Phonon Dispersion in Noble Metals

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A new lattice dynamical model comprising various interactions among the constituents of noble metals is developed. The model assumes central core-core coupling extending to the first neighbours only. Overlap interactions among neighbouring d-shells are expressed in terms of an angular parameter. Volume interactions for core-conduction electrons and d-shell-conduction electrons are described through a simple expression. Interactions between core and d-shell are also accounted for adequately.

The lattice is considered in equilibrium under the volume dependent energy of cores, conduction electrons and the d-shell electrons. The obtained dispersion relations for copper and silver are compared with (a) experimental data, (b) results of a recent first-principle calculation and (c) results of a recent phenomenological study.

1. Introduction

Recent years have seen a rapid advance in lattice dynamical studies. Phenomenological [1–5] as well as first principle [6–10] approaches have been employed to develop various models. In spite of this progress the lattice dynamical behaviour of non-simple metals remains to be a complex problem of immense interest. The complexities in these metals can obviously be attributed to the presence of d-shell and conduction electrons. In most of the classical studies [1–5] the interactions among these electrons and their environment in the lattice are ignored. Only Fielek [11] and Jani and Gohel [12] have considered the interactions of d-shell with core and conduction electron, but in these studies the interactions among core and conduction electrons have been ignored. Moreover, all these studies [1–5, 11–12] are deficient in as much as they do not account for the equilibrium of the lattice properly but only with respect to the core-core interactions. Some authors [13–14] have also considered the fermi-energy of conduction electrons while arriving at the equilibrium constraint. Some others [15–18] have modified the equilibrium condition for the exchange and correlation parts of the energy associated with the conduction electrons. In all these studies the contribution of the d-shell electrons to the equilibrium of the lattice has been ignored.

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The present communication accounts in a realistic manner for the following interactions:

i) Core–core interaction,
ii) d-shell–d-shell interaction,
iii) Core–d-shell interaction,
iv) Volume interaction among core and conduction electrons,
v) Volume interaction among d-shell and conduction electrons.

The core–core interaction is considered to be purely central extending out to first neighbours only. This assumption is fully supported by (a) pseudo-potential studies [19–20] involving perturbation calculations of second order, which essentially deal with the central interactions among the cores and b) non-linear pseudopotential studies of Resolt and Taylor [21] and Dagens et al. [22], which show oscillations in the effective two body interaction with rapid decrease in magnitude. These studies show that the potential up to zero beyond the first minimum affects only the first neighbour in fcc metals. It is well known that the cubic field in complex metals removes the five fold degeneracy and destroys the sphericity of the charge distribution due to the electrons occupying d-shells. This non-sphericity involves a non-central character [23–27] of the interactions among the overlapping clouds of d-shell charges, which can be represented by angular interactions of the Clark et al. [28] type, coupling the nearest neighbours only. These short range forces are dominant because C_{44} is moderately

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high and $(C_{12}-C_{44})$ is relatively small for copper and silver. The interaction among core and d-shell is expressed by the scheme given by Fielek [11]. Volume interactions among core and conduction electrons and d-shell and conduction electrons are expressed [29] in the form of a simple expression which is compensated for its asymmetric character by the inclusion of an inference factor (G) and a damping factor (C).

The lattice equilibrium is considered under the cumulative effect of the energies due to core, conduction and d-shell electrons. The lattice equilibrium makes the potential energy rotationally invariant on one hand and maintains the equality [30] of statical and dynamical elastic constants on the other hand. Moreover, the inclusion of the equilibrium condition makes the model consistent with measurements of elastic constants and dispersion frequencies.

