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Effect of three-body forces on the lattice dynamics of noble metals

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Abstract. A simple method to generate an effective electron–ion interaction pseudopotential from the energy wave number characteristic obtained by first principles calculations has been suggested. This effective potential has been used, in third order perturbation, to study the effect of three-body forces on the lattice dynamics of noble metals. It is found that three-body forces, in these metals, do play an important role. The inclusion of such three-body forces appreciably improves the agreement between the experimental and theoretical phonon dispersion curves.

Keywords. Noble metals; three-body forces; lattice dynamics.

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1. Introduction

The measurements of phonon spectra, performed in the last 40 years, provide a very direct test of any microscopic theory of lattice dynamics of solids. The pseudopotential formalism, in which a weak effective interaction is set-up between atomic cores and valence electrons, does an unexpectedly good job of reproducing properties of closed packed metals in second order perturbation theory [1]. By considering terms up to second order in the electron-ion pseudopotential, a simple expression is obtained for the total energy and the dynamical matrix can be easily evaluated by taking second order derivative of the energy with respect to ionic displacements. In this way it has become possible to carry out calculations of phonon frequencies. It is well-known that second order term in the perturbation expansion of energy, in pseudopotential, gives the pair-wise central forces between the atoms. The higher order terms lead to many-body forces.

The importance of many-body forces in the lattice dynamics of metals has been realized by several workers [2–5]. Brovman and Kagan [3,4] have shown that if one neglects the terms higher than the second order in perturbation expansion, then values of compressibility calculated by long wave method and the method of homogeneous deformation are not equal. This shows that many body forces are essential to satisfactorily account for long wavelength phonons. In some cases, it has also been found that unpaired forces play a more important role on the entire phonon spectrum [5].

Datta *et al* [6] have attempted to identify the role of pseudopotential third order energy in different lattice mechanical properties of HCP metals. In order to account for third order term in pseudopotential, these authors imposed the consistency condition of matching the elastic constants, calculated in second order, by long wavelength method and the method of homogeneous deformation. This condition simulates the effects beyond second order to some extent and explains the typical features of phonon dispersion curves. Laziz and Chopra [7] have argued that microscopic theories indicate the existence of three-body forces in noble metals. These authors have represented three-body forces phenomenologically by the Clark, Gazis and Wallis angular forces [8]. A theory of calculating vibrational spectra of transition metals has also been given by Kushwaha *et al* [9]. This is a semi-first principles model. This theory uses the concept of a rigid shell moving relative to its nucleus to simulate the response of d-electrons. The long range interaction between ion–ion as well as shell–shell interaction via conduction electrons is described using the screened potential and a short range interaction is described using two- and three-body forces between cores and shells.

Antonov *et al* [10] wrote the total energy of a d-shell metal, at zero temperature, as follows:

$$E = \sum_{n=0}^{2} E_s^{(n)} + \sum_{n\geq 3} E_s^{(n)} + E_i - \phi_d,$$

where $\phi_d = E_d$ (d-electron energy) $+E_{ds}$ (s-d interaction energy) $+E_{\rm ol}$ (energy due to overlap of d states) and E_i is the energy of interaction of ion cores. Here E_i and $E_s^{(n)}$, for $n \leq 2$, correspond to pair interatomic interaction. $E_s^{(0)}$ and $E_s^{(1)}$ are volume dependent contributions. Based on *ab initio* analysis [11], Antonov *et al* assumed that many-body interactions in $\sum_{n\geq 3} E_s^{(n)}$ are cancelled with the contributions from the term ϕ_d. Mishra *et al* [12] have modified the Morse potential to simulate 3-body forces in transition metals. In a very important extension of his theory, based on density functional formalism, for d band metals, Moriarty [13,14] has obtained useful analytical expressions, in real space, for multi-ion interactions. These expressions retain the most important physics of the full first principles treatment. Singh *et al* [15] have used a force constant model which accounts for two- and three-body forces through adjustable force constants. Barrera and Batana [16] have given a general interionic interaction model which includes both two- and three-body uncoupled forces. They consider two-body interactions up to third neighbours and common nearest neighbours for three-body forces. Four independent parameters were estimated from experimental second order elastic constants and Gruneisen function for $T \to \infty$. The interionic potential proposed by these authors has the form:

$$\Phi = \frac{N}{2} \sum_{A} \Phi(r_A) + \frac{N}{2} \sum_{AB}{}' \chi[\cos(\theta_{AB})].$$

