A Non-Central Fielek Model for Lattice Vibrations in Platinum

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Abstract

The Fielek model is made simple and more effective by modifying it for (*a*) purely central and short-range ionic interactions, (*b*) angular interactions coupling the nearby *d* shells, (*c*) easily computable volume interactions and (*d*) for crystal equilibrium in complicated f.c.c. lattices. The model, involving a minimum number of input data, is tested for its validity in predicting the dispersion relations in platinum.

Introduction

Recently, much effort has been made to account for the lattice-dynamical behaviour of platinum. These studies involve first principle (Singh, Singh & Prakash, 1978; Tripathi & Nand, 1979) as well as phenomenological (Singh & Hemkar, 1974; Bertolo & Shukla, 1975; Kharoo, Gupta & Hemkar, 1977) calculations. The former calculations need drastic approximations to arrive at useful conclusions whereas the latter suffer from various shortcomings. Fielek (1975) developed a model which accounts for all the feasible interactions present among the constituents of a non-simple metal. This model has since been employed by Singh, Pathak & Hemkar (1978*a,b*) for the lattice-dynamical study of platinum. The model as compared to other contemporary models seems to be more sound in its mathematical footings, but suffers with some deficiencies, which are accounted for in the present study.

Rathore & Verma (1977) and Rathore (1978, 1979) have already established that the ionic interactions must be central pairwise. This conclusion is also supported by pseudopotential studies employing the second-order perturbation technique. The non-linear pseudopotential studies (Rasolt & Taylor, 1975; Dagens, Rasolt & Taylor, 1975) reveal that the interionic interactions should be limited to immediate neighbours in f.c.c. metals. In view of these findings, the present study modifies the Fielek model to express the interionic interactions as the first (α_1) and second (β_1) derivatives of the central pairwise energy coupling the first neighbours only.

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The electrons occupying the *d* shells overlap with the immediate environment leading to *sd* hybridization, which causes non-sphericity in charge distribution. This non-sphericity calls for unpaired or three-body forces, pointed out by Bertoni, Bisi, Calandra & Nizzoli (1973), Bertoni, Bertolani, Calandra & Nizzoli (1974), Brovman, Kagan & Kholas (1970) and Lloyd & Sholl (1968) in their pseudopotential studies. These forces significantly contribute towards the Cauchy discrepancy exhibited by the metals. However, the corresponding computations are highly involved and unrewarding. It is therefore convenient and reasonable to assume angular forces of the Clark, Gazis & Wallis (1964) type to couple the *d* shells. These angular forces inherit the characteristic features of the three-body forces and may be used as a phenomenological substitute for them. The screening effect of the nearby conduction electrons limits these forces also to nearest neighbours only.

The interactions among the ions and the *d* shells are accounted for on the lines of the Fielek (1975) model. Computational effort is reduced in calculating the volume interactions among the ions and the electrons [occupying *sp* (conduction) bands and the *d* shells] by adopting the scheme due to Bhatia (1955), which is modified for the inclusion of (i) a suitable inference factor G^2 required for the convergence of the expression and (ii) a proper dielectric function $\varepsilon(\mathbf{q})$ accounting for the exchange and correlation effects present among the electrons. The crystal equilibrium considered by Fielek (1978*a*) seems to be objectionable (Shukla, 1978; Fielek, 1978*b*) and tedious. It was therefore thought worthwhile to tackle the problem on simpler lines, which assume the equilibrium of the lattice under the combined effect of the volume-dependent energy of the ions, the *d*-shell electrons and the conduction electrons. The model is employed to derive the dispersion relations in platinum. It is found that the simple modified version of the Fielek model predicts the relations in platinum more reliably.

