevant to the calculation of the histogram, or if a preset, is changed. Only if MC steps is black can you rely on the right hand graph to show simulation results appropriate to the parameter values given on the panel

3.3 MEASUREMENTS

3.3.1 Effect of directions on dispersion relation along high symmetry for fcc metals

Arbitrary direction was selected from the menu, the miller indices for directions [100], [110], and [111] were entered one by one, *debye* automatically calculates the dispersion relation for directions. The same procedure was repeated for other directions [010], [001], [011], [101] and [222] to see if there is any difference in dispersion curves along these directions.

For waves propagating along [100], the two transverse polarizations have same frequency. The choice of q direction was changed to [110] to explain why the transverse modes are degenerate for propagation along [100] but not for [110]. The sliders were used to read in a q direction [20 0 0] and the second index was increased unit after unit to see the [100] plot again.

3.3.2 Dispersion relation

Symmetry direction was selected from the display menu in the program. The lattice constant and atomic mass from the display menu were changed to that of Aluminum, *debye* then automatically displayed the predicted dispersion relation for Al. Al was selected from the COMPARE WITH menu to see the data from neutron scattering which determines the dispersion curves experimentally. The slider for the nearest neighbor force constant B was adjusted to get a good fit to the predicted dispersion relation. The same procedure was repeated for Cu and Pb to obtain their dispersion relations.

3.3.3 Density of states

The density of states was calculated for Al, Cu and Pb using the simulation tool by changing the parameters to fit each of the crystals and then clicking the CALCULATE button. This was done with number of bins at 30 and the data was copied using COPY GRAPH button. The NUMBER OF BINS was increased to 200 and the density of states was calculated again. The two graphs were superposed using STEAL DATA button.

The density of states was calculated again using the lattice dynamics simulation of *debye*, the Debye toggle button was clicked to display the density of □□ slider was adjusted to get a good match between the density of states from *debye* and Debye model for small value of q. This was done for each of Al, Cu and Pb.

3.3.4 Internal Energy

The internal energy associated with each of the frequency bins was □□□□ slider and MC steps were doubled a few times to get a good statistics for each

□□□□ at 100k. The calculation was repeated with□□□□at 10k to see the effect of temperature on the internal energy.

3.3.5 Heat Capacity

The heat capacities of Al, Cu and Pb were calculated using the lattice dynamics simulation of *debye* and the Debye model. The results were compared with result of neutron scattering experiment.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 EFFECT OF DIRECTION ALONG HIGH SYMMETRY ON DISPERSION CURVES FOR FCC CRYSTALS

The program *debye* calculates the phonon dispersion curve for fcc structure based on the lattice constant, atomic mass and a single force parameter B. The graphs in Figs 4.1 to 4.8 show dispersion curves for q values along family of directions <100>, <110>, and <111> respectively. From Figs 4.1, 4.2, and 4.3, it is observed that the dispersion curves are the same along the family of directions <100>, similarly in Figs 4.4, 4.5 and 4.6 and Fig 4.7 and 4.8 the dispersion curves are the same. In cubic crystal system, directions having the same indices regardless of order or sign are equivalent. For the family of directions <100> and <111>, the dispersion curves have two branches while for <110> there are three branches in the dispersion curve. This is so because for wave propagating along <100> and <111>, the two transverse polarizations are degenerate (i.e. they have the same frequencies) as a result of the 4 fold and 3 fold rotational symmetry along them respectively. For propagation along <110>, the transverse waves have different frequencies (not degenerate) as a result of the 2-fold symmetry rotation.

Dispersion relations along families of direction <100> and <111> closely follow the sinusoidal relationship developed for the simple monatomic chain with nearest neighbor interaction. The more complex shape of the dispersion curve

along <110> arises from second neighbor interaction between the planes of atoms which arise when there is only interaction between the nearest neighbor atoms.

