PHONON DISPERSION IN TRANSITION METALS USING A NON-CENTRAL FORCE MODEL

By R. P. S. Rathore

Department of Physics, R. B. S. College, Agra*

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A non-central force model has been employed to compute the phonon-dispersion relations in transition metals. The model contains three types of interactions, i. e. radial interactions operating up to third neighbouring ions, Clark et al. type angular interactions for first and second neighbouring ions, and electron-ion interactions given by a modified Cheveau scheme, which has been modified to include an exact expression for Bardeen's *g*-function and the modified form of the screening parameter. The model is used to compute the dispersion-frequencies for palladium (fcc) and vanadium (bcc). Good agreement between computed and experimental data has been attained.

1. Introduction

In recent years the lattice dynamics of transitional metals has been studied on the basis of two different approaches i. e. pseudopotential [1–3] approaches and phenomenological [3–10] approaches. The former approaches, based on certain assumptions, preclude the possibility of their use in studying the complicated lattices. These potentials require further modifications with respect to their non-centrality and dielectric functions for yielding a good comparison between computed and experimental dispersion-data. These modifications make these methods more complex and difficult.

The phenomenological models [4–9] either use de-Launay [11] type angular interactions or Sharma Joshi [12] volume interactions. The former interactions suffer from the deficiency of rotational-invariance and the later are asymmetric as pointed out by Lax [13]. The Krebs [14] electron ion interactions used by Kulshrestha and Upadhyaya [3] suffer from the deficiency of internal inequilibrium as reported by Cochran [15]. The Bhatia [16] model used by Shukla and Bertolo [10] is also deficient in these regards.

In view of these deficiencies, a new non-central force model has been developed. The model assumes ion-ion interactions to be radial up to third neighbours and Clark et al. [17] type angular up to second neighbours. These more distant ion-ion interactions

* Address: Department of Physics, R. B. S. College, Agra-282002, India.

are needed because of tightly-bounded *d*-electrons in the transition metals. The electron-ion interactions are included on the lines suggested by the modified Cheveau [18] model. The model has been used to compute the dispersion-frequencies for palladium (fcc) and vanadium (bcc).

2. *Formulations and results*

The phonon-frequencies (w) are expressed by the following secular determinant:

$$[D - mw^2\,\mathrm{I}] = 0, \tag{1}$$

where m is the mass of the atom and I is the unit matrix of the order three. The dynamical matrix-elements $[D]$ are the sum of ion-ion $[D^{\mathrm{i}}_{\alpha\beta}]$ terms and electron-ion $[D^{\mathrm{e}}_{\alpha\beta}]$ terms.

The ion-ion $[D^{\mathrm{i}}_{\alpha\beta}]$ terms are expressed as

$$\begin{aligned}
D^{\mathrm{i}}_{\alpha\beta} &= (2\alpha_1 - 16y_1)S_\alpha S_\beta + \tfrac{4}{3}\,S_\alpha S_\beta \alpha_3[4C_\gamma(C_\alpha + C_\beta) - (1-2C_\gamma)^2], \\
D^{\mathrm{i}}_{\substack{\alpha\alpha \\ \alpha\neq\beta\neq\gamma\neq\alpha}} &= 2[\alpha_1 + 8(y_1+y_2)]\,[2 - C_\alpha(C_\beta + C_\gamma)] + 4\alpha_2 S_\alpha^2 \\
&\quad + \tfrac{16}{3}\,[1 + C_\beta C_\gamma(1-2C_\alpha^2)]\alpha_3 \\
&\quad \tfrac{8}{3} + \alpha_3\left[1 + \frac{C_\alpha}{2}(C_\beta + C_\gamma)\,(1 - C_\beta C_\gamma)\right] - 4y_1[2S'_\alpha - C'_\beta - C'_\gamma], \quad \text{fcc}
\end{aligned} \tag{2}$$

$$\begin{aligned}
D^{\mathrm{i}}_{\alpha\beta} &= 8(\alpha_1 - y_1 + \tfrac{3}{2}\,y_2)S_\alpha S_\beta C_\gamma + 8\alpha_3 S_\alpha S_\beta C_\alpha C_\beta, \\
D^{\mathrm{i}}_{\substack{\alpha\alpha \\ \alpha\neq\beta\neq\gamma\neq\alpha}} &= (8\alpha_1 + 16y_1 + 24y_2)\,(1 - C_\alpha C_\beta C_\gamma) + 4\alpha_2 S_\alpha^2 \\
&\quad - 2y_1(4C'_\alpha - C'_\beta - C'_\gamma - 2) + 3y_2(2 - C'_\beta - C'_\gamma) \\
&\quad + 4\alpha_3(2S_\alpha^2 + S_\beta^2 + S_\gamma^2 - 2S_\alpha^2 S_\beta^2 - 2S_\alpha^2 S_\gamma^2), \quad \text{bcc}
\end{aligned} \tag{3}$$

