Elastic behaviour and phonons in bcc tantalum

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Abstract : The generalised exponential potential is suitably extended to investigate the elastic and the lattice dynamical behaviour of bcc tantalum The role of three-body interactions which couple d-shell of non-simple metals like tantalum is taken into account in an indirect manner in the framework of extended generalised exponential potential (EGEP) through the parameter *n* The effect of dielectric screening functions is included into the model in a more simpler form through the parameter *m* The model successfully predicts cohesive energy, second-order elastic constants and phonon spectra of the bcc tantalum and the predictions show good agreement with experimental findings.

1. Introduction

Two different approaches have widely been employed in the study of the lattice dynamical behaviour of transition metals *i.e* pseudopotential [1-3] and phenomenological [4-6] and form the basis for the development of various models. The former studies [1 3] involve huge computation and various simplifying assumptions for discussing the crystal dynamics of non-simple metals The later studies [4-6] of these metals ignore the consideration of lattice stability or observe it extraneously and employ a large number of input data to evaluate the parameters. Inspite of this progress, the lattice dynamical behaviour of non-simple metals remains to be a complex problem of immense interest because of the presence of d-shell and conduction electrons. Moreover, the first principle theories [7-9] employed to study the lattice dynamics of transition metals, make use of varying approximations to arrive at useful conclusions and increases computer time considerably. Khanna and Rathore [10] have used modified and improved versions of Fielek model [11] to discuss the phonon dispersion in bcc transition metals, which makes use of the elastic constants and the zone boundary

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frequencies as input data, introducing relative standard error. Recently, Singh *et al* [12] have proposed a temperature dependent pair potential for the same purpose, which is basically a Heine-Abarenkov (HA) potential and suffers from many drawbacks.

Tantalum ($Z = 73$) is the third transition element of group V in the bcc phase with an outer electronic configuration $6s^2 5d^3$, high melting point ($3000°C$) and exhibit variable valency. Also, the density (d) of transition metals of group V increases significantly from vanadium ($d = 6.1$ gm/ml) to niobium ($d = 8.6$ gm/ml), then to tantalum ($d = 16.6$ gm/ml). Further, because of the lanthanide contraction, the covalent and the ionic radii of Nb and Ta are almost identical with a value of 1.34Å. Consequently, these two elements have very similar properties, occur together and are very difficult to separate. Vanadium forms many different positive ions, but niobium and tantalum form virtually none. Thus, though Nb and Ta are metals (highly unreactive and resistant to acids except HF), their compounds in the (+V) state are mostly covalent, volatile and readily hydrolysed – properties associated with nonmetals. Finally, it is worthwhile to mention that the vanadium is seldom used on its own, but it is used in metal alloys and acts as an important catalyst in oxidation reactions. Niobium is used in chromium

nickel stainless steel. Because it is unreactive and is not rejected by the human body, tantalum is used for making metal plates, screws and wires for repairing badly fractured bones.

The electrons occupying the d-shells overlap with the immediate environment leading to s-d hybridization which causes non-sphericity in charge distribution. This non-sphericity calls for unpaired or three-body forces, as pointed out by Bertoni *et al* [13]. The s-d hybridization in transition metals has also been explained on the basis of Ziman's resonance model [14] in the $l = 2$ phase shift. The extended generalised exponential potential (EGEP) has earlier explained successfully the implications of hybridization in thorium [15] as well as in vanadium and niobium [16] and capable to explain s-d hyhridization in d-band metals, which requires a repulsive term with exponential character in the interaction potential, as pointed out by Moriarty [1].

Therefore, the present communication proposes an empirical potential rather than pseudopotential and phenomenological approaches. This is an extension of the generalised exponential potential, known as extended generalised exponential potential (EGEP) and explains almost all the characteristic features [17] of the interatomic interactions and its physical basis rests on the following facts .

(ia) Moriarty [18] has shown that the multiparticle unpaired interactions assume the attractive as well as the repulsive characters.

