ORIGINAL PAPER

PHONON DYNAMICAL STUDY OF COPPER BY USING [VTBFS] MODEL

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Abstract. *The lattice dynamical investigation of Copper (Cu) has been made on the basis of improved by van der Waals three body force shell models [VTBFSM]. The present model includes van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of both ion polarizable rigid shell models (RSM). van der Waals interactions and three-body interactions in the structure of Rigid Shell model (RSM) with short-range interactions viable up to the second neighbor. In the present communication author has reported thermodynamic properties, dispersion relation and density of state (DOS) of copper by the utilization of the present model [VTBFS] and Phonon-programming. We concentrated on here the lattice dynamics, metal Cu on our approach by figuring phonon dispersion relations along the three principal symmetry directions, entropy, internal energy, free energy, heat capacity at the temperature of 300K and 1356K and density of state (DOS) in THz. The model expectations are sensible for the total harmonic dynamical conduct of the crystals and will concurrence with their experimental reported results.*

Keywords: *Phonon; Phonon properties, phonon dispersion curve, density of state & Van der Waals Interaction.*

1. INTRODUCTION

In recent years, there has been considerable interest in the theoretical and experimental studies of inelastic neutron scattering, a huge amount of experimental data has been accumulated for phonon dispersion curves of various lattice dynamics is one of the methods by help of it the complete structure properties of copper Cu can be analyze. The pioneer work of Kellerman [1] in the lattice dynamics of the alkali halides has been devoted a considerable attention theoretically as well as experimentally. Theory of ionic solids by Lowdin's [2] and Lundqvist's [3] leads to a many–body force of which the three-body component is the first important term, which explains the Couchy discrepancy in alkali halides in an approximate way. Science it is, considering that crystal lattice as static and thus completely ignores the displacements of the electron clouds relative to the corresponding nuclei. In the vibrating lattice the shells move relative to their respective cores and thus give rise to electronic polarization. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom become an electric dipole. The instantaneous dipole moment of a closed shell atom induces as the van der Waals interaction potential. The present model includes van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of both ion polarizable rigid shell model (RSM). Thus, the inclusion of (VWI) and (TBI) effects in (RSM) [4] will employ the Hietler London and the free-electron approximations. The effects of van der Waals interactions and three-body interactions in the

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framework of ion polarizable rigid shell model (RSM) with short-range interactions effective up to the second neighbour. Therefore, it may be inferred that the most realistic model for complete harmonic dynamical behavior of the crystals under consideration can be developed by introducing the effect of van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of (RSM). The present model is known as van der Waals three-body force shell model which is used in study of noble metal copper (Cu).The structure of Cu is fcc and each copper atom has 12 nearest neighbors .Copper is a soft, malleable and ductile metal with very high thermal and electrical conductivity. It became stronger and more ductile as temperature decreases. The electrical conductivity of copper can be reduced by thermal vibration and crystal imperfections. The lattice parameter from neutron diffraction at room temperature were found equal a=b=c=3.615^{0}A and ($\alpha=\beta=\gamma=90^0$) [5].

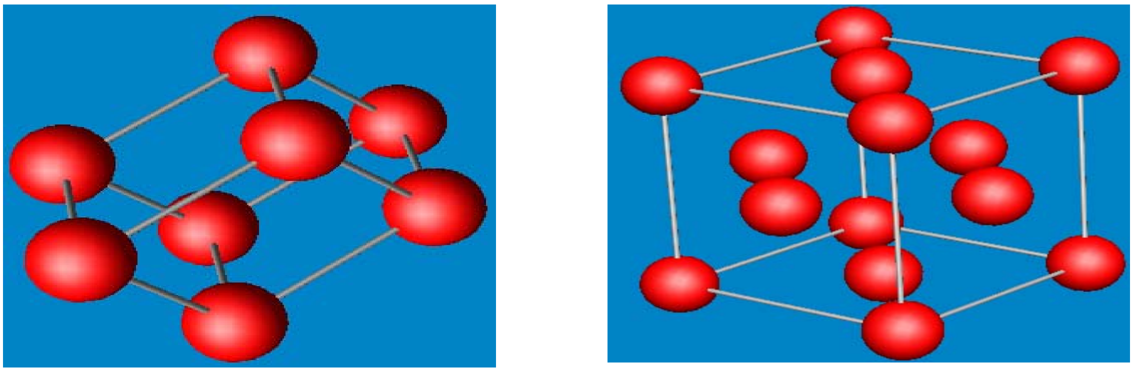

Figure 1.

