

Lattice vibronics of bcc phase metals (Ti, Zr and Hf) at higher temperatures

S K SAXENA, R M AGRAWAL and R P S RATHORE*

Department of Physics and Computer Science, Dayalbagh Educational Institute, Dayalbagh, Agra 282 005, India

*Department of Physics, R.B.S. College, Agra 282 002, India

MS received 13 December 1994

Abstract. Ashcroft's analytic bare ion pseudopotential form factor with a modified Hartree dielectric function has been employed to represent the temperature dependent interionic potential. This potential includes both direct ion-ion interaction and indirect ion-electron-ion interaction with and without the effects of 'd' bands, in some scantily studied complex bcc metals viz bcc Ti, Zr and Hf. The ab initio radial and tangential force constants extending out to 15th nearest neighbours are computed for the metals. The said potential is used for predicting the binding energy, elastic constants and phonon dispersion of the above mentioned metals and the results are satisfactorily compared with the corresponding measured data.

Keywords. Phonon dispersion; second ordered elastic constants; d-band electrons.

PACS No. 63·20

1. Introduction

The superconducting metals of groups III and IV namely Ti, Zr and Hf, have attracted attention in recent years on account of the anomalous features in several physical properties. These metals have *hcp* structure at low temperatures, and undergo a phase transition to a *bcc* phase well above room temperature. To understand the systematics of the phase stability of *bcc* metals, it is of fundamental interest to investigate the phonon dispersion i.e. dynamical response to the lattice potentials. The phonon dispersion of the *bcc* phases of Ti at 1293 K, Zr at 1188 K, and Hf at 2073 K are computed.

Recently Wills and Harrison [1] obtained an effective pair potential by taking advantage of the separation between free electron states exhibited in transition metal pseudopotential theory to treat the free electron like states with simple metal theory. The *s-s* interaction is treated within the Thomas Fermi approximation. The *d*-electrons have been treated by combining the Harrison and Froyen [2] formulation and a similar treatment has been meted out to the *d* state orthogonality matrix with a simple model of the *d* band density of states. The effective interaction between transition metal ions due to the *d*-electrons in combination with the simple metal repulsion due to the *s*-electrons describes the effect of the ion rearrangement at constant volume reasonably well. In real space, Singh *et al* [3] have taken the damped pair potential in combination with the ion-ion interaction due to *d* electrons obtained by Wills and Harrison [1] to calculate the phonon dispersion, elastic constants and binding energy. The study [3] characterizes (i) freedom from very long range Friedal oscillations (ii) cancellation of

the band structure term by the coulomb repulsion in the effective potential and (iii) saving of 9/10 computer time compared to that required to calculate it using wave number space.

The study [3] however, lacks the correct depiction of electron response toward the dynamical state of the metals. The proper behaviour of electron is accurately represented in wave number space. Therefore we have carried out the application of potential in wave number space and sufficient convergence is achieved by taking the interaction system extending up to the 15th shells, more than double the nearest neighbour shells considered by Singh *et al* [3].

The temperature dependent phonon spectra of *bcc* Ti, *bcc* Zr and *bcc* Hf have recently been measured respectively by Petry *et al* [4], Heiming *et al* [5], and Trampenau *et al* [6]. These workers have analyzed their results in terms of the Born-Von Karaman model by fitting twelve force constants of their model to the measured phonon frequencies. Recently Gupta *et al* [7] have applied the model potential of Nand *et al* [8] for some of these metals. The inclusion of interactions due to *d* band electrons, into the phonon dispersion of transition metals [3], as Wills and Harrison [1] have discussed require more elaborate and adequate adoption by the theory.

Most of the dynamical studies [9, 10] make use of the numerous parameters and resort to usual fitting procedure which undermines [11] the credibility and reliability of the model. Model pseudopotential [11–15] on the contrary invariably has a smaller number of fitting parameters.

The indiscriminate use of dielectric screening [16] makes coulombian interaction infructuous. The choice of dielectric screening function invariably leads to the proper adjustment of depth and width of the coupling potential representing the interactions. Fielek [17] has reported the need of incorporating the contribution of dielectric screening, into the elastic constants of the metals, which has so far been generally ignored by almost all the macroscopic studies. In cases where electron *d*-states are close to the valence electron states, the results are not so accurate since the pseudo-potential approach assumes that the cores do not overlap and core-core interactions can be treated using only Madelung terms. It is for this reason that the effect of '*d*' bands, on various structural, vibrational and elastic properties, require to be studied more adequately within the frame-work of pseudopotential studies.

Some earlier workers, Shapiro and Moss [18], Gupta *et al* [19], Singh *et al* [3] and Shyam *et al* [20] have considered the force constants up to 4th, 2nd, 7th and 10th nearest neighbours respectively. In complex metals, however the interatomic forces are found to possess long range character.

