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Electron pressure and lattice vibration in gold

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A central pair potential model, already developed by the authors, has been employed to investigate the lattice dynamical behaviour of gold. The model assumes the total interaction comprising of ion-ion and ion-electron-ion interactions. Former interactions being central (radial and transversal) extend out to the second neighbours due to the screening offered by the conduction electrons, Later interaction are considered on the lines suggested by Sharma-Joshi scheme, which yield good agreement with the experimental data on gold The whole lattice has been assumed to be in equilibrium under ionic and electronic pressures The electronic pressure and bulk-modulus derived from the model are compared with those given by independent theoretical formulations. Further, the model has been used to derive the phonon frequencies for gold. These frequencies are found to be in excellent agreement with the experimental ones

1. Introduction

Various authors Rathore (1976), Goel *et al* (1974), Singh & Hemkar (1975), Kumar & Tolpadi (1975) have used angular interactions de-Launay (1956), Clark *et al* (1964) for discussing the lattice dynamical behaviour of cubic metals These angular forces were initially thought of as the forces present in the covalently bonded crystals Since no such bonds exist in metals, hence there is hardly any justification for assuming such forces. Recently the present authors (Rathore & Verma 1977) have reported a successful replacement of angular forces with the central ones The central forces (Tewari 1975, Bertolo & Shukla 1975) considered so far, are derived as the second derivative of the ion-ion energy These studies (Hemkar *et al* 1973, Shukla & Salzberg 1973, Kushwaha 1974) ignore the contribution of ionic pressure (first order terms) in governing the lattice equilibrium. Recently Upadhyaya *et al* (1975) and Kulshrestha & Upadhyaya (1976) have considered the lattice equilibrium but their formulation do not account for the cohesion of electrons in metals

The present paper deals with the problem of lattice equilibrium and derive the quantitative values for electron-pressure and bulk modulus which are verified by the independent formulations

Pseudopotential—studies employing the second-order perturbation terms show that the total energy of ions surrounded by electrons may be divided in

two parts i e (a) two body central energy, and (b) volume-energy The present model includes the ion-ion interactions to be central one derived from the first and second order terms of iome-energy The volume-interactions are considered on the basis of the Sharma-Joshi (1963) scheme which introduces relatively small amount (about 5%) of asymmetry in reproducing phonon frequencies of gold. The computed phonon frequencies for gold are found to be in excellent agreement with experimental ones

2 Formulations

The central pair potentials binding the nearest (ϕ_1) and next nearest (ϕ_2) ions are used to derive first order (α_1, α_2) and second order (β_1, β_2) derivatives, which may be written as,

$$\left.\begin{aligned} \alpha_1 &= \frac{1}{r}\frac{\partial\phi_1}{\partial r}, & \alpha_2 &= \frac{1}{r'}\frac{\partial\phi_2}{\partial r'} \\ \beta_1 &= \frac{\partial^2\phi_1}{\partial r^2}, & \beta_2 &= \frac{\partial^2\phi_2}{\partial r'^2} \end{aligned}\right\} \quad \ldots (1)$$

where r and r' are the distances of nearest and next nearest ions from the central ion The elements of dynamical matrix $[D_{ij}{}^I]$ derived from the ion-ion interactions in fcc lattices may be expressed as

$$\left.\begin{aligned} D_{ii}{}^I &= 4(\beta_1+2\alpha_1)-2(\beta_1+\alpha_1)Ci(Cj+Ck)-4\alpha_1 CjCk+4\beta_2 Si^2+4\alpha_2(Sj^2+Sk^2) \\ D_{ij}{}^I &= 2(\beta_1-\alpha_1)SiSj \end{aligned}\right\} \quad (2)$$

where $i, j = 1, 2, 3$; $Ci = \mathrm{Cos}(\frac{1}{2}aqi)$, $Si = \mathrm{Sin}(\frac{1}{2}aqi)$. a is the cube edge and qi is the i-th component of the phonon wave-vector q Sharma-Joshi (1963) scheme yields the following elements ($D_{ij}{}^E$) of dynamical matrix

$$\left.\begin{aligned} D_{ij}{}^E &= \frac{a^3}{4}\, qi\, qj\, Ke G^2(qr_s) \\ D_{ii}{}^E &= \frac{a^3}{4}\, qi^2\, Ke\, G^2(qr_s) \end{aligned}\right\} \quad \ldots (3)$$

where Ke is the bulk modulus of the electron gas, r_s is the radius of the Wigner-Seitz sphere and G is the Bardeen (1937) function

The secular determinant solved for phonon-frequency (ν) may be written as

$$[D-4\pi^2 m\nu^2 I] = 0 \quad \ldots (4)$$

where $D(= D_{ij}{}^I + D_{ij}{}^E)$ is the total element of the dynamical matrix, m is the mass of the ion and I is the unit matrix of the order three. Eq (4) can be com-

pared with Christoffel's equation of electricity, yielding the following relations for fcc lattice

$$\begin{aligned} aC_{11} &= 2(\beta_1+\alpha_1)+4\beta_2+aKe \\ aC_{12} &= \beta_1-5\alpha_1-4\alpha_2+aKe \\ aC_{44} &= \beta_1+3\alpha_1+4\alpha_2. \end{aligned} \quad \ldots \quad (5)$$