a) Primitive unit Shell Structure of Cu. **b) Crystallographic unit shell of Cu.**

The crystal structures of Cu are illustrated in Fig.1 due to availability of experimental data, the theoretical lattice dynamical study for Cu has reported in present communication. The incorporation of the effects of van der Waals & three-body interactions [6-10] has used in lattice dynamical study of Copper. The present model is based on the framework of ion polarizable (RSM) by Dick and Over Hauser [11] and Woods et al [4] by two different groups of workers, which has been applied for study of lattice property with short-range interactions effective up to the second neighbor. In view of the remarkable success achieved from rigid ion model (RIM) and rigid shell model (RSM) to describe the complete lattice dynamics of alkali halides it seems worthwhile to explore the adequacies of (RIM) and (RSM) in doing so far Cu.

2. THEORETICAL FRAMEWORK OF THE PRESENT MODEL

The developed model has used for fcc structure, which includes the effect of van der Waal's interactions (VWI) and three body interactions (TBI) in the frame work of rigid shell model (RSM) where short range interactions are effective up to the second neighbours and known as van der Waal's three body force shell model [VTBFS].The general formalism of [VTBFSM] can be derived from the crystal potential whose relevant expression per unit cell is for fcc crystals, the cohesive energy for a particular lattice separation *(r)* has been expressed as

$$\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI} \tag{1}$$

where, First term Φ^C is Coulomb interaction potential. This interaction potential is long-range in nature. Thus, total Coulomb energy for the crystal is

$$\Phi^C(r) = \sum_j{}' \Phi^C \alpha_M \frac{Z^2 e^2}{r_0}\left(r_{ij}\right)$$

where α_m is the Modelung constant and r_0 is the equilibrium nearest neighbours distance. Second term Φ^R is short-range overlap repulsion potential.

$$\Phi^R\left(r_{ij}\right) = a r_{ij}^n \qquad \text{(Born Potential) and}$$

$$\Phi^R\left(r_{ij}\right) = b \exp.\left(-r_{ij}/\rho\right) \qquad \text{(B-M) Potential)}$$

where, a (or b) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively. Third term Φ^{TBI} is three-body interactions potential. As a natural consequence of the anti-symmetry requirement on the wave function[12], this alteration in the electronic charge density causes a charge depletion which depends on the inter nuclear separation and interacts with all other charges via Coulomb force law and gives rise to long-range TBI introduced by Lowdin [2] and Lundqvist [3]. This interaction potential is expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0}\left[\frac{2n}{Z} f(r)_0\right]$$

where, the term $f(r)_0$ is a function dependent on the overlap integrals of the electron wave-functions. Φ^{TBI} is also long-range in nature hence it is added to the $\Phi^{C\cdot}$ and last term Φ^{VWI} is van der Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms closely the method used by Wood et.al[4]. By using the potential energy expression (1), the equations of motion of two cores and two shells can be given as.

$$\omega^2 MU=(R+Z_m C Z_m)U+(T+Z_m C Y_m)W \tag{2}$$

$$0=(T^T+Y_m C Z_m)U+(S+K+Y_m C Y_m)W \tag{3}$$

Here, *U* and *W* are vectors describing the ionic displacements and deformations respectively, *Zm* and *Ym* are the diagonal matrices of modified ionic charges and shell charges, respectively, *M* is the mass of the core, *T* and *R* are the repulsive Coulombian matrix respectively; *C'* and *Ym* are the long-range interaction matrices which includes Coulombian and three-body interaction respectively; *S* and *K* are core-shell and shell-shell repulsive interaction matrices respectively T^T is the transpose of the matrix *T*. All these variables are as described in [3].The introduction of VWI and TBI in the framework of RSM with the elimination of *W* from eqs (2) and (3) leads to the secular determinant:

$$\left| D\left(\vec{q}\right) - \omega^2 MI \right| = 0 \tag{4}$$

Here $\underline{D}$ $(\vec{q})$ is the (6 x 6) dynamical matrix for Rigid Shell model expressed as:

$$\underline{D}(\vec{q}) = \left(\underline{R}' + \underline{Z}_m \underline{C}'\underline{Z}_m\right) - \left(\underline{T} + \underline{Z}_m \underline{C}'\underline{Y}_m\right)\times \left(\underline{S} + \underline{K} + \underline{Y}_m \underline{C}'\underline{Y}_m\right)^{-1}\left(\underline{T}^T + \underline{Y}_m \underline{C}'\underline{Z}_m\right) \tag{5}$$

The numbers of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells. This assumptions leads to $\underline{R} = \underline{T} = \underline{S}$ $\underline{C}'$ is modified long-range interaction matrix have been given by [12].

$$C' = C + \left(Z_m^{-2} Z r_0 f_0'\right)V \tag{6}$$

where f_0' is the first –order space derivative and Z_m modified ionic polarizability
If we consider only the second neighbour dipole-dipole van der Waals interaction energy, then it is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V\left|\frac{C_{++} + C_{--}}{6r^6}\right| = \Phi^V(r) \tag{7}$$

where, S_v is lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively.

2.1. VIBRATIONAL PROPERTIES OF Cu

The term fo is function dependent on overlap integrals of electron wave functions. Similarly, expressions for two distinct optical vibration frequencies (ω_L and ω_T) are obtained as:

$$\left(\mu\omega_L^2\right)_{q=0} = R' + \frac{(Z'e)^2}{Vf_L}\frac{8\pi}{3Vf}\left(Z_m^{\;2} + 6\zeta'^2\right) \tag{8}$$

$$\left(\mu\omega_T^2\right)_{q=0} = R_0' - \frac{(Z'e)^2}{Vf_T}\frac{4\pi}{3vf}Z_m^2 \tag{9}$$

$$R_0' = R_0 - e^2\left(\frac{d_1^{\;2}}{\alpha_1} + \frac{d_2^{\;2}}{\alpha_2}\right);\ Z' = Z_m + d_1 - d_2,\qquad R_0 = \frac{Z^2e^2}{V}(A_{12} + 2B_{12})$$

$$f_L = 1 + \left(\frac{\alpha_1 + \alpha_2}{V}\right)\frac{8\pi}{3V}\left(Z_m^2 + 6\xi'^2\right)$$

$$f_T = 1 - \left(\frac{\alpha_1 + \alpha_2}{\mathrm{v}}\right).\frac{4\pi}{3V}\left(Z_m^{\;2}\right)$$

where α_1, α_2 electrical polarizabilites and Y_1, Y_2 are shell charge parameters of positive and negative ions.

2.2. THERMODYNAMICALLY PROPERTIES OF Cu

The specific heat at constant volume C_υ at temperature *T* is expressed as

$$C_\upsilon = 3NK_B \frac{\int_0^{\upsilon_m} \left\{ \left(\frac{h\upsilon}{k_B T} \right)^2 e^{h\upsilon / k_B T} \right\} G(\upsilon) d\upsilon / \left(e^{h\upsilon / k_B T} - 1 \right)^2}{\int_0^{\upsilon_m} G(\upsilon) d\upsilon} \tag{10}$$

where, υ_m is the maximum frequency, *h* is the Planck's constant and K_B is the Boltzmann's constant. The equation (10) can be written as a suitable form for a computational purpose as

$$C_\upsilon = 3NK_B \frac{\sum_\upsilon \{E(x)\} G(\upsilon) d\upsilon}{\sum_\upsilon G(\upsilon) d\upsilon} \tag{11}$$

