Lattice Dynamics and Thermal Expansion of Ruthenium

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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 δ is calculated using the theoretical TOE constants, and the temperature variation of the bulk modulus is explained using Anderson's theory.

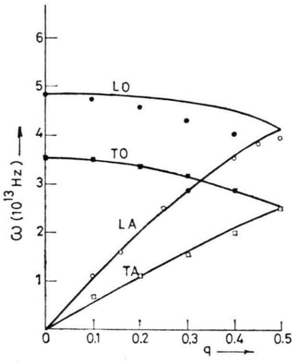
1. Introduction

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 upto 400 kbars. Gschneidner [5] reported a value of 3.25 for the thermal γ_{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 $C_v{}^l$, 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 $\binom{0}{1}$ atom at the origin are given in [6].

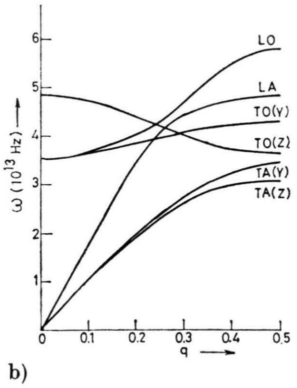
2. Lattice Dynamics

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 [01$\bar{1}$0] 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%).



a)

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



b)

Fig. 1b. Theoretical dispersion relations in [01$\bar{1}$0] direction of Ru.

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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].

Second order parameters	Value in 10^{11} dyn/cm^2	C_{ij}	Value in 10^{11} dyn/cm^2	Limiting frequencies in [0001] direction	in 10^{13} Hz
$(D^4/Va)\,\alpha$	3.294	C_{11}	56.26	LO (Γ_3^+)	4.838
$(D^4/Va)\,\beta$	0.865	C_{12}	18.78	TO (Γ_6^-)	3.525
$(D^4/Va)\,\gamma$	1.584	C_{13}	16.82		
$(D^4/Va)\,\varepsilon$	0.146	C_{33}	62.42		
$(D^4/Va)\,\sigma$	1.318	C_{44}	18.06		
$(D^4/Va)\,\delta$	0.275				
$(D^4/Va)\,\tau$	0.436				

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 $\boldsymbol{q}$ 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 (μ_2, μ_4, μ_6) for Ru on the present model have been calculated and are $\mu_2 = 16.799 \times 10^{26}/\text{sec}^2$; $\mu_4 = 33.052 \times 10^{53}/\text{sec}^4$; $\mu_6 = 72.438 \times 10^{80}/\text{sec}^6$. The value of the high temperature limit of the Debye temperature Θ_∞ for Ru, as calculated from μ_2 has the value 404 K. This agrees well with the value 415 K quoted by Gschneidner [5] for the Debye Θ 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.

$$C_v{}^l(T) = [3R \sum \sigma(\omega, T)\, g(\omega)]/[\sum g(\omega)]\,, \quad (3.1)$$

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 $C_v{}^l$ values are obtained by subtracting the dilation term $AC_p{}^2T$ and the electronic contribution γT from the experimental [3] C_p data. The experimental $C_v{}^l$ values are shown as full circles in

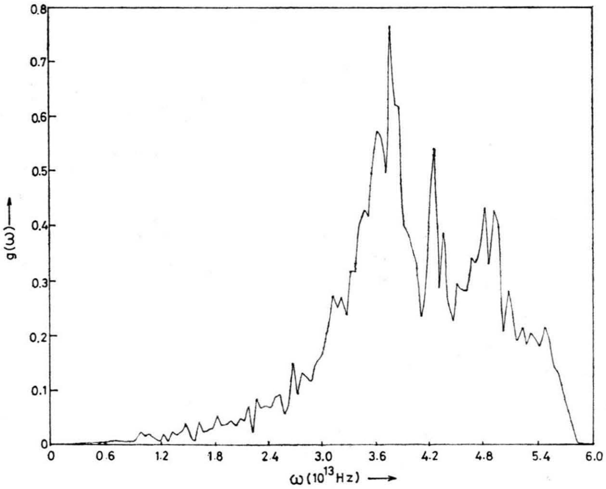

Fig. 2. Frequency distribution function obtained for Ru on the present model (reproduced computer plot).