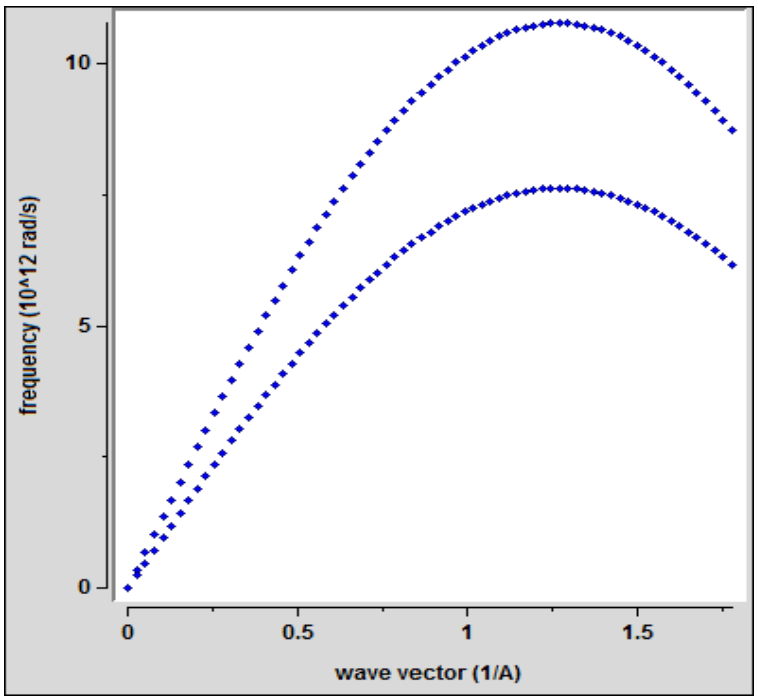


Fig 4.1: Dispersion curve along [100] direction

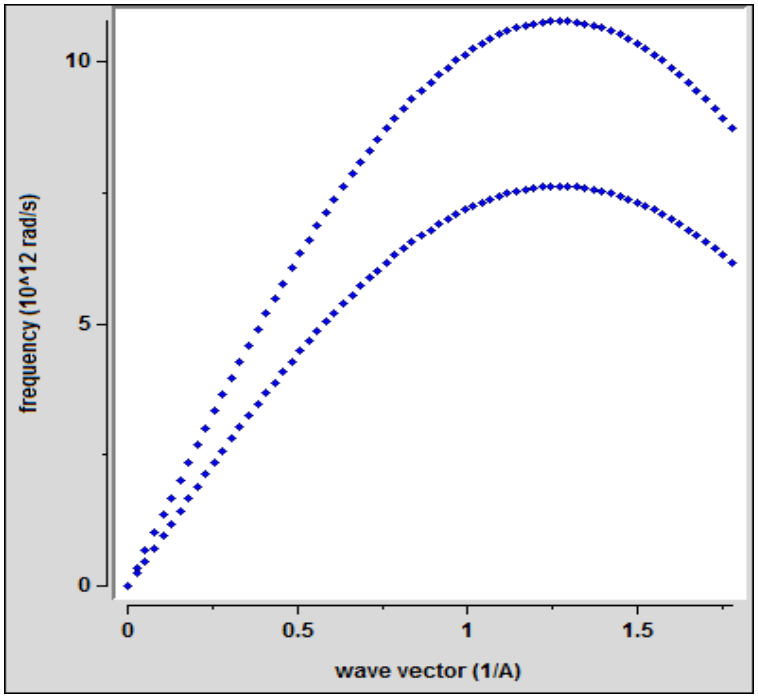


Fig 4.2: Dispersion curve along [010] direction

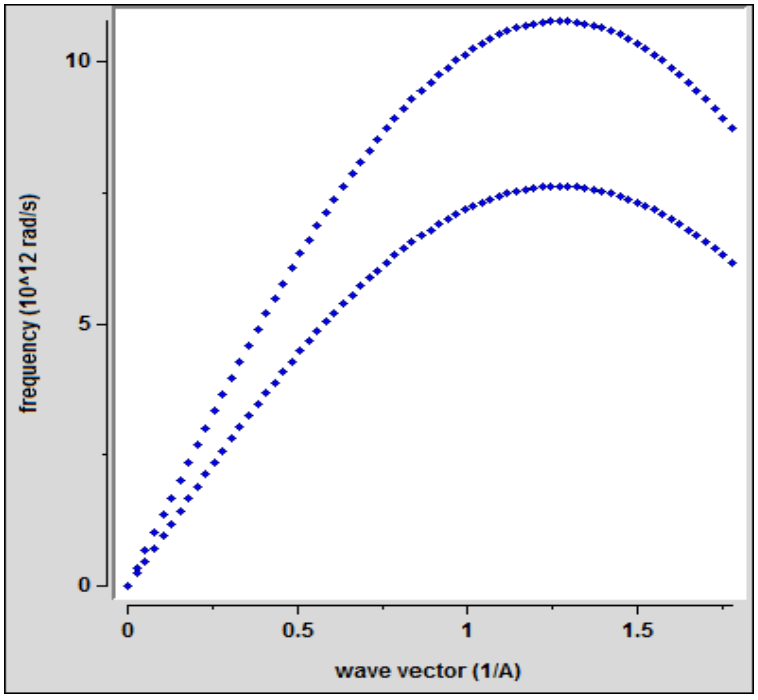


Fig 4.3: Dispersion curve along [001]

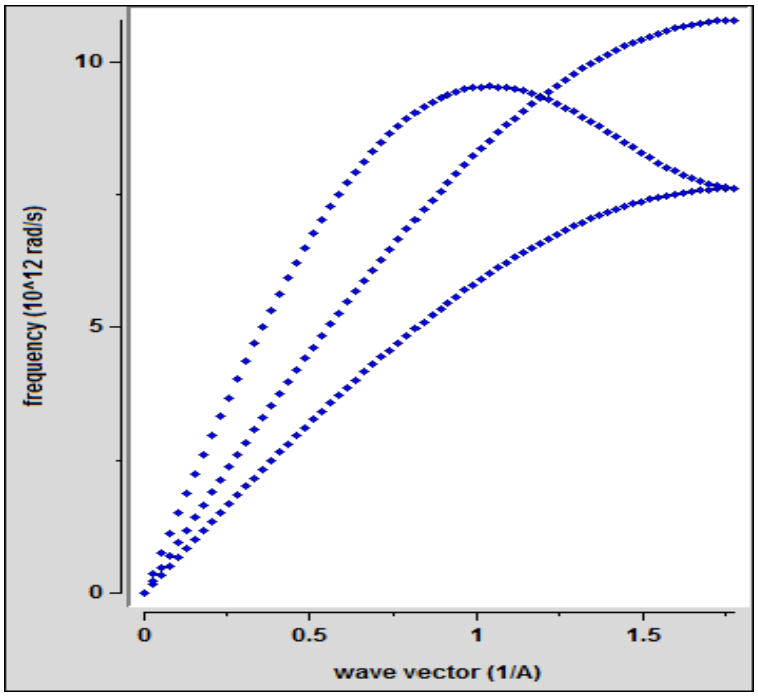


Fig 4.4: Dispersion along [110] direction

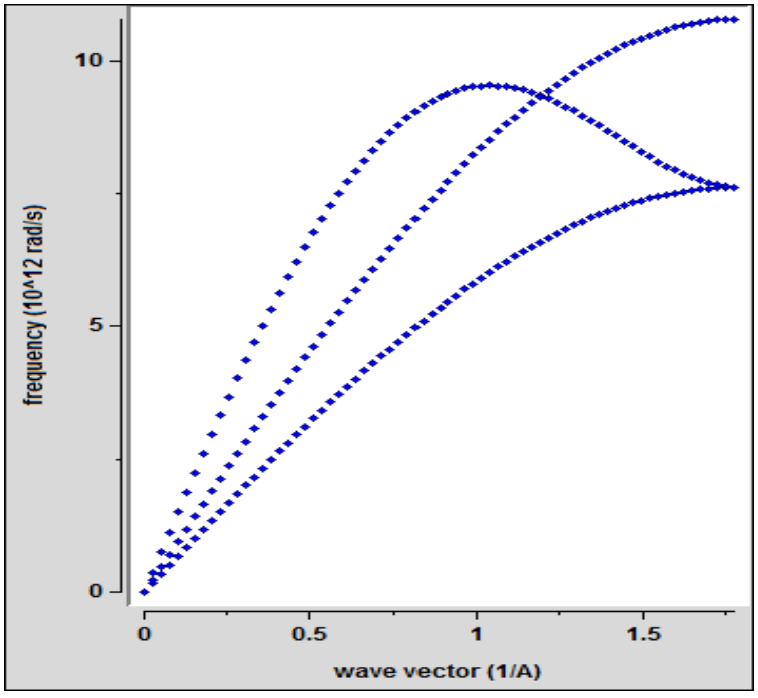


Fig 4.5: Dispersion curve along [101]

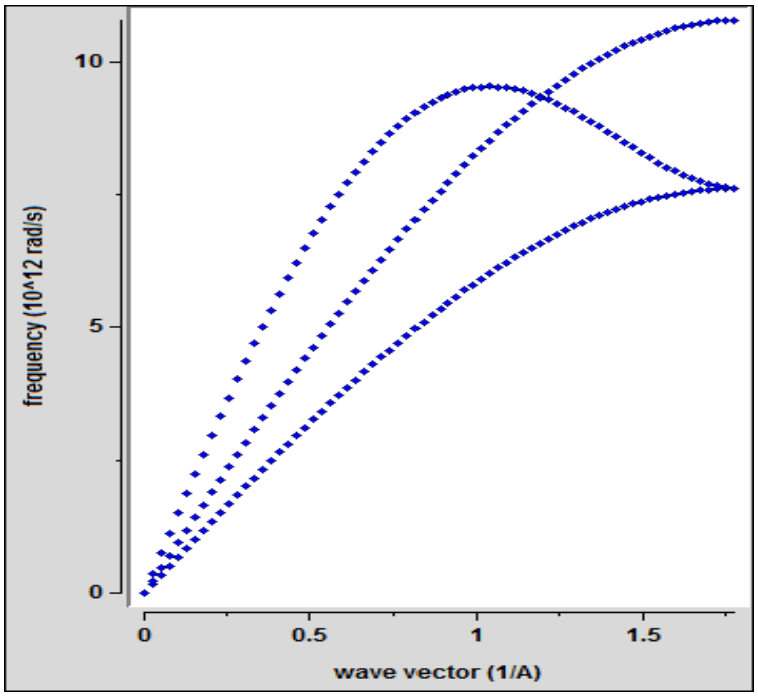


Fig 4.6: Dispersion curve along [011]