Here, N is number of atoms, r_A is distance of atom A from the origin and θ_{AB} is the angle structured by the bonds r_A and r_B. Inspired by the *ab initio* generalized valence-bond calculations of small metal clusters, Mo Li and Goddard [17] proposed a phenomenological many-body interaction model. This is the interstitial electron model (IEM) in which the valence electrons are treated as classical particles situated at the crystal lattice interstitial positions. Mishra *et al* [18] have proposed a generalized Morse potential which simulates,

in empirical manner, the three-body forces. Okoye and Pal [19] have studied the phonon dispersion in noble metals by incorporating a short range 3-body interaction potential coupled with Animalu's transition metal non local model potential [20]. Guong [21] has obtained a force constant tensor for Au, using a plane wave based linear response method. The use of optimized pseudopotential to model the electron–ion interaction requires only a modest number of plane waves. The excellent agreement with Born–von Karman fits were found when interactions were taken up to 4th neighbours. However, for better accuracy in specific heat calculations, long range interactions were found to be necessary. Akgun [22] has proposed an empirical many-body interatomic potential energy function. This potential function contains two- and three-body forces. Three-body interaction is expressed in terms of two-body interactions. The parameters were determined on the lines of Girifalco and Wiser [23]. Another empirical potential energy function to account for two- and three-body forces has been suggested by Isordi *et al* [24]. A generalized form of exponential potential was extended by Verma *et al* [25] to account for three body forces. The original model of Sarkar *et al* [26] was modified by Coelho and Shukla [27] to consider the three body forces in noble metals. These authors applied the crystal equilibrium condition to reduce one independent parameter. Akgun *et al* [28] have also proposed an empirical interatomic interaction potential which includes both two- and three-body forces. In a work by Barrera and Tendler [29], many-body interactions are taken into account by using potentials of the embedded atom method [11]. These authors carried out calculations of lattice dynamics in quasi harmonic approximation.

It can be seen that most of the attempts made to study the importance of three-body forces are empirical in nature. Also it is not clear as to how such empirical interatomic potentials explain the physics of the problem. These potentials do not correspond to quantitative theories of metals. They contain several parameters which are fixed by certain experimental inputs.

Pseudopotential theory has not only provided a convenient way of calculating a large number of lattice properties of metallic substances, but it shows quite transparently the complicated nature of interatomic interactions in metals.

It may be noted that description of a wide range of properties of metals (solids, liquids and glasses) is still beyond the capabilities of completely *ab initio* approaches. It is in this context, the importance of the development of pseudopotential theory for metals, for which it is valid, appears indisputable [1,30].

The effect of three body forces can be considered through third order perturbation theory in which weak electron–ion interaction acts as perturbation on a free electron gas [3,5].

In the pseudopotential theory the ground state energy of an electron–ion system is written in the form of an expansion in powers of electron–ion interaction. Retaining the terms up to third order, we have

$$E_{\rm el} = E^{(0)} + E_{\rm ii} + E^{(1)} + E^{(2)} + E^{(3)}, \tag{1}$$

where $E^{(0)}$ is the volume dependent part of the electron energy, while $E^{(1)}$, $E^{(2)}$ and $E^{(3)}$ give respectively the first, second and third order terms of perturbation expansion. $E_{\rm ii}$ is the ion–ion direct Coulomb interaction. Within the local approximation $E^{(2)}$ and $E^{(3)}$ can be written as

$$E^{(2)} = n_c^2 \Omega \frac{Z^{*^2}}{2\Omega_0^2} {\sum_{\vec{q}}}' |S(\vec{q})|^2 v_c(q) F_N(q), \tag{2}$$

$$E^{(3)} = n_c^3 \Omega \sum_{\vec{q}}{}' \sum_{\vec{q}}{}' \sum_{\vec{q}''}{}' S(\vec{q}) S(\vec{q}') S(\vec{q}'') g(\vec{q}, \vec{q}', \vec{q}'') \frac{v_i(q) v_i(q') v_i(q'')}{\bar{\epsilon}(q)\bar{\epsilon}(q')\bar{\epsilon}(q'')} \times \delta(\vec{q} + \vec{q}' + \vec{q}''), \tag{3}$$

where n_c is the number of ions per unit cell, Ω is total volume, $\bar{\epsilon}(q)$ is the dielectric function of electron gas corrected for exchange and correlation effects. $v_c = \frac{4\pi e2}{q2}$ is the Fourier transform of Coulomb potential. Z^* is effective charge of an ion and Ω_0 is volume per atom. $\delta(\vec{q} + \vec{q}' + \vec{q}'')$ takes care of conservation of momentum. $F_N(q)$ is known as energy wave number characteristic given by

$$F_N(q) = \frac{\Omega_0^2}{Z^{*2}} \frac{1}{v_c^2(q)} \frac{\epsilon(q) - 1)}{\epsilon(q)} v_i^2(q). \tag{4}$$