Formulations

The usual determinant solved for the normal frequencies (v) may be expressed as

$$|D(\mathbf{q}) - 4\pi^2 m \, v^2 \, I| = 0, \qquad (1)$$

where m is the mass of the ion, I is the unit matrix of order three and $D(\mathbf{q})$ is the dynamical matrix describing the various interactions present in the f.c.c. structure. The elements of the matrix $D(\mathbf{q})$ may be written

$$D_{\alpha\alpha}(\mathbf{q}) = -4(\beta_1 + 2\alpha_1) + 2(\beta_1 + \alpha_1)C_\alpha(C_\beta + C_\gamma)$$
$$+ 4\alpha_1 C_\beta C_\gamma + K + \frac{K^2}{N} + \frac{A\,q_\alpha^2\,G^2(qr_s)\Omega}{[1 + q^2/\lambda_e^2\,\varepsilon(\mathbf{q})]a},$$

$$D_{\alpha\beta}(\mathbf{q}) = -2(\beta_1 - \alpha_1)S_\alpha\,S_\beta + K + \frac{K^2}{N}, \qquad (2)$$

where $C_\alpha = \cos(\tfrac{1}{2}aq_\alpha)$, $S_\alpha = \sin(\tfrac{1}{2}aq_\alpha)$, a is the lattice constant, r_s the electron separation, Ω the atomic volume and q_α the αth component of the phonon wave vector $\mathbf{q}$. K is the parameter associated with the interactions among the ions and the d-shell electrons. The term N appearing in (2) may be obtained by solving the determinant

$$|D'(\mathbf{q}) - NI| = 0, \qquad (3)$$

where

$$D'_{\alpha\alpha} = 16K_1|2 - C_\alpha(C_\beta + C_\gamma)|$$

$$- 4K_1(2C_{2\alpha} - C_{2\beta} - C_{2\gamma})$$

$$+ k - \frac{A'\,q_\alpha^2\,G^2(qr_s I)\Omega}{[1 + q^2/\lambda_d^2\,\varepsilon(\mathbf{q})]a},$$

$$D'_{\alpha\beta}(\mathbf{q}) = -16K_1\,S_\alpha\,S_\beta + K, \qquad (4)$$

where $C_{2\alpha} = \cos(aq_\alpha)$, and K_1 is the angular force constant given by the scheme due to Clark, Gazis & Wallis (1964). A and A' are the deformability parameters associated with the conduction and the d-shell electrons respectively. The inference factor G^2 is evaluated for the actual shape of the polyhedron. The screening parameters λ_e and λ_d associated with the conduction and the d-shell electrons respectively are evaluated in Bohm–Pines (1953) and Thomas–Fermi (Thomas, 1927; Fermi, 1928) limits respectively. The dielectric function $\varepsilon(\mathbf{q})$ may be written as

$$\varepsilon(\mathbf{q}) = \varepsilon_H(\mathbf{q})[1 - S(\mathbf{q})], \qquad (5)$$

where $\varepsilon_H(\mathbf{q})$ is the usual Hartree function and $S(\mathbf{q})$ is the correction term, which is evaluated on the lines reported by Vasistha & Singwi (1972), i.e.

$$S(\mathbf{q}) = A\left[1 - \exp\left(\frac{Bq^2}{K_F^2}\right)\right]. \qquad (6)$$

K_F is the usual Fermi wave vector and A, B are the constants taken from the study of Vasistha & Singwi (1972).

For considering the equilibrium of the lattice, the total energy (E) may be written as the sum of that due to ions (E_I), conduction electrons (E_e) and d-shell electrons (E_d), i.e.

$$E = E_I + E_e + E_d. \qquad (7)$$

For equilibrium $\partial E/\partial\Omega$ should vanish, i.e.

$$\frac{\partial}{\partial\Omega}(E_I + E_e + E_d) = 0, \qquad (8)$$

which can be transformed as

$$\frac{4\alpha_1}{a} = -(P_e + P_d), \qquad (9)$$

where P_e and P_d are the pressures associated with the conduction and d-shell electrons respectively. Moreover,

$$A = -\Omega\,\frac{\partial P_e}{\partial\Omega}\,a. \qquad (10)$$

The values of P_e and A $(=aK_e)$ have already been reported by Rathore & Agrawal (1980) for electron separations (r_s) varying from 3 to 5. The present study adopts the quantitative values of P_e and A for $r_s = 3$ within the framework of the correlation scheme due to Wigner & Seitz (1934). The value of P_d is taken from the work of Khanna & Rathore (1980) for $r_s = 1.5$.

