

Multipole Interactions and Phonon Dispersion in B.c.c. Transition Metals

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Abstract

Multipole interactions arising out of the interband and intraband transitions of electrons occupying d shells are analysed classically. The ion–ion and volume interactions are modified and an equilibrium condition is derived on simple and realistic lines. A model incorporating these features is employed to discuss the dispersion relations in b.c.c. transition metals like tantalum and vanadium.

Introduction

Charged clouds associated with d -shell electrons of a transition-metal overlap, which leads to hybridization. During the lattice excitation these clouds are deformed resulting in interband and intraband transitions, which give rise to electrostatic multipole interactions possessing three-body character. The importance of these interactions in crystal mechanics has been studied by Lloyd & Sholl (1968), Upadhyaya (1977), Brovman, Kagan & Kholas (1969), Finnis (1974), Bertoni, Bisi, Calandra & Nizzoli (1975) and Bertoni, Bisi & Nizzoli (1974). These analyses, despite their computational complexities and mathematical rigour, could not lead to an explicit formulation for the interactions. Studies by Kharoo, Gupta & Hemkar (1979) and Sharma & Awasthi (1979) apparently employ angular forces for this purpose but these authors seem to assume these interactions among the ions, which is erroneous in view of the small ionic sizes. In fact, the ionic interactions are essentially central and pairwise (Rathore & Verma, 1977; Rathore, 1979) and the three-body character of the forces must be associated with the interactions among the d shells. We have developed a model which incorporates these forces among the d shells within the framework of the Fielek (1975) scheme.

The Fielek (1975) scheme ignores the volume dependence of the ionic interactions, implying that the total energy of the system is wholly ionic. This situation is artificial and needs rectification. The present model, therefore, expresses the ionic interactions more realistically. The volume interactions in the Fielek

(1975) scheme follow the Krebs (1965) model, which (a) assumes the electrons to be perfectly free (Upadhyaya, 1978), (b) treats the volume dependence of the screening parameter quite arbitrarily (Rathore, 1980), (c) introduces inequilibrium (Cochran, 1965) into the lattice, and (d) involves sophisticated computation. It is therefore thought worth while to replace the Krebs (1965) scheme by that due to Bhatia (1955), which is modified to (i) include the screening parameter (K_c) in the Bohm–Pines (Bohm & Pines, 1953) limit, (ii) correct the screening for exchange and correlation effects of conduction electrons, and (iii) incorporate a proper inference factor $G^2(x)$, which in turn (a) introduces the desired anisotropy into the interacting system, (b) ensures uniform distribution of the resulting stress over the whole of the atomic polyhedron and (c) makes the expression more convergent at large wave vector.

Some studies (Singh, Pathak & Hemkar, 1978; Singh & Hemkar, 1979; Jani & Gohel, 1976*a,b*), based on the Fielek (1975) scheme, have neglected the volume interactions among the ions and the conduction electrons. These interactions are adequately taken care of by the present study. Most of the authors could not treat the problem of crystal equilibrium in a self-consistent manner. Fielek (1978) has attempted to tackle this problem, but he could not apply his method to describe the lattice mechanics of any of the systems. The present communication derives an equilibrium condition in a self-consistent simple manner.

The model thus developed is employed to obtain the dispersion relations in tantalum and vanadium to test its predictability.

Theory

The dispersion frequencies (ν) along the major symmetry directions are given by the determinantal equation

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

where I is the unit matrix of 3×3 order, m the mass of the ion and $D(\mathbf{q})$ the matrix which describes the interactions of the ion with its environment, *i.e.* other ions, d shells and conduction electrons. If we consider the coupling energy (E_i) among the nearby ions as one

