

Cohesion, elastic constants and vibrational mechanics of fcc platinum

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Abstract : A model in real space has been developed by extending the generalized form of the exponential potential known as extended generalized exponential potential (EGEP) to account for (a) the correct nature of repulsive and attractive components of forces for all the separations in general and that of small separations in particular, (b) the three-body forces such as volume forces in an indirect way in the framework of EGEP through the parameter n , (c) the dielectric screening functions in an alternative and simpler form through the parameter m . The model is employed to compute the cohesive energy, second-order elastic constants and phonon spectra for fcc platinum. The predictions show promising agreement with experimental findings

Keywords : Cohesion, elastic constants, phonon dispersion

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1. Introduction

Platinum ($Z = 78$) is a silvery white transition metal of VIII group in VI period with an outer electronic configuration of $5d^9 6s$ and shows high catalytic activity. Platinum is highly malleable and ductile element with high melting point, high boiling point and high density. Platinum being a transition element shows a variable valency of two and four.

Needless to say, the phonon spectra play a pivotal role in determining the mechanical, electrical and thermodynamical properties of elements and their alloys. We have therefore, been motivated to study the cohesion, elastic and vibrational behaviour of fcc platinum with a renewed interest because of its above stated attractive properties.

The cohesion in metals has earlier been studied by many workers [1] following different approaches and using widely different approximations. Moriarty [2] has employed several approximations to compute the cohesive energy of twenty two metals using a simplified local-density theory. Cles [3] has

analysed the role of correlation effects in the cohesion of transition metals. Sethi *et al* [4] have employed their theory to compute cohesive energy of some cubic metals. Cheliskowsky [5] has determined the cohesive energy of twenty simple metals from atomic kinetic energies. The generalized gradient approximation has been employed by Asada and Terakura [6] to compute the cohesive and magnetic properties of bcc, fcc and hcp iron. The uniform electron gas model for transition metals has recently been employed by Rose and Shore [7] to calculate the cohesive energy of $3d$, $4d$ and $5d$ series of transition metals. In the light of widely different approaches adopted to explain cohesion in metals, we have employed the present model (EGEP) which involves the least approximations and employs the minimum number of input parameters to predict the cohesion in metals with remarkable success [8].

The importance of the study of elastic constants lies in the fact that they give information about the nature of the binding forces in solids, account for their thermodynamic behaviour and leads to the determination of the interatomic force constants of the metals. An exercise to compute the elastic constants has been undertaken from this point of view.

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Earlier, the dynamical behaviour of platinum has been studied by many workers using different approaches. These studies involve first principle [9,10] as well as phenomenological [11-13] calculations. The former calculations suffer from physical intractability, mathematical tediousness, conceptual obscurity and resort to various approximations to arrive at useful conclusions whereas the later suffers from various shortcomings such as lattice instability, combination of short range ion-ion interactions with long range electron-ion interactions in an abrupt manner and use of large number of force constants, which varies from metal to metal and from model to model. Fielek [14] model has been employed by Singh *et al* [15] for lattice dynamical study of platinum. Agrawal and Rathore [16] have employed a non-central Fielek model to study the lattice vibrations in platinum, considering the equilibrium of the lattice under the combined effect of the volume- dependent energy of ions, the *d*-shell electrons and the conduction electrons. The study [16] makes use of elastic constants and zone boundary frequency, thereby introducing relative standard error. Kulshrestha and Upadhyaya [17] have computed phonon dispersion curves of platinum using transition metal model potential (TMMP) in local approximation with the model parameters of Animalu [18] and the dielectric function of Hubbard modified by Sham [19]. In the local approximation, the dispersion results obtained, differ widely from experimental data. The author [17] themselves improved the results by including non-local effects in the scheme of Eschrig and Wonn [20]. Singh *et al* [21] have employed their isotropic non-interacting band model to calculate dielectric screening and phonon frequencies of palladium, platinum and vanadium using number of parameters. Prakash and Upadhyaya [22] have incorporated the effect of many body forces to study the dynamical behaviour of platinum using their [23] three-body potential which helps in improving the transverse branch of dispersion curves.

