CALCULATION OF PHONON DISPERSION FREQUENCIES FOR BCC TANTALUM USING RESONANCE PSEUDOPOTENTIAL MODEL

Laz Ezenwaka
Department of Industrial Physics, Anambra State University, Uli, Nigeria.
E-mail : ngoceee@yahoo.com

(Submitted: 30 November, 2006; Accepted: 3 June, 2007)

Abstract

The phonon dispersion frequencies are calculated from first principles for bcc Tantalum using a resonance pseudopotential model. It was also possible, using this scheme, to account for the anomalous feature of the Ta dispersion curve observed experimentally in the (ε,o,o,) direction where the frequencies of the transverse branch are higher than the frequencies of the longitudinal branch. The frequencies obtained were also used to calculate the phonon density of states by the linear – analytic tetrahedral method of zone integration. The results of these calculations are qualitatively in good agreement with experimental data, and provide further support to the interpretation of the anomalous behaviour in the (ε,o,o,) direction as arising from s-d hybridization.

Keywords: *Phonon dispersion, phonon frequency, resonance, pseudopotential model, phonon density of states.*

Introduction

Mizuki *et al.* (1985), obtained experimentally by the method of inelastic neutron scattering the phonon dispersion curves of bcc barium. One of the interesting features of their work which prompted the present calculations, is the surprising result that along the (ε,o,o,) symmetry direction, the frequencies of the longitudinal branch were found to be lower than those of the transverse branch, contrary to the normal behaviour in this symmetry direction. This anomalous feature of the dispersion curve was attributed to the hybridization of the free-electron-like s states with the d bands, which in this metal are just slightly above the Fermi level.

Lattice dynamical studies of the body centered cubic (bcc) ϒ-iron phase have been carried out (Okoye and Pal, 1993) Amah and Oli (2004), Ononiwu and Oli (2001), and Zarestky and Stasis (1966) obtained the phonon dispersion frequencies of face centered cubic (fcc) ϒ-iron. Usually, theoretical lattice-dynamical studies of metals are carried out using both phenomenological force constant approach or first-principles calculation based on an appropriate pseudopotential and dielectric function. The pseudopotential theory for metals indicates that the effective interaction between atoms contains a two-body and at least a three-body contribution (Brovman *et al.*, 1972) arising from the unpaired forces. The phonon frequencies calculated by Animalu (1967) and Sharma (1981), using simple local pseudopotentials gave substantially higher frequencies than the experimental values. Moriarity (1972) used a generalized pseudopotential approach which attempted to incorporate the effect of s-d hybridization, however, his results also deviated by about 40% as compared to the measured values. Recently Gupta *et al* (1986) have used an optimized form of model potential to include the influence of hybridization in the phonon

frequencies of barium. However, we find their potential in ϒ-space to be quite unrealistic.
In the present calculation, we use a more realistic model potential of the Heine-Abarenkov type and include the effect of s-d hybridization more consistently in our computation of the electronic band structure contribution to the dynamical matrix. In addition, we have calculated also the phonon density of states, which is an important quantity in elucidating the nature of electron-phonon interaction in a given material.

2. Outline of the Microscopic Theory

In a microscopic theory of lattice dynamics, within the adiabatic and harmonic approximations, the phonon frequencies (ω) are obtained by solving the dispersion equations.

$$[M\omega^2 \delta_{\alpha\beta} - D_{\alpha\beta}(q)]\ e^s_\beta(q) = 0 \qquad (1)$$

where α (or β) = 1, 2, 3; q is the phonon – wave vector restricted just to the Brillouin zone, e^s_β (q) is the β - component of the polarization vector with s as the longitudinal or transverse index and M is the mass of the ions. The dynamical matrix which is the Fourier transform of the force constants may be represented as a sum of the contributions due to the direct columbic ion-ion interaction, an indirect ion-ion interaction via the conduction electrons and a repulsive core – core contribution. Thus we can write for the total dynamic matrix

$$[D_{\alpha\beta}(q) = \underset{c}{D_{\alpha\beta}}(q) + \underset{E}{D_{\alpha\beta}}(q) + \underset{M}{D_{\alpha\beta}}(q) \qquad (2)$$

where $D^c_{\alpha\beta}$ (q) is the columbic part of the dynamical matrix due to the direct coulomb interaction between bare ions of effective valence z; $D_{\alpha\beta}$ (q) is the electronic band – structure contribution due to the polarization of the conduction electrons by the vibrating ions. It depends on the pseudopotential carried by the ions; by the ions; $D_{\alpha\beta}$ (q) is the three-body contribution which arise due to at least third-order terms in the pseudopotental analysis.