where *E(x)* is the Einstein function difiend as

$$E(x) = x^2 \frac{e^{(x)}}{\{e^{(x)} - 1\}^2}$$

and $\sum_\upsilon G(\upsilon) d\upsilon =$ Total number of frequencies considered lying in the interval *(v-dv/2)* to *(v+dv/2)*.The heat capacity, free energy, entropy and internal energy are compared with that computed from the phonon spectra. This comparison is usually done by plotting the heat capacity, free energy, entropy and internal energy with T. Lattice dynamics is also one of the important aspects in such studies, because it has been suggested that soft phonon mode mechanism is the major cause of phase transformations [13]. At high temperatures, quantum consideration carry significance changes shown in experimentally but at low temperature of shows significant properties and the validity of the present model. The heat capacity, free energy, entropy and internal energy at temperature T is calculating the exact variation of temperatures. Thermodynamic property of (Cu) is calculated and also carried out using the Package VASP [13-15] coupled with PHONON [16]. Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated and compared with experimental or others simulation results [17-24]. Specific heat capacity at constant volume (Cv) was calculated using the following equation (10).According to thermodynamics, the equilibrium of a solid at a temperature T is determined by the minimum value of the free energy.

$$F = E - TS \tag{12}$$

The change in entropy (ΔS) of a system was originally defined for a thermodynamically reversible process as

$$\Delta S = \int \frac{\delta Q_{\mathrm{Re}v}}{T} \tag{13}$$

2.3. DENSITY OF STATES

To determine the phonon density of states for each polarization is given by using Monte Carlo sampling method.

$$g(\omega) = dN / d\omega = N \int_{BZ} \sum_{j} \delta\left[\omega - \omega_j(q)\right] dq = \left(VK^2 / 2\pi^2\right) dK / d\omega \tag{14}$$

N = $(L/2\pi)^3$ $(4\pi K^3/3)$, K is wave vector and L^3=V, where N as a normalization constant such that $\int g(\omega) d\omega = 1$ and $g(\omega)d\omega$ is the ratio of the number of eigen states in the frequency interval $(\omega, \omega + d\omega)$ to the total number of eigen states $\omega_j(q)$ is phonon frequency of the jth normal mode of the phonon wave vector q.

2. COMPUTATIONS

By use of the first principles calculations, the properties of Cu have investigated in present paper. The Internal energy, entropy, free energy and heat capacity curve at temperature from at 300 K and 1356 K has shown in Figs. 2-5. Before staring calculation we have to optimize geometry of the crystal firstly then conducted PHONON-VASP software for calculations. All calculation carried out using (DFT) based Phonon-VASP code and [VTBFS] model. The effect of pressure on the crystal structure, electronic structure and vibrational properties are represented in our calculation. The calculated thermodynamical curve has shown the validity with an available experimental data. The internal energy value 1.8 (kcal/mol) has obtained at 300 K but at higher temperature the energy value is changed attended and 8(kcal/mol) at 1356 K.

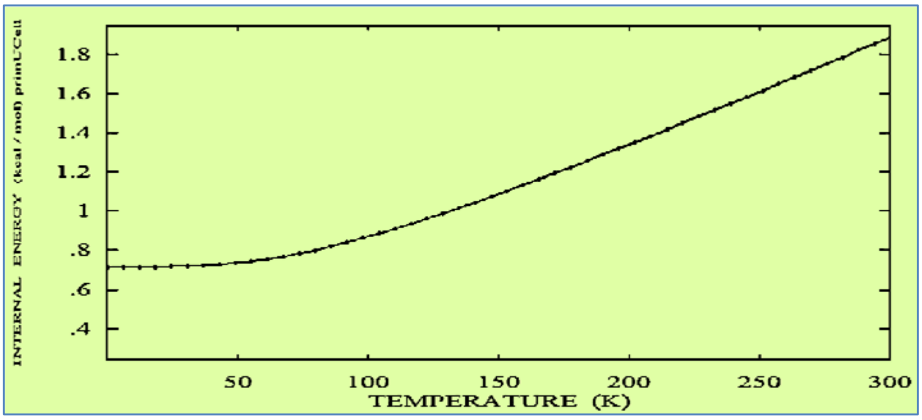

Figure 2. a) Internal Energy of Cu at 300 K.