Due to these inconsistencies it is necessary to develop an interaction model embodying the following characteristic features:

- (1) Present model accounts more appropriately for the repulsive interaction by making the first terms, of (1) and (4) each, $\Phi_{cp}(r)$ and $\Phi_d(r)$ characteristically repulsive
- (2) The role of *d*-band electrons has been included in a manner to make the resultant interaction more realistic and appropriate
- (3) The temperature dependence of the ensuing interaction has been made adequately effective within the framework of the present model
- (4) The dependence of elastic constants on dielectric screening has been sought through the force constants which are expressed as the function of the said screening. This procedure conforms with the requirements set by Fielek [17]

- (5) The field corrections due to Sham [21] have been applied to the modified dielectric function resulting in the proper adjustment of electron response to the ionic displacements
- (6) The interactions extending out to 15th nearest neighbour have been incorporated a) to account for the long range nature of interactions and b) to arrive at the desired convergence
- (7) A single parameter r_c has been fitted to the zone boundary frequency of [111] L mode.

The model is used to predict the binding energy, second order elastic constants (SOECs) and the phonon dispersion in *bcc* metals like Ti, Zr and Hf. The study being one of the first of its kind, reveals fair agreement with the experimental data on the said properties.

2. Theory

2.1 Screened ion-ion potential

A second order pseudopotential calculation transforms the interatomic interaction in the central pair wise form [22], i.e.

$$\Phi_{cp}(r) = Z^2 e^2 / r - 2 \cdot Z^2 e^2 / \pi \cdot \int G(q) \sin(qr) / qr \, dq, \quad (1)$$

where Z , is the valence, e the electronic charge and $G(q)$ the normalized energy wave number characteristics, given by

$$G(q) = (4\pi Z e^2 / \Omega q^2)^{-2} (W_b^2(q) / 1 - \epsilon(q)) (1 - 1 / (1 - \epsilon(q))). \quad (2)$$

with $W_b(q)$ being the bare ion model potential and $\epsilon(q)$ the modified Hartree dielectric function [23] inclusive of the exchange and correlation effects,

$$\epsilon(q) = 1 + [(1 - f(q))(4\pi Z e^2 / \Omega q^2) 3m^* / \hbar k_f^2] [0.5 + ((4k_f^2 + q^2) / 8k_f q) \ln |(2k_f + q) / (2k_f - q)|] \quad (3)$$

Table 1. Parameters to the Ashcroft's model potential [25]. (All quantities are in atomic units except M , which is given in amu.)

Parameters	Ti	Zr	Hf
r_c	1.191	1.342	1.267
Ω	86.709	109.642	113.81
a_{eff}	0.099	0.098	0.088
m^*	1	1	0
e	1	1	1
r_d	2.042	2.665	2.722
Z	2	2	2
M (amu.)	47.5	91.2	178.2

with

$$e^{*2} = (1 + a_{\text{eff}})e^2,$$

$$f(q) = 0.5[1 + (k_f/q)^2 + (k_s/q)^2]^{-1} \text{ and } k_s^2 = 2k_f/\pi \text{ (a.u.)}.$$

The temperature dependence of two body interaction between ions can be written as:

$$\Phi_i(r) = [\Phi_{\text{cp}}(r) + \Phi_d(r)] \cdot \exp[-T\pi k_b r / (\hbar v_f)]. \tag{4}$$

Here, the temperature dependent factor, $\exp(-T\pi k_b r / \hbar v_f)$ has been derived by Takanaka and Yamamoto [24] with $v_f (= \hbar k_f / m)$, the Fermi velocity and k_b is the Boltzmann constant.

Table 2. Computed radial and tangential force constants (accounting of the *d*-electrons effect).

Shell (no. of atoms)	Radial force constants (β_i) [10^{-3} Nm^{-1}]			Tangential force constants (α_i) [10^{-3} Nm^{-1}]		
	Ti	Zr	Hf	Ti	Zr	Hf
	1673 K	1188 K	2073 K	1673 K	1188 K	2073 K
1st (8)	20084.7	21097.6	18610.5	5347.7	3118.9	4784.3
2nd (6)	-11037.1	-5902.0	-11011.0	4763.3	3350.0	4095.2
3rd (12)	3421.0	-2641.0	-2537.5	194.5	108.0	171.0
4th (24)	257.4	328.0	151.9	22.6	-8.3	42.7
5th (8)	285.3	362.0	128	33.4	7.7	47.6
6th (6)	-249.8	-136.0	-258.9	29.0	21.6	27.0
7th (24)	-203.0	-165.2	-162.0	5.6	4.8	6.5
8th (24)	-139.8	-125.0	-103.7	1.1	1.1	2.3
9th (24)	50.6	28.0	41.3	-1.7	-2.6	1.0
10th (32)	56.6	50.4	32.8	2.0	-0.04	3.4
11th (12)	-22.4	-3.8	-29.0	3.0	2.39	2.2
12th (48)	-38.9	-24.7	-33	1.1	1.07	1.6
13th (30)	-37.2	26.5	-29.8	1.24	0.92	0.8
14th (24)	-11.9	-15.0	-5	-0.08	0.26	-0.4
15th (24)	7.3	-0.28	8.9	-1.24	-0.83	0.3

Table 3. Computed radial and tangential force constants (without *d*-electrons effect).

