

Phonon Dispersion Relation and Density of States in some Selected Fcc Metal Crystals

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Abstract: Phonon dispersion relation and density of states in Al and Cu were calculated using a theoretical model Debye. The calculations were done based on semi-classical approach within harmonic approximation considering only nearest neighbor interaction. The calculated results of phonon dispersion relation along the three principal symmetry directions were found to show reasonable agreement with the neutron scattering experimental results.

Keywords: density of states, dispersion relation, neutron scattering, phonon, wave vector

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I. Introduction

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 [1]-[3]. 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 [4], [5] and x-ray diffraction [6] 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 [7].

Several calculations of phonon spectra for fcc metal crystals have been published. Phonon dispersion relation calculated within density functional perturbation theory DFPT as implemented in ABINIT code using first principles have been performed [8]. The results were compared with experimental data as well as the results of previously done ab initio calculations based on the direct method and a slightly better agreement of density functional perturbation theory with experiment was observed. A new method of mapping phonon dispersion relations based on momentum-resolved x-ray calorimetry was developed by Xu et al [1]. X-ray scattering intensities were measured at selected points in reciprocal space with suitably chosen polarization configurations; 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 modified the original model of Sarkar *et al.* for cubic metals in extending the ion-ion interaction, ion-electron interaction and the introduction of crystal equilibrium condition [7]. 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. Born-von Kármán theory of lattice dynamics and the modified analytic embedded atom method were employed by Jun 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 [9]. The results show that the shapes of dispersion curves at high pressures are very similar to that at zero pressure. Direct method and ab initio force constants were also used to calculate phonon dispersion curves and phonon density in Al [10]. The force constants were determined from the Hellmann-Feynman forces induced by the displacement of an atom in the 2 x 2 x 2 fcc crystallographic super cell. This size of the super cell 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. Phonon dispersion relations for Al were also calculated using a small displacement method by a program PHON. The calculations were done with $4 \times 4 \times 4$ and $8 \times 8 \times 8$ super cell (small displacement) and equispaced grid of q-points (linear response) for each [11].

In this paper dispersion relation and density of states in harmonic approximation with nearest neighbor interaction is implemented using a theoretical model *debye* which utilizes experimentally determined macroscopic mechanical properties of the materials, aluminum and copper to deduce a value for the nearest neighbor interaction constant. This constant is 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.

II. Method

Aluminum and copper possesses an fcc structure in which every atoms under goes small oscillation round its equilibrium position. Given a harmonic inter atomic 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 \mathbf{q} [12]. As we will see below the phonon frequency ω of each mode is closely related to the eigen values of the dynamical matrix $D(\mathbf{q})$, which in turns depends on the atomic arrangement of the dynamical matrix and the inter atomic potential.

The total harmonic potential of a three-dimensional crystal can be written in terms of the displacement vector \mathbf{u} of each atom from its equilibrium position \mathbf{R} as:

$$U^{harm} = \sum_{RR'} \mathbf{u}(\mathbf{R}) \cdot \mathbf{D}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{u}(\mathbf{R}') \quad (1)$$

Where the sum extends over all pairs of atoms located at \mathbf{R} and \mathbf{R}' . The quadratic matrix $\mathbf{D}(\mathbf{R} - \mathbf{R}')$ can be specified in terms of the inter atomic pair potential $\Phi(\mathbf{R} - \mathbf{R}')$.

From the potential, it then follows that the motion of atom of mass M is determined by:

$$M\mathbf{u}(\mathbf{R}) = -\sum_{\mathbf{R}'} \mathbf{D}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{u}(\mathbf{R}') \quad (2)$$

The equation of motion has solutions of the form:

$$\mathbf{u}(\mathbf{R},t) = \epsilon_p e^{i[\mathbf{q} \cdot \mathbf{R} - \omega_p(\mathbf{q})t]} \quad (3)$$

Where ϵ_p ($p=1,2,3$) is one of the three polarization vectors and $\omega_p(\mathbf{q})$ is the phonon frequency associated with polarization p and wave vector \mathbf{q} . as it turns out, the polarization vectors and their associated phonon frequencies can be determined from the dynamical matrix $\mathbf{D}(\mathbf{q})$:

$$\mathbf{D}(\mathbf{q}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) e^{-i\mathbf{q} \cdot \mathbf{R}} \quad (4)$$

The three polarization vectors ϵ_p are the real three eigen vectors of $\mathbf{D}(\mathbf{q})$ and the angular frequency ω_p is given in terms of the corresponding eigen value λ_p :

$$\omega_p(\mathbf{q}) = \sqrt{\lambda_p(\mathbf{q})/M} \quad (5)$$

If we assume that the interatomic pair potential Φ contributes to the sum in equation (1) only for nearest neighbors then equation (4) reduces to a sum over 12 nearest neighbors \mathbf{R} in an fcc crystal:

$$\mathbf{D}(\mathbf{q}) = B \sin^2\left(\frac{1}{2}\mathbf{q} \cdot \mathbf{R}\right) \hat{\mathbf{R}}\hat{\mathbf{R}} \quad (6)$$