where $\alpha, \beta = 1, 2, 3$, $S_\alpha = \sin(\frac{1}{2}aq_\alpha)$, $C_\alpha = \cos(\frac{1}{2}aq_\alpha)$, $C'_\alpha = \cos(aq_\alpha)$, $\alpha_1, \alpha_2, \alpha_3$ are the radial force constants for the first, second and third neighbouring ions respectively, y_1 and y_2 are the angular force constants for the first and second neighbours respectively, a is the lattice parameter and q_α is the α-component of the wave-vector q.

The electron-ion term $[D^{\mathrm{e}}_{\alpha\beta}]$ can be written as

$$D^{\mathrm{e}}_{\alpha\beta} = \frac{a^3\lambda^2}{4}\,K_{\mathrm{e}} \sum \left[\frac{(q+G)_\alpha (q+G)_\beta g^2[(lq+Gl)B]}{(q+G)^2 + \lambda^2 f(t_1)} - \frac{G_\alpha G_\beta g^2[(lGlB)]}{(G)^2 + \lambda^2 f(t_2)}\right], \tag{4}$$

where K_{e} is the bulk modulus of the electron-gas. Equation (4) represents the modified form of the Cheveau [18] expression. The Bardeen [19] function g has been included to reduce the effective potential at the core-region of the ions and to admit the Bloch type electron-wave function as suggested by Toya [20] and Kohn [21]. This function has

been further modified for the Wigner-Seitzshell, as reported by Bross and Bohn [22] and successfully used by Goel et al. [9, 23] i. e. for fcc structure

$$g = \frac{-2}{x^2+y^2+z^2}\left\{\frac{x+y}{(x-y)^2-z^2}\left[\sin x+\sin y-\sin\left(\frac{x+y+z}{2}\right)\right.\right.$$

$$\left.\left.-\sin\left(\frac{x+y-z}{2}\right)\right]+\frac{x-y}{(x+y)^2-z^2}\left[\sin x-\sin y-\sin\left(\frac{x+y+z}{2}\right)+\ldots\right]\right\}, \qquad (5)$$

where

$$x = \frac{2\pi}{a}(lq+G), \quad y = \frac{\pi}{\sqrt{2}\,a}(lq+Gl), \quad z = \frac{\sqrt{3}\,\pi}{a}(lq+Gl).$$

For bcc structure

(a) along [100] direction

$$g = \frac{1}{x^3}\sin\frac{x}{2}\left[2x\sin\frac{x}{2}+8\sin^2\frac{x}{4}+\frac{x^2}{2}\cos\frac{x}{2}\right],$$

$$x = \frac{2\pi}{a}(lq+Gl), \qquad (6)$$

(b) along [110] direction

$$g = \frac{1}{y^3}\sin y\left[y\sin\frac{y}{2}+8\sin^2\frac{y}{2}\right],$$

$$y = \sqrt{2}\,\frac{\pi}{a}(lq+Gl), \qquad (7)$$

(c) along [111] direction

$$g = \frac{1}{8z^3}\sin^2\frac{z}{2}\left[(3z^2+4)\sin\frac{z}{2}+12z\cos\frac{z}{2}\right],$$

$$z = \sqrt{3}\,\frac{\pi}{a}(lq+Gl). \qquad (8)$$

The screening parameter (λ) is modified to take into account its dependence on wave number (k) and the repulsion due to electrons. These modifications suggested by Langer and Vosko [24] and Pines [25] lead to the modified screening parameter as

$$\lambda = 0.353\left(\frac{r_0}{a_0}\right)^{1/2} k_F, \qquad (9)$$

where r_0 = inter-electronic spacing = $r_s/Z^{1/3}$, r_s = radius of atomic sphere, Z = valence, a_0 = Bohr radius, k_F = Fermi-wave number, and

$$f(t) = \tfrac{1}{2}+\frac{1-t^2}{4t}\ln\left(\frac{1+t}{1-t}\right), \quad t_1 = \frac{lq+Gl}{2k_F}, \quad t_2 = \frac{lGl}{2k_F}. \qquad (10)$$