(ib) The core and shell charge densities responsible for the paired and unpaired interactions, have been represented by the exponential forms [19].

(ic) Analytical form of the pair potential [20] adopts the damped exponential character.

(id) Generalised pseudopotential theory [21] also seeks to incorporate the d-shell interactions through exponential form of the potential.

(ie) The broadening and shifting of centre of the bands results into the suitable changes [22] in the attractive and repulsive interactions.

Hence, the above said meritorious features of the pseudo/model potential are properly formulated by suitably adjusting the corresponding elements of the potential in the extended form of generalised exponential potential.

(ii) The formulation of the ion-ion interaction either in the phenomenological approach or in the pseudopotential scheme, does not account for the influence of the electron exchange and correlation effects. These effects which introduces the substantial change [23] into the width and depth of the potential by shifting the minima of the potential vertically have been accounted for, in an alternative form through a parameter m and therefore, properly substitutes for dielectric screening functions, which either enhances or reduces the Coulombian interaction in an arbitrary fashion.

(iii) The role of the three-body forces (such as volume forces [24]) responsible for shifting the minima of the potential horizontally, has effectively been expressed in an indirect manner through a parameter n, as this parameter affects [25] the position as well as the depth of the potential minima.

(iv) It accounts effectively for the characteristic feature of steep rise of Coulombic repulsion at small separations.

(v) The extended generalised exponential potential (EGEP) possesses all the virtues [26] of a well-behaved potential function including an empty core, smooth transition over the entire range and a well-defined minima.

(vi) The present form of potential is self-convergent and therefore, requires no exponential damping factor.

Since a heavy metal like tantalum embodies covalent to ionic texture, the relevant interactions are to be properly blended to reflect the transition smoothly. The pronounced role of the paired interactions have therefore been amalgamated with the desired infusion of the unpaired interactions in an indirect manner through the parameter n in the main expression of the potential. The extended generalised exponential potential (EGEP) accounts effectively for the range, strength and nature of the interactions involved in the structure under study.

The potential has earlier explained [26] successfully the elastic and dynamical behaviour of fcc metals. The present paper aims to investigate the elastic and dynamical behaviour of bcc tantalum.

2. Theory

2.1 Extended generalised exponential potential :

The attractive as well as the repulsive components of the generalised exponential potential (27) have been extended for representing their true and realistic nature. Extended generalised form of exponential potential (EGEP) so developed assumes the form

$$\Phi_m(r_j) =$$

$$D/2(m-1)\sum_j \left[c^{-m\alpha(r_j-r_0)} / (\alpha\theta_j)^n - m(\alpha\theta_j)^n c^{-\alpha(r_j-r_0)} \right], \quad (1)$$

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, D is the dissociation energy, α the hardness parameter and r_0 the equilibrium separation parameter and r_j is the distance of the j-th atom from the origin given by

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

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

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

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

where

$$\beta = \exp{(\alpha\, r_0)}. \tag{4}$$

The three defining parameters (α, r_0 and D of the potential require for their evaluation the precisely determined input data of equilibrium semi-lattice 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

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

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

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

where

$$P = \alpha \sum_{l_1 l_2 l_3} l_1^2 \; L_j^{n-1} \exp{(-\alpha a_0 L_j)}$$

$$Q = (n/a_0) \sum_{l_1 l_2 l_3} l_1^2 \; L_j^{n-2} \exp{(-\alpha a_0 L_j)}$$

$$R = m\alpha \sum_{l_1 l_2 l_3} l_1^2 \; L_j^{-(n+1)} \exp{(-m\alpha a_0 L_j)}$$

$$S = (n/a_0) \sum_{l_1 l_2 l_3} l_1^2 \; L_j^{-(n+2)} \exp{(-m\alpha a_0 L_j)}$$

The bulk modulus can be expressed as

$$B = \left(r^2 /9v \right) \left(d^2\phi/d r^2 \right)_{r=r_0}. \tag{7}$$

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 of D is obtained

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

where

$$X = \beta^m (\alpha a_0)^{-n} \Big\{ (m\alpha a_0)^2 \sum_{l_1 l_2 l_3} L_j^{-(n-2)} \exp{(-m\alpha a_0 L_j)}$$