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constituent of the total energy (E_T) then we could express E_I in the form of a Taylor expansion with the first and second derivatives of E_I denoted by α_1 and β_1 respectively. The diagonal and off-diagonal elements of $D(\mathbf{q})$ for b.c.c. metals can now be written as

$$D_{\alpha\alpha}(\mathbf{q}) = -\frac{8}{3}(\beta_1 + 2\alpha_1)(1 - C_\alpha C_\beta C_\gamma) + K + AM(\mathbf{q}) + \frac{K^2}{N}$$

$$D_{\alpha\beta}(\mathbf{q}) = -\frac{8}{3}(\beta_1 - \alpha_1)S_\alpha S_\beta C_\gamma, \quad (2)$$

where $C_\alpha = \cos(\frac{1}{2}aq_\alpha)$, $S_\alpha = \sin(\frac{1}{2}aq_\alpha)$, a is the cube edge and q_α the α th component of the phonon wave vector (\mathbf{q}). K denotes the coupling parameter among the ions and the d shells. A is the deformability parameter arising out of the response of conduction electrons towards the ionic motion and $M(\mathbf{q})$ is the corresponding dynamical matrix. The term N is evaluated from the secular equation

$$|D'(\mathbf{q}) - NI| = 0, \quad (3)$$

where the dynamical matrix $D'(\mathbf{q})$ defines the interactions of the d shells with its surroundings, *i.e.* other d shells, ions and conduction electrons. The literature on lattice-dynamical studies reveals various angular force schemes, *e.g.* De Launay (1956), Clark, Gazis & Wallis (1964), Rani & Gupta (1977). Khanna & Rathore (1979) have shown that out of these schemes, the one due to Clark *et al.* (1964) proves to be most appropriate for the system under consideration. Following the adiabatic approximation, which ensures that the centres of d shells are located at the site of the corresponding ions, we could define the angular forces (Clark, Gazis & Wallis, 1964) depending on the change of angles in the triangle formed by the d shells and its two neighbours. It is thus obvious that these forces inherit the three-body character, and the following elements of $D'(\mathbf{q})$ arise

$$\begin{aligned} D'_{\alpha\alpha}(\mathbf{q}) &= 2(2\gamma_1 + 3\gamma_2)(1 - C_\alpha C_\beta C_\gamma) \\ &\quad - 4\gamma_1(S_\beta^2 + S_\gamma^2 - 4S_\alpha^2) + 6\gamma_2(S_\beta^2 + S_\gamma^2) \\ &\quad + K - A'M(\mathbf{q}) \\ D'_{\alpha\beta}(\mathbf{q}) &= 8(\frac{3}{2}\gamma_2 - \gamma_1)S_\alpha S_\beta C_\gamma, \end{aligned} \quad (4)$$

where γ_1 and γ_2 are the force constants for the first and second neighbours. A' is the deformability parameter, representing the response of the conduction electrons to the motion of the d shells. The elements of the dynamical matrix $M(\mathbf{q})$ may be written as

$$M_{\alpha\alpha}(\mathbf{q}) = \frac{q_\alpha^2 \Omega G^2}{a \left[1 + \frac{q^2}{K_c^2 \epsilon(q)} \right]}, \quad (5)$$

where Ω is the atomic volume. The inference factor G^2

is evaluated from the relations given by Ramamurthy (1978). The dielectric function $\epsilon(\mathbf{q})$ may be written as

$$\epsilon(\mathbf{q}) = 1 + \frac{\epsilon_H(\mathbf{q})}{q^2} [1 - S(\mathbf{q})], \quad (6)$$

where $\epsilon_H(\mathbf{q})$ is the usual Hartree function and $S(\mathbf{q})$ is the correction term due to the exchange and correlation effects associated with the conduction electrons. The correction term $S(\mathbf{q})$ is evaluated by taking into consideration the exchange and correlation as described by Mandal, Rao & Tripathi (1978).

