Lattice Dynamics of Molybdenum and Chromium

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The frequency-wave vector dispersion relations, the frequency spectrum, the Debye temperature, the temperature dependence of the Debye-Waller factor and the mean square displacements of the atoms molybdenum and chromium, the metals for which long range forces are also important, have been computed on the basis of the extended improved Fielek model for BCC transition metals. The model considers, for the first time the d shell-d shell central interactions up to next-nearest-neighbours. The calculated results show a satisfactory agreement with the available experimental data.

1. Introduction

During the last two decades a number of phenomenological models [1—5] have been proposed for a priori calculations of the lattice vibrational properties of cubic metals. These models are fairly good for the lattice dynamical study of simple metals but do not yield equally good results for non simple metals. Fielek [6] has proposed a new lattice dynamical model for the study of non simple metals. In this model, the atoms are assumed to be composed of three entities: (i) the conduction electrons spread through out the solid, (ii) a shell of outermost d electrons and (iii) the ion core composed of the nucleus plus the remaining core electrons which move rigidly with the nucleus. We have applied this simple but powerful technique in the study of phonon dispersion relations of noble [7] and FCC and BCC transition [8, 9] metals. The results obtained were not very satisfactory. Recently we have proposed an improved Fielek model [10] for FCC transition metals by incorporating the next-nearest neighbours d shell-d shell central interactions and applied it quite successfully in studying the phonon dispersion curves of palladium and platinum and the ideal electrical resistivity and phonon dispersion relations of noble metals [11]. More recently, we have extended this model for BCC transition metals and computed the dispersion of lattice waves in α-iron and tungsten [12]. The results obtained were in fairly good agreement with the experimental data and were far better than those reported earlier on the basis of different lattice dynamical models.

In the present paper, to prove the adequacy of this extended model, we are reporting here the phonon dispersion curves, vibration spectra, the temperature variation of the Debye temperature and the Debye-Waller factor, and the mean square displacement of atoms in molybdenum and chromium.

2. Theory

The secular equation determining the angular frequencies of normal modes of vibration in a cubic crystal may be written as

$$|D(q) - m \omega^2 I| = 0,$$

where $q$ is the phonon wave vector restricted to the first Brillouin zone (BZ), $m$ is the mass of the atom and $I$ is the unit matrix of order three. The expressions for two typical elements of the dynamical matrix $D(q)$ are found to be

$$D_{11}(q) = -\frac{8}{3} z_1 (1 - C_1 C_2 C_3) - 4z_2 S_1^2 - K + K^2 / N,$$

$$D_{12}(q) = -\frac{8}{3} z_1 S_1 S_2 C_3,$$

where

$$C_i = \cos(a q_i),$$

$$S_i = \sin(a q_i); \quad i = 1, 2, 3,$$

“a” being the semi-lattice parameter, $N$ can be evaluated from the determinant

$$|D'(q) - NI| = 0.$$

The two typical elements of this secular determinant are

$$D'_{11}(q) = \frac{8}{3} \beta_1 (1 - C_1 C_2 C_3) + 4 \beta_2 S_1^2 + K - A' G(q),$$

$$D'_{12}(q) = \frac{8}{3} \beta_1 S_1 S_2 C_3 - A' G(q).$$
The solutions for six unknowns, viz. \( z_1, z_2, \beta_1, \beta_2, K \) and \( A' \) are discussed at length elsewhere [12].

An exponential factor \( e^{-2W} \), often referred to as the Debye-Waller factor, enters into a large number of solid state phenomena such as Mössbauer effect, neutron scattering, mean square displacement of atoms, thermal and electrical resistivity etc. of solids. The contribution to the DW factor (\( 2W \)) consists of two parts:

(i) the one which depends upon phonons and is obtained from the knowledge of the whole vibration spectra. Following James [13] this contribution is expressed as

\[
2W' = \frac{2}{3} \frac{h}{mN} \left( \frac{\sin \theta}{\lambda} \right)^2 \sum_{qj} \left( v_{qj} \right)^{-1} \coth \left( \frac{h v_{qj}}{2k_B T} \right),
\]

where the terms used have their usual meaning.