$\epsilon(q)$ is the well-known Hartree dielectric function of electron gas. The factor $G(q)$ gives exchange and correlation correction in $\epsilon(q)$. Note that $v_c(q)$ appearing in eq. (4) has the following form

$$v_c(q) = \frac{4\pi e^2}{q^2}\{1 - G(q)\}. \tag{5}$$

Also,

$$\bar{\epsilon}(q) = \epsilon(q) + G(q)[1 - \epsilon(q)]. \tag{6}$$

$v_i(q)$ is the electron–ion interaction in q-space. $S(\bar{q})$ is the static structure factor. The function $g(\vec{q}, \vec{q}', \vec{q}'')$ has been explicitly given by Lloyd and Sholl [2].

Equations (2) and (3) give structure dependent energy. We can write these contributions in terms of an indirect interaction between the ions in the following way:

$$E^{(2)} = \frac{1}{2} \sum_{\ell s \neq \ell' s'} V_{\rm ind}(|\vec{R}_{\ell s} - \vec{R}_{\ell' s'}|) + U^{(2)}(\Omega), \tag{7}$$

$$E^{(3)} = \frac{1}{2} \sum_{\ell s \neq \ell' s'} \sum_{\ell'' s''}{}' V_{\rm ind}^{(3)}(\vec{R}_{\ell s} - \vec{R}_{\ell'' s''}, \vec{R}_{\ell' s'} - \vec{R}_{\ell'' s''}) + \frac{1}{2} \sum_{\ell s \neq \ell' s'} V_{\rm ind}^{(2)}(|\vec{R}_{\ell s} - \vec{R}_{\ell'' s''}|) + U^{(3)}(\Omega). \tag{8}$$

These equations show that the second order energy arise from a central pair-wise interaction between the ions, while both central two body and non-central three body forces contribute to $E^{(3)}$. The last term in these equations represents a volume dependent part and does not give any contribution to dynamical matrix.

It is well-known that the use of a local pseudopotential or on Fermi sphere approximation with non-local pseudopotential leads to unreliable evaluations of third order term in the perturbation expansion in pseudopotential. In both cases the form factor presents spurious oscillations at large wave vectors, $\vec{q}$ which give rise to completely unphysical results owing to the considerable dependence of third order on the values of the pseudopotential at large

$\vec{q}$. To improve this situation one should carry out the whole calculation with a non-local, preferably first principles pseudopotential. However, the inclusion of non-locality leads to mathematical expressions for third order contributions whose evaluation is impossible in practice.

Long ago Bertoni *et al* [5] had suggested a method of constructing local potentials from the non-local ones. In their procedure an average potential is obtained from the relation

$$\nu_{\text{av}}(q) = \frac{G_q\{\vec{k}+\vec{q}|\nu|\,\vec{k}\}}{\frac{1}{2}[1-\epsilon(q)]/\left(\frac{4\pi e^2}{q^2}\right)},$$

where

$$G_q\{\phi(\vec{k})\} = \frac{2}{(2\pi)^3}\int_{k\le k_f}\frac{\phi(\vec{k})}{k^2-(\vec{k}+\vec{q})^2}\mathrm{d}\vec{k}.$$

It should be noted that energy wave number characteristic calculated by this $\nu_{\text{av}}(q)$ will not be the same as that generated in full non-local calculations.

In the present paper, we have two main objectives. First, we are interested in the study of relative importance of two- and three-body forces in the lattice dynamics of noble metals. And second, we wish to propose a simple scheme to generate a local electron–ion interaction potential from the energy wave number characteristic obtained from the first principles pseudopotential theory. We, then, use this local form for the study of effect of three-body forces on phonon frequencies. It may be noted that in most of the earlier works, on the same lines, either local empirical models or non-local empirical models have been used. We believe that first principles pseudopotentials are much more closer to reality. In the present study we have used the local form of electron–ion interaction extracted from the first principles pseudopotential due to Moriarty [31].