Shell (no. of atoms)	Radial force constants (β_i) [10^{-3}Nm^{-1}]			Tangential force constants (α_i) [10^{-3}Nm^{-1}]		
	Ti	Zr	Hf	Ti	Zr	Hf
	1673 K	1188 K	2073 K	1673 K	1188 K	2073 K
1st (8)	33920	29880	21820.1	2320	1392.7	2407.2
2nd (6)	-4336.1	-2101.2	-5622.0	3476	2655.3	2761.2
3rd (12)	-2661	-2245	-1628.5	61.5	40.6	6.455
4th (24)	520	461.99	476.9	-22.6	-30.91	-14.0
5th (8)	481.4	461.39	371	0.161	-9.003	5.35
6th (6)	-177.1	-100.1	-167.9	16.128	15.39	11.33
7th (24)	-164.1	-145	-111.0	-1.035	1.45	-2.12
8th (24)	-107	-108.9	-60.58	-4.468	-1.694	-4.99
9th (24)	69	36.9	63.3	-4.677	-4.00	-2.83
10th (32)	68	56.7	47.8	0.018	-1.01	0.88
11th (12)	-15	-0.63	-20.0	1.903	1.8	0.781
12th (48)	-34	-22.43	-27.67	0.298	0.69	0.627
13th (30)	-33	-24.39	-24.8	0.545	0.56	-0.175
14th (24)	-9.05	-13.53	-1	-0.568	0.014	-0.99
15th (24)	9.5	0.849	11	-1.63	-1.021	-0.133

The second potential term $\Phi_d(r)$ in (4) comprises of $\Phi_c(r)$ and $\Phi_b(r)$ i.e.

$$\Phi_d(r) = \Phi_c(r) + \Phi_b(r) \quad (5)$$

where $\Phi_c(r)$, is due to the overlap between *d*-states on different ions and $\Phi_b(r)$, the effects of *s* - *d* hybridization are included in an approximate manner as suggested by Wills and Harrison [1].

In the case of effective two body interactions, first and second derivatives of the potential provides for the two independent force constants pertaining to a particular set of neighbour [21]. We denote the radial force constants $(d^2\Phi_i(r)/dr^2)_{r_i}$ by β_i and tangential force constants $(r^{-1} \cdot d\Phi_i(r)/dr)_{r_i}$ by α_i for the *i*th set of neighbours.

Using function $G(q)$, one can easily evaluate the force constants. In this study we proceed with an analytic form for the bare ion pseudopotential form factor first proposed by Ashcroft [25].

The value of r_c , the core radius, Ω the atomic volume, k_f , the Fermi wave vector, Z , the valence, r_d , the d state electron radius and M the ionic mass are enlisted in table 1 for the metals under study. The computed force constants up to 15th set of neighbours are exhibited in tables 2 and 3.

2.2 Binding energy

The binding energy for the metals is computed on the lines of Wills and Harrison [1] making use of terms due to free electron gas, core, d -band and band structure components at temperature $T = 0$ K.

2.3 Phonon dispersion and second order elastic constants (SOECs)

The phonon frequencies for the present metals are calculated by solving the usual secular determinant.

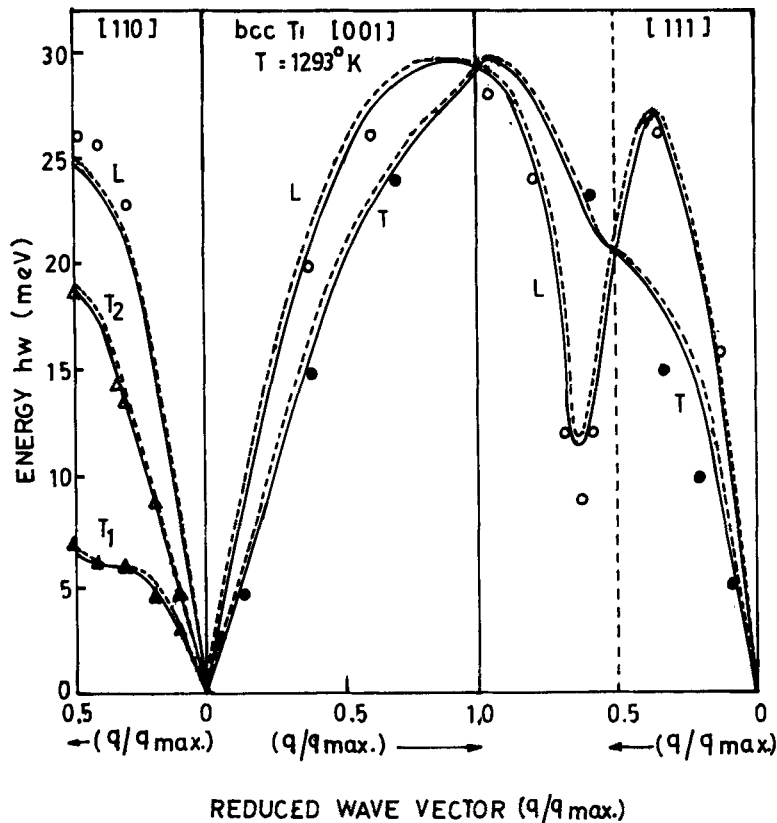


Figure 1. The phonon dispersion curve for the *bcc* Ti at temperature, $T = 1293$ K: present study; (—) with d -band effect, (---) without d -band effect. Experimental points are taken from Petry *et al* [4].