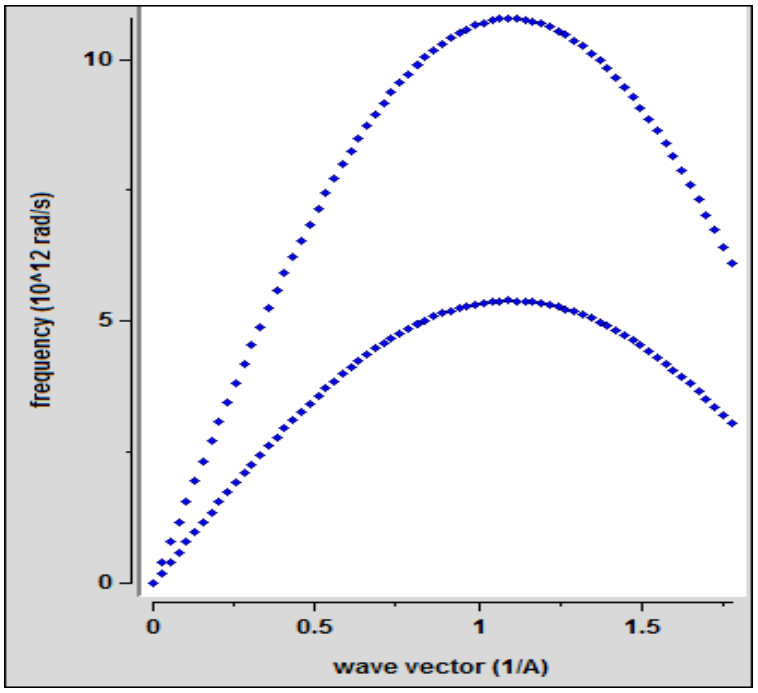


Fig 4.7: Dispersion curve along [111] direction

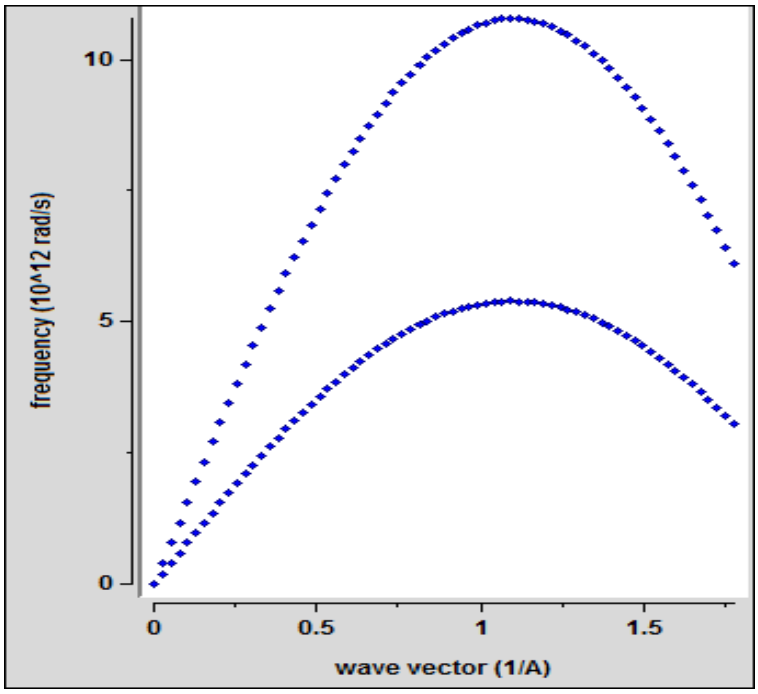


Fig 4.8: Dispersion curve along [222] direction

4.2 DISPERSION RELATION

Phonon dispersion curves for q values along high symmetry directions [100], [110] and [111] in reciprocal space are shown in Figs 4.9, 4.10 and 4.11 for Al, Cu and Pb respectively. The calculated result based on the *debye* model are compared with experimental data obtained from neutron scattering

A critical study of Fig 4.9 shows that the phonon dispersion relations along all the three principal symmetry directions of Al have been explained very well by the theoretical predictions. A look at Fig 4.10 shows that the calculated phonon dispersion relation of Cu has given an excellent account of experimental results quite close to experimental error. As far as phonons are concerned, like copper, the calculated results have almost reproduced the experimental results within the limits of the experimental error. The maximum deviation between the calculated and experimental phonons is of small order. In Fig 4.11, the agreement with

experimental data is satisfactory. The general observation is that all the computed results of phonon dispersion relation in Al, Cu and Pb reproduce very well the experimental results. However, in the case of Al and Cu the agreement is better.

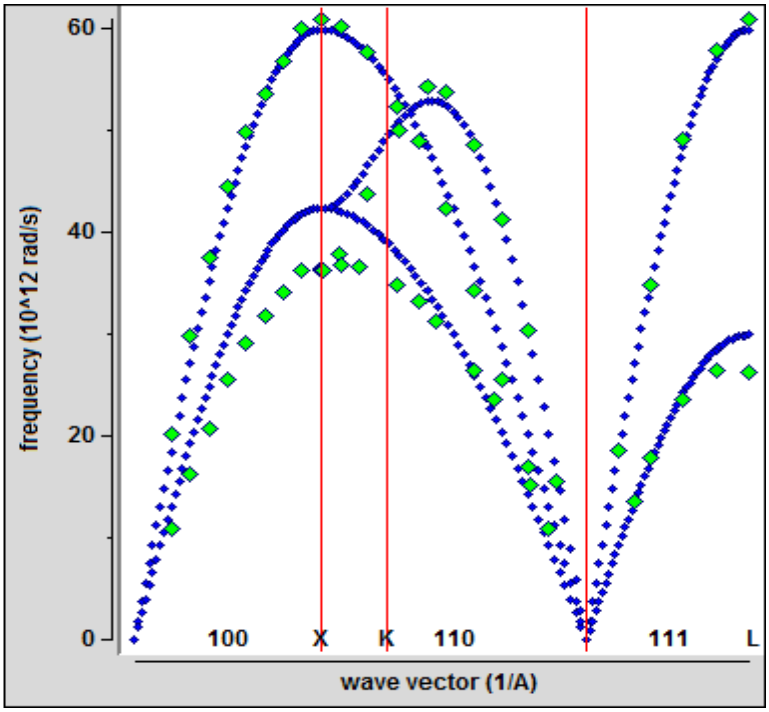


Fig 4.9: Phonon dispersion relations in Al. Blue dots represent simulation, green represent experimental result.