2. Calculations

In order to obtain a local form which includes the non locality in a way better than the on Fermi sphere approximation, we prefer to extract $v_i(q)$ from eq. (4). This requires $F_N(q)$ computed from first principles. We call $v_i(q)$ so generated, an effective electron–ion interaction. It is clear that it generates the same energy wave number characteristic as that generated by the original first principles pseudopotential. For the present work we use the numerical tables of $F_N(q)$ given by Moriarty [31] who has given a detailed discussion of pseudopotential theory of noble metals. For $G(q)$, appearing in eq. (4), we use the same form as that used by Moriarty. This is an interpolation formula due to Singwi *et al* [32].

The explicit expressions for matrix elements of dynamical matrix which is to be diagonalized to obtain phonon frequencies as a function of $\vec{q}$ are given by Brovman and Kagan [3]. These expressions include the third order contributions to matrix elements. We do not reproduce these lengthy expressions here.

Our method of generating $v_i(q)$ is simple and is better than that suggested by Bertoni *et al* [5]. It may be noted that $v_i(q)$ obtained through the procedure due to Bertoni *et al* can not reproduce the same $F_N(q)$ as that generated by the original full non-local calculations.

3. Results and discussion

We report, in figures 1–3, the form factors, $v(q) = v_i(q)/\bar{\epsilon}(q)$ of Cu, Ag and Au. It is seen that the differences between original on Fermi sphere approximation first principles form factors [31] and the presently obtained effective local form factors are large. This indicates that off-shell processes arising from non-locality of the potential are very important in Cu, Ag and Au. Notice that there is a drastic change in the height of the first maximum. The first few shells of reciprocal vectors fall in this part of the curve so that the results

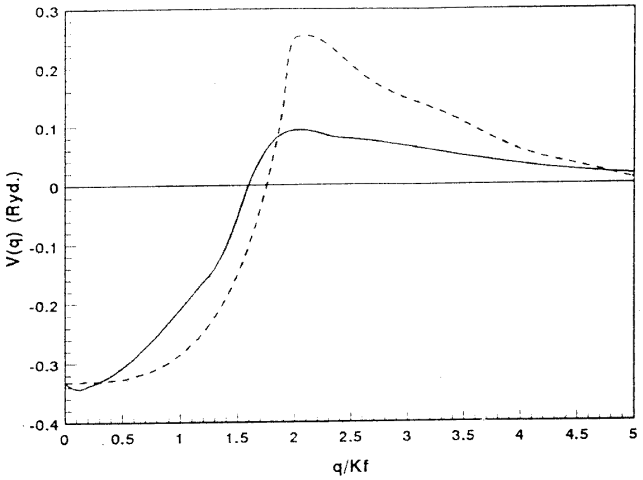

Figure 1. Pseudopotential form factors for copper. Dotted line shows $v(q)$ of Moriarty [31]. Continuous line (present work).

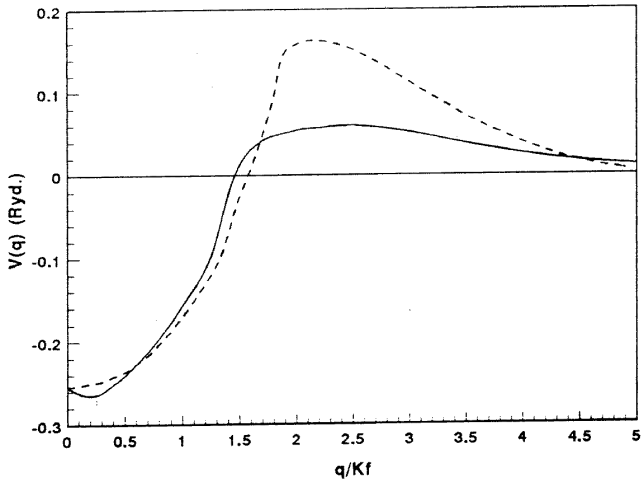

Figure 2. Pseudopotential form factors for silver. Dotted line shows $v(q)$ of Moriarty [31]. Continuous line (present work).

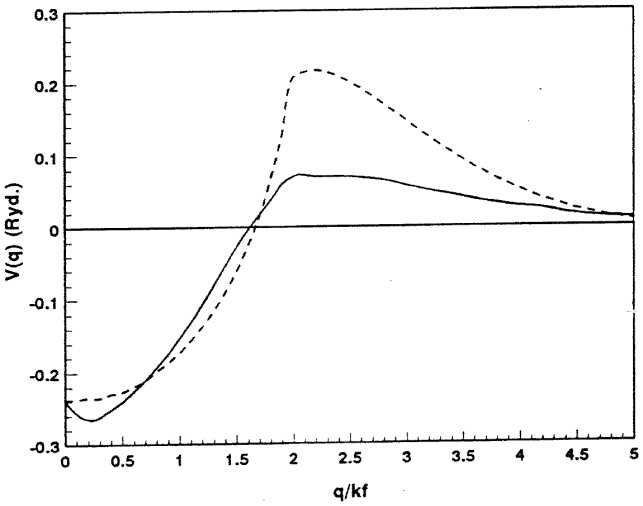

Figure 3. Pseudopotential form factors for gold. Dotted line shows $v(q)$ of Moriarty [31]. Continuous line (present work).

