

# LATTICE DYNAMICS OF NOBLE METALS ON EFFECTIVE THREE-BODY INTERACTION

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Quite recently we 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. We applied our scheme to alkali metals. We studied here the lattice dynamics of noble metals on our approach by calculating phonon dispersion relations along the three principal symmetry directions,  $[\xi 0 0]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  and the  $(\theta-T)$  curves of three noble metals: copper, silver and gold. We obtained reasonable agreement with the experimental findings.

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## 1. Introduction

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 i.e.  $(\theta-T)$  curves or  $(C_v-T)$  curves [1]. 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. The models which failed to predict well the experimental phonons were not trustworthy even for the thermal properties of metals. A close predictions of the experimental phonons by a theoretical model was only possible once the electron-ion interactions in metals was considered adequately [2]. In order to achieve this goal there emerged several techniques i.e. semiclassical models where electron-ion interaction was considered on a phenomenological basis, pseudopotential models, where a weak electron-ion potential was constructed on the physical basis and models on first principles [3]. 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.

In the present paper we confine our attention to a phenomenological model developed recently by Sarkar et al. [4, 5] for cubic and hcp metals by taking into account the ion-ion interaction on a two-body pair potential and the electron-ion interaction on three-body interaction. To evaluate the electron-ion interaction these authors averaged the local strain in the electronic medium in terms of the ionic displacements of all pairs of atoms which are equidistant and at equal phase difference to one of the atoms of the first, second and third etc., nearest neighbours to the origin atom forming different phases. The electron-ion interaction plays a crucial part in the model of Sarkar et al. [4, 5]. The electron-ion interaction in bcc metals [6] and hcp metals [5] were considered effective out to second nearest neighbours but for fcc metals out to first nearest neighbour [4]. Keeping in mind that the Cauchy deviation,  $C_{12} - C_{44}$  in fcc, and hence the bulk modulus of the electron gas,  $K_e$  in fcc metals is quite bigger in comparison to bcc and hcp metals, the use of first neighbour electron-ion interaction in these metals is questionable. Another reason for extending the electron-ion interaction for the dynamical matrix in the model of Sarkar et al. [4] is motivated by the fact that the electronic displacements are described in terms of the ionic displacements which means that this interaction becomes a short ranged interaction and not a type of long-range Coulomb interaction.

The statement of Sarkar et al. [4] that in fcc metals interionic interactions are of very short range, nearly the first nearest neighbour interaction has no physical justification. The experimentalists such as Woods et al. [7] have shown a necessity of including at least two neighbour ionic interactions. The use of ion-ion interaction effective between the first nearest neighbour is doubtful. We have, thus, extended the ion-ion interaction as well as electron-ion interaction for fcc metals out to second neighbours. We also introduced the crystal equilibrium condition of Upadhyaya et al. [8] to reduce one independent model parameter. The present paper is a continuation of our previous work on alkali metals [9] where we obtained a good fit with the experimental data on phonon dispersion relations and  $(\theta-T)$  curves. We have applied our scheme to noble metals as in fcc structure since these metals are very favorite metals of study. We calculated the phonon dispersion relations along all the three symmetry directions i.e.  $[\xi 00]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  and the thermal properties i.e.  $(\theta-T)$  curves and  $(C_v-T)$  curves of these metals. The comparison of the theoretical predictions with the experimental works forms the subject matter of this paper.

The general outline of the theory has been given by Sarkar et al. [4] and by us [9]. Here we will give only the necessary details.

The phonon frequencies of metals are calculated by solving the secular determinant

$$|D_{\alpha\beta}(q) - m\omega^2 I_{\alpha\beta}| = 0, \quad (1)$$

where  $D_{\alpha\beta}(q)$  is the dynamical matrix for the  $q$ -th phonon wave vector,  $m$  is the ionic mass and  $I$  is the unit matrix.

Each element of the dynamical matrix  $D_{\alpha\beta}(q)$  is split up into parts, the ion-ion interaction part i.e.  $D_{\alpha\beta}^{\text{ii}}(q)$  and the electron-ion interaction part,  $D_{\alpha\beta}^{\text{ie}}(q)$ .