The outer electronic configuration of platinum $5d^9 6s$ suggests that the electrons occupying the *d*-shells overlap with the immediate environment leading to *s-d* hybridization, which causes non-sphericity in charge distribution and hence calls for unpaired or three-body forces as pointed out by Bertoni *et al* [24] and recently by Verma *et al* [25]. Although several theories [26] have been put forward for providing much insight into the relative role played by the *s*- and *d*-like electrons in the bonding of the transition, but many of the details of the complex band structure are inessential to the understanding of the cohesive properties. Will and Harrison [27] have given a qualitative first principle analysis of the elastic and bonding properties of the transition metals, by computing their total energy as a function of volume and ionic configuration at constant volume, just by extending the nearly free electron theory of metals to include the effect of transition metal *d*-bands. A real space analysis of elastic and dynamical properties of transition metals have recently been investigated by Singh *et al*[28] by means of their temperature-dependent, exponentially-damped two-body

interaction potential which combines rational dielectric function (RDF) and Heine-Abarenkov (HA) model potential. The computations [27,28] being tedious and complex, require enormous time, money and efforts.

The present communication derives an empirical macroscopic potential in real space, which is an extension of the generalized exponential potential [29], known as extended generalized exponential potential (EGEP) and explains almost all the characteristic features of the interatomic interactions as detailed recently [30]. The present paper aims to investigate cohesion, the elastic and dynamical behaviour of fcc platinum.

2. Theory

2.1 Extended generalized exponential potential :

The extended generalized exponential potential (EGEP) representing the true and realistic nature of the repulsive as well as the attractive components of the interactions assumes the form

$$\Phi_m(r) = D/2(m-1) \sum_j \left[e^{-m\alpha(r_j-r_0)} / (\alpha r_j)^n - m(\alpha r_j)^n e^{-\alpha(r_j-r_0)} \right],$$

where *m* and *n* are the parameters which take care of electronic exchange and correlation effects and three-body forces such as volume forces in an alternative and simpler form respectively, *D* is the dissociation energy, α the hardness parameter and r_0 is the equilibrium separation parameter and r_j is the distance of the *j*-th atom from the origin given by

$$r_j = (l_1^2 + l_2^2 + l_3^2)^{1/2} = L_j a_0.$$

where l_1, l_2, l_3 (either even or odd) are the integers of the position co-ordinates such that

$$L_j = (l_1^2 + l_2^2 + l_3^2)^{1/2}$$

Eq. (1) can be put in the form to represent the cohesive energy at equilibrium semi-lattice constant (a_0) as under

$$\Phi(a_0) = D/2(m-1) \beta^m (\alpha a_0)^{-n} \sum_{l_1 l_2 l_3} L_j^{-n} e^{-m\alpha a_0 L_j}$$

$$-m\beta(\alpha a_0)^n \sum_{l_1 l_2 l_3} L_j^n e^{-\alpha a_0 L_j} \quad (3)$$

where $\beta = \exp(\alpha r_0)$. (4)

The three defining parameters (α , r_0 and *D*) of the potential require for their evaluation, the precisely determined input data of equilibrium semilattice constant (a_0) and bulk modulus (*B*) of

the metal only. For evaluating the three parameters α , r_0 and D of the potential function, the condition [31]

$$\sum_{l_1 l_2 l_3} \left[l_1^2 d\Phi(r) / dr^2 \right] = 0 \quad (5)$$

for the equilibrium of the crystal in the absence of external forces is employed which gives

$$\beta^{m-1} = \frac{m(\alpha a_0)^n (P-Q)}{(\alpha a_0)^{-n} (R+S)}, \quad (6)$$

where

$$P = \left[\alpha \sum_{l_1 l_2 l_3} l_1^2 L_j^{n-1} \exp(-\alpha a_0 L_j) \right],$$

$$Q = \left[(n/a_0) \sum_{l_1 l_2 l_3} l_1^2 L_j^{n-2} \exp(-\alpha a_0 L_j) \right],$$

$$R = \left[m\alpha \sum_{l_1 l_2 l_3} l_1^2 L_j^{-(n+1)} \exp(-m\alpha a_0 L_j) \right],$$

$$S = \left[(n/a_0) \sum_{l_1 l_2 l_3} l_1^2 L_j^{-(n+2)} \exp(-m\alpha a_0 L_j) \right].$$