For considering the equilibrium of the whole lattice, its total energy (E_T) may be written as

$$E_T = E_I + E_d + E_e, \quad (7)$$

where E_d and E_e are the energies associated with the d -shell and the conduction electrons respectively. The details regarding E_d and E_e are reported by Khanna & Rathore (1980) and Rathore & Agrawal (1980). For the equilibrium of the lattice $\partial E_T / \partial \Omega$ should vanish, which immediately gives the equilibrium constraint

$$\alpha_1 = -\frac{a}{2}(P_d + P_e), \quad (8)$$

where P_d and P_e are the pressures associated with the d shells and the conduction electrons respectively. Numerical values of P_d and P_e for the present study are taken from our reference quoted earlier. Moreover, the deformability parameter A is related to E_e as

$$A = -a\Omega \frac{\partial^2 E_e}{\partial \Omega^2}. \quad (9)$$

Calculations and results

The model consists of the seven disposable parameters α_1 , β_1 , γ_1 , γ_2 , K , A and A' . Three of these are evaluated from knowledge of elastic constants, C_{11} , C_{12} and C_{44} . Two are obtained from (8) and (9). The remaining two are given by the following zone-boundary frequency relations

$$\begin{aligned} 4\pi^2 m v_{T_1}^2(100) &= -\frac{16}{3}(\beta_1 + 2\alpha_1) - K + \frac{K^2}{K + 32\gamma_1 + 48\gamma_2} \\ 4\pi^2 m v_{T_1}^2(110) &= -8\alpha_1 - K + \frac{K^2}{K + 36\gamma_1 + 18\gamma_2}. \end{aligned} \quad (10)$$

The required input data for calculating the parameters for tantalum and vanadium are given in Table 1, and Table 2 lists the calculated parameters. These parameters when fed to (1) give the dispersion frequencies (ν) along the major symmetry directions. Dispersion relations for tantalum and vanadium are

Table 1. *Input data for tantalum and vanadium*

	Tantalum	Reference	Vanadium	Reference
C_{14} in 10^{11}	2.609		2.28	
C_{12} in 10^{11}	1.574	(a)	1.188	(c)
C_{44} in 10^{11}	0.818		0.426	
$\nu_T(100)$ in THz	5.03		8.2	
$\nu_{Ti}(110)$ in THz	2.63	(b)	4.6	(d)

References: (a) Kittel (1967); (b) Woods (1964); (c) Bolef (1961); (d) Collela & Batterman (1970).

Table 2. *Calculated model parameters for tantalum and vanadium (10 Nm^{-1})*

Model parameters	Tantalum	Vanadium
α_1	1.4525	1.338
β_1	-5.0373	-4.7512
γ_1	-0.4967	-0.5475
γ_2	-0.0316	0.1315
K	266.708	722.595
A	0.2953	0.2721
A'	0.7438	-0.5055

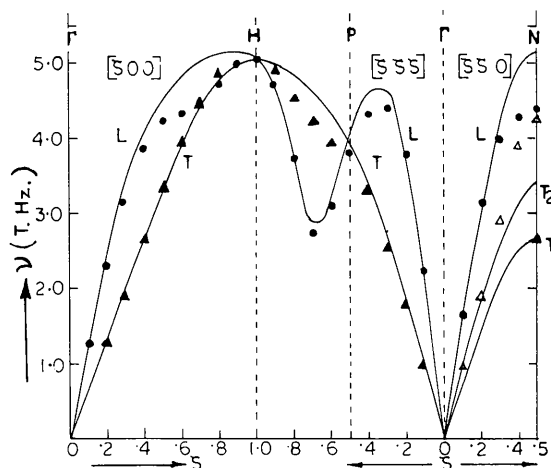


Fig. 1. Dispersion relation for tantalum. (—) Theoretical curve given by the present study; (●,▲,△) experimental points due to Woods (1964).