Written mathematically

$$D_{\alpha\beta}(q) = D_{\alpha\beta}^{\text{ii}}(q) + D_{\alpha\beta}^{\text{ie}}(q). \quad (2)$$

The evaluation of  $D_{\alpha\beta}^{\text{ii}}(q)$  and  $D_{\alpha\beta}^{\text{ie}}(q)$  is done on different schemes. General expression for  $D_{\alpha\beta}^{\text{ii}}(q)$  is given by

$$D_{\alpha\beta}^{\text{ii}}(q) = \sum_{l'} \phi_{\alpha\beta}'(l, l') \{1 - \exp[i(\omega t - qr_{l'})]\} \quad (3)$$

in Eq. (4)  $l'$  extends out to second neighbours and  $\phi_{\alpha\beta}'$  is given by

$$\phi_{\alpha\beta}' = \frac{r_{\alpha}' r_{\beta}'}{r_n^2} \left( \frac{d^2 \phi}{dr_n^2} - \delta_{\alpha\beta} \right) + \frac{r_{\alpha}' r_{\beta}'}{r_n^2} \frac{d\phi}{dr_n}. \quad (4)$$

By defining the first derivative divided by the distance of the neighbour from the origin by  $\phi_n''$  and second derivative of the potential energy  $\phi_n''$  i.e.

$$\phi_n' = \frac{1}{r_n} \frac{d\phi}{dr_n} \quad \text{and} \quad \phi_n'' = \frac{d^2 \phi}{dr_n^2}. \quad (5)$$

$\phi_n'$  and  $\phi_n''$  are the tangential and radial force constants for the  $n$ -th neighbour. Confining our attention to first two nearest neighbours, we have four parameters namely  $\phi_1', \phi_2', \phi_1'', \phi_2''$ . Substitution of Eq. (5) into (4) for all the 12 first neighbours and 6 second neighbours gives the typical diagonal and non-diagonal part of the dynamical matrix

$$D_{\alpha\beta}^{\text{ii}}(q) = 2(\phi_1'' + \phi_1') [2 - C_{\alpha}(C_{\beta} + C_{\gamma})] + 4\phi_1'(1 - C_{\beta}C_{\gamma}) + 4\phi_2'' S_{\alpha}^2 + 4\phi_2' [2 - (C_{\beta}^2 + C_{\gamma}^2)], \quad (6)$$

$$D_{\alpha\beta}^{\text{ii}}(q) = 2(\phi_1'' - \phi_1') S_{\alpha} S_{\beta}, \quad \alpha \neq \beta, \quad \alpha, \beta = 1, 2, 3. \quad (7)$$

The calculation of the dynamical matrix of the electron-ion interaction,  $D_{\alpha\beta}^{\text{ie}}(q)$  on the scheme of Sarkar et al. [4], or on our scheme [9] extending out to two neighbours is given by

$$D_{\alpha\beta}^{\text{ie}}(q) = \frac{1}{4} K_e V_0 \sum_l \chi_l^2 \{1 - \exp[i(qr - \omega t)]\}. \quad (8)$$

In Eq. (8)  $\chi_l$  is the average electronic strain calculated in terms of the ionic displacements in an effective three-body interaction introduced by Sarkar et al. [4] and is given by

$$\chi_{l'} = \frac{3}{n_{l'}} \sum_{l''} \frac{r(l, l'') u(l'')}{r^2(l, l'')}. \quad (9)$$

In Eq. (9) summation in  $l''$  is for the first two nearest neighbours, i.e.  $n_1', n_2'$  are for the 1st and 2nd nearest neighbours and are respectively 12 and 6. The typical diagonal and non-diagonal part of the dynamical matrix  $D_{\alpha\beta}^{\text{ie}}(q)$  is given by

$$D_{\alpha\beta}^{\text{ie}}(q) = 2aK_e \left\{ S_{\alpha} \left[ C_{\alpha} + \frac{1}{4}(C_{\beta} + C_{\gamma}) \right] \right\}^2, \quad (10)$$

$$D_{\alpha\beta}^{\text{ie}}(q) = 2aK_e S_{\alpha} S_{\beta} \left[ C_{\alpha} + \frac{1}{4}(C_{\beta} + C_{\gamma}) \right] \left[ C_{\beta} + \frac{1}{4}(C_{\beta} + C_{\gamma}) \right], \quad \alpha \neq \beta. \quad (11)$$

In Eqs. (6), (7), (10) and (11)  $C_\alpha = \cos(2\pi a K_\alpha)$  and  $S_\alpha = \sin(2\pi a K_\alpha)$ ,  $K_\alpha$ ,  $K_\beta$  and  $K_\gamma$  are the Cartesian components of the phonon wave vector  $K$  and  $2a$  is the lattice parameter.