The bulk modulus can be expressed as

$$B = (r^2/9V) \left(d^2\Phi/dr^2 \right)_{r=r_0}. \quad (7)$$

The parameter D can be evaluated through the expression for the bulk modulus following the condition given by eq. (5) for stress-free lattice. The following expression for D is obtained :

$$D = 18VB(m-1)/(X-Y), \quad (8)$$

where

$$X = \left[\beta^m (\alpha a_0)^{-n} \left\{ (m\alpha a_0)^2 \sum_{l_1 l_2 l_3} L_j^{-(n-2)} \exp(-m\alpha a_0 L_j) \right. \right. \\ \left. \left. + 2n(m\alpha a_0) \sum_{l_1 l_2 l_3} L_j^{-(n-1)} \exp(-m\alpha a_0 L_j) + n(n+1) \right. \right. \\ \left. \left. \sum_{l_1 l_2 l_3} L_j^{-n} \exp(-m\alpha a_0 L_j) \right\} \right],$$

$$Y = \left[m\beta (\alpha a_0)^n \left\{ (\alpha a_0)^2 \sum_{l_1 l_2 l_3} L_j^{(n+2)} \exp(-\alpha a_0 L_j) \right. \right.$$

$$\left. \left. - 2n(\alpha a_0) \sum_{l_1 l_2 l_3} L_j^{(n+1)} \exp(-\alpha a_0 L_j) + n(n-1) \right. \right.$$

$$\left. \left. \sum_{l_1 l_2 l_3} L_j^n \exp(-\alpha a_0 L_j) \right\} \right].$$

2.2 The second-order elastic constants :

The following expressions for the second-order elastic constants (SOEC) with present interatomic interactions are used [31] :

$$C_{11} = (n' a_0^4 / 2V) \sum_{l_1 l_2 l_3} l_1^4 d^2 \Phi(r) / (dr^2)^2, \quad (9)$$

$$C_{12} = (n' a_0^4 / 2V) \sum_{l_1 l_2 l_3} l_1^2 l_2^2 d^2 \Phi(r) / (dr^2)^2, \quad (10)$$

where n' is the number of atoms per unit cell (4 for fcc and 2 for bcc) and V represents the atomic volume.

The value of SOEC C_{44} for the metal under study has been computed by expanding the secular equation in the long wave limits ($q \rightarrow 0$) and the comparing with the usual Christoffel relation.

2.3 Lattice dynamical behaviour :

The elements of the dynamical matrix having explicit bearing on eq.(1) in case of fcc platinum, are :

$$D_{\alpha\alpha}^{(2)}(\mathbf{q}) = 2(\alpha_1 + \beta_1) \left[2 - C_\alpha (C_\beta + C_\gamma) \right] + 4\alpha_1 (1 - C_\beta C_\gamma)$$

$$+ 4\beta_2 S_\alpha^2 + 4\alpha_2 (S_\beta^2 + S_\gamma^2), \quad (11)$$

$$D_{\alpha\beta}^{(2)}(\mathbf{q}) = 2(\beta_1 - \alpha_1) S_\alpha S_\beta, \quad (12)$$

where

$$S_\alpha = \sin(aq_\alpha/2) \text{ and } C_\alpha = \cos(aq_\alpha/2), \quad (13)$$

$$\alpha_1 = [1/r (\partial\Phi/\partial r)]_N, \quad \alpha_2 = [1/r (\partial\Phi/\partial r)]_{NN}, \quad (14)$$

$$\beta_1 = [\partial^2\Phi/\partial r^2]_N, \quad \beta_2 = [\partial^2\Phi/\partial r^2]_{NN}. \quad (15)$$

q_α is the α - component of phonon wave vector \mathbf{q} , a is the lattice parameter and α_1, β_1 are the force constants for the first neighbour (N) and α_2, β_2 are these for the second nearest neighbour (NN) respectively.

The phonon frequencies (ν) are obtained by solving the usual secular equation *i.e.*

$$D_{\alpha\beta}(\mathbf{q}) - 4\pi^2 \nu^2 M \mathbf{I} = 0, \quad (16)$$

where \mathbf{I} is the unit matrix of 3×3 order and M is the mass of the atom.

3. Computations and results

The input data for the fcc platinum (Pt) *i.e.* the lattice constant and bulk modulus are given in Table 1, while the computed potential parameters are recorded in Table 2. The present study considers the 248 atoms extending to 12th neighbours in case of fcc platinum to compute potential parameters. The computed values of cohesive energy and second-order elastic constants are shown in Tables 3 and 4 respectively. Table 5 enlists the evaluated derivatives α_1, α_2 and β_1, β_2 for fcc platinum. Figure

Table 1. Input data for fcc platinum [Ref. 34]

