Lattice Dynamics and Thermal Expansion of Ruthenium

R. Ramji Rao and J. V. S. S. Narayana Murthy

Physics Department, Indian Institute of Technology, Madras-600 036, India

Z. Naturforsch. 34a, 724—730 (1979); received January 23, 1979

The lattice dynamics, lattice specific heat and thermal expansion of ruthenium are worked out using the model of Srinivasan and Ramji Rao, based on Keating's approach. A total number of 50,880 frequencies has been used in constructing the frequency distribution function. The anharmonic parameters are obtained from the data of Clendenen and Drickamer on the pressure variation of the lattice parameters of ruthenium. The Anderson-Grüneisen parameter $\delta$ is calculated using the theoretical TOE constants, and the temperature variation of the bulk modulus is explained using Anderson’s theory.

1. Introduction

Ruthenium is a hexagonal closepacked metal with $c/a$ ratio equal to 1.584. The second order elastic (SOE) constants of ruthenium single crystal were measured by Fisher and Dever [1] up to 923 K. The phonon dispersion curves for ruthenium were measured only in the $c$ direction by Smith et al. [2]. The heat capacity of Ru as a function of temperature has been reported and compiled [3]. Clendenen and Drickamer [4] measured the pressure dependence of the lattice parameters in Ru up to 400 kbars. Gschneidner [5] reported a value of 3.25 for the thermal $\gamma_H$ of Ru. Srinivasan and Ramji Rao [6] proposed a model for the lattice dynamics, third order elastic (TOE) constants and thermal expansion of hcp metals based on Keating’s approach [7] and applied the same to magnesium, zinc and beryllium. Recently this model was applied to thulium [8]. In this paper the lattice dynamics, lattice heat capacity $C_v$, TOE constants and thermal expansion of Ru have been calculated using the same model of Srinivasan and Ramji Rao.

In Keating’s approach, the potential energy of the crystal is written in terms of the powers of the changes in the scalar products of the interatomic vectors which automatically makes it invariant towards rigid translations and rigid rotations of the lattice. Two and three body interactions are used to write the potential energy of the lattice and third order parameters are included to calculate the anharmonic properties of the metal. The basis vectors and the position coordinates of the sets of neighbours of the $(1\over 2)$ atom at the origin are given in [6].

Reprint requests to Dr. R. Ramji Rao, Assistant Professor, Department of Physics, Indian Institute of Technology, Madras 600 036, India.

0340-4811/79/0600-0724 $ 01.00/0

2. Lattice Dynamics

The experimental SOE constants of Ru at room temperature and the experimental limiting frequencies $\Gamma_{3+}$ and $\Gamma_{6-}$ in the [0001] direction have been used to fit the 7 second order parameters. The seven second order parameters along with the room temperature SOE constants and the experimental frequencies $\Gamma_{3+}$ and $\Gamma_{6-}$ are given in Table 1. Figures 1a and 1b show the theoretical dispersion curves in the [0001] and [0110] directions on the present model for Ru. The experimental points in [0001] direction are the measurements of Smith et al. [2]. The theoretical acoustic branches LA and TA and the optic branch TO are in very good agreement with the experimental values while the theoretical optic branch LO deviates from the experiment above $q = 0.1$, and at $q = 0.4$ the discrepancy is maximum (11%).

Fig. 1a. Theoretical dispersion relations in [0001] direction of Ru. The experimental points are also shown: LO — o; TO — ; LA — o; TA — o.

Fig. 1b. Theoretical dispersion relations in [0110] direction of Ru.
R. Ramji Rao et al. • Lattice Dynamics and Thermal Expansion of Ruthenium

Table 1. Values of the second order parameters for Ru in the present model. The room temperature SOE constants are from [1] and the limiting frequencies are from [2].