A look at Eqs. (6), (7), (10), and (11) shows that there are five adjustable parameters in the model i.e.  $\phi'_1$ ,  $\phi''_1$ ,  $\phi'_2$ ,  $\phi''_2$  and  $K_e$ . We used crystal equilibrium condition of Upadhyaya et al. [8] to reduce one independent model parameter. According to these authors total pressure of the crystal at equilibrium volume is zero, meaning that electronic pressure and ionic pressure of the lattice are equal and opposite i.e.

$$p_i = -p_e, \quad (12)$$

$$p_i = \frac{d\phi}{d\Omega} = \frac{4}{a}[\phi'_1 + \phi'_2], \quad (13)$$

$$p_e = \frac{d\phi_e}{d\Omega} = -\frac{3}{5}K_e. \quad (14)$$

Thus, Eq. (12) takes the new form

$$aK_e = \frac{10}{3}[\phi'_1 + \phi'_2]. \quad (15)$$

By expanding the dynamical matrix in the long wavelength limit, we have relations between force constants and elastic constants given by

$$aC_{11} = (\phi''_1 + \phi'_1 + 2\phi''_2) + \frac{\phi}{4}aK_e, \quad (16)$$

$$aC_{12} = \frac{1}{2}(\phi''_1 - 5\phi'_1 - 4\phi'_2) + \frac{9}{4}aK_e, \quad (17)$$

$$aC_{44} = \frac{1}{2}(\phi''_1 + 3\phi'_1 + 4\phi'_2). \quad (18)$$

Substituting Eq. (15) in Eq. (16) to (18) eliminates one independent model parameter. Thus in the present study we have only four independent model parameters in comparison to the scheme of Sarkar et al. [4] where crystal equilibrium condition was not utilized and the introduction of  $p_e$  and  $K_e$  in the expression of elastic constants had increased two additional model parameters.

The lattice heat capacities are evaluated by the expression

$$C_\nu = 3R \int_0^{\nu_1} E(x)g(\nu)d\nu, \quad (19)$$

where  $g(\nu)$  is the frequency distribution function and  $E(x)$  is the Einstein specific heat function given by

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2}, \quad (20)$$

$$x = \frac{h\nu}{k_B T}, \quad (21)$$

$h$  is the Planck constant,  $k_B$  is the Boltzmann constant,  $\nu_1$  is the largest frequency in the frequency spectrum and  $R$  is the gas constant.

## 2. Numerical computation

In order to determine all the four parameters of the model we have used there experimental elastic constants and one longitudinal frequency from the zone boundary of the  $[\xi 00]$  direction. The experimental phonons for copper were measured by various researchers, Buhner et al. [10], Nicklow et al. [11], Sinha [12], Miller and Brockhouse [13] and Svensson et al. [14]. We chose the paper of Svensson et al. [14] for the present study. The experimental phonons for silver was also measured by more than one researcher, Drexel et al. [15] and Kamitakahara and Brockhouse [16]. We chose the paper of Kamitakahara and Brockhouse [16] in our study. The experimental phonons of gold was measured by Lynn et al. [17]. The experimental elastic constants of copper was taken from the paper of Overton and Gaffney [18]. The experimental elastic constants of silver was taken from the paper of Hiki and Granato [19]. The experimental elastic constants of gold was taken from the paper of Alexandrov and Ryzhova [20].

TABLE I

Input values of the experimental data.

Metal	$\nu_L(\xi, 0, 0)$ [ $10^{12}$ Hz]	$\nu_L(\xi, \xi, 0)$ [ $10^{12}$ Hz]	$C_{11}$ [ $10^{11}$ d/cm <sup>2</sup> ]	$C_{12}$ [ $10^{11}$ d/cm <sup>2</sup> ]	$C_{44}$ [ $10^{11}$ d/cm <sup>2</sup> ]
Gold	4.61	3.34	19.40	16.60	4.00
Silver	4.71	4.09	12.22	9.07	4.54
Copper	7.19	5.73	16.84	12.15	7.55

TABLE II

Output values of the atomic force constants.

Metal	$\phi_1''$ [ $10^3$ d/cm]	$\phi_1'$ [ $10^3$ d/cm]	$\phi_2''$ [ $10^3$ d/cm]	$\phi_2'$ [ $10^3$ d/cm]
Gold	39.2341	-4.9431	0.5074	5.3123
Silver	24.0501	-2.8295	1.8541	2.9615
Copper	27.0307	-0.1166	-2.4681	0.6123

In Table I there are shown the input data to calculate the atomic force constants and in Table II there are shown the output values of them.