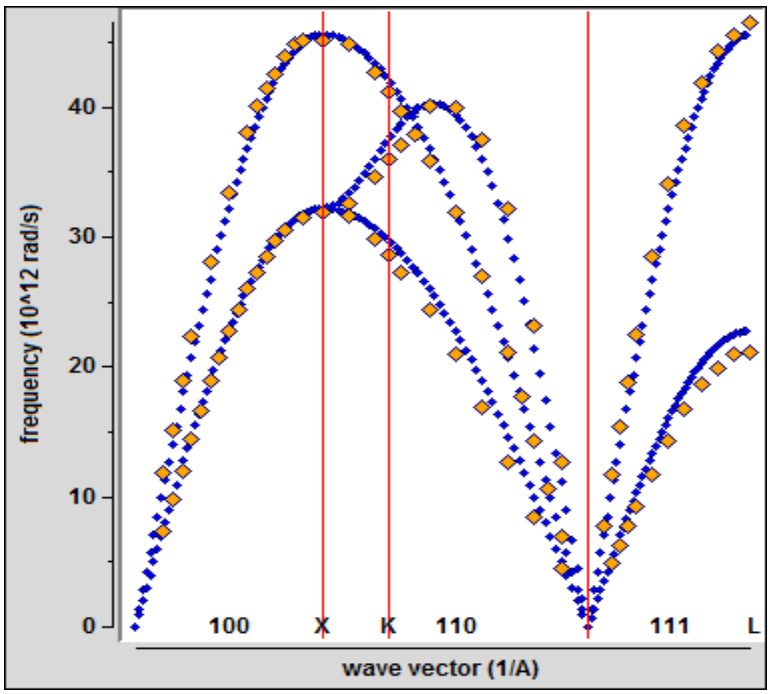


Fig 4.10: Phonon dispersion relation in Cu. Blue dots represent simulation, orange represent experimental result.

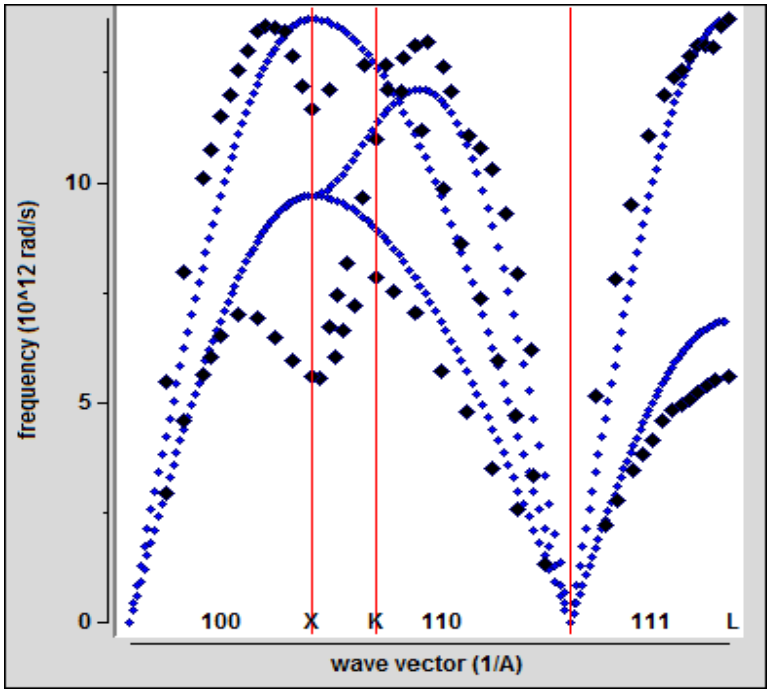


Fig 4.11: Phonon dispersion relation in Pb. Blue dots represent simulation, black represent experimental result.

4.3 DENSITY OF STATES

The phonon dispersion curves along high symmetry directions enable the computation of phonon density of states of a solid which has been done for Al, Cu and Pb by fitting the simulated curves with dispersion curve from neutron scattering. Figs 4.12, 4.13 and 4.14 show the calculated density of states for Al, Cu and Pb respectively. The calculations were done with number of bins at 30 and at 200. It is clearly seen from the figures that increasing the NUMBER OF BINS improve the resolution with finer and a lot more structures. But increasing the NUMBER OF BINS to get better resolution in frequency decreases the number of samples per bin. High resolution in frequency give a fine structure with a high signal to noise ratio but when the resolution is low, the structure is coarse with low signal to noise ratio. The trade-off between resolution and signal to noise ratio is a major problem not only in computational physics but in much of experimental physics. A two-fold increase in signal to noise ratio requires a four-fold increase in observing time.

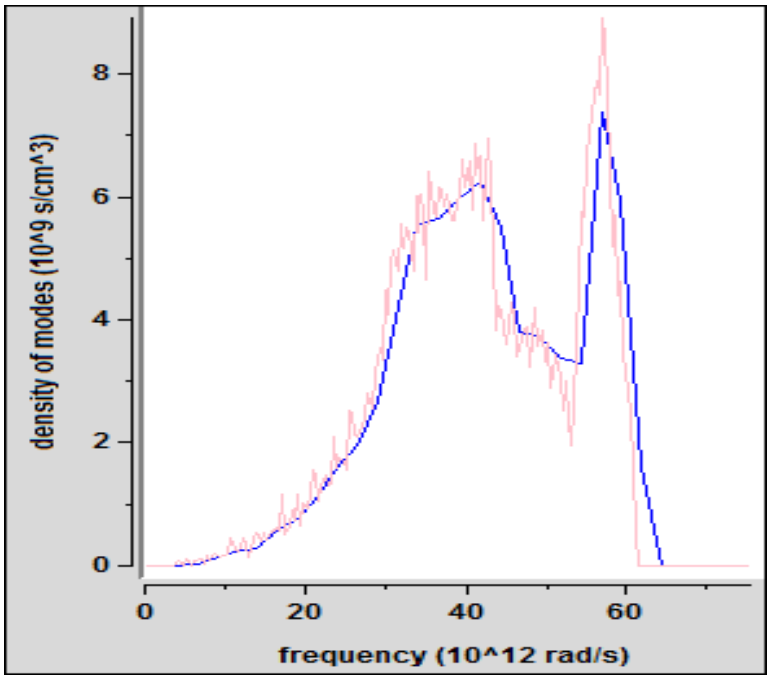


Fig 4.12: Density of State for Al with number of bins at 30 (blue line) and 200 (red line)

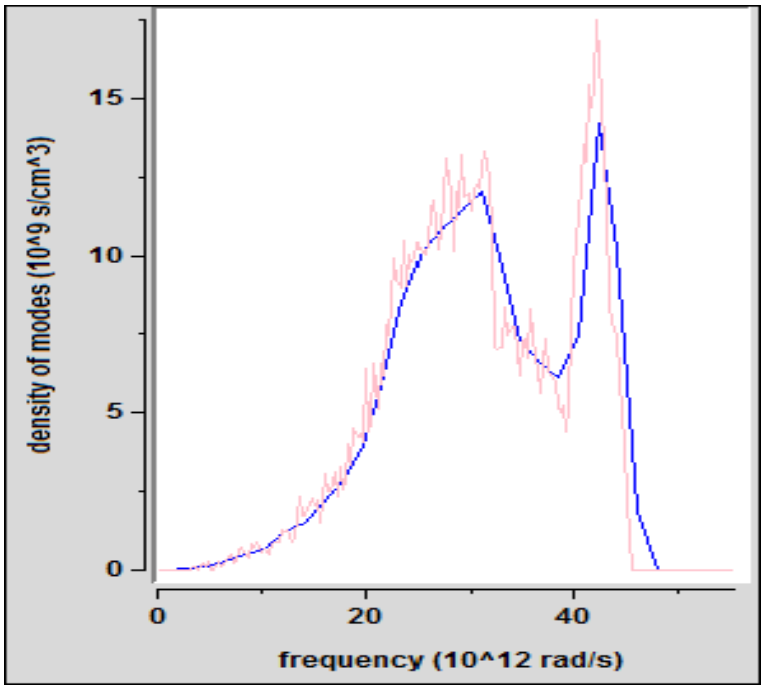


Fig 4.13: Density of State for Cu with number of bins at 30 (blue line) and 200 (red line)

