MODIFIED SHARMA–JOSHI MODEL AND PHONON DISPERSION IN β-ZIRCONIUM

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A new model is proposed. This model assumes the ion-ion interaction to be purely central and expresses the ion-ion coupling through the first and second derivatives of the potential. An equilibrium criterion, considering the volume dependent energies of ions and electrons, makes the model quite sound in its applicability. The volume-term due to Sharma–Joshi is modified to include the factors like G^2 and $K_c^2\varepsilon(q)$. The latter factor account for the exchange and correlation effects of conduction electrons in their screening-action and the former factor includes the Umklapp processes, which essentially control the symmetry of the lattice. The model thus developed reproduces the phonon-dispersion in bcc zirconium quite successfully.

1. Introduction

A large number of theoretical studies [1–7] employing Sharma–Joshi model [8] have been reported in the recent past. All of these studies use non-central forces to couple the neighbouring ions. The validity of angular part of these forces is doubtful and unjustifiable. Moreover these studies assume the lattice at equilibrium under the ionic energy only. Actually the crystal comprises of ions and electrons and their energies altogether should be considered while arriving at the proper equilibrium condition. Further, the electron-ion expression due to Sharma–Joshi needs some modifications: (a) a proper inference factor G^2 depending on the actual shape of the atomic polyhedron. Dayal and Srivastava [9] have pointed out the importance of this factor. Further the results on phonon-dispersion have been greatly improved (Goel et al. [10, 11], Ramamurthy and Neelkandan [12]) by using the correct form of the factor G^2, and (b) a screening parameter properly modified for the exchange and correlation effects of the conduction electrons.

Present communication expresses the ionic coupling between the first and second neighbours in terms of the first and second derivatives of the pair potentials coupling them. A proper equilibrium condition, envolving the volume dependent energy of ions and electrons, have been derived and it has been shown that the Cauchy's discrepancy in β-zir-

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conium is sufficiently explained for the crystal under equilibrium. The Sharma–Joshi volume term is adequately modified to include the correct inference and screening factors.

The model in its reported form reproduces the dispersion relations in body centered zirconium quite successfully. An independent stimuli for this study is provided by the availability of the experimental phonon-energies on bcc zirconium [13] quite recently.

2. Formalism

The usual secular determinant for dispersion frequencies (ν) along the principal symmetry directions $[\zeta, 0, 0]$, $[\zeta, \zeta, 0]$, $[\zeta, \zeta, \zeta]$ may be written as

$$|D(\vec{q}) - 4\pi^2 m\nu^2 I| = 0, \tag{1}$$

where m is the mass of the ion and I is the unit matrix of the order 3. The dynamical matrix $D(\vec{q})$ may be expressed as the sum of two parts, one due to ion-ion coupling $D^{\mathrm{I}}_{\alpha\beta}(\vec{q})$ and other due to electron-ion coupling $D^{\mathrm{E}}_{\alpha\beta}(\vec{q})$. The former may conveniently be expressed within the central pair potential scheme [14] as

$$\begin{aligned} D^{\mathrm{I}}_{\alpha\alpha}(\vec{q}) &= \tfrac{8}{3}(\beta_1 + 2\alpha_1)(1 - C_\alpha C_\beta C_\gamma) + 4\beta_2 S_\alpha^2 + (1 - C_{z\beta} - C_{z\gamma})2\alpha_z, \\ D^{\mathrm{I}}_{\alpha\beta}(\vec{q}) &= \tfrac{8}{3}(\alpha_1 - \beta_1) S_\alpha S_\beta C_\gamma, \end{aligned} \tag{2}$$

where $C_\alpha = \cos(\frac{1}{2}aq_\alpha)$, $C_{z\alpha} = \cos(aq_\alpha)$ and $S_\alpha = \sin(\frac{1}{2}aq_\alpha)$, q_α is the α-component of the phonon-wave vector $\vec{q}$, and

$$\alpha_i = \frac{1}{r_i}\left(\frac{\partial w}{\partial r_i}\right), \qquad \beta_i = \frac{\partial^2 w}{\partial r_i^2}, \qquad j = 1, 2 \tag{3}$$

w is the pairwise potential coupling the ions.

