The Study of Three Body Effects in Phonons using Parameter Free Pseudopotential in Symmetric Directions: Cu as a Test Case

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***Abstract*— In the present study, using parameter free local form of pseudopotential with inclusion of three body effects we have study phonon dispersion curves. The overall agreement with experimental results are fairly well. Further, the temperature variations of Debye-Waller factor and mean square displacement have been calculated by using computed phonon density of states. From present study, we conclude that three body forces in the study of phonons play an important role for the understanding of lattice mechanical properties of transition metals.**

***Keywords*— Phonons in symmetric directions, three body forces, Pseudopotential, Transition metals**

I. INTRODUCTION

Looking to the need of the study of many mechanical and thermodynamical properties at ambient condition and at extreme environment (High Temperature and High Pressure) there is a need of experimental as well as theoretical studies of lattice dynamics of metals, liquid metals and glasses. Experimentally phonon spectra are measured by using neutron scattering experiments. Theoretically phonon spectra has been calculated by using empirical potential pseudopotential and embedded atom method. Very recently with the increasing computational power of modern workstations ab initio calculations of phonons have become possible. The study of phonon spectra helps to understand the peculiarities of interatomic interactions in crystals. An experimental investigation of lattice dynamics together with a theoretical analysis gives the best possibility to study interatomic forces and related phenomena. The theoretical investigations based on density functional theory (DFT) differ, however in the treatment of the tightly bound core electrons and/or in the basis set used for describing the wave functions. Since very accurate full potential calculations (e.g. FLAPW) are very time consuming, even with modern workstations most studies have been restricted to selected phonon modes by using the frozen phonon approach. Baroni and co-workers [1] as well as other groups have used the formalism within a plane-wave basis and with pseudopotentials linearized Muffin Tin (MT) orbital versions and FLAPW versions have also been developed. The embedded atom method is also used for the study of lattice dynamics which is based on empirical assumptions. Tight Binding [TB] method is found to be the most reliable for such study. Phonon anomalies are also observed due to the treatment given to d electrons for the calculation of total energy in this method. Such model contains three or more adjustable parameters which are obtained by favouring some physical properties like elastic constants, phonon frequencies and bulk-modulii etc.

On the other hand, pseudopotentials in its different form, local, non-local and first principles, are used successfully for the description of not only lattice dynamics and lattice mechanical properties but also wide range of physical properties of all types of materials. Among all this forms of the pseudopotential, local pseudopotential method are used widely due to its computational simplicity and physical transparency alongwith transferability to extreme environment even for metals with complicated electronic structure like transition metals, rare earth metals, actinides and lanthanides [2]. Local pseudopotential can be used for the theoretical description of many physical properties with adjustment of valency [3]. Recently using second order perturbation theory sophisticated pseudopotential with proper dielectric function were used for the study of lattice mechanical properties of many transition metals [4-5]. In such research work, the short range d-d electrons interaction is accounted by Born-Mayer type of repulsive potential.

Looking to the aforesaid facts we find that the study of lattice mechanical properties require more adjustable parameter and such study is limited up to second order perturbation theory. The prime aim of the present paper is to carry out the study of lattice dynamics and lattice mechanical properties of FCC Cu as a test case using local form of the pseudopotential without adjustment of any parameters. The pseudopotential used is free from adjustment of parameters it means it is equivalent to first principles pseudopotential. There are several indications that third and fourth order terms play an important role in the lattice mechanical properties of metals [6]. In this context, for the complete description of lattice mechanical properties we also include three body forces which are found to be very rare for such studies. Kumar [7] has proposed local form of the pseudopotentialwith two

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parameters r_c – core radius and r_m – some atomic radius which is discontinuous in r-space has the following form,

$$V_{ion}(r) = \frac{-Ze^2 r}{r_m r_c} \quad for\ 0 < r < r_c$$
$$= \frac{-Ze^2}{r_m} \quad for\ r_c < r < r_m$$
$$= \frac{-Ze^2}{r} \quad for\ r_m < r \tag{1}$$