2. Theory

The secular determinant, which is solved to obtain the dispersion frequencies (ν) along the main symmetry directions, assumes the form a characteristic equation.

$$|D(\boldsymbol{q}) - 4\pi^2 m \nu^2 I| = 0 \tag{1}$$

where m is the mass of the core and I the unit matrix of the order 3. Elements of total dynamical matrix $D(\boldsymbol{q})$ are derived from the interactions among the various constituents of the metal under consideration

$$\begin{aligned} D_{xx}(\boldsymbol{q}) &= D'_{xx}(\boldsymbol{q}) + K^2/M\,, \\ D_{xy}(\boldsymbol{q}) &= D'_{xx}(\boldsymbol{q})\,, \end{aligned} \tag{2}$$

where the elements of $D'(\boldsymbol{q})$ arise out of the interactions of cores with its environment i.e. interactions among core–core, core–d-shell and core–conduction electrons:

$$\begin{aligned} D'_{xx}(\boldsymbol{q}) &= -4(\beta_1 + 2\alpha_1) + 2(\beta_1 + \alpha_1) \\ &\quad \cdot C_x(C_y + C_z) + 4\alpha_1 C_y C_z \\ &\quad + K + E(\boldsymbol{q})\,, \\ D'_{xx}(\boldsymbol{q}) &= -2(\beta_1 - \alpha_1) S_x S_y\,. \end{aligned} \tag{3}$$

The interactions of d-shells with their surrounding constituents contribute to the total dynamical matrix $D(\boldsymbol{q})$ through the term M appearing in (2). The term M involving interactions for d-shell-d shell, core-d shell and d shell-conduction electron is the eigenvalue of the equation

$$|D''(\boldsymbol{q}) - MI| = 0 \tag{4}$$

where

$$\begin{aligned} D''_{xy}(\boldsymbol{q}) &= 16K_1[2 - C_x(C_y + C_z)] \\ &\quad - 4K_1(C_x' - C_y' - C_z') \\ &\quad + K - E'(q)\,, \\ D''_{xx}(\boldsymbol{q}) &= -16K_1 S_x S_y\,, \end{aligned} \tag{5}$$

$C_x = \cos(\frac{1}{2}aq_x)$ and $C_x' = \cos(aq_x)$. a is the lattice constant and q_x the x-component of the phonon wave vector $\boldsymbol{q}$. α_1, β_1 are, respectively, the first and second derivatives of the central potential coupling the nearest cores. K is the force constant due to core-d-shell interaction. K_1 is the angular force constant, which describes the overlap interaction among the clouds of neighbouring d-shells. E and E' represent the matrix contribution of conduction electrons with the core and the d-shells, respectively, i.e.

$$E_{xx}(\boldsymbol{q}) = \frac{2\zeta_x^2 D G^2(qr) C(\eta)}{K_1 + 4K_2|\zeta|^2}\,, \tag{6}$$

$$E'_{xx}(\boldsymbol{q}) = \frac{2\zeta_x^2 D' G^2(qr) C(\eta)}{K_1 + 1 + K_2|\zeta|^2}\,, \tag{7}$$

where ζ_x is the x-component of the reduced wave vector ζ. D and D' are the deformation parameters associated with conduction electrons due to the motion 1 care and d-shells respectively.

$$K_1 = 1/\pi^2\,, \quad K_2 = 1/a^2 K_c^2\,. \tag{8}$$

K_c is the secreening parameter which has been evaluated in the Bohm-Pine [31] limit. The inference factor $G(qr)$ is defined as the overlap integral of the form

$$G(qr) = \frac{\int_{\Omega} \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})}{\Omega}\,\mathrm{d}\tau \tag{9}$$

and is determined explicitly for the fcc structure. The damping factor $C(\eta)$ is expressed as

$$C(\eta) = \exp(-0.03\,\eta^4)\,, \tag{10}$$

where $\eta = q/2K_F$. K_F is the fermi wave vector

$$K_F = \left(\frac{3\pi^2 z}{\Omega}\right)^{1/3}\,, \tag{11}$$

Z the effective valence and Ω the atomic volume. The total energy (E_T) of the system is

$$E_T = E_c + E_e + E_d, \tag{12}$$

where E_c is the energy due to cores and E_e, E_d are the corresponding terms for conduction and d-shell electrons, respectively. For equilibrium $\partial E_T/\partial\Omega$ should vanish, i.e.

$$\frac{\partial E_c}{\partial\Omega} = -\frac{\partial}{\partial\Omega}(E_e + E_d). \tag{13}$$