Knowledge of the force constants allowed us to solve the secular determinant for various wave vectors in all the three principal symmetry directions and to plot the phonon dispersion relations in  $[\xi 00]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  for copper, silver and gold respectively in Figs. 1, 2 and 3. Also shown in these figures are experimental phonons for comparison purpose.

In order to determine the phonon density of states,  $g(\nu)$  versus  $\nu$ , we subdivided the Brillouin zone into 8000 miniature cells and found 282 independent wave vectors to describe the total 8000 wave vectors given by the crystal symmetry. We solved the dynamical matrix for all these wave vectors and constructed a histogram of  $\Delta\nu = 0.05$  Hz. This histogram was utilized to compute  $C_\nu$  from Eq. (19).

The experimental heat capacities of copper, silver and gold were taken from the paper of respectively Martin [21], Meads et al. [22] and that of Geballe et al. [23].

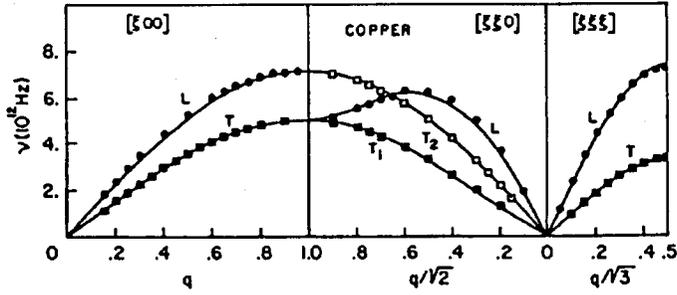


Fig. 1. Phonon dispersion relations in copper along  $[\xi 0 0]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  directions. Solid lines represent present calculations. Signs represent experimental points.

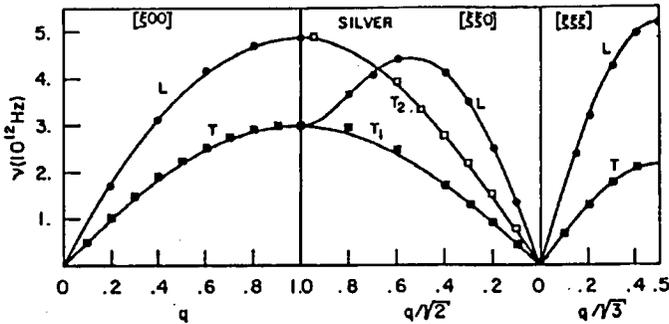


Fig. 2. Phonon dispersion relations in silver along  $[\xi 0 0]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  directions. Captions are the same as for Fig. 1.

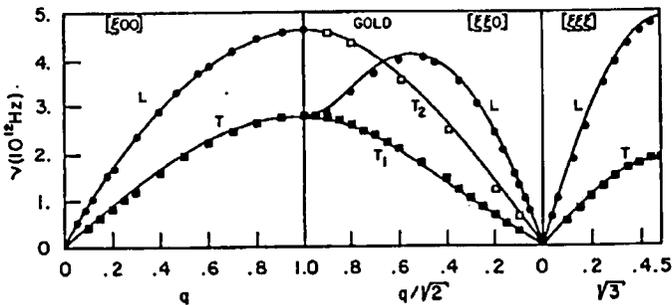


Fig. 3. Phonon dispersion relations in gold along  $[\xi 0 0]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  directions. Captions are the same as for Fig. 1.

The electronic heat capacities were subtracted from the experimental  $C_v$  in order to extrapolate  $(\phi-T)$  curves. The calculated and experimental  $(\theta-T)$  curves of copper, silver and gold are shown in Figs. 4 and 5.

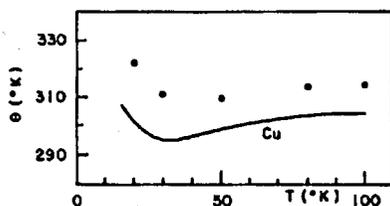


Fig. 4.  $(\theta-T)$  curves of copper. Solid line represent present calculations and experimental points are shown by.