<table>
<thead>
<tr>
<th>Second order parameters</th>
<th>Value in $10^{11}$ dyn/cm²</th>
<th>$C_{ij}$</th>
<th>Value in $10^{11}$ dyn/cm²</th>
<th>Limiting frequencies in [0001] direction</th>
<th>in $10^{13}$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>($D^4/V_a$) $\alpha$</td>
<td>3.294</td>
<td>$C_{11}$</td>
<td>56.26</td>
<td>LO ($F_2^+$)</td>
<td>4.838</td>
</tr>
<tr>
<td>($D^4/V_a$) $\beta$</td>
<td>0.865</td>
<td>$C_{12}$</td>
<td>18.78</td>
<td>TO ($F_6^-$)</td>
<td>3.525</td>
</tr>
<tr>
<td>($D^4/V_a$) $\gamma$</td>
<td>1.584</td>
<td>$C_{13}$</td>
<td>16.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($D^4/V_a$) $\epsilon$</td>
<td>0.146</td>
<td>$C_{33}$</td>
<td>62.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($D^4/V_a$) $\sigma$</td>
<td>1.318</td>
<td>$C_{44}$</td>
<td>18.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($D^4/V_a$) $\tau$</td>
<td>0.275</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Lattice Specific Heat

The normalized frequency distribution function has been obtained by the root sampling method. The secular equation is solved for different wave vectors $q$ and the corresponding normal mode frequencies are obtained using a computer program written for the IBM 370/155. A grid of equally spaced 484 points in the irreducible volume of the Brillouin zone is chosen for the wave vectors. This is equivalent to 8,480 points in the entire volume of the Brillouin zone, taking into account the crystal symmetry. The number of frequencies in each frequency interval ($\Delta \omega = 0.05 \times 10^{13}$ Hz) is counted and a histogram is constructed for $g(\omega)$. In the low frequency region where there are not sufficient frequencies to draw a reliable histogram, the Debye parabolic equation $g(\omega) = C \omega^2$ is used to obtain $g(\omega)$. The reproduced computer plot for the normalized frequency distribution curve is shown in Figure 2. The even moments of the frequency distribution function ($\mu_2$, $\mu_4$, $\mu_6$) for Ru on the present model have been calculated and are $\mu_2 = 16.799 \times 10^{26}$/sec²; $\mu_4 = 33.052 \times 10^{43}$/sec⁴; $\mu_6 = 72.438 \times 10^{60}$/sec⁶. The value of the high temperature limit of the Debye temperature $\Theta_\infty$ for Ru, as calculated from $\mu_2$ has the value 404 K. This agrees well with the value 415 K quoted by Gschneidner [5] for the Debye $\Theta$ at 298 K obtained from specific heat data.

The theoretical frequency distribution function has been used to calculate the lattice contribution to the specific heat as a function of temperature.

\[ C_v(T) = \left[ 3 R \sum \sigma(\omega, T) g(\omega) \right] / \left[ \sum g(\omega) \right], \tag{3.1} \]

where $\sigma(\omega, T)$ is the Einstein specific heat function and $R$ the gas constant expressed in cal/mole K.

The calculated lattice specific heat of Ru versus temperature is shown in Figure 3. The experimental $C_v$ values are obtained by subtracting the dilation term $AC_p^2T$ and the electronic contribution $\gamma T$ from the experimental $C_p$ data. The experimental $C_v$ values are shown as full circles in

Fig. 2. Frequency distribution function obtained for Ru on the present model (reproduced computer plot).

Fig. 3. Calculated specific heat as a function of temperature. Full circles show the experimental points.
Figure 3. The values \( A = 1.472 \times 10^{-5} \) g atom/cal and \( \gamma = 7.9 \times 10^{-4} \) cal/g atom K\(^2\) for Ru are taken from Gschneidner's compilation [5]. The overall general agreement between the lattice specific heat \( C_v \) and the experimental \( C_v \) is good, particularly very good above 100 K.

4. TOE Constants

Anharmonic interactions up to 2nd neighbours only are taken into account. The first two neighbours of the (i) atom in Ru are J and I atoms and the corresponding anharmonic parameters are \( \xi \) and \( \zeta \) respectively. The theoretical expressions for the pressure derivatives of the SOE constants of a hep crystal in terms of its TOE constants were derived by Ramji Rao and Srinivasan [9]. The TOE constants are functions of anharmonic parameters. The anharmonic parameters \( \xi \) and \( \zeta \) are obtained by fitting the experimental data of Clendenen and Drickamer [4] on the pressure variation of lattice parameters of Ru to Thurston’s [10] extrapolation formula which involves the pressure derivatives of the SOE constants.