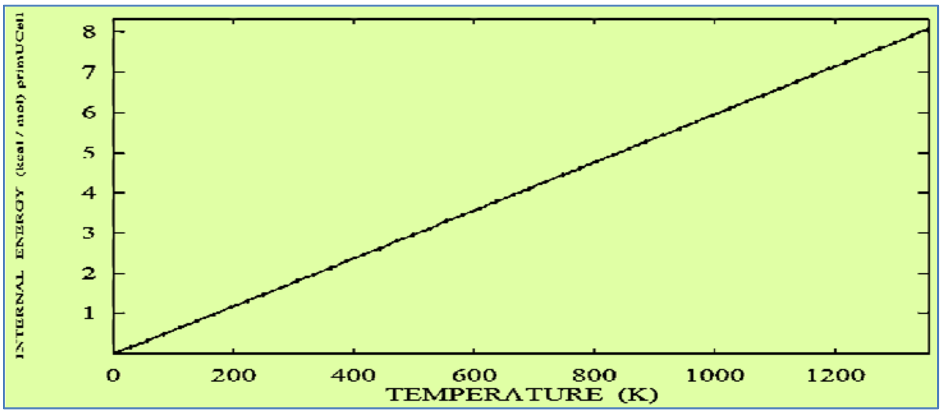

Figure 2. b) Internal Energy of Cu at 1356 K.

The curve for free energy has shown in Fig. 3 a) value of free energy decreasing gradually till attaining the value of 300 K. But at temperature 1356 K the linear falling in energy value can be seen, starting from zero to -35 (kcal/mol) is shown in Fig 3 b).

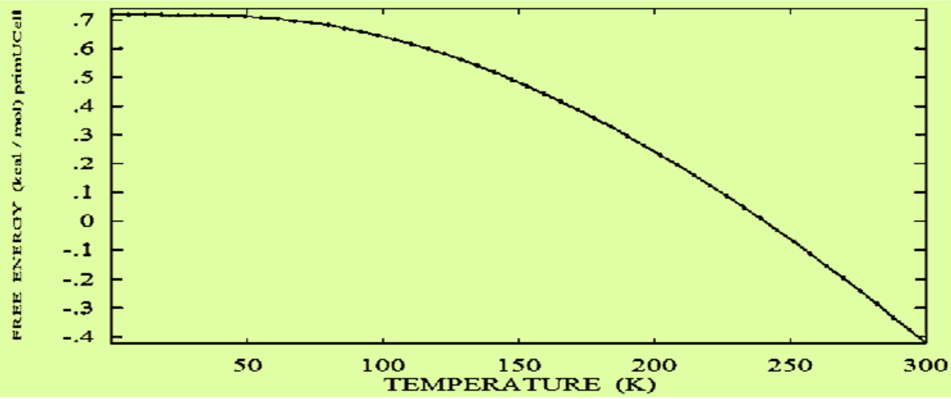

Figure 3. a) Free Energy of Cu at 300 K.

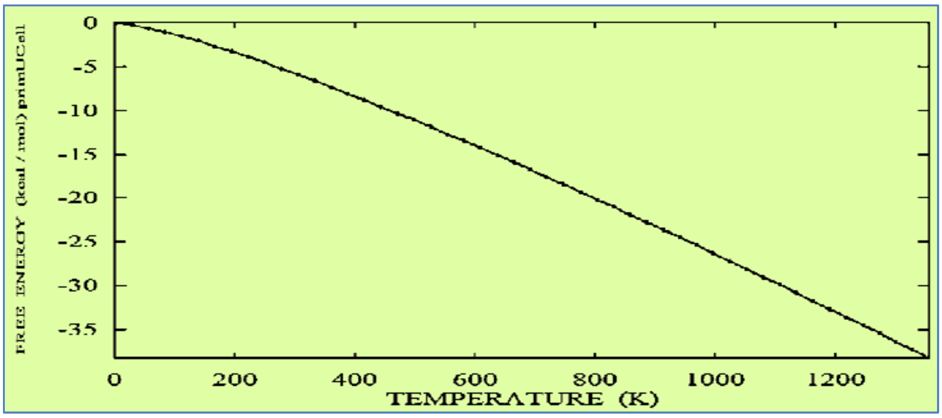

Figure 3. b) Free Energy of Cu at 1356 K.