Obviously

$$\partial E_c/\partial\Omega = 4\alpha_1/a \tag{14}$$

and

$$\partial E_e/\partial\Omega = -P_e, \quad \partial E_d/\partial\Omega = -P_d. \tag{15}$$

Here P_e and P_d are the pressures associated with conduction and d-shell electrons. The deformation parameter D for the conduction electrons may now be expressed as

$$D = -a\Omega\,\partial P_e/\partial\Omega. \tag{16}$$

The energy of the conduction electrons may be written as the sum of fermi, exchange and correlation terms. The fermi and exchange terms are well known, but different expressions for the correlation energy of the electrons are reported from time to time. In a recent communication [32] we have reported the values of P_e and K_e ($=D/a$) for almost all the schemes of correlations added to the usual fermi and exchange terms. The electron separation used in these calculations varies from 1 to 6. In view of the cohesion in metals, it has been found that suitable values of P_e and K_e are found for the separations 3, 4 and 5. In noble metals like copper and silver, the separation is close to 3 and the proper values of P_e and K_e ($=D/a$) are obtained by describing the electron correlation by the Wigner-Seitz [33] scheme.

For evaluating P_d we can write the expression for E_d following Slater [34] and Lindgren and Schwarz [35], i.e.

$$E_d = -1\cdot 47\left(\frac{3}{2}\right)\left(\frac{6}{\pi}\right)^{1/3}\varrho_\alpha^{1/3}, \tag{17}$$

where ϱ_d is the probable density of the d-shell electrons.

3. Evaluation of Model Parameters

Our model contains six free parameters (α_1, β_1, K, K_1, D, D'). D is evaluated using (15) and (16). As mentioned earlier, the expression for E_e is written using usual terms for the fermi and exchange energies. The correlation part of the energy is given by the expression of Winger-Seitz [33]. Thus

$$E_e = \frac{2\cdot 21}{r^2} - \frac{0\cdot 916}{r} - \frac{3}{2\pi\alpha r}, \tag{18}$$

where $\alpha = (4/q\pi)^{1/3}$ and r is the electron separation, which can be evaluated by the knowledge of the atomic volume, i.e.

$$\Omega = \tfrac{4}{3}\pi r^3 a_0{}^3 = a^3/4, \tag{19}$$

where a_0 is the Bohr-radius, which is needed to make r dimension less.

Three of the remaining model parameters are evaluated using elastic relations. These elastic relations are obtained by comparing (1) in the long wave length limit to Christoffel's equation [36] of elasticity: The measured elastic constants reported by Overton et al. [37] and Kittel [38] for copper and silver, respectively, are used in the present calculations.

One of the model parameters is evaluated by the constraint defining the equilibrium of the metallic lattice. This constraint can be derived using (13), (14) and (15). The resulting expression, known as equilibrium condition, may be written as

$$\alpha_1 = \frac{a}{4}(P_e + P_d). \tag{20}$$

For copper and silver, P_d assumes insignificantly small values because of the dominance of the short range forces. The last model-parameter is evaluated by the knowledge of the Zone-boundary frequency for the transverse mode (ν_T) along the [ζ 0 0] direction. The needed expression is written as

$$4\pi^2 m \nu_{T[100]}^2 = 4(\beta_1 + 3\alpha_1) + K + \frac{K^2}{-K - 32K_1}. \tag{21}$$

Input data required to evaluate the model parameters for copper and silver are enlisted in Table 1, while Table 2 gives the calculated values of the required parameters.

Table 1. Model parameters.

Parameters	Copper	Silver
C_{11}	1.6839×10^{12} dyne/cm^2	1.240×10^{12} dyne/cm^2
C_{12}	1.2142×10^{12} dyne/cm^2	0.934×10^{12} dyne/cm^2
C_{44}	0.7539×10^{12} dyne/cm^2	0.461×10^{12} dyne/cm^2
a	3.615 A°	4.09 A°
m	105.4746×10^{-24} gm.	179.0642×10^{-24} gm.

Table 2. Calculated values of the model parameters in 10 dyne/cm.