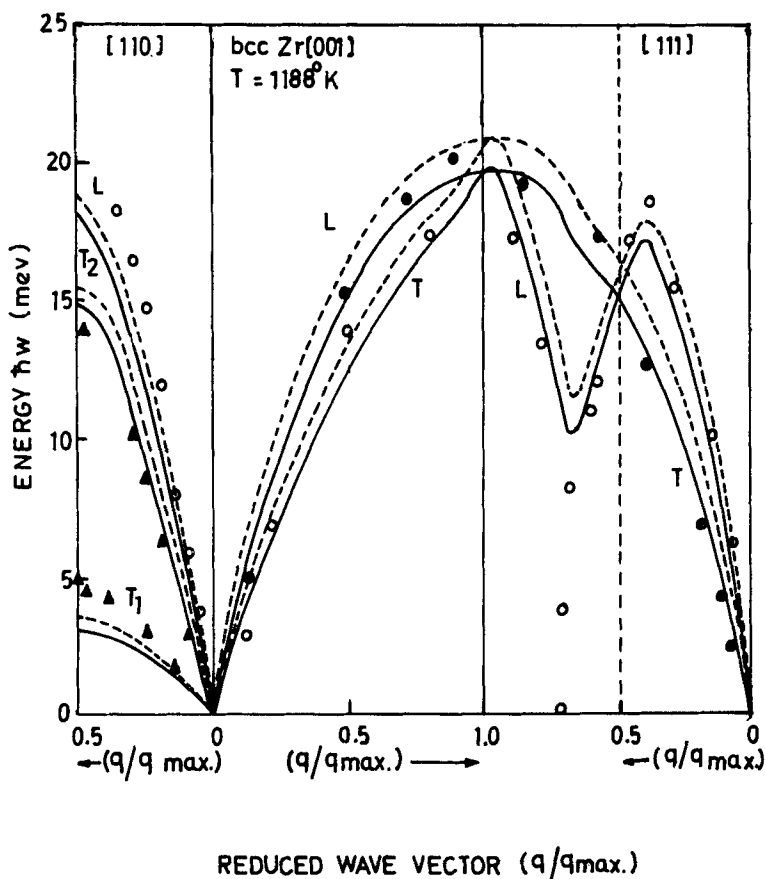


Figure 2. The phonon dispersion curves for the *bcc* Zr at temperature $T = 1188$ K present study; (—) with *d*-band electrons effects and (---) without *d*-band effects. Experimental results are taken from Heiming *et al* [5].

In the present microscopic study we have therefore computed the force constants extending up to 15th nearest neighbours and evaluated the dynamical matrix accordingly. The dynamical matrix elements are given in Appendix A.

The expressions for the SOECs of the metals under study are obtained by expanding the secular equation in long wave limits ($q \rightarrow 0$) and comparing with the usual Christoffel's relation.

3. Computation and results

The number of electrons Z_s in the *s*-shell of Ti, Zr and Hf may be equated to 1.5. Obviously the number of electrons in the *d* shell comes out to $(2 - Z_s)$. The r_d , the *d*-state radius [1] for the metals cited above is shown in table 1. We obtain the parameter r_c by matching the calculated values of phonon frequencies with experimental results of the L and T mode along [111] direction.

The contribution up to 15th shell have been found sufficient to achieve the needed convergence. The integration term appearing in the usual expressions of radial and

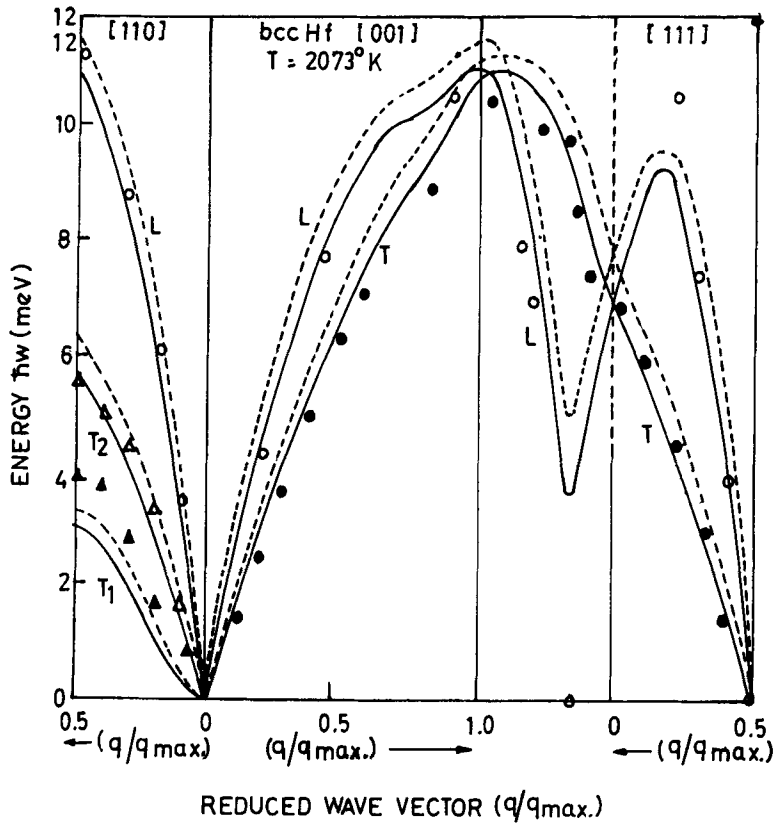


Figure 3. The phonon dispersion curve for the *bcc* Hf at temperature $T = 2073$ K, present study; (—) with the *d*-band effect and (---) without *d*-band effects, experimental results are taken from Trampenau *et al* [6].