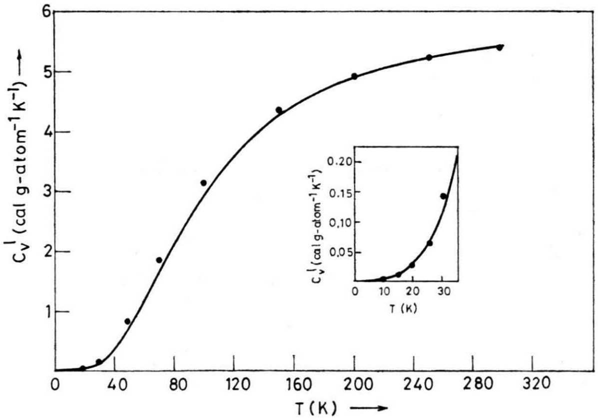

Fig. 3. Calculated specific heat as a function of temperature. Full circles show the experimental points.

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 $C_v{}^l$ and the experimental $C_v{}^l$ is good, particularly very good above 100 K.

4. TOE Constants

Anharmonic interactions upto 2nd neighbours only are taken into account. The first two neighbours of the $\binom{0}{1}$ atom in Ru are J and I atoms and the corresponding anharmonic parameters are ξ and ζ respectively. The theoretical expressions for the pressure derivatives of the SOE constants of a hcp 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 ξ and ζ 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 λ_i $(i = 1, 2, 3)$ that is consistant with a linear pressure dependence of the bulk modulus is

$$\lambda_i = \left[\left(\frac{B}{B_0}\right)^{-(B_0{}^2 y_{i0}/B_0'^2)}\right] \exp\left(a_i + \frac{B_0\, y_{i0}}{B_0'}\right) p\,. \tag{4.1}$$

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

$$\begin{aligned}\lambda_\perp &= \frac{a}{a_0} \\ &= \left[\left(\frac{B}{B_0}\right)^{-(B_0{}^2 y_{\perp 0}/B_0'^2)}\right] \exp\left(a_\perp + \frac{B_0\, y_{\perp 0}}{B_0'}\right) p\,, \\ \lambda_\parallel &= \frac{c}{c_0} \\ &= \left[\left(\frac{B}{B_0}\right)^{-(B_0{}^2 y_{\parallel 0}/B_0'^2)}\right] \exp\left(a_\parallel + \frac{B_0\, y_{\parallel 0}}{B_0'}\right) p\,.\end{aligned} \tag{4.2}$$

Here a_0, c_0 are the lattice parameters at zero pressure while a and c are the lattice parameters at pressure p. B is the bulk modulus at pressure p, B_0 and B_0' are the bulk modulus and its pressure derivative at zero pressure. The expressions for the parameters in Eqs. (4.2) are given in Thurston's [10] paper and are not repeated here. From Eqs. (4.2) the volume ratio is

$$\frac{V}{V_0} = \lambda_\perp{}^2\, \lambda_\parallel = \left(1 + p\,\frac{B_0'}{B_0}\right)^{-1/B_0'}. \tag{4.3}$$

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 ξ and ζ are so chosen 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 upto 400 kbars. The values of ξ and ζ are reported in Table 2. The calculated and experimental a/a_0, c/c_0 and V/V_0 upto 400 kbars are shown in Figure 4. The dots are experimental points. The calculated values of $a_\perp$,

Table 2. Values of the Third-order parameters, the TOE constants and the pressure derivatives of the SOE constants of ruthenium

Third-order parameters	Value in 10^{11} dyn/cm^2	TOE constants	Value in 10^{11} dyn/cm^2	Pressure derivatives of the SOE constants	
				$\mathrm{d}C_{ij}/\mathrm{d}p$	Obtained from the present calculations
$(D^6/Va)\,\xi$	-60.65	C_{111}	-925.1	$\mathrm{d}C_{11}/\mathrm{d}p$	11.55
		C_{112}	-197.2		
$(D^6/Va)\,\zeta$	-57.27	C_{113}	-179.5	$\mathrm{d}C_{12}/\mathrm{d}p$	2.38
		C_{123}	78.1		
		C_{133}	-190.7	$\mathrm{d}C_{13}/\mathrm{d}p$	2.87
		C_{144}	8.0		
		C_{155}	-109.4	$\mathrm{d}C_{33}/\mathrm{d}p$	8.93
		C_{222}	-1013.3		
		C_{333}	-717.1	$\mathrm{d}C_{44}/\mathrm{d}p$	1.86
		C_{344}	-190.7		