Thurston’s extrapolation formula for the principal stretches \( \lambda_i \ (i = 1, 2, 3) \) that is consistent with a linear pressure dependence of the bulk modulus is

\[
\lambda_i = \frac{a}{a_0} = \left( \frac{B}{B_0} \right)^{-(\frac{\beta}{B_0} y_{\beta/0} B_0^{-1})} \exp \left( a_\perp + \frac{B_0 y_{\beta/0}}{B_0'} \right) p ,
\]

\( (4.1) \)

For a uniaxial crystal \( \lambda_1 = \lambda_2 = \lambda_\perp , \lambda_3 = \lambda_\parallel \) and Eq. (4.1) becomes respectively

\[
\frac{V}{V_0} = \frac{\lambda_\parallel^2 \lambda_\perp}{\lambda_3} = (1 + p \frac{B_0'}{B_0})^{-1/B_0'} \quad (4.3)
\]

Equation (4.3) is Murnaghan’s [11] equation.

The Eqs. (4.2) involve pressure derivatives of the SOE constants which are functions of the anharmonic parameters. The values of \( \xi \) and \( \zeta \) are chosen so as to yield a close agreement (to within 0.25%) between the calculated and experimental [4] values of \( a/a_0 \) and \( c/c_0 \) at all pressures up to 400 kбарs. The values of \( \xi \) and \( \zeta \) are reported in Table 2. The calculated and experimental \( a/a_0 \), \( c/c_0 \) and \( V/V_0 \) up to 400 kбарs are shown in Figure 4. The dots are experimental points. The calculated values of \( a_\perp , \)

<table>
<thead>
<tr>
<th>Third-order parameters</th>
<th>Value in ( 10^{11} ) dyn/cm(^2)</th>
<th>TOE constants</th>
<th>Value in ( 10^{11} ) dyn/cm(^2)</th>
<th>Pressure derivatives of the SOE constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\frac{D}{V)a} ) ( \xi )</td>
<td>-60.65</td>
<td>( C_{111} )</td>
<td>-925.1</td>
<td>( dC_{11}/dp )</td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \zeta )</td>
<td>-57.27</td>
<td>( C_{112} )</td>
<td>-197.2</td>
<td>( dC_{12}/dp )</td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \gamma )</td>
<td></td>
<td>( C_{113} )</td>
<td>-179.5</td>
<td>( dC_{13}/dp )</td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \beta )</td>
<td></td>
<td>( C_{123} )</td>
<td>78.1</td>
<td>( dC_{23}/dp )</td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \zeta )</td>
<td></td>
<td>( C_{133} )</td>
<td>190.7</td>
<td>( dC_{33}/dp )</td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \gamma )</td>
<td></td>
<td>( C_{144} )</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \beta )</td>
<td></td>
<td>( C_{155} )</td>
<td>109.4</td>
<td></td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \gamma )</td>
<td></td>
<td>( C_{222} )</td>
<td>-1013.3</td>
<td></td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \beta )</td>
<td></td>
<td>( C_{233} )</td>
<td>717.1</td>
<td></td>
</tr>
<tr>
<td>( (\frac{D}{V}a) ) ( \gamma )</td>
<td></td>
<td>( C_{244} )</td>
<td>190.7</td>
<td></td>
</tr>
</tbody>
</table>
0.98
0.96
0.90
0.88
0.86

Fig. 4. Pressure dependence of lattice parameters and volume of Ru. The scale for \( c/c_0 \) is on the r.h.s. The dots are the experimental values.

The ten TOE constants and the pressure derivatives of the SOE constants are calculated using the two anharmonic parameters and these are reported in Table 2.

Table 3. Parameters used in the Thurston’s extrapolation formulae for ruthenium.

<table>
<thead>
<tr>
<th>( a_\perp )</th>
<th>( y_\perp )</th>
<th>( y_0 )</th>
<th>( y_0' )</th>
<th>( B_0 )</th>
<th>( B_0' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M bar)(^{-1})</td>
<td>(M bar)(^{-1})</td>
<td>(M bar)(^{-2})</td>
<td>(M bar)(^{-2})</td>
<td>(M bar)</td>
<td>(M bar)</td>
</tr>
<tr>
<td>(-0.1108)</td>
<td>(-0.1006)</td>
<td>(0.215)</td>
<td>(0.130)</td>
<td>(3.1037)</td>
<td>(5.36)</td>
</tr>
</tbody>
</table>