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

$$\sum_{l_1 l_2 l_3} L_j^{-n} \exp{(-m\alpha a_0 L_j)} \Big\}$$

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

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

$$\sum_{l_1 l_2 l_3} L_j^n \exp{(-\alpha a_0 L_j)} \Big\}$$

2.2 The second-order elastic constants :

The following expressions for the second-order elastic constants (SOEC) with present interatomic interactions are used [28]

$$C_{11} = \left(n' a_0^4 /2V \right) \sum_{l_1 l_2 l_3} l_1^4 \; d^2\phi(r)/(dr^2)^2, \tag{9}$$

$$C_{12} = \left(n' a_0^4 /2V \right) \sum_{l_1 l_2 l_3} l_1^2 \; l_2^2 d^2\phi(r)/(dr^2)^2. \tag{10}$$

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 extending the secular equation in long wave limits $(q \to 0)$ and comparing with the usual Christoffel relation.

2.3 Lattice dynamical behaviour :

The elements of the dynamical matrix having explicit bearing on eq. (1) may be written as

$$D_{\alpha\alpha}^{(2)}(q) = \frac{8}{3}\beta_1 \left[1 - C_\alpha C_\beta C_\gamma \right] + 4\beta_2 S_\alpha^2, \tag{11}$$

$$D_{\alpha\alpha}^{(2)}(q) = \frac{v}{3}\beta_1 \; S_\alpha S_\beta C_\gamma, \tag{12}$$

where

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

$$\beta_1 = \left[\partial^2 \phi / \partial r^2\right]_N, \quad \beta_2 = \left[\partial^2 \phi / \partial r^2\right]_{NN} \tag{14}$$

q_α is the α - component of phonon wave vector q, a is the lattice parameter, β_1 and β_2 are the force constants for the first neighbour (N) and the second nearest neighbour (NN) respectively. It may be mentioned that the inclusion of the first derivatives (α_1, α_2) of the potential deteriorates the dispersion curves in the alloys and metals beyond repairs. For this reason, we have considered only the second derivatives (β_1, β_2) while considering the two-body contribution towards the phonon dispersion in bcc metals

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

$$D_{\alpha\beta}(q) - 4\pi^2 v^2 M I = 0. \tag{15}$$

where I is the unit matrix of 3×3 order and M is the mass of the atom.

2.4 Parameter evaluation :

Eq. (6) is treated repeatedly for a chosen value of n and m to yield a value of dimensionless quantity (αa_0) which reproduces such values of β and D [from eq. (8)] which on subsequent substitution in eq. (3), yields exactly measured value of cohesive energy. This proper value of αa_0 is employed to evaluate α from the measured value of equilibrium semi-lattice constant. The value of r_0 is evaluated using eq. (4)

3. Computations and results

A machine program was developed on the theoretical lines given in the preceding section and the same was fed to the computer to obtain the results given in Tables 2 to 5.

Table 1. Input data for bcc tantalum

Metal	Lattice constant 10^{-10} m	bulk modulus 10^{11}N/m^2
Ta	3.3	2.0

The input data for bcc tantalum (Ta) *i.e.* lattice constant and bulk modulus are given in Table 1. For a given value of parameter n, we have computed potential parameters for four different values of m (= 1.5, 2, 3, 6). However, due to limitations of the space, we have shown our parameters in Table 2 only for the

most suitable value of m. The present study considers the 306 atoms extending to 16-th neighbours to compute these 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 β_1 and β_2 for bcc tantalum (Ta). Figure 1 depicts the computed phonon dispersion curves alongwith the measured data of Woods [29] for bcc Ta.