In the region $r < r_c$, there is no complete cancellation of potential but it decreases linearly and in the region r_c to r_m it remains constant. It possesses pure coulombic behaviour for the region outside r_m. The potential between region r_c to r_m accounts hybridization effects because in case of d-band metals there is no complete cancellation of potential within this range. This local form of the pseudopotential is found to be successful for the description of lattice dynamics of actinide thorium. The Fourier transform of Eq. (1) gives unscreened pseudopotential in momentum space [7]. Such unscreened pseudopotential is screened by using method discussed in Wallace [8]. In the present communication we have computed phonons in Cu in symmetric directions, the temperature variation of Debye-Waller factor (W_T) and mean square displacement ($\overline{U}^2$).

II. Theory

The lattice dynamics of metals has been discussed in complete detail by several authors. The total dynamical matrix $D_{\alpha\beta}(q)$ will consist of two terms,

$$D_{\alpha\beta}(q) = D^C_{\alpha\beta}(q) + D^E_{\alpha\beta}(q) \tag{2}$$

Here superscripts stand for Columbic and Electronic contributions. Also,

$$D^C_{\alpha\beta}(q) = \frac{2}{M}\Big[\sum_Q G_1\big(|\vec{Q}+\vec{q}|\big)\big(\vec{Q}+\vec{q}\big)_\alpha\big(\vec{Q}+\vec{q}\big)_\beta - \sum_Q G_1\big(|\vec{Q}|\big)Q_\alpha Q_\beta + \sum_R \{\varphi_1'(R)\delta_{\alpha\beta} + 2\varphi_1''(R)R_\alpha R_\beta\big(1 - cos\big(\vec{q}.\vec{R}\big)\big)\}\Big] \tag{3}$$

M is the mass of the ion.

$$G_1\big(|\vec{Q}|\big) = \frac{2\pi Z^2 e^2}{\Omega Q^2} e^{-Q^2/4\eta^2} \tag{4}$$

$$\varphi_1(R) = Z^2 e^2 R^{-1} erfc(\eta R) \tag{5}$$

η is an adjustable parameter and erfc(ηR) is a complimentary error function. $\varphi_1'(R)$ and $\varphi_1''(R)$ are first and second order derivatives of $\varphi_1(R)$. $D^E_{\alpha\beta}(q)$ describes electron-ion interaction which is made up of $D^{(2)E}_{\alpha\beta}(q)$ and $D^{(3)E}_{\alpha\beta}(q)$ i.e. second order and third order contributions to $D^E_{\alpha\beta}(q)$ due to pseudopotential, where,

$$D^{(2)E}_{\alpha\beta}(q) = \frac{2}{M}\Big[\sum_Q F\big(|\vec{Q}+\vec{q}|\big)\big(\vec{Q}+\vec{q}\big)_\alpha\big(\vec{Q}+\vec{q}\big)_\beta - \sum_Q{}' F\big(|\vec{Q}|\big)Q_\alpha Q_\beta\Big] \tag{6}$$

$$D^{(3)E}_{\alpha\beta}(q) = \frac{6\Omega}{M}\sum_{\vec{Q}_1,\vec{Q}_2,\vec{Q}_3}[(\vec{q}+\vec{Q}_1)_\alpha\,(\vec{q}+\vec{Q}_2)_\beta\ x\ \Gamma^{(3)}\big(\vec{q}+ Q1,-q-Q2,Q3\ x\ Vionq+Q1Vion-q+Q2VionQ3x \Delta(\vec{Q}_1-\vec{Q}_2+\vec{Q}_3)\big]$$

$$\Delta\big(\vec{Q}_1-\vec{Q}_2+\vec{Q}_3\big) = 1\ for\ \vec{Q}_1+\vec{Q}_3 = \vec{Q}_2 \tag{7}$$
$$= 0\ otherwise \tag{8}$$

The expression for $\Gamma^{(3)}\big(\vec{q}+\vec{Q}_1,-\vec{q}-\vec{Q}_2,\vec{Q}_3\big)$ is taken from [7].