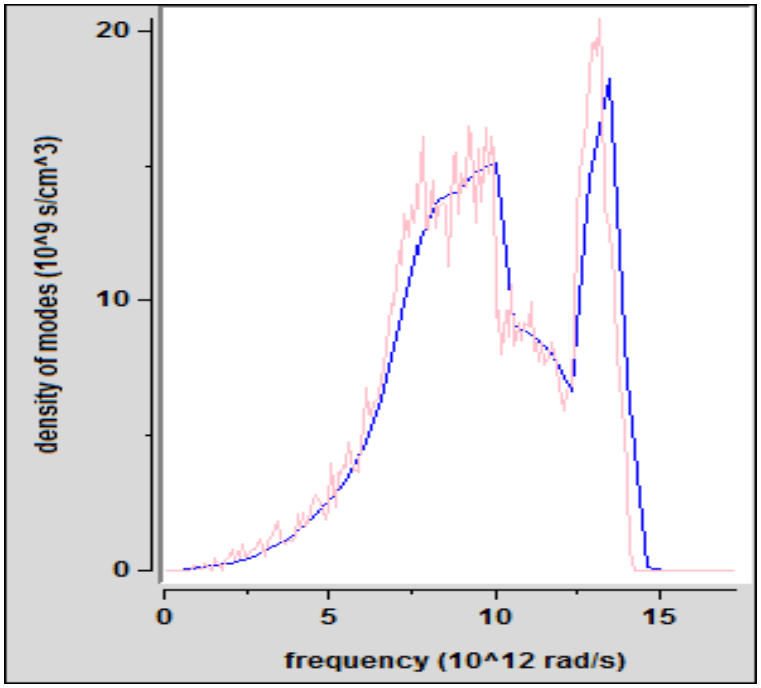


Fig 4.14: Density of State for Pb with number of bins at 30 (blue line) and 200 (red line)

Figures 4.15, 4.16 and 4.17 shows the plots for the predicted density of state from “debye” compared with density of state from the Debye model for Al, Cu and Pb respectively. For all the three crystals (Al, Cu and Pb), the calculated densities of states are in good agreement with the Debye density of state at low frequencies. Largest deviations are where the phonon modes approaches zero. The calculated density of states curves are complex because the 3-D zones have complicated shape and the longitudinal and transverse modes have different dispersions as seen earlier.

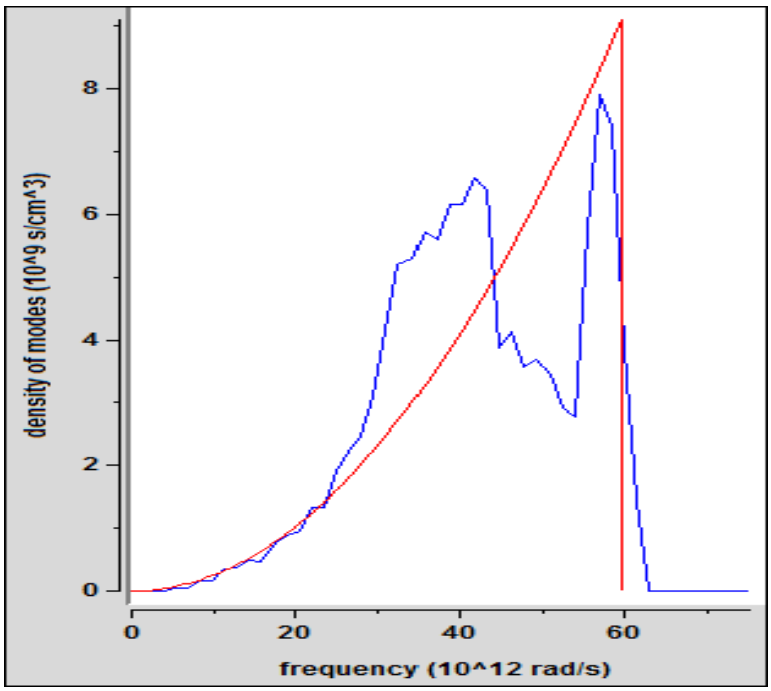


Fig 4.15: Calculated Density of State (blue line) compared with the Debye Density of State (red line) for Al

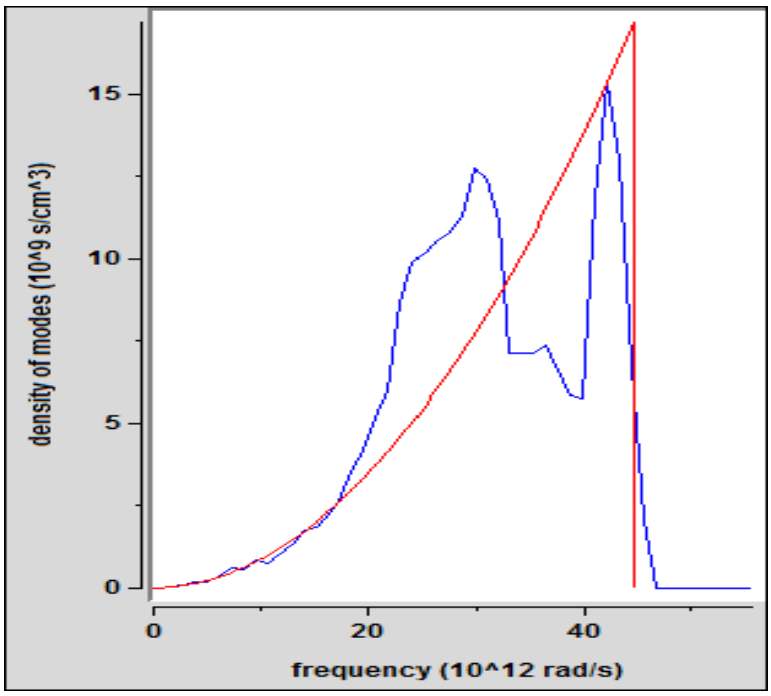


Fig 4.16: Calculated Density of State (blue line) campared with the Debye Density of State (red line) for Cu