Parameters	Copper	Silver
α_1	− 0.0468505	− 0.0530066
β_1	2.8659	2.0445098
K	− 0.0812031	0.2126841
K_1	− 0.0174996	− 0.00879
D	0.0649868	0.0735259
D'	0.9442001	1.2963513

4. Results

The calculated dispersion curves for copper and silver are shown by solid lines in Figs. 1 and 2, respectively. The experimental points (●, ○, ×), of Sinha [39] and Drexel et al. [40] for copper and silver, respectively, are shown for comparison. To show further the efficiency of the model, we have compared our curves with these given in one of the recent phenomenological studies of Rai and Hemkar [41] and that given in one of the recent pseudopotential studies of George et al. [42].

5. Conclusion

In noble metals, the filled d-shell lies just below the Fermi level. Further this band is located in the middle of the free-electrons (s-p). It is therefore important to consider the effect of these d-electrons when describing the dispersion-relations for these metals. The present study is very much in keeping with this situation and expresses explicitly (a) the interaction of these electron with their environment and (b) the contribution of these electrons towards the lattice stability. Our study expresses Cauchy's discrepancy as a function of (a) volume dependent core-electron interaction energy, (b) isotropic energy of the conduction electrons and (c) non-central energy arising from many body

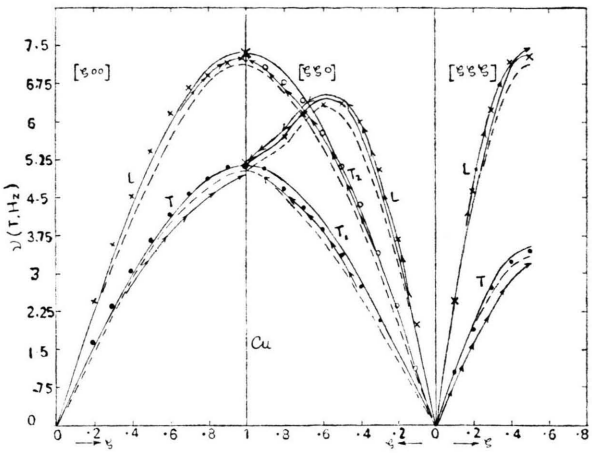

Fig. 1. Dispersion curves for copper. (———) theoretical results of the present model, (-------) theoretical results of Rai and Hemkar [41], (→→→) theoretical results of George et al. [42], (●, ○, ×) experimental points of Sinha [39].

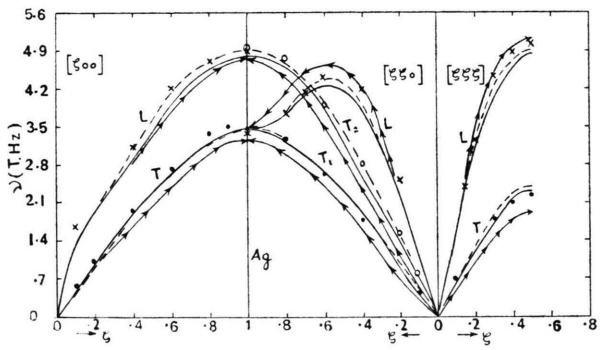

Fig. 2. Dispersion curves for silver. (———) theoretical results of the present model, (-------) theoretical results of Rai and Hemkar [41], (→→→) theoretical results of George et al. [42], (●, ○, ×) experimental points of Drexel et al. [40].

interactions due to the overlap of the non-spheric charge-distribution of the d-shell electrons. The model thus satisfies partially the mathematical contents of the recent studies of Finnis [43], Upadhyaya [44] and Cousins and Martin [45].

The dispersion relations for copper and silver obtained from the present model fit the experimental data rigorously. The maximum errors for copper and silver lie in the T- and L-mode, respectively, near the zone boundary along the direction [ζ ζ ζ]. These errors, being 3.2% and 4.4% for copper and silver, respectively, are unimportant in view of the experimental errors. Our results are

in much better agreement with the experimental observations than those of other calculations [41—42]. It is thus evident that the interactions in complicated structures like copper and silver can best be described within the frame work of the present model.

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