III. Results and Discussion

In the present study, r_c is calculated using the formula given in [7] and experimental value of atomic radii is taken as r_m. As suggested by Moriarity, we have selected value of the valency within narrow range 1.1<Z<1.7. First time using above philosophy we have studied phonon dispersion relation including three body effects. The calculated frequencies in symmetric directions along with the experimental points due to [9] is as shown in Fig. 1. It is quite interesting to note here that the overall agreement with the experimental points for all branches are fairly well.

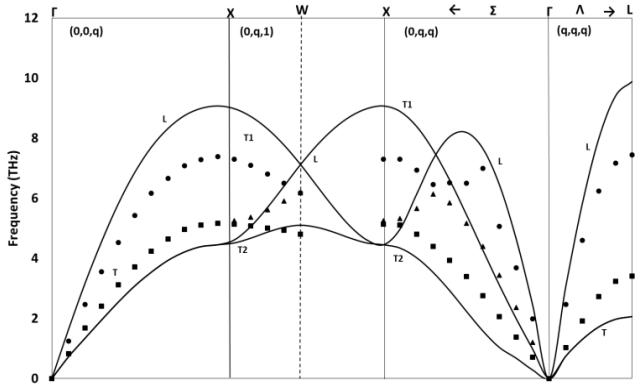

Fig. 1 Phonon dispersion curves of Copper in symmetric directions

paper The maximum deviation observed is less than 25%. Presently calculated results are better in the sense that no

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fitting and re-fitting of potential parameters have been done during the course of calculation to yield better agreement with experimental results at zone boundary. It has been noted by many researchers, for local and non-local pseudopotential, that for transition metals in order to account core-core repulsion, one must use Born-Mayer type of potential. Present calculation is free from adjustments of the parameters and potential itself accounts s, p and d hybridization. In this sense, presently used pseudopotential can be treated as first principles pseudopotential and three body forces do play an important role for the better understanding of phonons. Further in the harmonic approximation, we have computed phonon density of states using root sampling method. In such calculation the mesh of 64000 wavevectors have been taken in the first brillouin zone. With the help of calculated frequency distribution we have computed Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$) using expressions described in [3]. The variations of W_T and $\bar{U}^2$ with temperature alongwith experimental points (Δ-W_T and • - $\bar{U}^2$) due to Penget. al. [10] are as shown in Fig. 2. The agreement between experiments and theory are quite well.

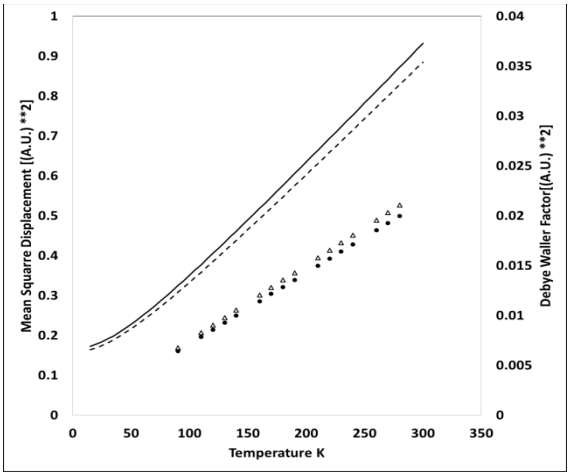

Fig. 2 Temperature variations of W_T and $\bar{U}^2$

IV. Conclusions

From the present study we conclude that even local pseudopotential without adjustments of any parameters with inclusion of three body forces can be used for the study of lattice dynamics and lattice mechanical properties in metals. The three body forces cannot be ignored for the better understanding of ion's vibrations. Such approach of calculation with local form of pseudopotential is equivalent to the study based on first principles pseudopotentials.

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