For maintaining the equilibrium of the lattice as a whole the algebraic sum of ionic (P_I) and electronic (Pe) pressure must vanish i.e

$$P_I - Pe = 0. \quad \ldots \quad (6)$$

Screened repulsive interactions present among the ions generate the positive ionic pressure. Cohesion of electrons with the ions necessarily demand negative electron pressure. Eq. (6) may be written interms of the model parameters α_1 and α_2 i.e

$$\alpha_1+\alpha_2 = \frac{a}{4} Pe = \frac{a}{4} \gamma Ke \quad (7)$$

The value of γ ($= Ke/Pe$) i.e $-0{\cdot}985$ used in the model is determined by ascertaining the best agreement of computed phonon-frequencies with the experimental ones. Further, this value of γ is obtained by the Bohm-Pine formulations in association with the free-electron-gas-expression reported by Noziers & Pines (1958). Moreover the value of γ lies within the range of screened coulombian computations [assuming $Ke/K_f = 0{\cdot}4$ as given by **H$_0$** (1968)] in association with the Noziers & Pines (1958) expressions.

Four of the model parameters are evaluated by using the set of eq. (5) and eq. (7). The fifth model parameter is evaluated by the knowledge of the transverse zone-boundary frequency ν_T along [100] direction. The needed expression may be written as

$$4\pi^2 m\nu_T^2 = 4(\beta_1+3\alpha_1). \quad \ldots \quad (8)$$

3 Results

As mentioned earlier, the value of γ used in the model is $-0{\cdot}985$, which agrees well with the value ($= -0{\cdot}961$) given by independent computations based on Bohm-Pine screened coulombian energy (ϕ_e) of bunded electron [Eq. (1)] in association with the Noziers and Pines [Eq. (10)] free electron—gas energy (ϕ_{fe}) for upper limit ($r_0 = 1{\cdot}8$) of electron-density

$$\phi_e = -\frac{3e^2}{r_s}\left[\frac{1}{K_c^2 r_s^2} - \exp(-K_c r_s)\left(\frac{1}{K_c^2 r_s^2} - \frac{1}{K_c r_s}\right)\right] \quad (9)$$

$$\phi_{fe} = \frac{2{\cdot}21}{r_0^2} - \frac{0{\cdot}916}{r_0} - 0{\cdot}458\frac{\beta^2}{r_0} + 0{\cdot}866\frac{\beta^3}{r_0^{3/2}} - \frac{0{\cdot}98\beta^4}{r_0^2}$$

$$+0{\cdot}019\frac{\beta^4}{r_0} + 0{\cdot}706\frac{\beta^5}{r_0} + \quad (10)$$

where r_0 is the inter-electronic spacing, K_c is the screening parameter and β is related to long wave-length momentum-transfers.

The volume derivative of ϕ_e and ϕ_{fe} yield the electron pressure, which amount to $-0{\cdot}002552$ au (the unit of energy is ry and that of length is Bohr radius) for gold. This value is in good agreement with that ($= -0{\cdot}002762$ au) computed from the model. The electron bulk modulus (Ke) given by the model is $+0{\cdot}002719$ au which falls well within the range ($0{\cdot}001378$ au–$0{\cdot}003272$ au) provided by Gellmann & Brueckner (1957) and Wigner (1934, 1938) formulations

The input data and the computed model parameters for gold are given in table 1.

Table 1. Input data and computed model parameters for Au

Input data		Computed model parameters	
*C_{11} = $1{\cdot}9234\times10^{12}$	dyne/cm^2	α_1 = $-0{\cdot}2299\times10^{4}$	dyne/cm
*C_{12} = $1{\cdot}6314\times10^{12}$	,,	α_2 = $-0{\cdot}1833\times10^{4}$	,,
*C_{44} = $0{\cdot}4195\times10^{12}$	,,	β_1 = $3\ 1301\times10^{4}$	,,
a = 4·07Å	,,	β_2 = $0{\cdot}1002\times10^{4}$	,,
†ν_T = 2·75 THZ	,,	aKe = $1{\cdot}6272\times10^{4}$	,,

*Neighbours & Alers (1958 †Lynn *et al* (1973),

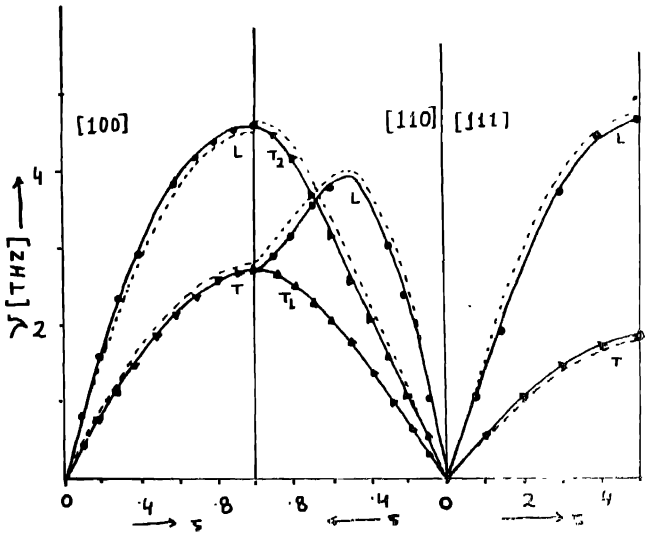

Fig. 1

The computed dispersion frequencies for gold are shown in figure 1. The dashed curves are due to the most recent study reported by Tewari (1975) The experimental points due to Lynn *et al* (1973) shown by circles and triangles closely follow the computed curves.

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