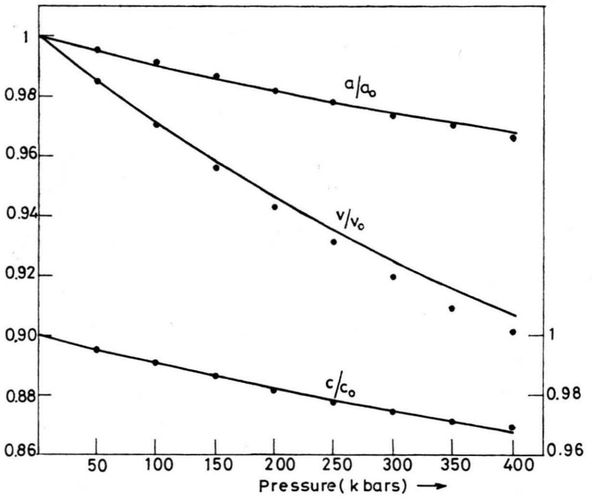

Fig. 4. Pressure dependence of lattice parameters and volume of Ru. The scale for c/c_0 is on the r.h.s. The dots are the experimental values.

$a_\parallel$, $y_{\perp 0}$, $y_{\parallel 0}$ and those of B_0 and B_0' are given in Table 3.

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.

$a_\perp$ (M bar)$^{-1}$	$a_\parallel$ (M bar)$^{-1}$	$y_{\perp 0}$ (M bar)$^{-2}$	$y_{\parallel 0}$ (M bar)$^{-2}$	B_0 (M bar)	B_0'
−0.1108	−0.1006	0.215	0.130	3.1037	5.36

5. Thermal Expansion

a) Low Temperature Limit of the Lattice Thermal Expansion

The low temperature limit γ_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

$$\gamma'(\omega) = -\frac{\partial \ln \omega}{\partial \varepsilon'}; \quad \gamma''(\omega) = -\frac{\partial \ln \omega}{\partial \varepsilon''}. \tag{5.1}$$

Here ε' is a uniform areal strain in the basal plane and ε'' a uniform longitudinal strain parallel to the unique axis. We define the effective Grüneisen function $\bar{\gamma}_\perp{}^l(T)$ and $\bar{\gamma}_\parallel{}^l(T)$ for a uniaxial crystal as the weighted averages of the generalised GPs. The superscript "l" on the gammas indicate that these are lattice Grüneisen functions. We have

$$\bar{\gamma}_\perp{}^l(T) = \Big[\sum_{\boldsymbol{q}j} \gamma'(\boldsymbol{q},j)\, C_v{}^l(\boldsymbol{q},j)\Big] \Big/ \Big[\sum_{\boldsymbol{q}j} C_v{}^l(\boldsymbol{q},j)\Big],$$
$$\bar{\gamma}_\parallel{}^l(T) = \Big[\sum_{\boldsymbol{q}j} \gamma''(\boldsymbol{q},j)\, C_v{}^l(\boldsymbol{q},j)\Big] \Big/ \Big[\sum_{\boldsymbol{q}j} C_v{}^l(\boldsymbol{q},j)\Big]. \tag{5.2}$$

where $\boldsymbol{q}$ is the wave vector, j the polarisation index and $C_v{}^l(\boldsymbol{q},j)$ the contribution of a single normal mode frequency $\omega(\boldsymbol{q},j)$ to the specific heat of the lattice. The temperature variation of the linear expansion coefficients $\alpha_\perp$ and $\alpha_\parallel$ are expressed in terms of the effective Grüneisen functions $\bar{\gamma}_\perp{}^l(T)$ and $\bar{\gamma}_\parallel{}^l(T)$ as follows:

$$\begin{aligned} V\alpha_\perp &= [(S_{11}+S_{12})\,\bar{\gamma}_\perp{}^l(T) + S_{13}\,\bar{\gamma}_\parallel{}^l(T)]\,C_v \\ &= \bar{\gamma}_\perp{}^{\mathrm{Br}}(T)\,C_v\,\chi_{\mathrm{iso}}, \\ V\alpha_\parallel &= [2S_{13}\,\bar{\gamma}_\perp{}^l(T) + S_{33}\,\bar{\gamma}_\parallel{}^l(T)]\,C_v \\ &= \bar{\gamma}_\parallel{}^{\mathrm{Br}}(T)\,C_v\,\chi_{\mathrm{iso}}. \end{aligned} \tag{5.3}$$

Here S_{ij} are the elastic compliance coefficients, V is molar volume, C_v the molar specific heat at temperature T and χ_{iso} the isothermal compressibility. $\bar{\gamma}_\perp{}^{\mathrm{Br}}(T)$ and $\bar{\gamma}_\parallel{}^{\mathrm{Br}}(T)$ are the average Grüneisen functions used by Brugger and Fritz [12].

At very low temperatures the acoustic modes are predominant and $\bar{\gamma}_\perp{}^l(T)$ and $\bar{\gamma}_\parallel{}^l(T)$ approach the limits conventionally represented by the symbols $\bar{\gamma}_\perp{}^l(-3)$ and $\bar{\gamma}_\parallel{}^l(-3)$, respectively. These limits are defined as

$$\bar{\gamma}_\perp{}^l(-3) = \Big[\sum_{j=1}^{3} \int \bar{\gamma}_j{}'(\Theta,\varphi) \cdot V_j{}^{-3}(\Theta,\varphi)\,\mathrm{d}\Omega\Big] \Big/ \Big[\sum_{j=1}^{3} \int V_j{}^{-3}(\Theta,\varphi)\,\mathrm{d}\Omega\Big],$$
$$\bar{\gamma}_\parallel(-3) = \Big[\sum_{j=1}^{3} \int \bar{\gamma}_j{}''(\Theta,\varphi) \cdot V_j{}^{-3}(\Theta,\varphi)\,\mathrm{d}\Omega\Big] \Big/ \Big[\sum_{j=1}^{3} \int V_j{}^{-3}(\Theta,\varphi)\,\mathrm{d}\Omega\Big]. \tag{5.4}$$

In Eqs. (5.4) $V_j(\Theta,\varphi)$ is the wave velocity of the acoustic wave of polarisation index j propagating in the direction (Θ,φ); $\gamma_j{}'(\Theta,\varphi)$ and $\gamma_j{}''(\Theta,\varphi)$ 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 $\bar{\gamma}_\perp{}^l(-3)$ and $\bar{\gamma}_\parallel{}^l(-3)$ 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 Θ and not on the azimuth φ. The calculated values of $\bar{\gamma}_{\perp}{}^{l}(-3)$ and $\bar{\gamma}_{\parallel}{}^{l}(-3)$ are found to be 2.22 and 2.76 respectively. The low temperature limit of the Grüneisen function is given by $\bar{\gamma}_{\mathrm{L}} = 2\bar{\gamma}_{\perp}{}^{\mathrm{Br}}(-3) + \bar{\gamma}_{\parallel}{}^{\mathrm{Br}}(-3)$ 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 $\bar{\gamma}_{\perp}{}^{l}(T)$ and $\bar{\gamma}_{\parallel}{}^{l}(T)$. The normal mode frequencies $\omega(\boldsymbol{q}, j)$ and the GPs $\gamma'(\boldsymbol{q}, j)$ and $\gamma''(\boldsymbol{q}, j)$ have been evaluated at 484 points equally distributed over 1/24th volume of the Brillouin zone using a computer program. The individual GPs γ' and γ'' 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 $\bar{\gamma}_{\perp}{}^{l}(T)$ and $\bar{\gamma}_{\parallel}{}^{l}(T)$ are then calculated as follows:

$$\bar{\gamma}_{\perp}{}^{l}(T) = \left[\int_{0}^{\omega_{\max}} \bar{\gamma}'(\omega)\, g(\omega) \cdot \sigma(\omega, T)\, \mathrm{d}\omega\right] \Big/ \left[\int_{0}^{\omega_{\max}} g(\omega)\, \sigma(\omega, T)\, \mathrm{d}\omega\right],$$

$$\bar{\gamma}_{\parallel}{}^{l}(T) = \left[\int_{0}^{\omega_{\max}} \bar{\gamma}''(\omega)\, g(\omega) \cdot \sigma(\omega, T)\, \mathrm{d}\omega\right] \Big/ \left[\int_{0}^{\omega_{\max}} g(\omega)\, \sigma(\omega, T)\, \mathrm{d}\omega\right]. \tag{5.6}$$

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

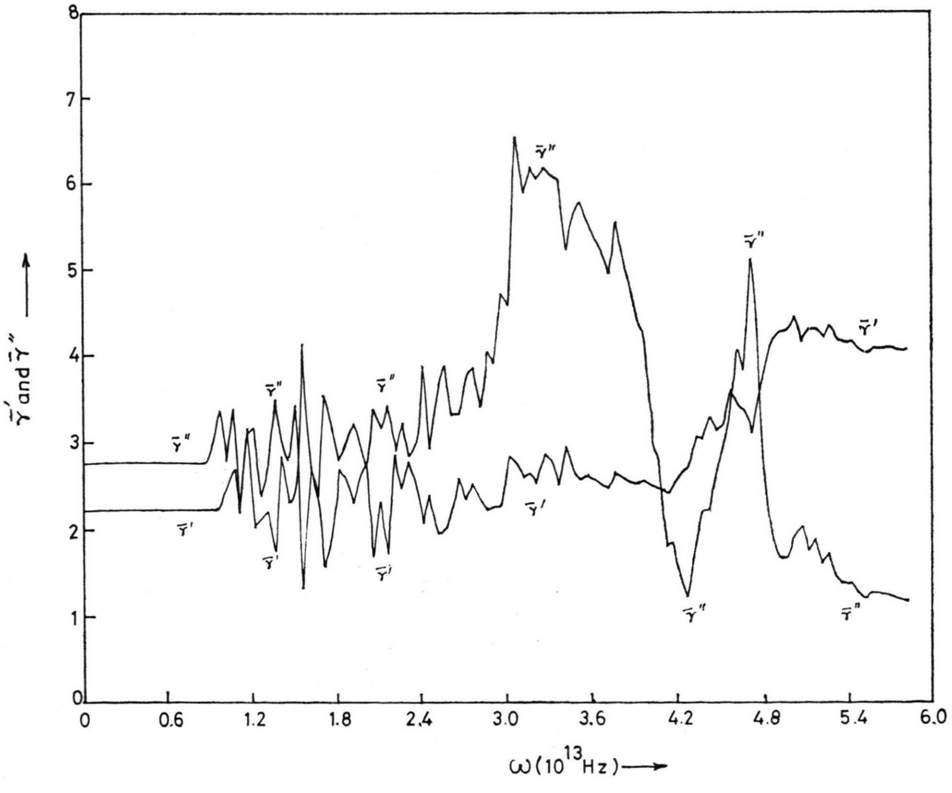

Fig. 5. $\bar{\gamma}'(\omega)$ and $\bar{\gamma}''(\omega)$ versus ω for Ru (reproduced computer plot).

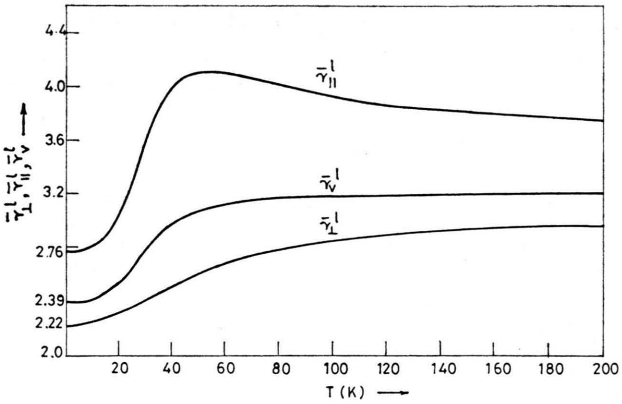

Fig. 6. $\bar\gamma_\perp{}^l(T)$, $\bar\gamma_\parallel{}^l(T)$ and $\bar\gamma_v{}^l(T)$ versus T for Ru.