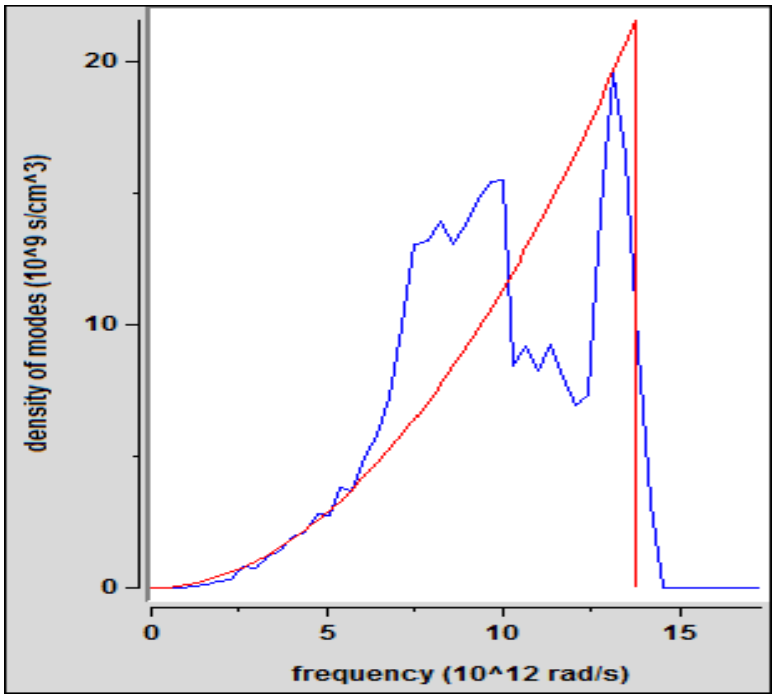
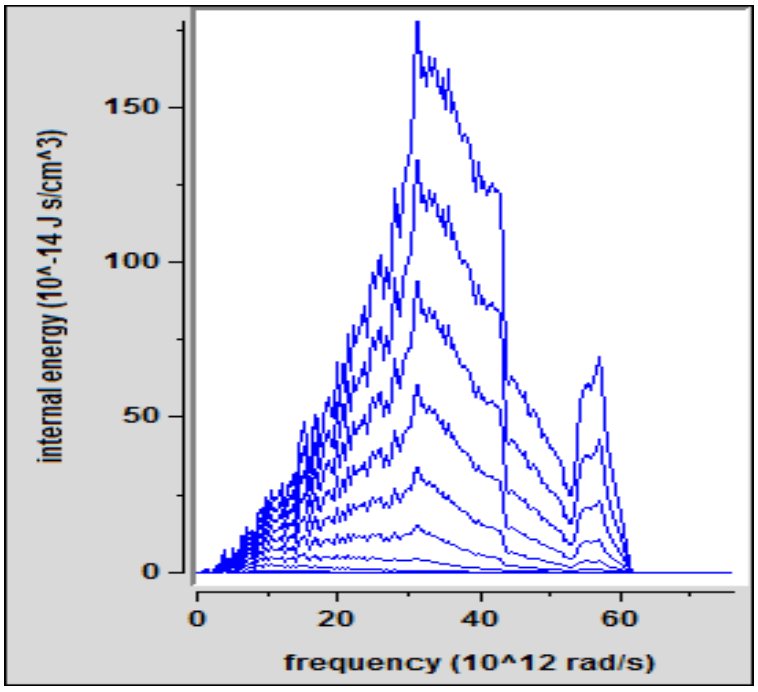


Fig 4.17: Calculated Density of State (blue line) campared with the Debye Density of State (red line) for Pb

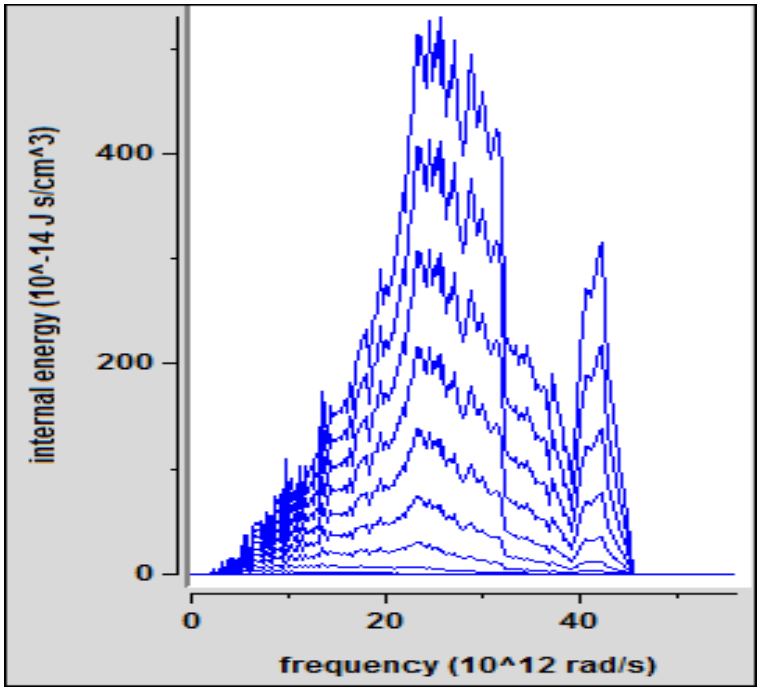
There are several peaks in the density of states. They correspond to high phonon density regions of the dispersion curve. The density of states is high in the regions where dispersion curve is flat. For frequencies at which the dispersion relation has a horizontal tangent, the derivative of density of states with respect to frequency has a singularity. The density of states for a crystal at small frequencies and wave vectors increases quadratically with frequency.

4.4 INTERNAL ENERGY

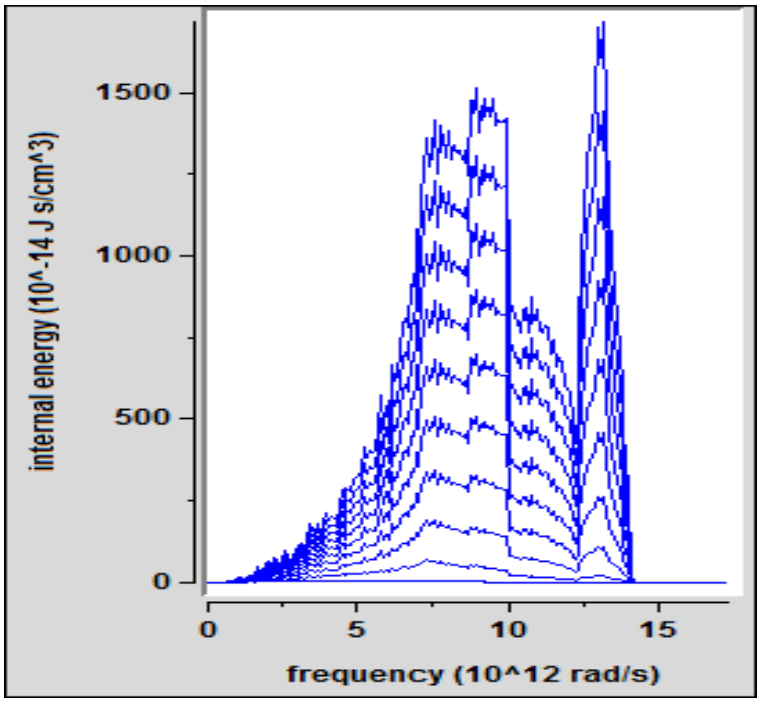
Figs 4.18, 4.19 and 4.20 show the plot of internal energy for ten different □□□□ at 100k for Al, Cu and Pb respectively. The plots are similar to density of states plots but in place of the number of modes in each bin of the density of states histogram, it shows the internal energy associated with each of the frequency bins. The area under any one of the curve is the internal energy of the crystal at the corresponding temperature. The area between two curves is the energy (heat) that must be added to the crystal to raise its temperature from the lower temperature to the higher of the two temperatures.