tangential force constants are converged up to 10^{-09} . To achieve this the ranges of wave vector \mathbf{q} ($= 10^{-5}k_f$ to $75k_f$) and ($= 10^{-05}k_f$ to $100k_f$) are considered for the radial and tangential force constants respectively.

Values of the force constants for the said metals (tables 2 and 3) are fed into the dynamical matrix and then the usual secular equation is solved to obtain the dispersion relations along the three major symmetry directions. The phonon dispersions (reduced wave vector (q/q_{\max}) versus energy $\hbar\omega$ (meV)) so computed are shown in figures (1 to 3) for Ti at 1293 K, Zr at 1188 K, and Hf at 2073 K respectively.

The binding energies, at $T = 0$ K, for the metals under study are computed and shown in table 4 which also displays the experimental values which agree remarkably well with the present results.

The second order elastic constants (C_{11} , C_{12} and C_{44}), at various temperatures, for the metals under study are computed and shown in table 5, along with the calculated values of Petry *et al* [4], Heiming *et al* [5] and Trampenau [6]. These calculated values show fair agreement with those computed herein.

The present temperature dependent model proves to be efficacious in predicting the binding energy, SOECs and the phonon dispersion satisfactorily in *bcc* phase of Ti, Zr and Hf at relatively higher temperatures, which have so far been not studied adequately

Table 4. Binding energy in Ry for bcc Ti, Zr and Hf at $T = 0$ K.

Binding-energy	Ti	Zr	Hf
with d -electrons	1.268	1.41	1.45
without d -electrons	1.10	1.20	1.32
experimental	1.361*	1.484*	1.521*

* values are esimated by the relation

$E_{\text{bind}}(\text{Exp.}) = -E_{\text{coh}} - E_1 - (E_1 + E_{II})/4$, where E_{coh} , is the cohesive energy and E_1 and E_{II} are first and second ionization energy. And all these data are at $T = 0$ K, taken from the Kittel [26].

Table 5. Computed SOECs at different temperatures for bcc, Ti, Zr and Hf (10^{12} dyn/cm²).

Metal	Temperature		C_{11}	C_{12}	C_{44}
Ti	1293 K	with d -electrons	1.434	1.244	0.385
		without d -electrons	1.00	1.05	0.3825
		experimental values	1.34 ^a	1.10 ^a	0.36 ^a
Zr	1188 K	with d -electrons	1.21	1.11	0.452
		without d -electrons	1.89	1.75	0.621
		experimental values	1.04 ^b	0.93 ^b	0.38 ^b
Hf	2073 K	with d -electrons	1.41	1.2	0.58
		without d -electrons	1.95	1.92	0.825
		experimental values	1.31 ^c	1.03 ^c	0.45 ^c

where a , b and c data are taken from refs [4], [5] and [6] respectively.

by the theoretical workers. The model however reveals somewhat less pronounced dip in [111] L branch.

The present study establishes that the d -band electrons play a crucial role in the determination of the electronic properties of the transitional metals; phonon frequencies, for the metals by ignoring the d -band electrons contribution, rule over those computed by considering the d -band electrons. The later frequencies, however, lie close to the experimental ones. On the other hand the non-inclusion of the effects of d -band shell in the Zr and Hf leads to less satisfactory result and in the case of Ti, the non-inclusion of these electrons makes, however, little difference.

We have further carried out the computations on the phonon dispersion for the above mentioned metals at different temperatures with and without the inclusion of the interactions due to d -electrons. It was found that the phonon dispersion for each of the said metals at low temperatures in association with the interaction due to d electrons corresponds to those at higher temperatures without the inclusion of the interaction due to d -electrons. It may therefore be concluded that,

- (1) The comparison between computed and experimental frequencies improves upon by including the d -band electrons
- (2) The inclusion of d -band contribution at lower temperatures leads to the frequencies computed by ignoring the contribution of these electrons at higher temperatures.

It may therefore be inferred that the increase of the lattice temperature freezes down the effect of *d*-band electrons as far as the phonon frequencies are concerned.

Acknowledgements

The authors wish to thank Dr J C Upadhayay for many useful discussions during the course of this work. One of the authors (SKS) is also thankful to the University Grants Commission, New Delhi for providing JRF and financial assistance through the major research project sanctioned to Dr R M Agrawal.