Metal	Lattice constant 10^{10} m	Bulk modulus 10^{11} N/m ²
Pt	3.92	2.783

Table 2. Computed potential parameters of platinum

n	m	αa_0	$\alpha \times 10^{10} \text{m}^{-1}$	β	$D \times 10^{-21} \text{J}$	$r_0 \times 10^{10} \text{m}$
0.5	2.0	3.10466	1.584010	415.6055	11.160770	3.806628
1.0	2.0	3.13644	1.600225	1794.5240	1.092589	4.682153
2.0	2.0	3.23935	1.652730	40802.6000	0.009026	6.423617
3.0	2.0	3.35498	1.711751	1172507.0000	5.68E-05	8.164080
4.0	2.0	3.42325	1.746556	3.65E+07	2.92E-07	9.976552

Table 3. Computed values of cohesive energy of Pt [eq. (3)] in eV/atom

n	m	Cohesive energy		Magnitudes of cohesive energy	
		repulsive part	attractive part	comp	exp. [34]
0.5	2.0	5.3708	11.2108	5.8400	
1.0	2.0	4.2207	10.0606	5.8399	
2.0	2.0	2.8345	8.6753	5.8399	5.84
3.0	2.0	2.0843	7.9243	5.8400	
4.0	2.0	1.6645	7.5043	5.8398	

Table 4. Computed second-order elastic constants (in 10^{11} N/m²).

Metal	n	m	C_{11}	C_{12}	C_{44}	Ref
Pt	0.5	2.0	3.6403	2.3543	1.3353	
			3.6568	2.3461	1.3276	
			3.6935	2.3278	1.3094	
			3.7350	2.3069	1.2819	
			3.7830	2.2829	1.2391	
Exp.			3.580	2.536	0.774	35

Table 5. Computed force constants (N/m).

Metal	n	m	α_1	α_2	β_1	β_2
Pt	3.0	2.0	-3.092918	0.5720612	57.23967	-1.3785450

1 depicts the computed phonon dispersion curves along with the measured data of Dutton *et al* [32] for fcc Pt.

4. Conclusions

The successful prediction of cohesive energy [eq. (3)] of the fcc Pt for any positive value of n effectively points to the efficacy of the present potential (EGEP). Although the dissociation energy parameter (D) of the present potential appears as the consequence of the cohesive energy but the model parameters depend sparingly on the cohesive energy because the said parameters describe the mean average binding over a large number of neighbouring atoms.

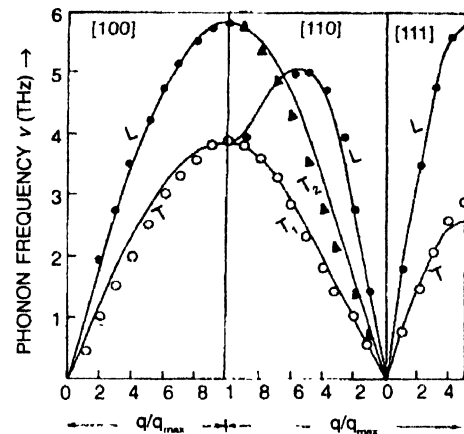


Figure 1. Phonon dispersion in fcc platinum – present study (●, ○) ▲ experimental findings of Dutton *et al* [32]

The extended form of the generalized exponential potential explains quantitatively the second-order elastic constants (SOEC) of fcc platinum and their intimate relation with the strength of the metal further establishes the importance of the present study. The study of the second-order elastic constants provides direct knowledge to the response of metallic ions to its environment and therefore, further reveals the nature of the resultant interactions.

The computed values of second-order elastic constants C_{11} and C_{22} of fcc platinum compare reasonably well with the experimental values, but the computed value of C_{44} override the experimental value as the contribution of attractive interactions in β_1, α_1 and α_2 predominates in their values calculated in the long wave limit. The dominant values of β_1, α_1 and α_2 based on reasonable nature of operative interactions which eventually enhances the value of C_{44} determined by the slope of the dispersion curves occupying the proximity of zone center. The strong attractive forces at zone center have also been exploited by the first principles calculations as well as by the phenomenological models.

The computed phonon frequencies of fcc platinum [Figure 1] in the framework of extended generalized exponential potential agree satisfactorily with the experimental values of Dutton *et al* [32] and that too by employing the minimum number of input data, are encouraging. The computed values slightly exceed the

experimental values along $[100 T]$ and $[110 T_2]$ except along the zone boundaries, whereas the computed values fall short of the measured data along $[111 T]$ the zone boundary. The results along the transverse branches can be further improved by explicit inclusion of appropriate three-body forces and the suitable electronic contribution in a more direct manner. Anyway, our results are free from the relative standard error [16], complex formulation [22,23], various approximations [27,28] and these fact enhances the reliability [33] of our model.

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