3. Phonon Density of States for Tantalum

The density of phonon states N(ω) is usually defined such that N(ω) dω is the number of phonon states per unit cell with frequencies between w and ω + dω. It is calculate from the expression

$$N(\omega) = \frac{\Omega}{(2\pi)^3} \sum_j \int_{\omega j(q) = \omega} \frac{ds}{|\nabla q\omega j(q)|} \qquad (3)$$

where the integral is taken over the surface of constant frequency ω, and j is the polarization index. In the tetrahendron method, one divides the irreducible wedge of the Brillouin zone into tetrahedral, and the integral in eqn. (3) is then evaluated as the sum

$$N(\omega) = \frac{\Omega}{(2\pi)^3} \sum_{j,i} Nj, i(\omega) \qquad (4)$$

over these tetrahedral. When the frequencies at the four corners of the ith tetrahedron are ordered such that $\omega_1 \leq \omega_2 \leq \omega_3 \leq \omega_4$
the density of frequency states N(ω) and the number of states n(ω) at frequency w from this single tetrahedron are given by the simple analytic expressions given below (Table 1):

Table 1: Analytic expression for density of states from single tetrahedron

$n(\omega_1, \omega_2, \omega_3, \omega_4, v_i, \omega)$		$n(\omega_1, \omega_2, \omega_3, \omega_4, v_i, \omega)$
$\omega_2 \leq \omega_1$	O	O
$\omega_1 \leq \omega \leq \omega_2$	$\frac{3v_i}{D} \frac{(\omega-\omega_1)^2}{(\omega_1-\omega_2)D_1}$	$\frac{v_i}{D} \frac{(\omega-\omega_1)^3}{(\omega_1-\omega_2)D_1}$
$\omega_2 \leq \omega \leq \omega_3$	$\frac{3v_i}{D} \frac{D_1D_2 - (\omega-m)}{D_1D_2}$	$\frac{3v_i}{D}(\omega-m) - \frac{v_i}{D}\left[D_1+D_2+\frac{(\omega-m)^2}{D_1D_2}\right]$
$\omega_3 \leq \omega \leq \omega_4$	$\frac{3v_i}{D} \frac{(\omega-\omega_4)^2}{(\omega_3-\omega_4)D_4}$	$\frac{vi}{D}\left[D + \frac{\omega - \omega_4}{(\omega_4-\omega_3)D}\right]$
$\omega_4 \leq \omega$	O	vi

where

D = $\omega_4 + \omega_3 - \omega_2 - \omega_1$; M = $(\omega_4\omega_3 - \omega_3\omega_1)/D$

Dn = $\omega_n - M$, n = 1, 2, 3, 4; Vi = Volume of the ith tetrahedron

4. Model Potential Parameters

The model potential parameters for Tantalum have been determined and listed in Table 2.

Table 2: Model potential parameters for bcc tantalum

A_0	A_1	A_2	A_3	Rm	Ω	z	m*	Rc	α	\ Ec \
0.900	1.400	1.7500	1.410	2.00	252.2	3.0	1.00	1.21	0.081	0.096

e (density)	Vp(plasma frequency)	a (lattice constant) Å	Wf (F-band-width) eV
16.66	8.698	3.30	1.00

E_f(Fermi level) Ryd	M(ω mass) g	E_f [location of F-band and (Ryd)]
0.438	230.59×10^{-24}	0.597

The mesh is now constructed and the mesh – point numbers N_1, N_2,.... N_7 are established before the actual summation is done to give the required density of phonon states.

5. Results and Discussion

Solving the phonon dispersion eqn. (1), the phonon frequencies were computed along the principal symmetry directions for metallic bcc Ta.