Where $\hat{\mathbf{R}}\hat{\mathbf{R}}$ is the dyadic (the outer product) $(\hat{\mathbf{R}}\hat{\mathbf{R}})_{ij} = \hat{R}_i \hat{R}_j$ of the unit vectors $\hat{\mathbf{R}} = \mathbf{R}/R$. The force parameter B is given in term of the inter atomic potential Φ as $B = 2 \Phi''(d)$, where d is the equilibrium nearest neighbor distance ($d=a/\sqrt{2}$) for an fcc crystal.

A numerical simulation was carried out by a computer program *debye* to obtain the atomic force constant, solve the dynamical matrix from Eq.4 for the wave vectors and plot the phonon dispersion relation from Eq.5 in all the three principle symmetry directions ([100], [110] and [111]) for Al and Cu.

To determine the phonon density of states, $g(\omega)$, a simple Monte Carlo scheme was used to calculate the number of phonon frequency $N(\omega)$ in the frequency interval ω to $\omega + \Delta \omega$ by randomly sampling the wave vector in the first brillouin zone, determine the dynamical matrix \mathbf{D} in Eq.6 for each of the sampled wave vectors \mathbf{q} , and then compute the three phonon frequencies $\omega_p(\mathbf{q})$ from the three eigen values according to Eq.5. $N(\omega)$ is then used to calculated the density of state using:

$$g(\omega) = \frac{N(\omega)}{N_{MC} \Delta \omega} \frac{4}{a^3} V \quad (7)$$

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 $n = 4/a^3$.

III. Result And Discussion

The simulated phonon dispersion curves along high symmetry directions [100], [110] and [111] are shown in Figs.1 and 2 for Al and Cu, respectively, together with available experimental results from neutron scattering for comparison, where the blue curves represent the present simulations, the green and orange points are the experimental data for Al and Cu respectively, the notations X, K and L are assigned to various symmetry points on the surface of the first Brillouin zone for fcc lattice.

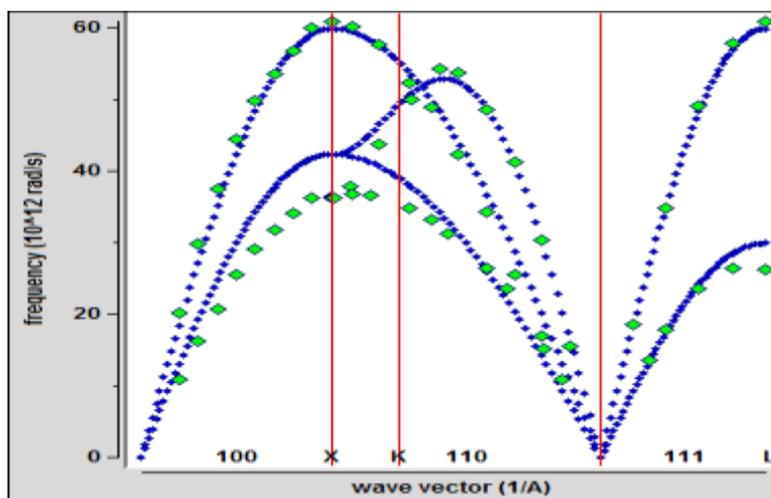


Fig1: Phonon dispersion relation in Al. Blue points represents present calculation, green represent experimental points

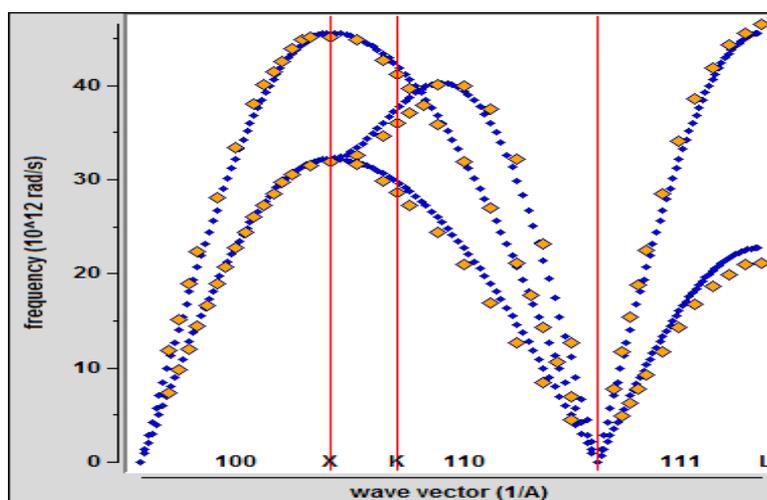


Fig 2: Phonon dispersion relation in Cu. Blue points represents present calculation, orange represent experimental points