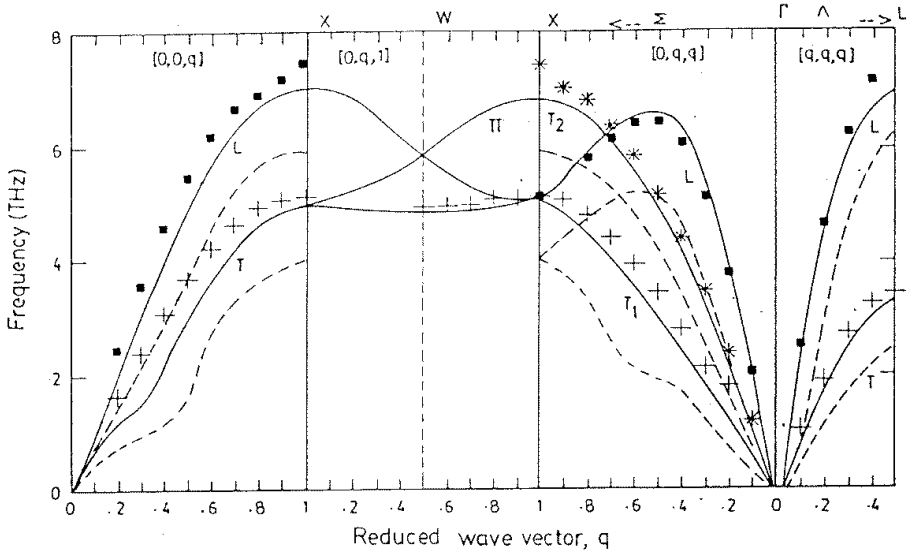

Figure 4. Phonon dispersion curves for copper. Continuous lines show results of third order (present work) and dotted lines show results due to Moriarty [31]. Experimental points are due to Nillson and Rolandsson [36].

of third order calculations of phonon frequencies would differ appreciably from the second order calculations. The presently obtained $v(q)$'s do not have any spurious oscillations at large $\vec{q}$ and hence unphysical contributions to off-shell elements are removed.

The phonon dispersion curves calculated in third order (full lines) are reported in figures 4–6 for Cu, Ag and Au respectively along with second order calculations by Moriarty [31]

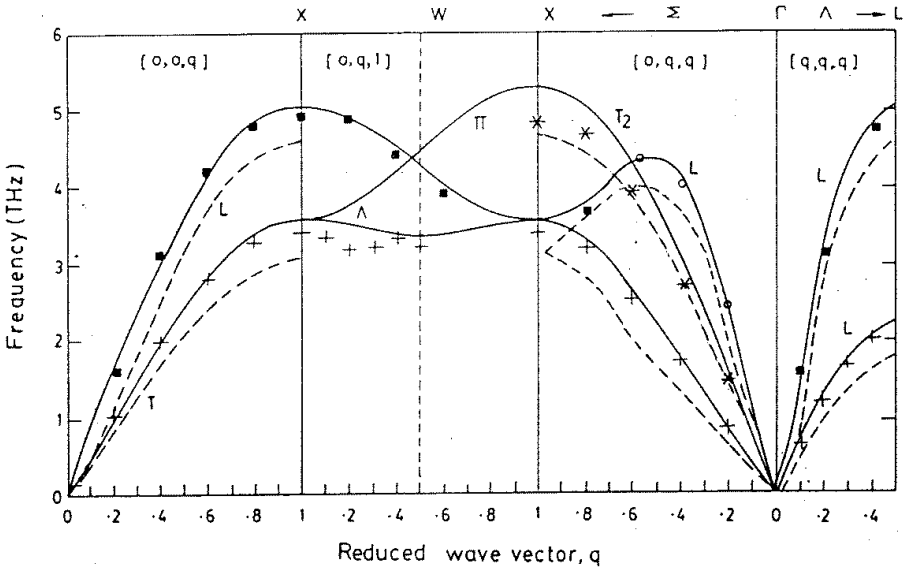

Figure 5. Phonon dispersion curves for silver. Continuous lines show results of third order (present work) and dotted lines show results due to Moriarty [31]. Experimental points are due to Kamitakahara and Brockhouse [37].