5. Thermal Expansion

a) Low Temperature Limit of the Lattice Thermal Expansion

The low temperature limit \( \gamma_L \) of a uniaxial crystal can be calculated from a knowledge of the generalised Grüneisen parameters (GPs) of the elastic waves propagating in the crystal. The GPs of the normal mode frequencies are defined by the expressions

\[
\gamma'(\omega) = -\frac{\partial \ln \omega}{\partial \varepsilon'}; \quad \gamma''(\omega) = -\frac{\partial \ln \omega}{\partial \varepsilon''}.
\]

Here \( \varepsilon' \) is a uniform areal strain in the basal plane and \( \varepsilon'' \) a uniform longitudinal strain parallel to the unique axis. We define the effective Grüneisen function \( \gamma_{L}^{I}(T) \) and \( \gamma_{L}^{II}(T) \) for a uniaxial crystal as the weighted averages of the generalised GPs. The superscript ‘‘I” on the gammas indicate that these are lattice Grüneisen functions. We have

\[
\gamma_{L}^{I}(T) = \frac{\sum_{ij} \gamma'(q, j) C_{ij}(q, j)}{\sum_{ij} C_{ij}(q, j)},
\]

\[
\gamma_{L}^{II}(T) = \frac{\sum_{ij} \gamma''(q, j) C_{ij}(q, j)}{\sum_{ij} C_{ij}(q, j)}. \quad (5.2)
\]

where \( q \) is the wave vector, \( j \) the polarisation index and \( C_{ij}(q, j) \) the contribution of a single normal mode frequency \( \omega(q, j) \) to the specific heat of the lattice. The temperature variation of the linear expansion coefficients \( a_\perp \) and \( a_\parallel \) are expressed in terms of the effective Grüneisen functions \( \gamma_{L}^{I}(T) \) and \( \gamma_{L}^{II}(T) \) as follows:

\[
V a_\perp = \left[ (S_{11} + S_{12}) \gamma_{L}^{I}(T) + S_{13} \gamma_{L}^{II}(T) \right] C_v = \gamma_{L}^{I}(T) C_v X_{iso},
\]

\[
V a_\parallel = \left[ 2 S_{13} \gamma_{L}^{I}(T) + S_{33} \gamma_{L}^{II}(T) \right] C_v = \gamma_{L}^{II}(T) C_v X_{iso}. \quad (5.3)
\]

Here \( S_{ij} \) are the elastic compliance coefficients, \( V \) is molar volume, \( C_v \) the molar specific heat at temperature \( T \) and \( X_{iso} \) the isothermal compressibility. \( \gamma_{L}^{I}(T) \) and \( \gamma_{L}^{II}(T) \) are the average Grüneisen functions used by Brugger and Fritz [12].

At very low temperatures the acoustic modes are predominant and \( \gamma_{L}^{I}(T) \) and \( \gamma_{L}^{II}(T) \) approach the limits conventionally represented by the symbols \( \gamma_{L}^{I}(-3) \) and \( \gamma_{L}^{II}(-3) \), respectively. These limits are defined as

\[
\gamma_{L}^{I}(-3) = \frac{3}{\sum_{j=1}^{3} \gamma_j^{I}(\Theta, \varphi)} \cdot \int \left[ \sum_{j=1}^{3} \gamma_j^{I}(\Theta, \varphi) \right] d\Omega,
\]

\[
\gamma_{L}^{II}(-3) = \frac{3}{\sum_{j=1}^{3} \gamma_j^{II}(\Theta, \varphi)} \cdot \int \left[ \sum_{j=1}^{3} \gamma_j^{II}(\Theta, \varphi) \right] d\Omega. \quad (5.4)
\]

In Eqs. (5.4) \( \gamma_j^{I}(\Theta, \varphi) \) is the wave velocity of the acoustic wave of polarisation index \( j \) propagating in the direction \( (\Theta, \varphi) \); \( \gamma_j^{I}(\Theta, \varphi) \) and \( \gamma_j^{II}(\Theta, \varphi) \) are the GPs for this mode. The GPs for the elastic waves can be calculated from a knowledge of the TOE constants of the crystal and hence the low temperature limits \( \gamma_{L}^{I}(-3) \) and \( \gamma_{L}^{II}(-3) \) can be obtained from the procedure suggested by Ramji Rao and Srinivasan [13a, b]. In hexagonal crystals the acoustic wave velocities and the GPs depend
only on $\Theta$ and not on the azimuth $\varphi$. The calculated values of $\bar{\gamma}_\perp(-3)$ and $\bar{\gamma}_\parallel(-3)$ are found to be 2.22 and 2.76 respectively. The low temperature limit of the Grüneisen function is given by $\bar{\gamma}_L = 2\bar{\gamma}_\perp^{Br}(-3) + \bar{\gamma}_\parallel^{Br}(-3)$ and is found equal to 2.39.