Appendix A

Undefined

$$\begin{aligned}
 D_{11}(q) = & \frac{8}{3} \cdot (\beta_1 - \alpha_1) \cdot (1 - c_1 \cdot c_2 \cdot c_3) + 8 \cdot \alpha_1 \cdot (1 - c_1 \cdot c_2 \cdot c_3) \\
 & + 2 \cdot (\beta_2 - \alpha_2) \cdot (1 - c_{21}) + 2 \cdot \alpha_2 \cdot (3 - c_{21} - c_{22} - c_{23}) \\
 & + 2 \cdot (\beta_3 - \alpha_3) \cdot (2 - c_{21} \cdot c_{22} - c_{21} \cdot c_{23}) + 4 \cdot \alpha_3 \cdot (3 - c_{21} \cdot c_{22} - c_{21} \cdot c_{23} - c_{22} \cdot c_{23}) \\
 & + \frac{8}{11} (\beta_4 - \alpha_4) \cdot (2 - c_1 \cdot c_2 \cdot c_{33} - c_1 \cdot c_{32} \cdot c_3) + \frac{72}{11} (\beta_4 - \alpha_4) \cdot (1 - c_{31} \cdot c_2 \cdot c_3) \\
 & + 8 \cdot \alpha_4 \cdot (3 - c_1 \cdot c_2 \cdot c_{33} - c_1 \cdot c_3 \cdot c_{32} - c_2 \cdot c_3 \cdot c_{31}) + \frac{8}{3} (\beta_5 - \alpha_5) \cdot (1 - c_{21} \cdot c_{22} \cdot c_{23}) \\
 & + 8 \cdot \alpha_5 \cdot (1 - c_{21} \cdot c_{22} \cdot c_{23}) \\
 & + 2 \cdot (\beta_6 - \alpha_6) \cdot (1 - c_{41}) + 2 \cdot \alpha_6 \cdot (3 - c_{41} - c_{42} - c_{43}) \\
 & + \frac{8}{19} (\beta_7 - \alpha_7) \cdot (1 - c_1 \cdot c_{32} \cdot c_{33}) + \frac{72}{19} (\beta_7 - \alpha_7) \cdot (2 - c_{31} \cdot c_2 \cdot c_{33} - c_{31} \cdot c_{32} \cdot c_3) \\
 & + 8 \cdot \alpha_7 \cdot (3 - c_1 \cdot c_{32} \cdot c_{33} - c_{31} \cdot c_2 \cdot c_{33} - c_{31} \cdot c_{32} \cdot c_3) \\
 & + \frac{4}{5} (\beta_8 - \alpha_8) \cdot (2 - c_{21} \cdot c_{42} - c_{21} \cdot c_{43}) + \frac{16}{5} (\beta_8 - \alpha_8) \cdot (2 - c_{41} \cdot c_{22} - c_{41} \cdot c_{23}) \\
 & + 4 \cdot \alpha_8 \cdot (6 - c_{21} \cdot c_{42} - c_{21} \cdot c_{43} - c_{41} \cdot c_{22} - c_{41} \cdot c_{23} - c_{22} \cdot c_{43} - c_{23} \cdot c_{42}) \\
 & + \frac{4}{3} (\beta_9 - \alpha_9) \cdot (2 - c_{21} \cdot c_{22} \cdot c_{43} - c_{21} \cdot c_{42} \cdot c_{23}) + \frac{16}{3} (\beta_9 - \alpha_9) \cdot (1 - c_{41} \cdot c_{22} \cdot c_{23}) \\
 & + 8 \cdot \alpha_9 \cdot (3 - c_{21} \cdot c_{22} \cdot c_{43} - c_{21} \cdot c_{42} \cdot c_{23} - c_{41} \cdot c_{22} \cdot c_{23}) \\
 & + \frac{8}{3} (\beta_{10} - \alpha_{10}) \cdot (1 - c_{31} \cdot c_{32} \cdot c_{33}) + \frac{8}{27} (\beta_{10} - \alpha_{10}) \cdot (2 - c_1 \cdot c_2 \cdot c_{53} - c_1 \cdot c_{52} \cdot c_3) \\
 & + \frac{200}{27} (\beta_{10} - \alpha_{10}) \cdot (1 - c_{51} \cdot c_2 \cdot c_3) \\
 & + 8 \cdot \alpha_{10} \cdot (4 - c_1 \cdot c_2 \cdot c_{53} - c_1 \cdot c_3 \cdot c_{52} - c_2 \cdot c_3 \cdot c_{51} - c_{31} \cdot c_{32} \cdot c_{33}) \\
 & + 2(\beta_{11} + \alpha_{11}) \cdot (2 - c_{41} \cdot (c_{42} + c_{43})) + 4 \cdot \alpha_{11} \cdot (1 - c_{42} \cdot c_{43})
 \end{aligned}$$