(ii) The other one due to the central part of the BZ corresponding to \( q \to 0 \) and evaluated in the Debye approximation as

\[
2W'' = \frac{16a^3}{3m} \left[ D(C_L) + 2D(C_T) \right] \left( \frac{\sin \theta}{\lambda} \right)^2,
\]

where \( C_L \) and \( C_T \) correspond to the average velocities for the longitudinal and transverse phonons, respectively, in the region \( q \to 0 \) and \( D(C) \) can be evaluated from

\[
D(C) = \frac{P}{2 \pi k_B T} \int_0^\infty \frac{t \, dt}{e^t - 1} + \frac{1}{4} \frac{P \, x}{x}.
\]

Here \( P = 2 \pi k_B T q_{\text{max}}/C^2, \ x = h q_{\text{max}} C/k_B T, \)

\[
t = \frac{h q C}{2 \pi k_B T} \quad \text{and} \quad q_{\text{max}} = \frac{\pi}{10a} (3/2\pi)^{1/3}.
\]

Thus the total DW factor (\( 2W \)) is

\[
2W = 2W' + 2W''.
\]

In the harmonic approximation, the mean square displacement of atoms \( \overline{U^2} \) is given by

\[
\overline{U^2} = \frac{3}{16\pi^2} \left( \frac{\lambda}{\sin \theta} \right)^2 (2W).
\]

### 3. Numerical Computation

The phonon dispersion curves of molybdenum and chromium are calculated from the secular Eq. (1) along the three highly symmetric directions. The experimental input parameters and the calculated values of the force constants are listed in Table 1 and Table 2, respectively.

The frequency distribution function \( G(v) \) has been computed by Blackman's sampling method. In order to get fairly a large number of frequencies, the translational vector in reciprocal space is

<table>
<thead>
<tr>
<th>Metal</th>
<th>Elastic constants ((\times 10^{11} \text{ dyn cm}^{-2}))</th>
<th>Lattice constant (2\alpha(\text{Å}))</th>
<th>Zone boundary frequencies ((\text{THz}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_{11} )</td>
<td>( C_{12} )</td>
<td>( C_{44} )</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>44.077</td>
<td>17.243</td>
<td>12.165</td>
</tr>
<tr>
<td>Chromium</td>
<td>35.00</td>
<td>6.78</td>
<td>10.08</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Metal</th>
<th>( z_1 )</th>
<th>( z_2 )</th>
<th>( \beta_1 )</th>
<th>( \beta_2 )</th>
<th>( K )</th>
<th>( A' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>-43.9698</td>
<td>-40.3576</td>
<td>0.4363</td>
<td>-0.2679</td>
<td>-3.48</td>
<td>-34.7491</td>
</tr>
</tbody>
</table>

**Table 1. Input parameters.**

**Table 2. Output values of force constants (in units of 10⁹ dyn cm⁻¹).**
divided into 20 equal parts so as to give a grid of 8000 equally spaced points inside the first BZ. On account of the symmetry properties of the lattice and Born’s cyclic boundary condition, these 8000 points reduce to 256 non-equivalent points including the origin, lying within the 1/48th irreducible sector of the first BZ. The 24000 frequencies corresponding to 8000 points are calculated from (1).

From the knowledge of frequency spectra, one can easily calculated the lattice specific heat at constant volume from the relation

\[ C_v = k_B \int \frac{v^n e^v}{(e^v - 1)^2} G(v) \, dv, \quad (10) \]

where

\[ x = \frac{h v}{k_B T} \quad \text{and} \quad \int_0^x G(v) \, dv = 3N, \quad (11) \]

\( N \) being the number of atoms per gram molecule.

The results obtained for the specific heat \( (C_v) \) are expressed in terms of the effective Debye temperature \( \Theta \) after substracting the electronic specific heat contribution from the experimental \( C_v \) values. For this purpose, the coefficients of the electronic specific heat for molybdenum and chromium have been taken to be \( 50 \times 10^{-5} \) and \( 3.6 \times 10^{-5} \) cal (gram atom)\(^{-1}\) deg\(^{-2}\), respectively as reported by Clusius and Franzolini [14] and Feldman [15].

