

# ELASTIC BEHAVIOUR AND LATTICE VIBRATIONS IN bcc V AND Nb

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A model is developed by extending the generalised form of exponential potential known as extended generalised exponential potential to account for: (a) a realistic realization of interactions in all separations in general and that of small separations in particular, (b) three-body and electronic effects into the interaction in an alternative and simpler form, (c) a model free from usual fitting procedure. The model is employed to compute the cohesive energy, phonon spectra and second- and third-order elastic constants for group VA bcc metals V and Nb. The computed results showing good agreement with the experimental findings lend reliability and credibility to the potential.

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## 1. Introduction

The lattice dynamical behaviour of transition metals has been studied on the basis of two different approaches, i.e. pseudopotential and phenomenological. The former studies [1-4] involve huge computation and various simplifying assumptions for discussing the crystal dynamics of non-simple metals. These model potentials require further modifications with respect to their non-centrality and dielectric functions for yielding a good comparison between the computed and experimental dispersion data. The later studies [5-8] of these metals suffer from the deficiency of lattice instability and use extensive fitting procedures. Not only this, the first principle theories [9-11] to study the lattice dynamics of transition metals make use of drastic approximations to arrive at useful conclusions and increases computer time many times. A non-central force model with six input data has been employed by Rathore [12] to predict the phonon dispersion in bcc vanadium. Khanna and Rathore [13] have used simplified forms of Fiełek model [14] to discuss the phonon dispersion in bcc niobium with the same number of input data.

Both the studies [12, 13] make use of the elastic constants and the zone boundary frequencies as input data, introducing relative standard error. Recently, Singh et al. [15] have proposed a temperature dependent pair potential for discussing the lattice vibrations in bcc V and Nb, which is basically a deficient Heine–Abarenkov (HA) potential.

Vanadium ( $Z = 23$ ) and niobium ( $Z = 41$ ) are the first and the second transition elements of group VA in bcc phase with outer electronic configurations as  $3d^34s^2$  and  $4d^35s^2$ , respectively and exhibit variable valency. The presence of electrons occupying the  $d$ -shells in non-simple metals like V and Nb makes their lattice dynamical behaviour interestingly complicated and stresses on the importance of the inclusion of short and long range electron response to the ionic motion in the central pair-wise potential. The displacement of cores and shells gives rise to mechanical polarization resulting in the paired interactions of central type. These interactions being short-ranged effectively couple the cores and the shells. Secondly, during a lattice vibration, the electron shells around each core get deformed due to their overlap leading to  $s$ - $d$  hybridization and this in turn alters their charge density distribution, which gives rise to unpaired or three-body forces, as pointed out by Bertoni et al. [16]. The non-orthogonality associated with the overlap of electron wave functions and quantum mechanical treatment of overlap interactions also suggest the unpaired nature of these interactions which are quite dominant between the  $d$ -shells in these metals. The  $s$ - $d$  hybridization in transition metals has also been explained on the basis of Ziman's resonance model [17] in the  $l = 2$  phase shift. The extended generalised exponential potential (EGEP) has earlier explained [18] successfully the implications of hybridization in thorium and is capable to explain  $s$ - $d$  hybridization in  $d$ -band metals, which requires a repulsive term with exponential character in the interaction potential, as pointed out by Moriarty [1].

The present communication derives an empirical potential, which is an extension of the generalised exponential potential, known as extended generalised exponential potential and explains almost all the characteristic features of the interatomic interactions such as

- (i) The broadening and shifting of centre of the bands results into the suitable changes [19] in the attractive and repulsive interactions. The corresponding elements of the potential are properly formulated to account for the effective inclusion of these forces.
- (ii) The electronic exchange and correlation effects, which introduces the substantial change [20] into the width and depth of the potential, have been accounted for in an alternative form through a parameter  $m$  and therefore properly substitutes for dielectric screening functions [21].
- (iii) The role of the three-body forces such as volume forces [22] has been effectively expressed in an indirect manner through a parameter  $n$ , because this parameter affects [23] the position as well as the depth of the potential minima.
- (iv) It accounts effectively for the characteristic feature of a steep rise of Coulombic repulsion at small separations.