Lattice vibronics at high temperatures

$$\begin{aligned}
 &+ (25 \cdot \beta_{12} + 10 \cdot \alpha_{12}) \cdot \frac{8}{35} \cdot (2 - c_{51} \cdot (c_{32} \cdot c_3 + c_2 \cdot c_{33})) \\
 &+ (9 \cdot \beta_{12} + 26 \cdot \alpha_{12}) \cdot \frac{8}{35} \cdot (2 - c_{31} \cdot (c_{52} \cdot c_3 + c_2 \cdot c_{53})) \\
 &+ (\beta_{12} + 34 \cdot \alpha_{12}) \cdot \frac{8}{35} \cdot (2 - c_1 \cdot (c_{32} \cdot c_{53} + c_{52} \cdot c_{33})) + 2 \cdot \beta_{13} \cdot (1 - c_{61}) \\
 &+ 2 \cdot \alpha_{13} \cdot (2 - c_{62} - c_{63}) + \frac{8}{9} \cdot (4 \cdot \beta_{13} + 5 \cdot \alpha_{13}) \cdot (1 - c_{41} \cdot c_{42} \cdot c_{23}) \\
 &+ \frac{8}{9} \cdot (4 \cdot \beta_{13} + 5 \cdot \alpha_{13}) \cdot (1 - c_{41} \cdot c_{22} \cdot c_{43}) \\
 &+ \frac{8}{9} \cdot (\beta_{13} + 8 \cdot \alpha_{13}) \cdot (1 - c_{21} \cdot c_{42} \cdot c_{43}) + \frac{4}{10} \cdot (9 \cdot \beta_{14} + \alpha_{14}) \cdot (2 - c_{61} \cdot (c_{22} + c_{23})) \\
 &+ \frac{4}{10} \cdot (\beta_{14} + 9 \cdot \alpha_{14}) \cdot (2 - c_{21} \cdot (c_{62} + c_{63})) + 4 \cdot \alpha_{14} \cdot (2 - c_{62} \cdot c_{23} - c_{22} \cdot c_{63}) \\
 &+ 4 \cdot \alpha_{14} \cdot (2 - c_{62} \cdot c_{23} - c_{22} \cdot c_{63}) + \frac{8}{43} \cdot (25 \cdot \beta_{15} + 18 \cdot \alpha_{15}) \cdot (1 - c_{51} \cdot c_{32} \cdot c_{33}) \\
 &+ \frac{8}{43} \cdot (9 \cdot \beta_{15} + 34 \cdot \alpha_{15}) \cdot (2 - c_{31} \cdot c_{52} \cdot c_{33} - c_{31} \cdot c_{21}) \\
 \\
 D_{12}(q) &:= \frac{8}{3} \cdot (\beta_1 - \alpha_1) s_1 \cdot s_2 \cdot c_3 + 2 \cdot (\beta_3 - \alpha_3) s_{21} \cdot s_{22} \\
 &+ 8 \cdot (\beta_4 - \alpha_4) s_1 \cdot s_2 \cdot c_{33} + \frac{24}{11} \cdot (\beta_4 - \alpha_4) \cdot (s_{31} \cdot s_2 \cdot c_3 + s_1 \cdot s_{32} \cdot c_3) \\
 &+ \frac{8}{3} \cdot (\beta_5 - \alpha_5) \cdot s_{21} \cdot s_{22} \cdot c_{23} + \frac{24}{19} \cdot (\beta_7 - \alpha_7) \cdot (s_1 \cdot s_{32} \cdot c_{33} + s_{31} \cdot s_2 \cdot c_{33}) \\
 &+ \frac{72}{19} \cdot (\beta_7 - \alpha_7) \cdot s_{31} \cdot s_{32} \cdot c_3 + \frac{8}{5} \cdot (\beta_8 - \alpha_8) \cdot (s_{21} \cdot s_{42} + s_{41} \cdot s_{22}) \\
 &+ \frac{4}{3} \cdot (\beta_9 - \alpha_9) \cdot s_{21} \cdot s_{22} \cdot c_{43} + \frac{8}{3} \cdot (\beta_9 - \alpha_9) \cdot (s_{21} \cdot s_{42} \cdot c_{23} + s_{41} \cdot s_{22} \cdot c_{23}) \\
 &+ \frac{8}{3} \cdot (\beta_{10} - \alpha_{10}) \cdot s_{31} \cdot s_{32} \cdot c_{33} + \frac{8}{27} \cdot (\beta_{10} - \alpha_{10}) \cdot s_1 \cdot s_2 \cdot c_{53} \\
 &+ \frac{40}{27} \cdot (\beta_{10} - \alpha_{10}) \cdot (s_{51} \cdot s_2 \cdot c_3 + s_1 \cdot s_{52} \cdot c_3) + 2 \cdot (\beta_{11} - \alpha_{11}) \cdot s_{41} \cdot s_{42} \\
 &+ \frac{40}{35} \cdot (\beta_{12} - \alpha_{12}) \cdot (s_{51} \cdot (3 \cdot s_{32} \cdot c_3 + s_2 \cdot c_{33})) \\
 &+ \frac{40}{35} \cdot (\beta_{12} - \alpha_{12}) \cdot (s_{52} \cdot (3 \cdot c_3 \cdot s_{31} + c_{33} \cdot s_{32}))
 \end{aligned}$$