□□□□ at 100k

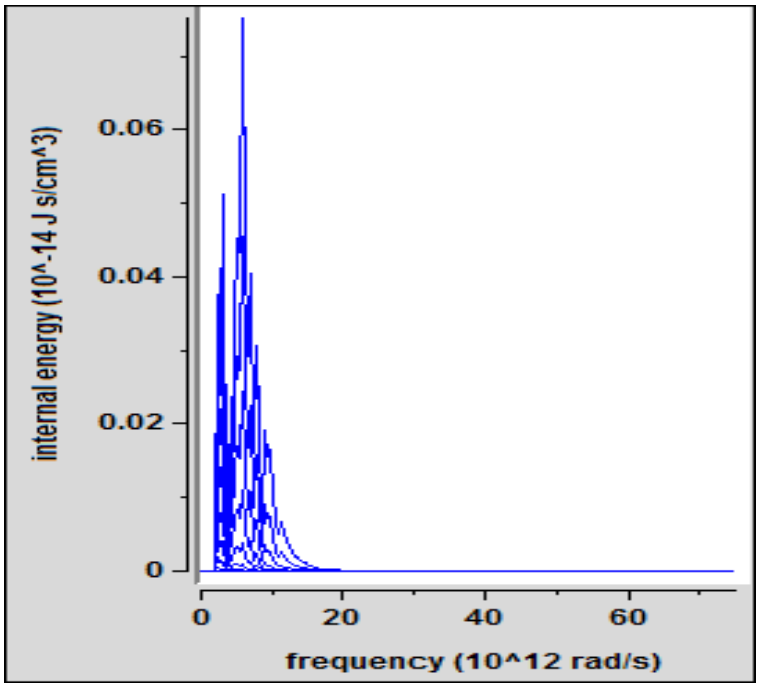


□□□□ at 100k

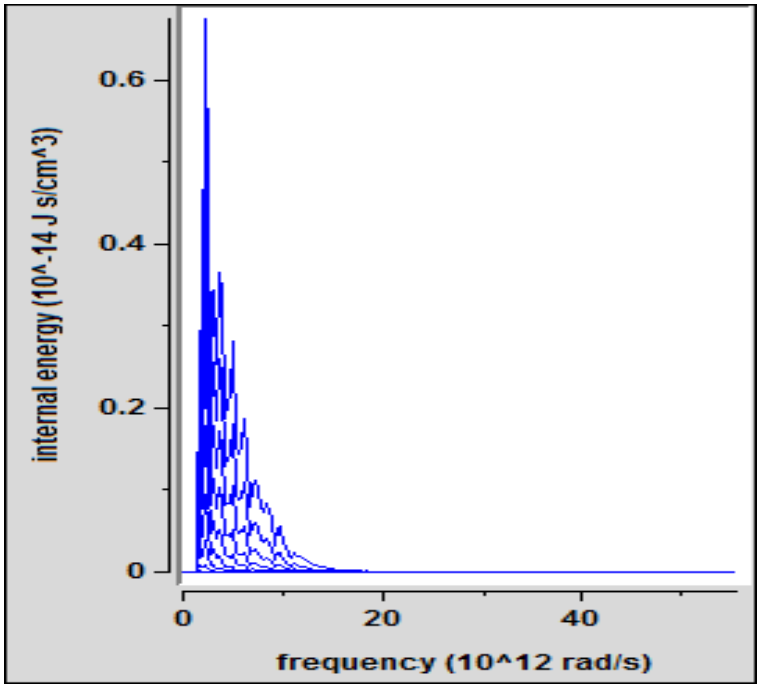


□□□□ at 100k

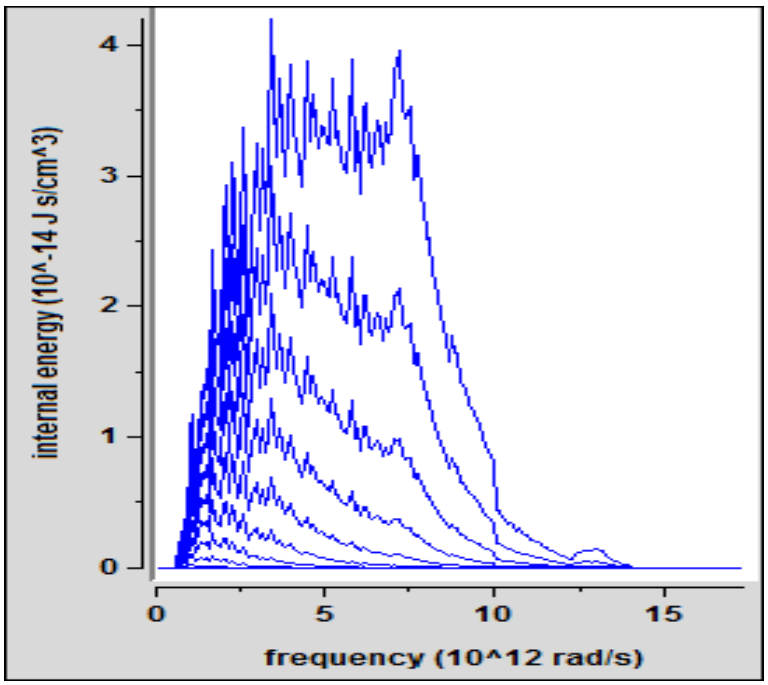
□□□□ at 10k. Comparing the plots for low and high □□□□, it is clearly seen that curves in the low temperature family are so distorted from the shape of the density of states curves. This is so because most of the thermal excitation energies of the crystals are associated with the low frequency modes.


internal energy (10^-14 J s/cm^3)
0.06
0.04
0.02
0
0
20
40
60
frequency (10^12 rad/s)

□□□□ at 10k


internal energy (10^-14 J s/cm^3)
0.6
0.4
0.2
0
0
20
40
frequency (10^12 rad/s)

□□□□ at 10k



□□□□ at 10k

4.5 HEAT CAPACITY

Figs 4.24, 4.25 and 4.26 compared the predicted heat capacity from the *debye* lattice dynamics simulation, the Debye model and heat capacity from neutron scattering experiment for Al, Cu and Pb respectively. A look at Fig 4.24 shows that both the predicted heat capacity from *debye* and heat capacity from Debye model are in good agreement with the heat capacity obtained from neutron scattering experimental but the agreement is better between the Debye heat capacity and the experimental result. A critical study of Fig 4.25 shows that the calculated and the Debye heat capacities have given an excellent account of the experimental results. Similarly Fig 4.26 gave a good agreement between the three results. In all the Figs, the agreements are better at low temperatures.