The six model parameters (α_1, α_2, α_3, y_1, y_2 and aK_e) are reduced to five by assuming a proper ratio between y_1 and y_2, i. e. $y_1/y_2 = -9/2$. The remaining five parameters have been computed independently making use of known values of three elastic constants (C_{11}, C_{12}, C_{44}) and two transverse zone-boundary frequencies ν_1 and ν_2 in the directions [100] and [111], respectively. The resulting equations are expressed as

$$\alpha_1 = \tfrac{1}{2}(9\pi^2 m\nu_1^2 - 7aC_{44} + 306y_2), \quad \alpha_2 = \tfrac{1}{2}(2\pi^2 m\nu_2^2 - \pi^2 m\nu_1^2 + 64y_2),$$

$$\alpha_3 = \tfrac{1}{6}(aC_{44} - \alpha_1 - 8y_2), \quad y_2 = \tfrac{1}{74}(aC_{12} + aC_{44} - aC_{11} + 4\pi^2 m\nu_2^2 - 2\pi^2 m\nu_1^2),$$

$$aK_e = aC_{12} - aC_{44} + 32y_2, \quad \text{fcc} \tag{11}$$

and

$$\alpha_1 = \frac{a}{4}(C_{12} - C_{44}) + \tfrac{1}{2}\pi^2 m\nu_1^2 - \tfrac{1}{4}aK_e,$$

$$\alpha_2 = \frac{a}{4}(C_{12} - C_{44}) - \frac{\pi^2 m(\nu_1^2 - 2\nu_2^2)}{2} - \tfrac{1}{4}aK_e,$$

$$\alpha_3 = \frac{a}{4}(C_{12} - 3C_{44}) - \frac{\pi^2 m\nu_1^2}{4} + \tfrac{1}{4}aK_e, \quad y_2 = \frac{a}{24}(C_{12} - C_{44} - K_e),$$

$$aK_e = \frac{4a(C_{11} + 2C_{12} - 4C_{44}) + 2\pi^2 m(\nu_1^2 - \nu_2^2)}{12}, \quad \text{bcc} \tag{12}$$

The input data and the computed model parameters for palladium and vanadium are given in Table I.

TABLE I

Input data and computed model parameters for palladium and vanadium

Metal	Input data	Computed model parameter in 10^4 dyne/cm
	$C_{11} = 2.271 \times 10^{12}$ dyne/cm^2	$\alpha_1 = 8.70043$
Ref. [26]	$C_{12} = 1.761 \times 10^{12}$ dyne/cm^2	$\alpha_2 = 0.30523$
palladium	$C_{44} = 0.717 \times 10^{12}$ dyne/cm^2	$\alpha_3 = -0.99858$
	$a = 3.89$ Å	$y_1 = -0.04511$
	$\nu_1 = 4.56$ THz	$y_2 = 0.010024$
Ref. [27]	$\nu_2 = 3.21$ THz	$aK_e = 3.49979$
	$C_{11} = 2.28 \times 10^{12}$ dyne/cm^2	$\alpha_1 = 0.49949$
Ref. [28]	$C_{12} = 1.188 \times 10^{12}$ dyne/cm^2	$\alpha_2 = 0.3864$
	$C_{44} = 0.426 \times 10^{12}$ dyne/cm^2	$\alpha_3 = -0.46267$
vanadium	$a = 3.04$ Å	$y_1 = 0.20476$
	$\nu_1 = 7.50$ THz	$y_2 = -0.04550$
Ref. [29]	$\nu_2 = 6.00$ THz	$aK_e = 3.40854$

3. Conclusion

The computed dispersion curves for palladium and vanadium are shown in Figs. 1 and 2, respectively. The experimental points (○ △ ▲) as reported by Brockhouse [27] and Colella and Batterman [29] for palladium and vanadium respectively, are also marked in the figures. A close inspection of the figures reveals that the computed curves are in

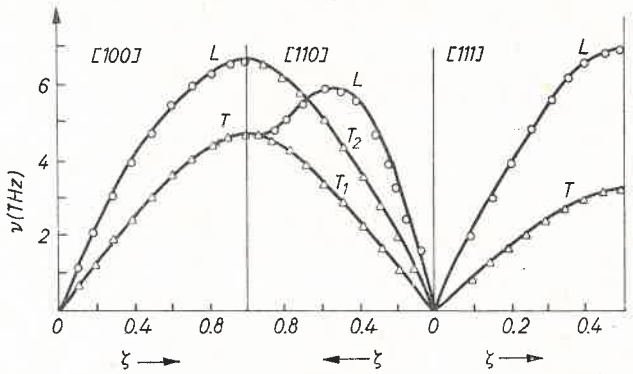

Fig. 1. Computed phonon dispersion for palladium. Experimental points are marked by circle and triangle