The entropy versus temperature curve for Copper has shown in Fig. 4 a) and b) the curve spread over a wide range of temperature. In Fig. 4 a) entropy value continuously increases up to 7 (Cal/K.mol) at temperature of 300 K value which shows orderliness. While in Fig. 4 b) entropy value increase smoothly up to the temperature of 600 K and then shows constant nature upto the range of 1356 K. abrupt changes noted till the value of 357(cal/K.mol) in case of higher temperature entropy is ordered then at 300 K.

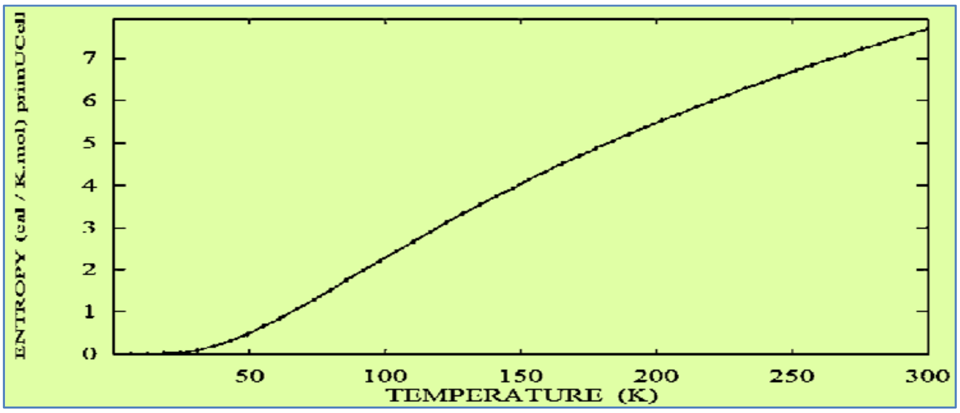

Figure 4. a) Entropy of Cu at 300 K.

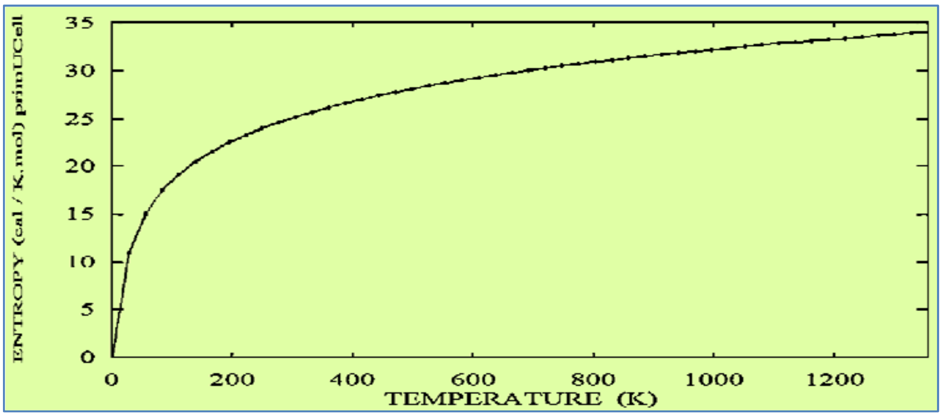

Figure 4. b) Entropy of Cu at 1356 K.

In the Fig. 5 a) and b) the temperature verses heat capacity graph has shown. The specific heat curve increases sharply up to 200 K and then remains constant for the temperature of 300 K. The value heat capacity at the temperature for 1356 K increases rapidly at the value of 6 (cal/K.mol) and then for the further value of temperature the constant condition obtained till the temperature of 1356 K. As the temperature of Cu raised the involvement of different type of mechanism of heat absorption become apparent.