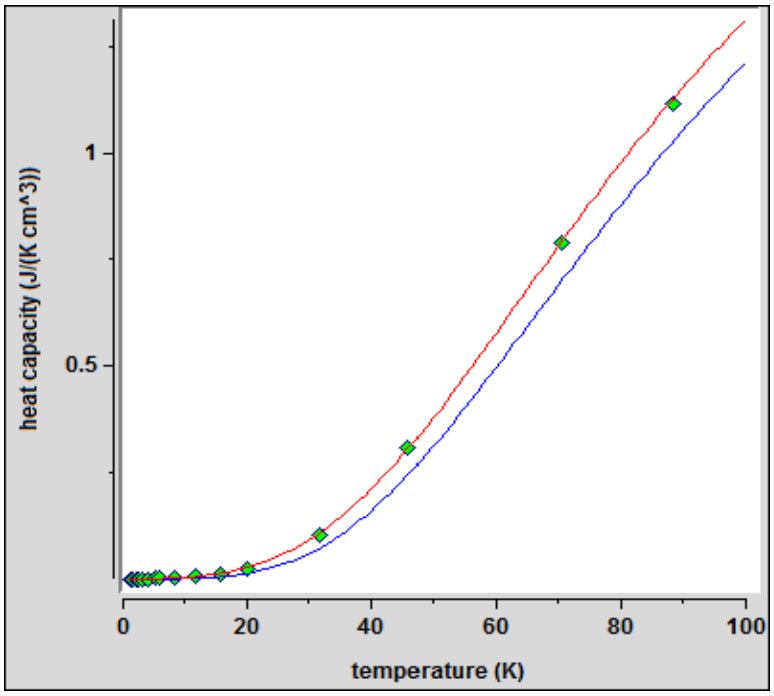


Fig 4.24: Heat capacity of Al. Numerical simulation in blue, the Debye model in red and the point represent neutron scattering experimental result (Landolt-Bornstein, 1981).

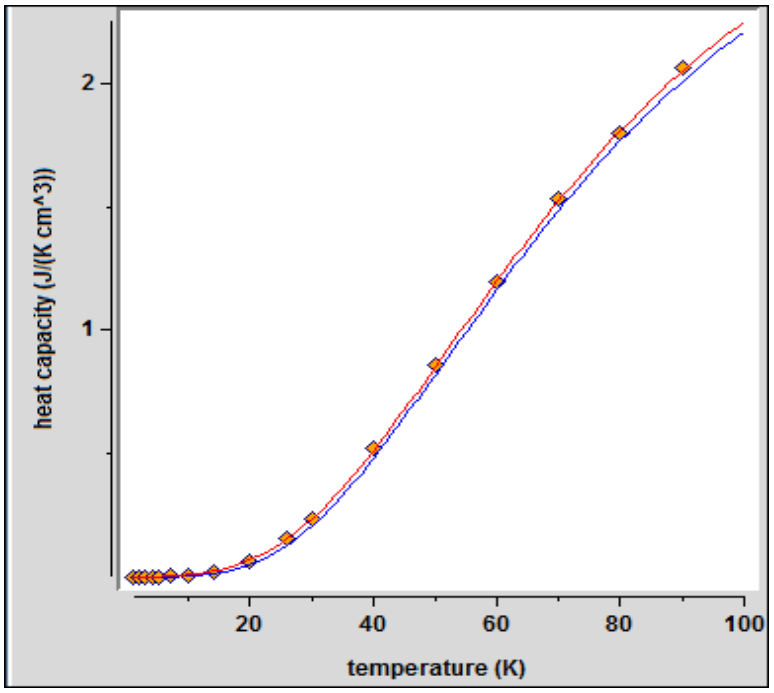


Fig 4.25: Heat capacity of Cu. Numerical simulation in blue, the Debye model in red and the point represent neutron scattering experimental result (Landolt-Bornstein, 1981).

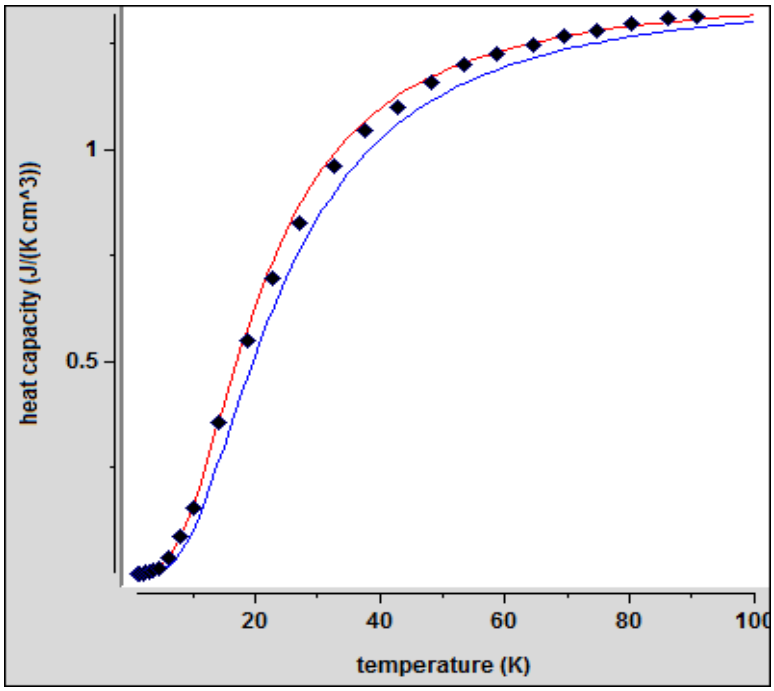


Fig 4.26: Heat capacity of Pb. Numerical simulation in blue, the Debye model in red and the point represent neutron scattering experimental result (Landolt-Bornstein, 1981).

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 SUMMARY

Lattice dynamical properties (dispersion relation, density of state and heat capacity) of fcc crystals have been presented based on lattice dynamics simulation code *debye* and the Debye model. The model is based on a harmonic interatomic potential with one free parameter, the force constant of the nearest neighbor interaction. Detailed solution of the equation of motion gives the dispersion relation for different branches along the three high symmetry directions and the results were compared with experimental data from neutron scattering. A simple

Monte-Carlo was used to determine the number of modes with frequencies in a given frequency interval and the density of phonon states. The heat capacity can be calculated once the density of states is known. The results obtained were compared with experimental data from neutron scattering.

The computed phonon dispersion relations for all the three metals, aluminum, copper, and lead reproduced well the experimental phonons within the limit of experimental error but the agreements are better in the case of aluminum and copper. The predicted densities of states from *debye* are in good agreement with the Debye density of state at low frequencies for all the three metals. Largest deviations are where the phonon modes approaches zero. Finally in comparing the experimental heat capacities with the predictions from *debye*, it was observed that there is a good agreement between the two results.

5.2 CONCLUSION

In conclusion, there is an excellent agreement between all the computed results of phonon dispersion relation, density of states and heat capacity with neutron scattering experimental result. Though the results were obtained with only one free adjustable parameter but the results are accurate. This demonstrates the efficiency and possibility of using this code in calculation and analysis of lattice dynamics properties.

5.3 RECOMMENDATION

The success of computer simulation of lattice dynamics is measured by the extent to which it can reproduce the experimental data on well studied structures. The simulation tool provides neutron scattering experimental result for only aluminum, copper and lead for comparison. It will be highly desirable if the force constant can be obtained mathematically for other fcc metal crystals and then used to simulate the lattice dynamics properties (dispersion relation, density of states and heat capacity) of these crystals.

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