Using the computed frequency spectra, the temperature variation of the DW factor is studied with the help of (5)—(8), and the corresponding mean square displacement of atoms is evaluated from (9). The calculated DW factor has been compared in terms of a temperature parameter \( Y \) which is defined as

\[ Y = (\lambda/\sin \theta)^2 \log_{10} \epsilon [2 W_{T_0} - 2 W_T], \quad (12) \]

where \( W_{T_0} \) and \( W_T \) are the DW exponents at the temperatures \( T_0 \) and \( T \) and are quite independent of \( \lambda \) and \( \Theta \). The DW exponent is directly assessed from the measurements of X-ray intensities of Bragg reflections as

\[ I_T/I_0 = \exp(-2 W_T)/\exp(-2 W_{T_0}), \quad (13) \]

where \( I_T \) and \( I_0 \) are the X-ray intensities at the temperatures \( T \) and \( T_0 \), respectively. From (12) and (13) we obtain

\[ Y = (\lambda/\sin \theta)^2 \log_{10}(I_T/I_0). \quad (14) \]
The calculated frequency spectrum is plotted in Figure 2. Experimental observations, being absent, no conclusion can be drawn as to the adequacy of the theoretical curve. Using this spectrum, the calculated specific heat is expressed in terms of the Debye temperature in Figure 3 along with the experimental values of Clusius and Franzosini and that of Simon and Zeidler. The calculated $\Theta - T$ curve agrees well at lower temperatures with the experimental data of Clusius and Franzosini but does not agree with the data of Simon and Zeidler throughout the temperature range.

Korsunskii [18] measured the intensity ratio $I_{291}/I_T$ of the crystal for the (232) and (322) reflection planes in the temperature range 100—400 K. His results are plotted in Figure 4 along with our theoretical values for $Y$ and $U^2$ with 291 K as reference temperature. It is evident from the figure that our theoretical curves approach the experimental value of the (322) reflecting plane.

Chromium. Shaw and Muhlestein [19] have measured the detailed phonon dispersion curves at room temperature by means of thermal neutron scattering. Their dispersion curves show four regions of anomalous behaviour which are related with the departure of the Fermi surface from sphericity. The calculated phonon dispersion curves are plotted in Figure 5 along with the experimental values [19]. Our curves are in fairly good agreement. The crossing over of the $A_L$ and $A_T$ branches in the P-H region, which had never been obtained by any lattice dynamical model, is the most salient feature of the present calculations. The slight deviations of the theoretical curves from the experimental values are generally in the anomalous
behaviour regions because in the present computations the Fermi surface is considered as spherical.

The theoretical vibration spectrum for chromium is shown in Fig. 6 along with the experimental values of Shaw and Muhlestein [19]. It is seen from the figure that our calculated $G(v)$ values agree in their broad features with the experimental spectrum. The calculated spectrum has two prominent peaks, the lower frequency peak being more intense. The temperature variation of the Debye temperature is shown in Fig. 7 together with the experimental values of Clusius and Franzosini [20] and Heiniger's [21] estimated values. The calculated curve agrees well with the estimated values of Heiniger throughout the whole temperature range but does not match with the experimental data of Clusius and Franzosini.

![Frequency spectrum of chromium](image)

**Fig. 6.** Frequency spectrum of chromium. Solid curve from the present calculations. Experimental curve (-----) from Shaw and Muhlestein [19].

![Temperature variation of the equivalent Debye temperature of chromium](image)

**Fig. 7.** Temperature variation of the equivalent Debye temperature of chromium. Solid curve from the present calculations. Experimental points (●●●) from Clusius and Franzosini [20] and (○○○) as estimated by Heiniger [21].

The calculated $Y - T$ and $U^2 - T$ curves are compared with the experimental results of Wilson et al. [22] in Fig. 8 with $T_0$ (298 K) as reference temperature. A reasonable agreement between theory and experiment is observed.

The discrepancies may, however, be attributed to the neglect of:

(i) the temperature variation of elastic constants and normal modes frequencies,

![Temperature variation of $Y$ and $U^2$ of chromium](image)

**Fig. 8.** Temperature variation of $Y$ and $U^2$ of chromium. Solid curves from the present calculations. Experimental points (○●) from Wilson et al [22].
(ii) the anharmonicity effects [23, 24],
(iii) the ion core-conduction electrons interaction,
(iv) the flexibility of d-orbitals.

As the things stand, it emerges from the present study that various lattice dynamical properties of non simple metals are adequately expressed with the present model.

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