The electron – phonon matrix element for the bare ion pseudopotential between plane wave states was screened linearly with the Hartree type of dielectric function. Using the Hubbard approximation, the exchange and correlations corrections were included. The residual oscillation in the large q region (q > 4 kf) which is inherent in the Heine Abarenkov type of potential were reduced by a damping factor D(q) of the form (Bortolani, 1976)

$$D(q) = \exp[-0.65\ (^{q}/_{2k_f})^4] \qquad (5)$$

For the present calculation, we have used the rare – earth model potential derived from spectroscopic term values. These values are shown in Table 2. In order to obtain convergence, the summations in reciprocal space for calculating the dynamical matrices were performed over 285 reciprocal lattice vectors.

In Fig. 1 and Table 3, we present the numerical results obtained for phonon frequencies of bcc tantalum and compared them with the recent experimental results of Stasis et al (1982). The agreement between theory and experiment is good within the framework of a microscopic theory and in particular at the $q \rightarrow 0$ limit where the velocity of sound in a solid is reproduced by theory and experiment.

The phonon density of states $N(\omega)$ for bcc Ta was calculated theoretically by the method outlined in section 3 above, and is shown in Fig. 1. The overall width and shape of the phonon spectrum and the position of the main peak (at 2.2 THz) are in relatively good agreement with the results obtained by Stassis et al (1982) using the phenomenological force constant fit method of Gilat and Raubenheimer (1966).

In general the microscopic theory of lattice dynamics of the rare – earth metal Tantalum – presented here is satisfactory enough to justify our support of the view that Tantalum can be regarded as an f – band metal where d – f hybridization between the conduction and unoccupied 4f band just above the Fermi level is of importance in understanding the occurrence of its low melting point and high superconducting transition temperature. This can lead to a process of phonon softening of modes when compared to Ce, as observed experimentally at the L and X zone boundaries by Stassis et al. (1982) and which is present also in our theoretically calculated results. Recent experiments on the anomalous thermal expansion of bcc Ta below 37k supports this itinerant nature of electrons in Tantalum (Andres, 1968) and indicates that low frequency (short-wavelength) phonons may become even softer with increase in pressure. This is a feature that certainly needs further investigation from a theoretical point of view, i.e. the effect of increase in pressure on the vibrational frequency spectrum of superconducting Tantalum.

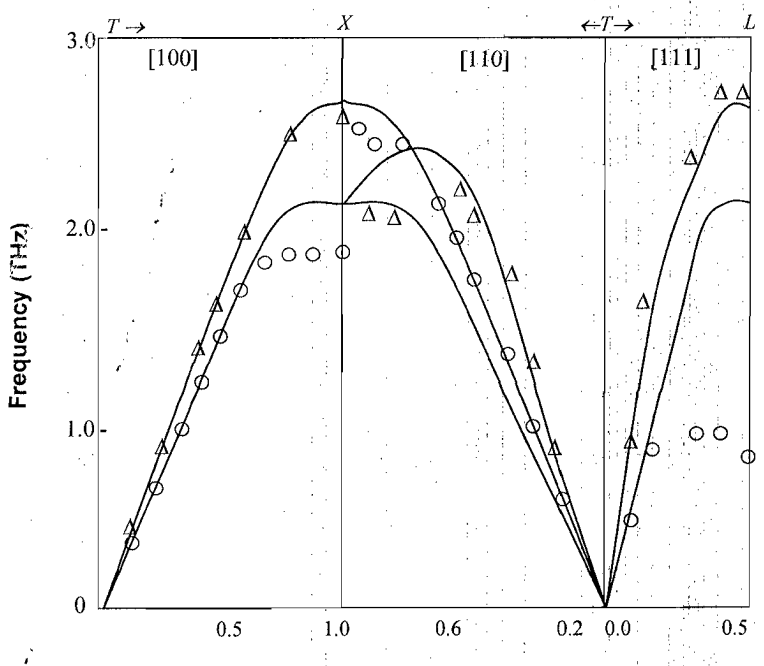

Fig. 1: Calculated (continuous curves) and measured (∇, O, x) phonon frequency dispersion curves of fcc ta at 660 K.