6. Anderson-Grüneisen Parameter δ, Second Grüneisen Constant q and Temperature Dependence of Bulk Modulus

The Anderson-Grüneisen (AG) parameter of Ru has been calculated from its TOE constants using the procedure given by Ramji Rao [15], it has the value 4.36. The temperature dependence of the bulk modulus is derived by Anderson [16] and the relation is

$$B_s = B_{00} - (\delta\gamma_G/V_0)\int_0^T C_v\,dT', \tag{6.1}$$

where V_0 is the specific volume per "average" atom at 0 K, γ_G the usual Grüneisen constant, and $\int_0^T C_v dT'$ the internal energy content at temperature T. The specific heat at constant volume C_v obtained by subtracting the dilation correction term $AC_p{}^2T$ from the experimental [3] C_p data on Ru is plotted against T. The area enclosed between the ordinate at T and the curve gives the internal energy content $\int_0^T C_v dT'$ at T.

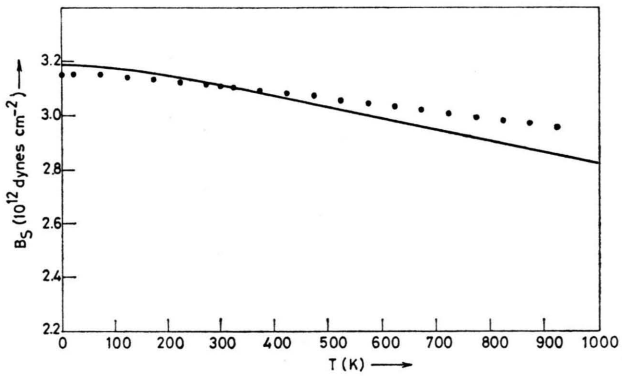

Fig. 7. Temperature variation of Bulk modulus of Ru. The dots represent the experimental points.

Table 4. Values of the constants of Ru used in the present calculations.

V_0	B_0 10^{11} dyn/cm^2	γ_H	β	δ	q
8.284	31.863	3.22	20.1 $\cdot 10^{-6}$/K	4.36	3.305

The bulk modulus of Ru has been evaluated at different temperatures upto 1000 K, using the calculated δ parameter and Eq. (6.1), and is shown in Figure 7. The values of the parameters V_0 and B_{00} for Ru are given in Table 4. The experimental SOE constants have been used to evaluate B_s and are shown as full circles. The agreement is good between the experimental and the present calculations, with a maximum discrepancy of about 3.5% that occurs at 923 K.

The volume dependence of the Grüneisen constant is described by the second Grüneisen constant q and is given by

$$q = (\partial \ln \gamma_G/\partial \ln V)_T\,. \tag{6.2}$$

The second Grüneisen constant q of Ru at room temperature has been calculated from the modified formula of Basset et al. [17] derived by Ramji Rao [18]

$$q = \gamma_G(1 + \delta\,\beta\,T)\,, \tag{6.3}$$

where β is the volume coefficient of thermal expansion and the value for Ru is given in Table 5. The calculated value of q is 3.305 and is presented in the same Table.

7. Discussion

The agreement between the calculated dispersion curves and the experimental values of Smith et al. [2] in [0001] direction, and the overall general agreement of the calculated lattice specific heat values with the experimental [3] values imply that the normalized distribution function of Ru obtained from the present model is good enough to explain its thermal properties. The high temperature limit of $\bar\gamma_v{}^l(T)$ (3.22) is in very good agreement with the value of γ_H (3.25) quoted by Gschneidner [5]. This shows that the anharmonic interactions upto second neighbours in Ru are enough to explain its 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 $\mathrm{d}C_{44}/\mathrm{d}p$ 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.

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