The potential has earlier explained [24] successfully the elastic and dynamical behaviour of fcc metals. The present paper aims to investigate the elastic and dynamical behaviour of bcc vanadium and niobium.

## 2. Theory

### 2.1. Extended generalised exponential potential

The attractive as well as the repulsive components of the generalised exponential potential [25] have been extended for representing their true and realistic nature. Extended generalised form of exponential potential so developed assumes the form

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

where  $m$  and  $n$  are the parameters which take care of electronic exchange and correlation effects and the three-body forces such as volume forces in an alternative and simpler form respectively,  $D$  is the dissociation energy,  $\alpha$  — 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

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

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

$$\Phi(a_0) = [D/2(m-1)] \times \left[ \beta^m (\alpha a_0)^{-n} \sum_{l_1 l_2 l_3} e^{-m\alpha a_0 L_j} L_j^{-n} - m\beta (\alpha a_0)^n \sum_{l_1 l_2 l_3} e^{-\alpha a_0 L_j} L_j^n \right], \quad (3)$$

where

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

The three defining parameters ( $\alpha$ ,  $r_0$  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 metals only. For evaluating the three parameters function, the condition

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

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

$$\beta^{m-1} = \frac{m(\alpha a_0)^n (U - V)}{(\alpha a_0)^{-n} (X + Y)}, \quad (6)$$

where

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

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

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

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

The bulk modulus can be expressed as

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

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

$$D = 18VB(m-1)/(P-Q), \quad (8)$$

where

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

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

## 2.2. The second-order and third-order elastic constants

The following expressions for the second-order elastic constants (SOEC) and third-order elastic constants (TOEC) with present interatomic interactions are used [26]

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

$$C_{111} = (n' a_0^6 / V) \sum_{l_1 l_2 l_3} l_1^6 d^3\Phi(r) / (dr^2)^3, \quad (10)$$

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

Equation (9) transforms to represent  $C_{12}$  when  $l_1^4$  in the mentioned equation is replaced by  $l_1^2 l_2^2$ . Similarly, Eq. (10) transforms to represent  $C_{112}$  ( $= C_{166}$ ) and  $C_{123}$  ( $= C_{456} = C_{144}$ ) when  $l_1^6$  in the mentioned equation is replaced by  $l_1^4 l_2^2$  and  $l_1^2 l_2^2 l_3^2$ , respectively.

The value of SOEC  $C_{44}$  for the metals under study have been computed by expanding the secular equation in long wave limits ( $q \rightarrow 0$ ) 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

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

$$D_{\alpha\beta}^{(2)}(q) = \frac{8}{3}\beta_1 S_\alpha S_\beta C_\gamma, \quad (12)$$

where

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

$$\beta_1 = (\partial^2\Phi/\partial r^2)_N, \quad \beta_2 = (\partial^2\Phi/\partial r^2)_{NN}, \quad (14)$$

$q_\alpha$  is the  $\alpha$  component of phonon wave vector  $q$ ,  $a$  is the lattice parameter,  $\beta_1$  and  $\beta_2$  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 ( $\alpha_1$ ,  $\alpha_2$ ) of the potential deteriorates the dispersion curves in the alloys and metals beyond repairs. For this reason, we have considered only the second derivatives ( $\beta_1$ ,  $\beta_2$ ) while considering the two-body contribution towards the phonon dispersion in bcc metals.

The phonon frequencies ( $\nu$ ) are obtained by solving the usual secular equation, i.e.

$$D_{\alpha\beta}(q) - 4\pi^2\nu^2 MI = 0, \quad (15)$$

where  $I$  is the unit matrix of  $3 \times 3$  order and  $M$  is the mass of the atom.