The electron-ion coupling term due to Sharma–Joshi [8] may be written as

$$D^{\mathrm{E}}_{\alpha\beta}(\vec{q}) = q_\alpha q_\beta K_{\mathrm{e}} G^2 \Omega, \tag{4}$$

where Ω is the atomic volume, K_{e} is the bulk modulus of the electron gas and G^2 is the inference factor evaluated over the Wigner–Seitz sphere.

In place of usual G^2 factor we have used the correct form of the factor which can be obtained by evaluating the following integral over the actual atomic polyhectron of the cubic metal.

$$G^2 = \frac{1}{\Omega}\int_{\Omega} \exp(i\vec{q}\cdot\vec{r})\,d\tau. \tag{5}$$

The resulting expressions along the symmetry directions have been reported by Ramamurthy [15]. These relations are exploited in the present study. The screening effect due to conduction electrons is accounted for by introducing a factor $K_{\mathrm{c}}^2\,\varepsilon(q)$. The modified form of equation (4) may now be written as

$$D^{\mathrm{E}}_{\alpha\beta}(\vec{q}) = q_\alpha q_\beta K_{\mathrm{e}} G^2 \Omega \frac{K_{\mathrm{c}}^2}{a_0^2}\varepsilon(q), \tag{6}$$

where K_c is the screening parameter, which has been evaluated in the Bohm–Pine [16] limit using the following expression

$$K_c = 0.353\left(\frac{r_s}{a_0}\right)^{1/2} K_F, \tag{7}$$

where γ_s is the separation between the electrons and a_0 is the Bohr radius, K_F — the Fermi-surface wave vector, may be expressed as

$$K_F = \left(\frac{3\pi^2 z}{\Omega}\right)^{1/3}. \tag{8}$$

The dielectric function $\varepsilon(q)$ in Habbard [16] and Sham [17] formulations, is given as

$$\varepsilon(q) = [1-f(q)]\varepsilon_H(q), \tag{9}$$

where Hartree dielectric function $\varepsilon_H(q)$ is expressed as

$$\varepsilon_H(q) = \frac{2K_F m_e^2}{\pi\hbar^2 q^2}\left\{1+\frac{4K_F^2-q^2}{4K_F q}\ln\left|\frac{2K_F+q}{2K_F-q}\right|\right\} \tag{10}$$

and the factor $f(q)$ needed for exchange and correlation correction is written as

$$f(q) = \tfrac{1}{2}\frac{q^2}{(q^2+K_F^2+K_s^2)}, \tag{11}$$

where

$$K_s^2 = 2K_F/\pi a_0. \tag{12}$$

For considering the equilibrium of the lattice, the volume derivative of total energy E_T should vanish, i.e.

$$\partial E_T/\partial\Omega = 0, \tag{13}$$

where E_T may be written as the sum of that due to ions (E_I) and electrons (E_e), i.e.

$$E_T = E_I + E_e. \tag{14}$$

The volume derivative of E_I can be easily expressed in terms of α_i

$$\frac{\partial E_i}{\partial\Omega} = (\alpha_1+\alpha_2)\frac{2}{a} \text{ for bcc.} \tag{15}$$

The electron-energy E_e comprises of fermi (E_f), exchange (E_x) and correlation parts (E_c). The fermi and exchange parts may be expressed as

$$E_f = \frac{2\cdot 21}{r_s^2}, \quad E_x = -\frac{0.916}{r_s}. \tag{16}$$

The correlation (E_c) part has been the subject of various studies on dielectric screening. Recently Agrawal and the present author [18] have analysed all these expressions. From this study [18] it could be inferred that for the electron separation 4 for β-Zr the most suitable schemes for electron correlation are those due to Gellmann and Brueckner [19], DuBois [20] Tiogo and Woodruff [21] Singwi et al. [22] and Mandal et al. [23]. For the purpose of the present study the latter three schemes [21, 22, 23] give the identical results on electron pressure (P_e), which can be expressed as

$$\frac{\partial E_e}{\partial \Omega} = -P_e. \tag{17}$$

The scheme due to Mandal et al. [23], which seems to be most appropriate and is used here, expresses E_c as

$$E_c = -\frac{4}{\pi \alpha r_s} \int_0^{r_s} \bar{Y}(r_s) dr_s, \tag{18}$$

where $\alpha = (4/9\pi)^{1/3}$ and the value of $\bar{Y}(r_s)$ at $r_s = 4$ equals 0.5386. The required equilibrium condition assumes the form