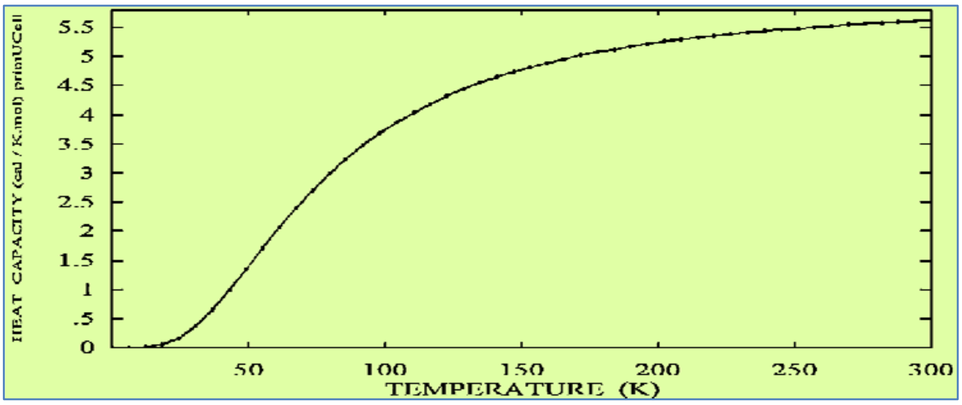

Figure 5. a) Heat Capacity of Cu at 300 K.

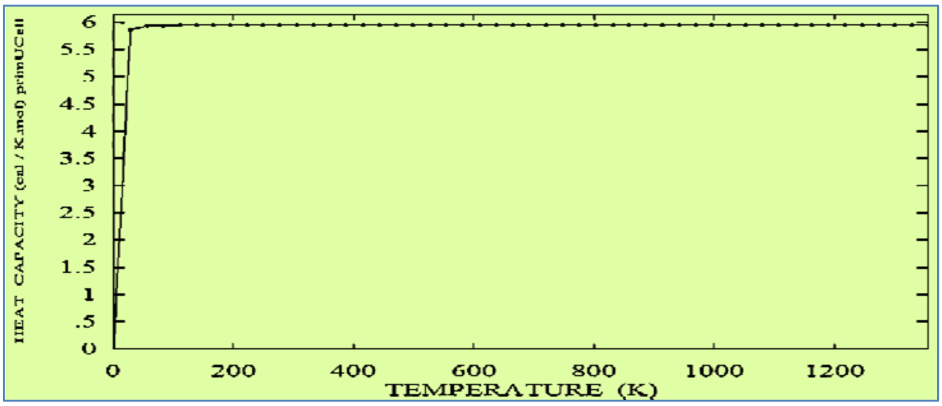

Figure 5. b) Heat Capacity of Cu at 1356 K.

The illustrated thermodynamic properties obtained and confirmed the ceramic characteristics of Cu.The phonon dispersion relation curve has shown in Fig. 6 and theoretical data along symmetry direction is reported in Table 1. The effective charge along transverse and longitudinal mode with real and imaginary frequency along three coordinates has reported in Table 2.

Table 1. Phonon dispersion relations along the symmetry directions of Cu.

Index	SymP	q1	q2	q3	Kx	Ky	Kz
1	Γ	1.0000	1.0000	1.0000	0.2770	0.2770	0.2770
2	X	0.5000	0.5000	1.0000	0.2770	0.2770	0.0000
3	K	0.3750	0.3750	0.5000	0.1385	0.1385	0.0693
4	L	0.5000	0.5000	0.5000	0.1385	0.1385	0.1385
5	Γ	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

An accurate description of phonon frequencies is a stringent test for a theoretical model. The lower section of Γ-X direction indicates higher longitudinal energy, while most of the branches in the X-L directions converge as non-degenerate, thus leading to the expected nine branches for a typical cubic structure has shown in dispersion relation curve in Fig. 6.

The energy of the Cu is used as a reference to properly the theoretical study of density of states DOS.This theoretical finding is in qualitative agreement with the experimental observations.

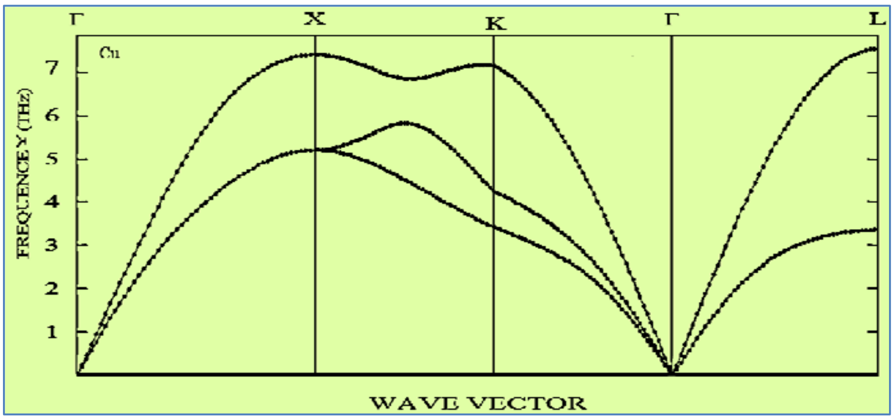

Figure 6. Phonon dispersion curve of Cu.