### 2.4. Parameter evaluation

Equation (6) is treated repeatedly for a chosen value of  $n$  and  $m$  to yield such a value of dimensionless quantity ( $\alpha a_0$ ) which reproduces such values of  $\beta$  and  $D$  (from Eq. (8)) which on subsequent substitution in Eq. (3) yield an exactly measured value of cohesive energy. This proper value of  $\alpha a_0$  is employed to evaluate  $\alpha$  from the measured value of equilibrium semi-lattice constant ( $a_0$ ). 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 II to V.

The input data for bcc vanadium (V) and niobium (Nb), i.e. the lattice constant and bulk modulus are given in Table I. For a given value of parameter  $n$ , we have computed potential parameters for four different values of  $m$  ( $= 1.5, 2, 3, 6$ ) but keeping in mind the limitations of the space, we have recorded our parameters in Table II for the most suitable value of  $m$ . The present study considers the 306 atoms extending to 16th neighbours to compute these parameters. The computed values of cohesive energy and the evaluated derivatives  $\beta_1$  and  $\beta_2$  for bcc

TABLE I

Input data for bcc V and Nb.

Metal	Lattice constant [ $10^{-10}$ m]	Bulk modulus [ $10^{11}$ N/m <sup>2</sup> ]
V	3.03	1.619
Nb	3.30	1.702

TABLE II

Computed potential parameters.

Metal	$n$	$m$	$\alpha a_0$	$\alpha \times$ $10^{10}$ m <sup>-1</sup>	$\beta$	$D$ [ $10^{-21}$ J]	$r_0$ [ $10^{-10}$ m]
V	0.5	6	0.85905	0.567029	7.3592	18.885760	3.520002
	1.0	6	0.87434	0.577122	8.5225	9.398328	3.712749
	2.0	6	0.93020	0.613993	12.4945	1.986921	4.112892
Nb	0.5	3	1.34594	0.815721	27.8713	26.392890	4.079332
	1.0	3	1.32423	0.802564	43.5279	7.924340	4.692944
	2.0	3	1.27880	0.775030	106.1244	0.655338	6.018619

TABLE III

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.
V	0.5	6.0	1.9256	7.2355	5.3099	5.31
	1.0	6.0	1.5647	6.8747	5.3100	
	2.0	6.0	1.0399	6.3498	5.3099	
Nb	0.5	3.0	5.3875	12.9575	7.5700	7.57
	1.0	3.0	4.4397	12.0095	7.5698	
	2.0	3.0	3.1458	10.7157	7.5699	

vanadium (V) and niobium (Nb) are recorded in Tables III and IV, respectively. Figures 1 and 2 depict the computed phonon dispersion curves along with the measured data of Colella and Batterman [27] and Powell et al. [28] for bcc V and Nb, respectively. The computed second- and third-order elastic constants for bcc V and Nb are shown in Table V.

TABLE IV  
Computed force constants for bcc V and Nb [N/m].

Metal	$n$	$m$	$\beta_1$	$\beta_2$
V	2.0	6	37.20970	06.09253
Nb	2.0	3	49.44374	12.63353

TABLE V  
Computed second- and third-order elastic constants in [ $10^{11}$  N/m $^2$ ].

Metal	$n$	$m$	$C_{11}$	$C_{12}$	$C_{44}$	$C_{111}$	$C_{112}$	$C_{123}$	Ref.
V	0.5	6.0	1.7879	1.5269	0.7042	-18.6816	-6.8217	-7.6080	
	1.0	6.0	1.7961	1.5233	0.6798	-18.9321	-7.2183	-7.7580	
	2.0	6.0	1.8026	1.5216	0.6491	-19.2036	-8.0335	-8.2101	
Exp.			2.280	1.187	0.426	—	—	—	[33]
			1.960	1.330	0.670	—	—	—	[34]
Nb	0.5	3.0	1.8412	1.6228	0.8468	-18.0951	-5.9293	-7.7992	
	1.0	3.0	1.8505	1.6169	0.8209	-18.3766	-6.3536	-7.8605	
	2.0	3.0	1.8986	1.5921	0.7130	-19.5633	-7.0727	-7.8223	
Exp.			2.460	1.340	0.287	—	—	—	[34]
			2.480	1.530	1.160	—	—	—	[35]