$$\alpha_1 + \alpha_2 = \frac{a}{2} P_e. \tag{19}$$

3. *Calculations and results*

The model reported here uses five disposable parameters ($\alpha_1, \alpha_2, \beta_1, \beta_2, aK_e$). The three of them are evaluated using elastic relations. These elastic relations are obtained by comparing Eq. (1) in long wave length limit with the Christoffel [24] relation of elasticity. The relations thus obtained are

$$\begin{aligned} aC_{11} &= 2/3(2\alpha_1 + \beta_1) + 2\beta_2 + aK_e, \\ aC_{12} &= 2/3(\beta_1 - 4\alpha_1) - 2\alpha_2 + aK_e, \\ aC_{44} &= 2/3(2\alpha_1 + \beta_1) + 2\alpha_2. \end{aligned} \tag{20}$$

The fourth model parameter is evaluated using equation (19) and the last model parameter is obtained by the knowledge of a zone boundary frequency (ν_T) at the point (1, 0, 0). The relation used in the following:

$$\pi^2 m \nu_T^2 = 4/3(2\alpha_1 + \beta_1). \tag{21}$$

The input data and the calculated model parameters for bcc zirconium are shown in Table I. The calculated dispersion curves for the said metal are shown in Fig. 1. To

TABLE I

Input data and calculated model parameters for β-zirconium

Input data	References	Calculated model parameters (10^4 dyne/cm)
$C_{11} = 0.783 \times 10^{12}$ dyne/km^2		$\alpha_1 = 0.2773$
$C_{12} = 0.503 \times 10^{12}$ dyne/km^2	[25]	$\alpha_2 = -0.3474$
$C_{44} = 0.290 \times 10^{12}$ dyne/km^2		$\beta_1 = 2.07103$
$a = 3.64$ Å		$\beta_2 = 0.3024$
$m = 91.22$ amu		
$z = 4$	[26]	$aK_e = 0.4949$
$\nu_T = 4.84$ THZ	[13]	

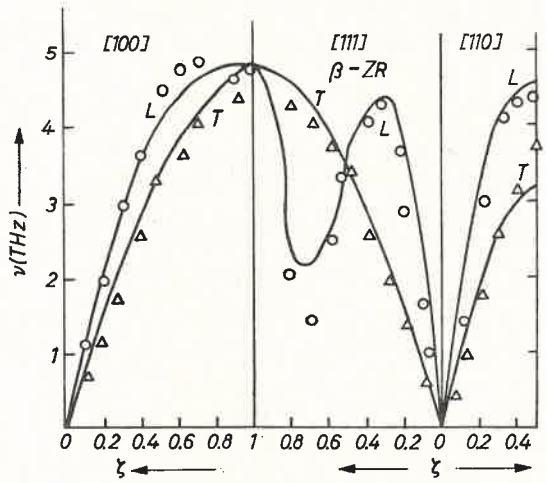

Fig. 1

compare our results, we have plotted the experimental phonon frequencies alongside our curves. These experimental phonon frequencies are calculated from the recently published data on phonon-energy [13] for β-zirconium.

4. Conclusions

From equations (19) and (20) it is evident that Cauchy's discrepancy for the metal is given by

$$C_{12} - C_{44} = K_e - 2P_e. \tag{22}$$

Our analysis (18) reveals that for $r_s = 4$ negative value for P_e and positive value for K_e is obtained what clearly explains the positivity of Cauchy's discrepancy in general. The exact magnitude of the discrepancy is yielded by considering effective valency of the

metal. Further, the negative value of P_e speaks about the cohession in metal. It is thus obvious that our equilibrium-criterion sufficiently explain Cauchy's discrepancy and cohesion in metal on one hand and makes the model consistent with the experimental findings of C_{11}, C_{12}, C_{44} and v_T on the other.

The inclusion of the factor G^2 and $K_c^2\varepsilon(q)$ has improved our results a lot. It is thus obvious that the proper inference factor and the dielectric screening effectively control the volume coupling between electron and ion. The model, in its simple form, explains the phonon dispersion in a complex metal like β-zirconium, with a reasonable degree of success.

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