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

Metal	n	m	Cohesive energy		Magnitude of cohesive energy	
			repulsive part	attractive part	comp.	exp
Ta	0 5	6.0	2.9018	11 0018	8 1000	
	1 0	6.0	2.3771	10.4770	8 0999	
	2 0	6 0	1 6044	9 7042	8.0998	
	3 0	6 0	1.0984	9 1984	8 1000	
	4 0	6.0	0 7711	8 8710	8 0999	

Table 4. Computed second-order elastic constants (in 10^{11} N/m^2)

Metal	n	m	C_{11}	C_{12}	C_{44}	Ref
Ta	0 5	6 0	2 1761	1.9029	0.8894	
	1 0	6 0	2 1862	1 8982	0 858	
	2 0	6 0	2.1971	1 8943	0 8184	
	3 0	6 0	2.1969	1 8958	0 7989	
	4 0	6 0	2 1963	1 8974	0 7888	
Exp			2 609	1 574	0 818	[35]

Table 5. Computed force constants for bcc Tantalum (N/m)

Metal			β_1	β_2
Ta	0 5	6 0	57.17932	12 35096

4. Conclusions

The empirical nature of the potential is established by successful prediction of cohesive energy of the bcc tantalum for any positive value of n, which in turn, explains all the qualitative features of phonon dispersion relations and therefore effectively supports the efficacy of present interactions coupling the metallic ions.

The intimate relation of second-order elastic constants with the strength and stability [30] of the metal further establishes

Table 2. Computed potential parameters for bcc tantalum.

Metal	n	m	αa_0	$\alpha \times 10^{10}$ m^{-1}	β	$D \times 10^{-21}$ J	$r_0 \times 10^{-10}$ m
Ta	0 5	6.0	0 88598	0 536976	7 6797	29.813030	3 796537
	1 0	6 0	0 90083	0.545957	8.9367	14.662160	4.011614
	2 0	6 0	0.95435	0 578294	13 1758	3.029311	4 457827
	3 0	6 0	1.03913	0 629776	22.1478	0.486622	4.918793
	4.0	6 0	1.14874	0 696206	42.4454	0 059276	5.383779

the importance of the present study. The study on the second-order elastic constants provides direct knowledge to the response of metallic ions to its environment, nature of the binding forces in solids and therefore, further reveals the nature of the resultant interactions. The computed values of the second-order elastic constants compare reasonably well with the available experimental values.
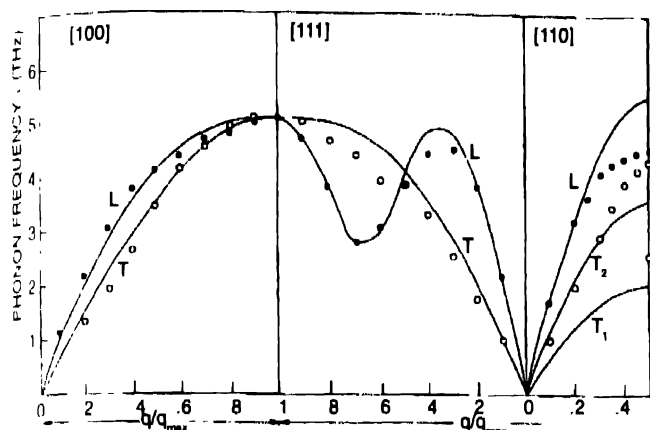

Figure 1. Phonon dispersion in bcc tantalum ___ Present Study, ●, o experimental findings of Woods [29]

A close scrutiny of the literature reveals that the phonon dispersion curves in bcc transition metals are notoriously full of anomalies [31], but these anomalies have been accounted for in a satisfactory way [32] to some extent. Previous attempts to devise potentials have met with limited success [33] and it is not surprising to find discrepancies as high as 100% between the computed and experimental phonon frequencies in the literature. High structural density and low degree of hybridization of the energy levels due to increase in the atomic size causing softness of the orbitals from vanadium to tantalum, tends to narrow down the phonon dispersional anisotropy at large wave vectors along [110L] and [110T] directions. The optimisation of the model parameters *m* and *n* in a coherent and composite manner, may achieve the said narrow-down. Even then, a comparison of the experimental [29] and the presently computed phonon frequencies in the framework of EGEP using minimum number of input data are encouraging. The computed phonon frequencies 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 and this fact enhances the reliability [34] of our model