Calculations

The present model comprises six model parameters, three of which are calculated by the use of elastic relations, which are obtained by comparing the long-wave form of (1) with the usual Christofell equation of elasticity. Two of the model parameters are obtained from (9) and (10). The last model parameter is evaluated in terms of the zone-boundary frequency for the T mode along the direction $[\zeta\zeta\zeta]$, i.e.

$$4\pi^2 m\,v_T^2 = -\left[2(\beta_1 + 5\alpha_1) + K\right] + \frac{K^2}{K + 48\,K_1}. \qquad (11)$$

The input data and the computed model parameters are shown in Table 1. The calculated dispersion relations for platinum are shown in Fig. 1. The experimental

Table 1. *Input data and model parameters for platinum*

Input data		Model parameters (10 N m⁻¹)	
C_{11}^*	$= 3.580$ ⎫	$\alpha_1 =$	1.9725
C_{12}^*	$= 2.536$ ⎬ $\times 10^{11}$ N m⁻²	$\beta_1 =$	-8.948
C_{44}^*	$= 0.774$ ⎭	$K_1 =$	-0.1864
a	$= 3.9156$ Å	$K =$	31.0019
$v_{T[111]}^\dagger$	$= 2.90$	$A =$	0.0704
m	$= 195.02$ a.m.u.	$A' =$	-5.9688

* MacFarlane, Rayne & Jones (1965).
† Dutton, Brockhouse & Miller (1972).

points (▲, △, ●) due to Dutton, Brockhouse & Miller (1972) are also depicted on the same figure.

Conclusions

The present model expresses the interactions among the various constituents of the non-simple metal in a consistent manner. The crystal equilibrium is properly accounted for in terms of α_1, P_d and P_e. The quantitative values of P_e and A used in the present study sufficiently explain the cohesion and the lattice stability. The use of the Bhatia (1965) scheme makes the model less involved computationally. The simple model, using a minimum number of input data, is capable of reproducing all the essential features of the dispersion curves of platinum. The deviations for the L modes in the proximity of the zone boundary may be attributed to the well known aperiodic nature of the Bhatia (1955) scheme. The well known anomaly in the branch $[\zeta\zeta 0]T_1$ may be associated with the volume-dependent interionic forces (Finnis, 1974). The anharmonic effects (Taole, Glyde & Taylor, 1978) may also contribute towards this anomaly.
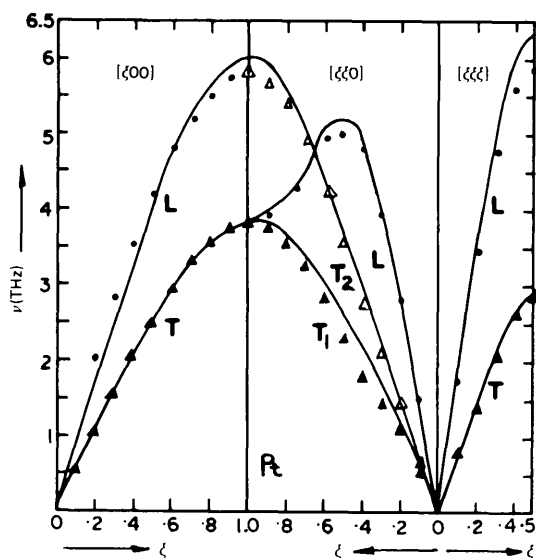

Fig. 1. Dispersion curves for platinum: (———) computed from the model; ▲, △, ● experimental points due to Dutton, Brockhouse & Miller (1972).

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