The DOS curve versus frequency value is reported in Fig .7.At lower frequency at 2.5 THz the DOS value is small and at frequency of 4.3 THz curve increases continuously and attended the maximum value and further decrement can seen upto value of 6.2 THz and again atttend the maximum value and then for further increment in frequencey value the DOS fall for zero value sarplly and then raim const for other higher value of frequencey.There are many states available for occupation and on increasing the frequency value a local density of states (LDOS) available, frequency of 6.8 THz.

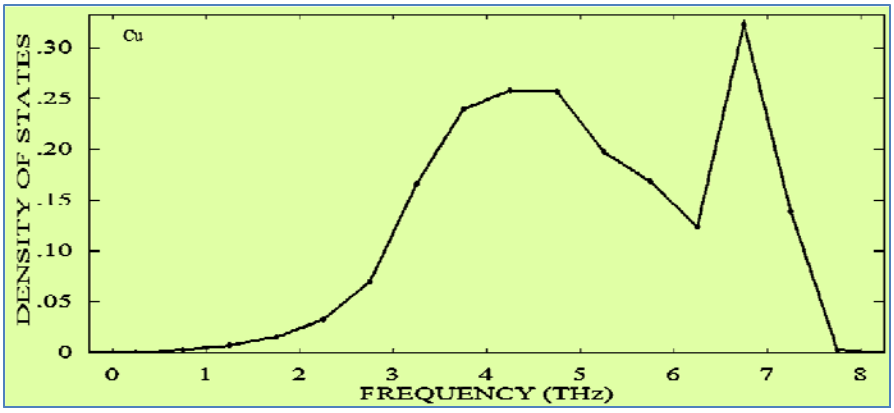

Figure 7. Density of states curve of Cu.

4. RESULT

The present model is based on this concept that in solid phase the lattice vibrations are quantized and can be described by quasi-particles, phonons. It is assumed that the photons represent a normal mode vibration, thus all parts of the lattice vibrate with the same frequency**.** This has been applied for study of lattice property with short-range interactions effective up to the second neighbor. In present study despite the lower symmetry direction of Cu the uncertainty as to the exact nature of the distortion of the lower–temperature structure can be seen. A tremendous change in the nature of slope has been observed in 300 K and 1356K temperature. Our theoretical study at the lower temperature side shows a better agreement, but at the higher temperature side, slight disagreement may be ascribed to the non-inclusion of the harmonic interactions in using present model, which it may be inferred that the incorporation of van der Waals interactions is essential. The Complete phonon dynamical properties of Cu theoretically reported has been agreed with experimental reported data.

5. CONCLUSION

To aggregate up, we can state that the contributions of (VWI) and (TBI) have a fundamental part in the portrayal of the entire lattice dynamical investigation of Cu. By utilizing the present [VSTBFS] model, we have effectively figured the estimation of internal energy, free energy, heat capacity, entropy value, phonon dispersion relation and density of states of copper . In this way, it is inferred that the most sensible model for investigation of complete harmonic dynamical conduct of the Cu can be totally reported by presenting the impact of van der Waals interactions (VWI) and expression for the contribution of (TBI) to the dynamical matrix, which has been thoroughly determined and assessed effectively in the present study. The (TBI) has satisfactorily depicted the lattice dynamic, dielectric, photo-elastic, relative stability, polymorphic phase-transition, a consonant-elastic and thermal properties. So the present model has given another device to future specialists in complete theoretical investigation of crystal in the accessibility of the some required test information. The present model [VTBFS] has been effectively utilized by some scientists [25-37] for the entire theoretical phone dynamics of different alkali halide crystal furthermore for semiconductor materials which had demonstrated the significance and legitimacy of the present model.

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