b) The Temperature Dependence of the Effective Grüneisen Functions of Ruthenium

Blackman's [14] procedure has been used to calculate the temperature dependence of the effective Grüneisen functions $\bar{\gamma}_\perp(T)$ and $\bar{\gamma}_\parallel(T)$. The normal mode frequencies $\omega(q,j)$ and the GPs $\gamma'(q,j)$ and $\gamma''(q,j)$ have been evaluated at 484 points equally distributed over 1/24th volume of the Brillouin zone using a computer program. The individual GPs $\gamma'$ and $\gamma''$ for various normal mode frequencies in each frequency interval ($\Delta\omega = 0.05 \times 10^{13}$ Hz) are noted and the average values $\bar{\gamma}'$ and $\bar{\gamma}''$ of these GPs are found for each interval. The plots of $\bar{\gamma}'(\omega)$ and $\bar{\gamma}''(\omega)$ are shown in Fig. 5 in which the low frequency range $\bar{\gamma}'(\omega)$ and $\bar{\gamma}''(\omega)$ tend to their low temperature limits 2.22 and 2.76, respectively. The effective Grüneisen functions $\bar{\gamma}_\perp(T)$ and $\bar{\gamma}_\parallel(T)$ are then calculated as follows:

$$\bar{\gamma}_\perp(T) = \int_0^{\omega_{\text{max}}} \bar{\gamma}'(\omega) g(\omega) \sigma(\omega, T) d\omega$$

$$\bar{\gamma}_\parallel(T) = \int_0^{\omega_{\text{max}}} \bar{\gamma}''(\omega) g(\omega) \sigma(\omega, T) d\omega$$

Knowing $\bar{\gamma}_\perp(T)$ and $\bar{\gamma}_\parallel(T)$ we calculate $\bar{\gamma}_\perp^{Br}(T)$ and $\bar{\gamma}_\parallel^{Br}(T)$ using Equations (5.3). The lattice volume Grüneisen function at any temperature $T$ is given by $\bar{\gamma}_V(T) = 2\bar{\gamma}_\perp^{Br}(T) + \bar{\gamma}_\parallel^{Br}(T)$. The variation of the effective Grüneisen functions $\bar{\gamma}_\perp(T)$, $\bar{\gamma}_\parallel(T)$ and $\bar{\gamma}_V(T)$ of Ru with temperature is shown in Figure 6. The high temperature limit of $\bar{\gamma}_V(T)$, also referred to as $\gamma_H = 3.22$ agrees well with the value 3.25 quoted by Gschneidner [5], obtained from thermal expansion and lattice specific heat data.

![Fig. 5. $\bar{\gamma}'(\omega)$ and $\bar{\gamma}''(\omega)$ versus $\omega$ for Ru (reproduced computer plot).](image-url)
thermal properties. Ramji Rao and Ramanand [19] investigated the same properties of Ru studied in this paper, using the nearest neighbour central force (C.F.) model proposed by Srinivasan and Ramji Rao [20, 13a], which is much simpler and less general than the one presently employed. On the C.F. model, the pressure derivatives of Ru are consistently larger than those obtained on the present model. The present set of TOE constants may be considered more reliable in view of the fact that the anharmonic parameters used in this calculation have got direct bearing on the experimental $a/a_0$ and $c/c_0$ data of Ru [4]. The calculated pressure derivative $dC_4/dp$ for Ru is positive, from which it may be inferred that the pressure induced phase transformation from hcp to bcc structure is not possible in this metal.

**Acknowledgement**

One of us (Murty) is grateful to the Council of Scientific and Industrial Research, Government of India, for the award of a Research fellowship. The authors wish to thank Mr. A. Ramanand and Mr. A. Rajput for their helpful discussions.