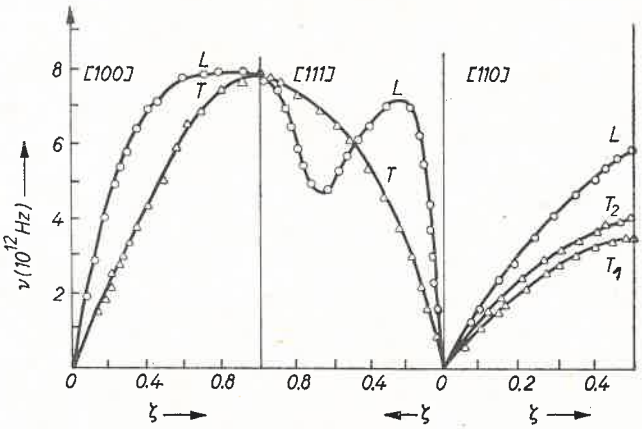

Fig. 2. Computed phonon dispersion for vanadium. Experimental points are marked by circle and triangle

good agreement with the experimental ones in all the three symmetry directions. Such satisfactory results have not been obtained so far. It may be concluded that the model presents correctly the actual interactions responsible for the lattice vibrations in the transition metals.

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REFERENCES

[1] J. Singh, N. Singh, S. Prakash, *Phys. Rev.* **B12**, 3166 (1975).
[2] B. A. Oli, A.O.E. Animalu, *Phys. Rev.* **B12**, 3166 (1976).
[3] O. P. Kulshrestha, J. C. Upadhyaya, *Ind. J. Pure Appl. Phys.* **14**, 253 (1976).

[4] S. Pal, *Phys. Rev.* **B9**, 5144 (1974).
[5] J. C. Upadhyaya, S. S. Sharma, O. P. Kulshrestha, *Phys. Rev.* **B12**, 2236 (1975).
[6] V. P. Singh, J. Prakash, M. P. Hemkar, *Nuovo Cimento* **B28**, 47 (1975).
[7] J. Behari, B. B. Tripathi, *J. Phys. Soc. Jap.* **23**, 1207 (1972).
[8] J. Prakash, L. P. Pathak, M. P. Hemkar, *Aust. J. Phys.* **28**, 57 (1975).
[9] C. M. Goel, B. P. Pandey, B. Dayal, *Phys. Status Solidi* (b) **66**, 759 (1974).
[10] L. A. Bertolo, M. M. Shukla, *J. Phys. Soc. Jap.* **38**, 1439 (1975).
[11] J. de-Launay, *Solid State Physics*, Edited by Seitz and Turnbull, Academic Press, New York 1956, 2, p. 276.
[12] P. K. Sharma, S. K. Joshi, *J. Chem. Phys.* **39**, 2633 (1963).
[13] M. Lax, Proc. Int. Conf. Lattice Dynamics, Pergamon Press, New York 1963.
[14] K. Krebs, *Phys. Rev.* **138**, 143 (1965).
[15] W. Cochran, Proc. Int. Conf. Lattice Dynamics, Pergamon Press, New York 1968, p. 183.
[16] A. B. Bhatia, *Phys. Rev.* **97**, 363 (1955).
[17] B. C. Clark, D. C. Gazis, R. F. Wallis, *Phys. Rev.* **134**, 1486 (1964).
[18] L. Cheveau, *Phys. Rev.* **169**, 496 (1968).
[19] J. Bardeen, *Phys. Rev.* **52**, 688 (1937).
[20] T. Toya, *J. Res. Inst. Catalysis, Kokkaido Univ.* **6**, 161, 183 (1958).
[21] E. J. Woll, W. Kohn, *Phys. Rev.* **A126**, 1693 (1969).
[22] H. Bross, B. Bohn, *Phys. Status Solidi* **20**, 277 (1967).
[23] C. M. Goel, B. P. Pandey, B. Dayal, *Phys. Status Solidi* (b) **69**, 589 (1975).
[24] J. S. Langer, S. H. Vosko, *Phys. Chem. Solids* **12**, 196 (1959).
[25] D. Pines, *Solid State Physics*, Academic Press, New York 1955, p. 367.
[26] C. Kittel, *Ind. Solid State Physics*, John Wiley, New York 1971, p. 149.
[27] B. N. Brockhouse, *Phonons*, edited by R. W. H. Stevenson, Plenum Press, New York 1966, p. 110.
[28] I. D. Bolef, *J. Appl. Phys.* **32**, 100 (1961).
[29] R. Colella, B. W. Batterman, *Phys. Rev.* **B1**, 3913 (1970).