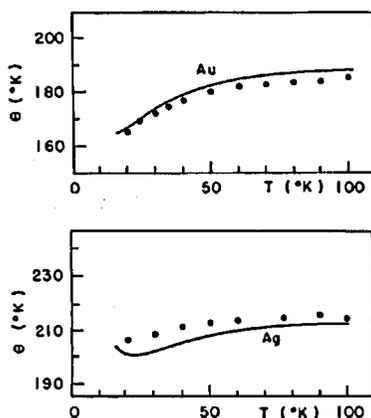


Fig. 5.  $(\theta-T)$  curves of gold and silver. Captions are the same as for Fig. 4.

### 3. Comparison with experimental work

A look at Fig. 1 and Fig. 4 shows that our calculated phonon dispersion relations and  $(\theta-T)$  curve of copper has given an excellent account of experimental results. While calculated phonon dispersion relations have almost reproduced the experimental results quite close to experimental error, the calculated  $(\theta-T)$  curve lies about 5% below the experimental one but it demonstrates the correct course of the experimental curve.

A critical study of Figs. 2 and 5 shows that the phonon dispersion relations along all the three principal symmetry directions of silver and  $(\theta-T)$  of this metal have been explained very well by the theoretical predictions. As far as phonons are concerned, like copper, our theoretical results have almost reproduced the experimental papers within the limits of the experimental error. The maximum deviation between the calculated and experimental phonons is of the order of 2%. The calculated  $(\theta-T)$  curve has reproduced the entire course of the experimental curve but lies about 3.5% below the experimental one.

Finally, a close glimpse of Figs. 3 and 5 shows that there is an excellent agree-

ment between the calculated and experimental phonons in all the three principal symmetry directions for gold. For gold the calculated curves show a discrepancy in the longitudinal branches of all the three directions,  $[\xi 00]$ ,  $[\xi \xi 0]$  and  $[\xi \xi \xi]$  but in no way the difference between the experimental and theoretical phonon is more than 5%. A critical study of Fig. 5 shows that the theoretical ( $\theta-T$ ) curve of gold has reproduced the entire course of the experimental curve but lies about 3% above it.

#### 4. Discussion and conclusions

We have presented here the lattice dynamics and thermal properties of noble metals on an extended model of Sarkar et al. [4] recently done by us [9]. The computed phonon dispersion relations for all the three metals, copper, silver and gold reproduced well the experimental phonons within the limit of experimental error. Calculated ( $\theta-T$ ) curves of them gave also an excellent agreement with the experimental findings.

Sarkar et al. [4] have studied only copper on their model. Our result for copper is superior to their work due to the inclusion of higher neighbour ionic and electronic interactions. While Sarkar et al. [4] used three independent parameters, we used four, one more than they. We can say boldly that the ionic interactions in fcc metals should be considered out to second neighbour and the electron-ion interaction should be extended beyond the first neighbour which is confirmed from the present study.

As has been pointed out in our paper of alkali metals [9], the effect of extending the electron-ion interaction out to second neighbour has a pronounced effect in the elastic constants. This can be explained by splitting the experimental elastic constant,  $C_{ij}$ , in terms of elastic constant on ion-ion interaction,  $C_{ij}^{ii}$ , and elastic constant on electron-ion interaction,  $C_{ij}^{ie}$ , i.e.

$$C_{ij} = C_{ij}^{ii} + C_{ij}^{ie}. \quad (22)$$

If we take the electron-ion interaction effective between nearest neighbour, we have

$$C_{11} = C_{11}^{ii} + aK_e, \quad (23)$$

$$C_{12} = C_{12}^{ii} + aK_e, \quad (24)$$

$$C_{44} = C_{44}^{ii}. \quad (25)$$

But if we take the electron-ion interaction out to second neighbour, we have

$$C_{11} = C_{11}^{ii} + \frac{9}{4}aK_e, \quad (26)$$

$$C_{12} = C_{12}^{ii} + \frac{9}{4}aK_e, \quad (27)$$

$$C_{44} = C_{44}^{ii}. \quad (28)$$

Equations (23), (24) and (26) and (27) confirm the similar kind of results obtained by us (see Eqs. (19), (20) and (21) of our paper [9]). There is a misprint in that paper, on the right hand side of these equations there is  $C_{11}$  and not  $C_{12}$ .

We further extended the model of Sarkar et al. [4] by including third and fourth neighbour ion-ion and electron-ion interaction for fcc metals but that

scheme did not show any significant improvement over the present results. We can thus conclude our paper by the statement that the model of Sarkar et al. [4] extended by us gives a good description of cubic metals either for the fcc structure or bcc structure. We have to see whether our scheme is good or not for transition metals. Such a study is in progress.

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