Table 3: Measured and calculated phonon frequencies of bcc

L100			Ta[100]		
q	**Expt.**	**Theory**	**q**	**Expt.**	**Theory**
0.1	0.42	0.39	0.1	0.25	0.32
0.2	0.81	0.78	0.2	0.64	0.64
0.3	1.027	1.28	0.3	0.89	0.94
0.4	1.59	1.55	0.4	1.10	1.23
0.5	-	1.79	0.5	1.42	1.49
0.6	2.10	2.01	0.6	1.67	1.73
0.7	-	2.25	0.7	1.80	1.93
0.8	2.43	2.62	0.8	1.87	2.93
0.9	-	2.73	0.9	1.90	2.23
1.0	2.56	2.72	1.0	1.95	2.15

L[100]			T[110]			T[110]		
q	Expt.	Theory	q	Expt.	Theory	q	Expt.	Theory
0.1	0.70	0.53	0.1	0.46	0.47	0.1	-	0.45
0.2	1.34	1.10	0.2	0.90	0.92	0.15	0.35	-
0.3	1.83	1.70	0.3	1.40	1.39	0.20	-	0.89
0.4	2.07	2.00	0.4	1.78	1.66	0.30	0.75	1.29
0.5	2.20	2.28	0.5	2.00	1.86	0.4	-	1.67
0.6	2.25	2.40	0.6	2.20	2.01	0.5	1.17	2.01
0.7	2.06	2.41	0.7	2.42	2.20	0.6	-	2.24
0.8	2.16	2.39	0.8	-	2.42	0.7	-1.66	2.43
0.9	1.95	2.32	0.9	2.50	-	0.8	-	2.66
1.0	-	2.15	1.15	-	2.30	0.9	-	2.74
1.1	-	-	1.00	2.60	2.20	1.0	-	2.72

L[111]			T[111]		
q	**Expt.**	**Theory**	**q**	**Expt.**	**Theory**
0.1	0.84	0.70	0.10	0.33	0.56
0.2	1.73	1.30	0.20	0.79	1.10
0.3	2.30	2.02	0.30	0.90	1.56
0.4	2.55	2.41	0.40	0.91	1.76
0.5	2.50	2.40	0.50	0.84	1.75

References

Amah, A. and Oli, B.A. (2005): Tetrahalral Method of Calculating Phonon Density of States, Phy. Rev. B21, 431 – 436.

Animalu A.O.E. and Upadyaya, J.C. (1977): Pseudopotential and the Resonance Model of S-D Hybridization, Phys. Rev. B15. 325 – 360.

Andres, K. (1968): Linear Analytical Tetrahedral Method of Zone Integration, Phys. Rev. 161, 445 – 451.

Bortolani, V and Guiunchi, G. (1976): Model-Potential Transformation of the Dielectric Matrix, J. Phys. F: metal Physics 6: 34 – 53.

Brovman, E.G., Kagan, Y.U. and Holas, A. (1971): Pseudopotential Theory for Metals, Sov. Phys. Jet Phys. 394 – 401.

Gupta, H.C., Raddy G.S., Vijai B.G. and Tripathi, B.B. (1986): An Optimized Form of Model Potential, Phys. Rev. B33, 5839 – 5853.

Gilat, G. and Ranbenleimer (1966): Calculation of the Phonon Density of States Using the Phenomenological Force Constant Fit Method, Phys. Rev. 44, 390.

Harrison, W.A. (1966): Pseudopotential in the Theory of Materials Benjamin, New York.

Moriarity, J.A. (1972): Effect of s – d Hybridization In Generalized Pseudopotential Approach, Phy. Rev. B6, 4445 – 44501.

Mizuki, J., Chem, Y, Ho, K.O. and Stassis, C. (1985): Phonon Dispersion Curves of BCC Barium Using Method of Inelastic Neutron Scattering, Phys. Rev. B32, 666 – 669.

Okoye, C.M.I. and Pal, S.P. (1993): Lattice Dynamics of ϒ-iron; Phys. B 183, 279-282.

Ononiwu, J. S. and Oli, B. A. (2001): Microscopic Theory of the Phonon Frequencies In BCC Barium; Phy. B 195, 135 – 141.

Sharma, K. S. (1981): Effect of Non-Locality in the Calculation of the Phonon Frequencies of Transition Metals, Phy. B134, 325 – 331.

Stassis, C, Loong, C.K. and Zarestky, J. (1982): Loong, C.K. Zarestky, J. (1982): Lattice Dynamics of Transition Metals in the Resonance Model, Phys. Rev. B13, 2398 – 2410.

Zarestky, J. and Stassis, C. (1966): The Phonon Dispersion Frequencies of Face Centred Cubic ϒ-iron, Phy. Rev. B184, 2143 – 2162.