$$\begin{aligned}
 & + \frac{24}{35} \cdot (\beta_{12} - \alpha_{12}) \cdot (c_{53} \cdot (s_{31} \cdot s_2 + s_1 \cdot s_{32})) \\
 & + \frac{16}{9} \cdot (\beta_{13} - \alpha_{13}) \cdot (2 \cdot s_{41} \cdot s_{42} \cdot c_{23} + s_{41} \cdot s_{22} \cdot c_{43} + s_{21} \cdot s_{42} \cdot c_{43}) \\
 & + \frac{12}{10} \cdot (\beta_{14} - \alpha_{14}) \cdot (s_{61} \cdot s_{22} + s_{21} \cdot s_{62}) \\
 & + \frac{24}{43} \cdot (\beta_{15} - \alpha_{15}) \cdot (5 \cdot s_{51} \cdot s_{32} \cdot c_{33} + 5 \cdot s_{31} \cdot s_{52} \cdot c_{33} + 3 \cdot s_{31} \cdot s_{32} \cdot c_{53})
 \end{aligned}$$

where

$$\begin{aligned}
 s_i & := \sin \left[\frac{aq_i}{2} \right] & c_i & := \cos \left[\frac{aq_i}{2} \right] \\
 s_{2i} & := \sin [aq_i] & c_{2i} & := \cos [aq_i] \\
 s_{3i} & := \sin \left[\frac{3aq_i}{2} \right] & c_{3i} & := \cos \left[\frac{3aq_i}{2} \right] \\
 s_{4i} & := \sin [2aq_i] & c_{4i} & := \cos [2aq_i] \\
 s_{5i} & := \sin \left[\frac{5aq_i}{2} \right] & c_{5i} & := \cos \left[\frac{5aq_i}{2} \right] \\
 s_{6i} & := \sin [3aq_i] & c_{6i} & := \cos [3aq_i]
 \end{aligned}$$

with $i = 1, 2, 3, 4, 5$ and 6

References

- [1] J M Wills and W A Harrison, *Phys. Rev.* **B28**, 4363 (1983)
- [2] W A Harrison and S Froyen, *Phys. Rev.* **B21**, 3214 (1980)
- [3] N Singh, N S Banger and S P Singh, *Phys. Rev.* **B38**, (1988) 7415; *Phys. Rev.* **B39**, 3097 (1989)
- [4] W Petry, A Heiming, J Trampenau, M Alba, C Herzig, H R Schober and G Vogl, *Phys. Rev.* **B43**, 10933 (1991)
- [5] A Heiming, W Petry, J Trampenau, M Alba, C Herzig, H R Schober and G Vogl, *Phys. Rev.* **B43**, 10948 (1991)
- [6] J Trampenau, A Heiming, W Petry, M Alba, C Herzig, W Meikeley and H R Schober, *Phys. Rev.* **B43**, 10963 (1991)
- [7] H C Gupta, M M Sinha and B B Tripathi, *Indian J. Pure Appl. Phys.* **30**, 409 (1992)
- [8] S Nand, B B Tripathi and H C Gupta, *Phys. Lett.* **A53**, 229 (1975); *J. Phys. Soc. Jpn.* **41**, 1237 (1976)
- [9] V K Thakur and T N Singh, *Phys. Status Solidi* **B138**, 407 (1986); *Phys. Status. Solidi* **B135**, 67 (1986)
- [10] B L Ficlek, *J. Phys.* **F11**, 2381 (1980)
- [11] P S Lay, B Szigitte and V K Tewari, *Proc. R. Soc. (London)* **A320**, 505 (1971)
- [12] K M Ho, C L Fu and B N Harman, *Phys. Rev.* **B29**, 2575 (1984); *Phys. Rev.* **B28**, 6687 (1983)
- [13] J A Moriarty, *Phys. Rev. Lett.*, **55**, 1505 (1985)
- [14] B N Onwuaga, *Phys. Status Solidi* **B141**, 105 (1987); *Nuovo Cimento* **D10**, 271 (1988); *Can. J. Phys.* **667**, 489 (1989)
- [15] A Ramaji Rao and A Rajput, *Phys. Status Solidi* **B147**, K-11 (1988)
- [16] R Taylor, *J. Phys.* **F8**, 1699 (1978)

Lattice vibronics at high temperatures

- [17] B L Fielek, *J. Phys.* **F14**, 61 (1984)
- [18] S M Shapiro and S C Moss, *Phys. Rev.* **B15**, 2726 (1977)
- [19] O P Gupta, *Solid State Commun.* **42**, 31 (1982)
- [20] R Shyam, S C Upadhyaya and J C Upadhyaya, *Phys. Status Solidi* **B161**, 565 (1990)
- [21] L J Sham, *Proc. R. Soc. (London)* **A283**, 33 (1965)
- [22] Wei-Mei Shyu and G D Gaspari, *Phys. Rev.* **170**, 687 (1968)
- [23] J Hubbard, *Proc. R. Soc. (London)* **A283**, 33 (1965)
- [24] K Takanaka and R Yamamoto, *Phys. Status Solidi* **B84**, 813 (1977)
- [25] N W Ashcroft, *Phys. Lett.* **23**, 48 (1966); N W Ashcroft and Langreth, *Phys. Rev.* **155**, 682 (1967)
- [26] C Kittel, *An introduction to solid state physics*, 5th ed. (Wiley, New York, 1976)