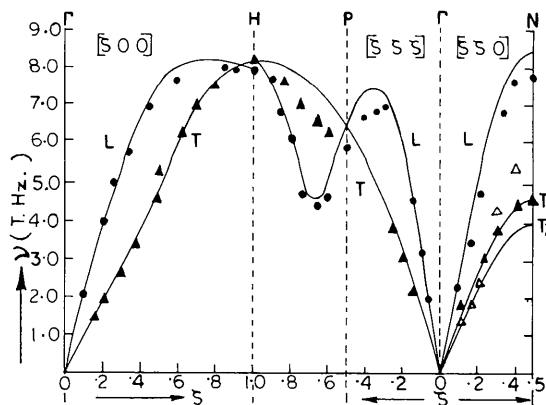


Fig. 2. Dispersion relation for vanadium. (—) Theoretical curve given by the present study; (●,▲,△) experimental points due to Collela & Batterman (1970).

plotted in Figs. 1 and 2 respectively. The experimental points due to Woods (1964) and Collela & Batterman (1970) for tantalum and vanadium, respectively, are also depicted in the figures for comparison.

Conclusion

The Cauchy discrepancy exhibited by the metals under study is given by the model as

$$C_{12} - C_{44} = \frac{1}{a} [A + A' - 2a(P_d + P_e) + 8\gamma_1 + 12\gamma_2]. \quad (11)$$

It is thus evident that the non-central character of the deformability parameter, the angular parameters γ_1 and γ_2 bearing the three-body character and the pressures P_d and P_e associated with the d shell and the conduction electrons, respectively, all contribute towards the discrepancy. The positive values of A and A' and the negative values of P_e and P_d , contributing positively towards the discrepancy, explain the pronounced cohesion exhibited by transition metals like tantalum and vanadium. The simple and realistic equilibrium condition makes the model more sound in its mathematical footings.

The simple model successfully reproduces the dispersion relations in tantalum and vanadium. To show the relative merits of the present model we have compared its predictions on phonon dispersion with those given by two of our models reported earlier: (a) the model which expresses the ion-ion and the d -shell- d -shell interactions each by a Taylor's expansion of their central pairwise potential energy coupling the first neighbours only—all the other interactions are assumed to follow the lines of the present model (called model 1); and (b) the model which is similar to the present model with the difference that the d -shell- d -shell interactions are three-bodied extending to first neighbours only (called model 2).

The mean maximum percentage deviation from experimental data for tantalum and vanadium for the said models and also in the present model are depicted in Fig. 3.

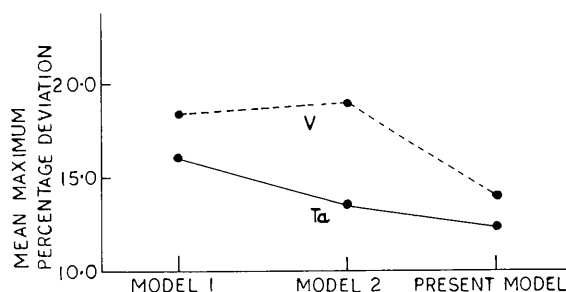


Fig. 3. Mean maximum percentage deviation from experimental data: (—) for tantalum; (---) for vanadium.

It can now be inferred that the interactions controlling the phonon dispersion in the complicated metals under study are well accounted for by the present model.

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Deriving the Equilibrium Conformation in Molecular Crystals by the Quasi-Harmonic Procedure: Some Critical Remarks

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Abstract

Owing to progress in lattice-dynamical computing routines, free-energy calculations for perfect molecular crystals are no longer prohibitive in the quasi-harmonic approximation. Thus the consistent derivation of an equilibrium conformation at various temperatures and pressures, and even the stability range of various phases, may become a routine possibility, starting from semi-empirical potentials only. An example of such conformational calculations is given and discussed for the tetragonal phase of adamantane at 163 and 1 K. The effect of vibrational energy (even zero-point) and

entropy upon molecular orientation and position in the unit cell is shown not to be negligible by several examples. This precludes the possibility of calculating the cell parameters on free-energy grounds and the molecular coordinates by considering the minimum packing energy. For crystals with molecules fixed by symmetry, the quasi-harmonic approximation becomes particularly appropriate, since in this case for any unit cell the first derivatives of energy with respect to any molecular shift are zero. Some critical steps of such calculations are examined and discussed, especially in connection with converging processes. No particular problem is encountered in sampling the Brillouin zone,