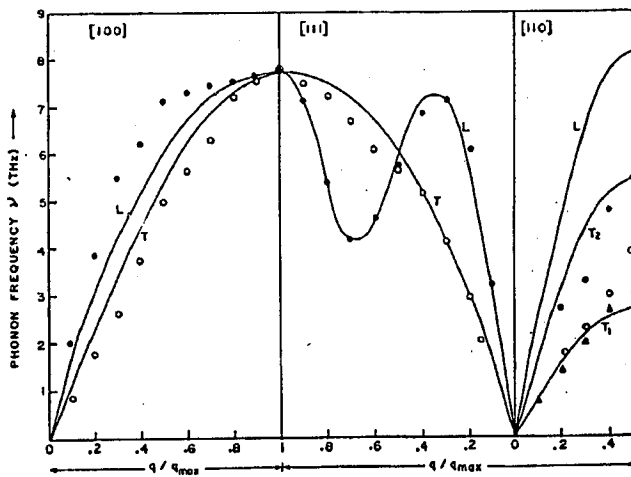


Fig. 1. Phonon dispersion in bcc vanadium; — present study, ●, full triangle, ○ experimental findings of Colella et al. [27].

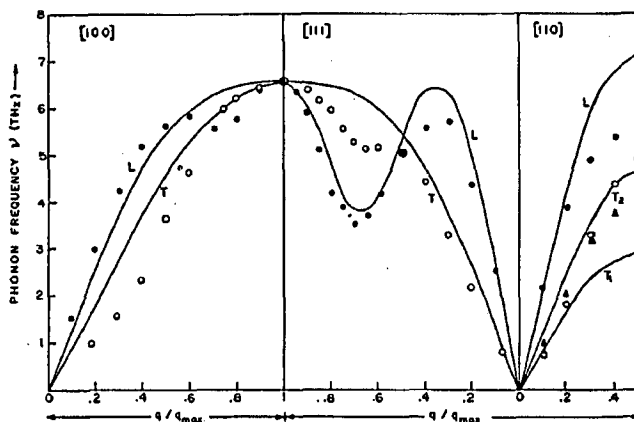


Fig. 2. Phonon dispersion in bcc niobium; — present study, ●, full triangle, ○ experimental findings of Powell et al. [28].

#### 4. Conclusions

The successful prediction of cohesive energy of the bcc V and Nb bears eloquent testimony to the efficacy of the present potential (EGEP) in explaining all the qualitative features of phonon dispersion relations of the bcc metals like V and Nb as well as the interactions coupling the metallic ions. This fact also establishes the empirical nature of the potential.

The phonon dispersion curves in bcc transition metals are notoriously full of anomalies [29]. It is only recently that these anomalies have been accounted for in a satisfactory way [30] to some extent. Previous attempts to devise potentials have met with a limited success [31] and it is not surprising to find discrepancies as high as 100% between the computed and experimental phonon frequencies in the literature. In this light, a comparison of the experimental [27,28] and the presently computed phonon frequencies in the framework of EGEP and that too, with minimum number of input data are encouraging. However, the difference of 10% to 30% between the presently computed phonon frequencies and the measured frequencies [27,28] can be further reduced 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 [32] of our model.

The intimate relation of second-order elastic constants with the strength of the metal further establishes 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 and therefore, further reveals the nature of the resultant interactions. The computed values of second-order elastic constants compare reasonably well with the available experimental values. The third-order elastic constants in the framework of EGEP have been also computed.



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