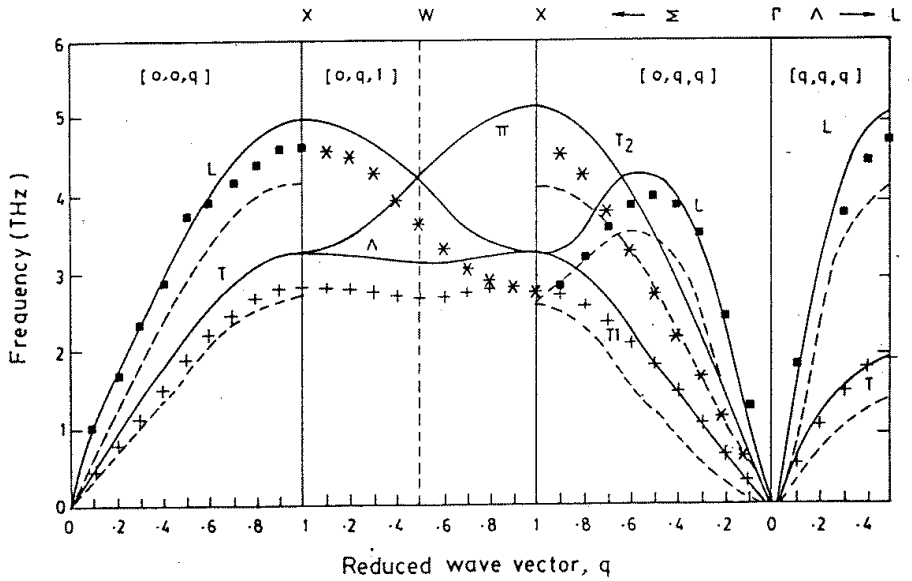

Figure 6. Phonon dispersion curves for gold. Continuous lines show results of third order (present work) and dotted lines show results due to Moriarty [31]. Experimental points are due to Lynn *et al* [38].

(dashed lines). These figures show clearly the importance of three-body forces in noble metals. Introduction of third order correction improves considerably the calculated frequencies at almost all the modes of vibrations in major symmetry directions. The overall agreement between third order calculations and experimental results is excellent.

The second order calculations by Moriarty show Kohn anomalies in [001] T and [011] T_1 branches for Cu. Moriarty argued that s-d hybridization is responsible for the strong anomalous behaviour of metal Cu. However, no such Kohn anomalies have been reported experimentally in Cu. It is interesting to see, in this context, that in our third order calculations the anomaly in [001] T branch has greatly weakened and it has disappeared in [011] T_1 branch. This again, speaks in favour of necessity of third order calculations.

A close look at figure 6 shows that [001] T branch for Au shows a maximum difference of about 12% with experimental results at the zone boundary. It may be noted that third order calculations are highly sensitive to the form of the pseudopotential. Even a slight change in the form factor can cause considerable change in the phonon frequencies [33]. In addition to this, there may be some uncertainty, in the calculated frequencies, due to some inaccuracy in exchange and correlation function $G(q)$. Effective charge of ion also plays an important role in determining the phonon frequencies [30]. All these factors can change the phonon frequencies by about 10–15%. This, we believe, has happened with Au in our calculations. However, overall results for all the three metals are far better than those obtained in second order calculations.

It is interesting to mention a recent calculation of phonon dispersion curves of Au by Singh [34]. This author has used transition metal pair potential which is basically equivalent to the effective pair potential obtained by Wills and Harrison [35]. Our results for Au are better than those due to Singh. It should be noted that present calculations are based on first principles pseudopotential, while, in the work of Singh, some parameters have to be fixed by experimental inputs.

4. Conclusion

In this paper we have investigated the importance of three-body forces on lattice dynamics of noble metals. In order to evaluate the third order perturbation terms, which represent these forces, we have constructed a local potential from the first principles energy wave number characteristic. This local pseudopotential, used in third order, accounts for the off-shell processes arising from the non-locality in the first principles pseudopotential. Our method of constructing the effective local potential is simple and more realistic as it gives the same energy wave number characteristic as generated from full non-local calculations.

Our method of studying three-body forces is more realistic as compared to many other previous works in which non-central forces were accounted for in either phenomenological way or by appropriate adjustable force constants.

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