Acknowledgments

References

[1]   J A Moriarty *Phys. Rev.* **B1** 1362 (1970), **B6** 1239 (1972)

[2]   B A Oli and A O E Animalu *Phys Rev.* **B13** 2398 (1976)

[3]   J Singh, N Singh and S Prakash *Phys Rev.* **B12** 3166 (1975)

[4]   L A Bertolo and M M Shukla *J. Phys Soc. Jpn.* **38** 1439 (1975)

[5]   J Prakash, L P Pathak and M P Hemkar *Aust J. Phys.* **28** 57 (1975)

[6]   P K Sharma and R K Awasthi *Phys. Rev* **B18** 1963 (1979)

[7]   J C Upadhyaya and L Dagens *J. Phys* **F8** L 21 (1978)

[8]   J Singh, N Singh and S Prakash *Phys Rev* **B18** 2954 (1978)

[9]   R Rebonato and J Q Broughton *Phil Mag Lett* **55** 225 (1987)

[10] R N Khanna and R P S Rathore *Acta Phys Pol* (Poland) **A58** 745 (1980), *Z Naturforsch* **35A** 920 (1980)

[11] B L Fielek *J. Phys* **F5** 17 (1975); *ibid* **F8** 577 (1978)

[12] N Singh, N S Banger and S P Singh *Phys Rev* **B39** 12915 (1989)

[13] C M Bertoni, V Bertolani, C Calandra and F Nizzoli *J Phys* **F4** 19 (1974)

[14] J M Ziman *Proc. Phys Soc* **86** 337 (1965)

[15] M L Verma and R P S Rathore *Phys. Stat Sol* (b) **185** 93 (1994)

[16] A Verma, M L Verma and R P S Rathore *Acta Phys Polon.* **A90** 547 (1996)

[17] A Verma, M L Verma and R P S Rathore *Mod Phys Lett* **B11** 209 (1997)

[18] J A Moriarty *Phys. Rev* **B44** 1609 (1991)

[19] Y R Wang and A W Overhauser *Phys Rev* **B35** 501 (1987)

[20] D G Pettifor and W A Ward *Solid State Commun* **49** 281 (1984)

[21] J A Moriarty *Phys. Rev* **B34** 6738 (1986)

[22] J M Wills and W A Harrison *Phys Rev* **B28** 4363 (1983)

[23] N K Khanna *Phys Status Solidi*, (b) **101** K117 (1980)

[24] S K Sarker, S K Das, D Roy and S Sengupta *Phys Stat Sol* (b) **83** 6757 (1977)

[25] J Hafner *Phys Stat Sol* (b) **56** 1579 (1973)

[26] M L Verma and R P S Rathore *Indian J Pure Appl Phys.* **32** 308 (1994), M L Verma, R P S Rathore and A Verma *Czech J. Phys* **45** 79 (1995)

[27] F Milstein *J Appl. Phys* **44** 3825 (1973)

[28] M Born *Proc Camb Phil. Soc* **36** 160 (1940)

[29] A D B Woods *Phys Rev* **136** 781A (1964)

[30] A Verma, M L Verma and R P S Rathore *Acta Phys Polon* **A91** 583 (1997)

[31] S T Chui *Phys Rev* **B9** 2097 (1974)

[32] W Weber in *Superconductivity in d- and f-Band Metals* (ed) D H Douglass (New York · Plenum) (1976)

[33] A O E Animalu *Phys Rev.* **B8** 3555 (1973) K Terakura *J. Phys* **F14** 3255 (1984)

[34] R S Leigh, B Szigett and V K Tewari *Proc. Roy Soc.* **320A**, 505 (1971)

[35] C Kittel *Introduction to Solid State Physics* (3rd edn) (New York . Wiley) P111 (1967)