From Figs. 1 and 2, we can see that the simulated phonon dispersion curves of the fcc metals Al and Cu are generally in good agreement with the available experiment results. The phonon dispersion curves reproduced very well the experimental results along high symmetry directions near lower frequency. In the high-frequency limit, it can be seen that there is a slight deviation from the result obtained experimentally. The deviations of the simulation results from experimental results appear more in Al especially between the frequency range of $20 \times 10^{12} \text{ rad/s}$ to $40 \times 10^{12} \text{ rad/s}$. The deviations may be as a result of the simulation done within harmonic approximation with only one adjustable parameter. Consequently, the above results indicate that the “debye” model provides a satisfactory description of the phonon dispersion in fcc metals Al and Cu. It can also be observed from the figures that the shapes of dispersion curve of Al and Cu are very similar to each other though the numerical size varies. The similarity of the dispersion curves for these metals is due to the fact that they are both fcc metals with similar arrangement of atoms in crystal structure.

The phonon dispersion curves along high symmetry directions enable the computation of phonon density of states. The calculated density of states function, conventionally normalized to $\int_0^\infty d\omega g(\omega) = 3N$, (where $3N$ is the number of phonon modes in a crystal with N atoms) are shown in Fig3 and Fig4 for Al and Cu respectively

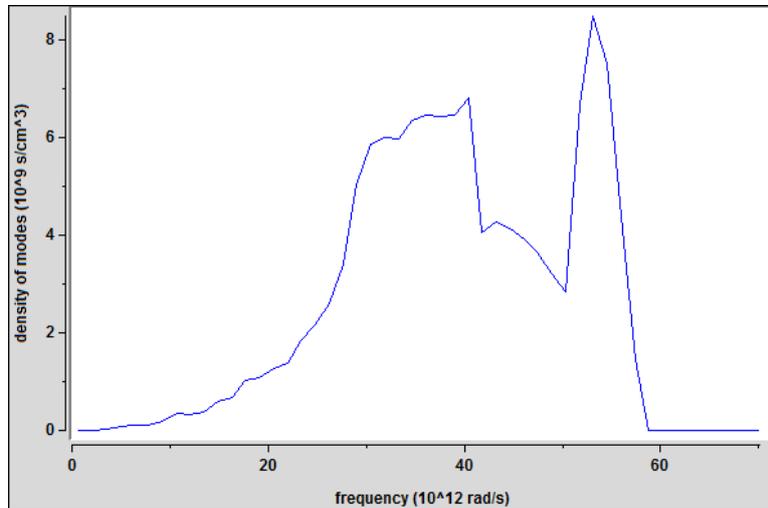


Fig 3: The calculated phonon density of states in Al.

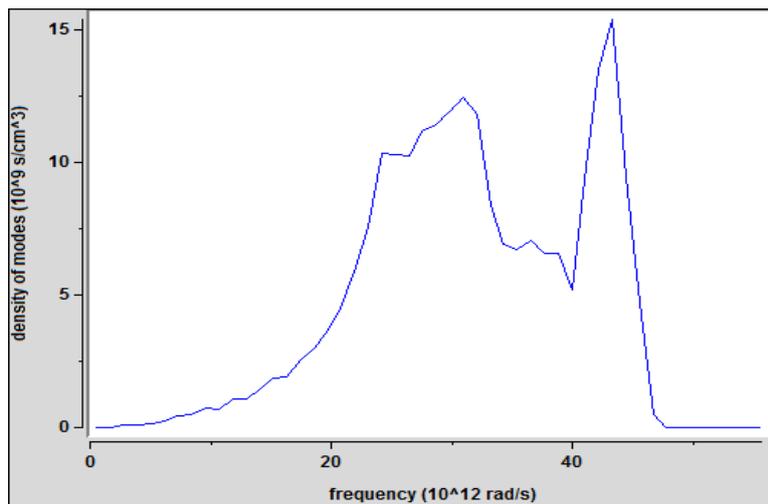


Fig 3: The calculated phonon density of states in Cu.

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. The density of state curves shows the most resonant behavior at the frequency of $53.38 \times 10^{12} \text{ rad/s}$ and $42.86 \times 10^{12} \text{ rad/s}$ for Al and Cu respectively at 100K. 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.

IV. Conclusion

Phonon dispersion relation and density of state for Al and Cu investigated. There is an excellent agreement between the computed results of phonon dispersion relation and neutron scattering experimental result in both Al and Cu. The fact that the characteristics features in the dispersion relation were well reproduced by the calculation demonstrates a successful test of the validity of modern theory to reproduce experimental results. This shows efficiency and possibility of using the code *debye* in calculation and analysis of other lattice dynamics properties.

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