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Résumé. — On applique un modèle basé sur l'approche de Keating au calcul de la chaleur spécifique, des constantes élastiques du 3e ordre et des coefficients d'expansion thermique du thallium (métal de structure hexagonale compacte). Les constantes élastiques du 3e ordre calculées sont utilisées pour déterminer la limite à basse température du coefficient d'expansion thermique et pour étudier la variation en pression des paramètres du réseau et du volume du thallium. Les résultats des calculs sont en bon accord avec les résultats expérimentaux.

Abstract. — A model based on Keating's approach is applied to the hcp metal thallium to work out its lattice heat capacity, third-order elastic (TOE) constants and thermal expansion. The calculated TOE constants are used to determine the low-temperature limit of volume thermal expansion and to investigate the pressure variation of the lattice parameters and volume of thallium. The results of calculations show good agreement with the corresponding available experimental data.

1. Introduction. — Thallium has a hexagonal-close-packed structure at room temperature and atmospheric pressure. At about 510 K it transforms to body centered cubic structure. The specific heat of Tl below 4.2 K was measured by van der Hoeven and Keesom [1]. The measurements of specific heat for this metal at elevated temperatures have also been reported and compiled [2]. Worlton and Beyerein [3] have recently measured the c/a ratio and the volume of Tl as a function of pressure by time of flight neutron diffraction. Earlier Vaidya and Kennedy [4] obtained the volume measurements of Tl with pressure. At about 36 K bar this metal is observed to transform from hcp to fcc. In this paper we present the results of the calculations of lattice heat capacity, third-order-elastic (TOE) constants and the temperature variation of the volume Grüneisen function for hcp Tl employing the model of Srinivasan and Ramji Rao [5], based on Keating's [6] approach wherein the potential energy of the lattice is expressed in a manner that makes it automatically invariant under rigid translations and rotations of the lattice. The pressure variation of the lattice parameters and volume is also investigated for this metal using its calculated TOE constants in Thurston's [7] extrapolation formulae.

2. Frequency distribution function and lattice heat capacity. — The lattice dynamics of Tl was earlier studied on the present model by Menon and Ramji Rao [8]. The twelve second-order parameters, appropriate for Tl at 296 K, have been taken from reference [8] and are shown in table I. The normalized frequency distribution function \( g(\omega) \) for Tl is obtained by the root-sampling technique and its computer plot is shown in figure 1. The normal mode frequencies have been determined using a program written for the computer IBM 370/155. The grid chosen for the wave vectors \( q \) contains 484 evenly spaced points in the irreducible volume of the Brillouin zone, this being equivalent to 8 480 points in the whole volume of the

Table I. Values of the second-order parameters for Tl at 296 K on the present model (ref. [8]).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value in ( 10^{11} ) dyn/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>((D^*/a)) (\alpha)</td>
<td>0.753 6</td>
</tr>
<tr>
<td>((D^*/a)) (\tau)</td>
<td>-0.720 0</td>
</tr>
<tr>
<td>((D^*/a)) (\rho)</td>
<td>-0.011 4</td>
</tr>
<tr>
<td>((D^*/a)) (\gamma)</td>
<td>0.427 0</td>
</tr>
<tr>
<td>((D^*/a)) (\sigma)</td>
<td>0.053 7</td>
</tr>
<tr>
<td>((D^*/a)) (\beta)</td>
<td>-0.127 3</td>
</tr>
<tr>
<td>((D^*/a)) (\beta')</td>
<td>-0.015 1</td>
</tr>
<tr>
<td>((D^*/a)) (\epsilon)</td>
<td>-0.491 9</td>
</tr>
<tr>
<td>((D^*/a)) (\kappa)</td>
<td>-0.247 2</td>
</tr>
<tr>
<td>((D^*/a)) (\kappa')</td>
<td>0.003 0</td>
</tr>
<tr>
<td>((D^*/a)) (\delta)</td>
<td>1.191 1</td>
</tr>
<tr>
<td>((D^*/a)) (\delta')</td>
<td>0.029 8</td>
</tr>
</tbody>
</table>
Brillouin zone. In the low-frequency region of $g(\omega)$, where the number of frequencies is insufficient, we have adopted the formula $g(\omega) = C\omega^2$, the constant $C$ being known from the average value of

$$\sum_{j=1}^{3} v_j^{-3}(\theta, \varphi)$$

over all directions. Here $v_j(\theta, \varphi)$ denotes the acoustic wave velocity of the $j$th mode propagating in the direction $(\theta, \varphi)$.

The even moments of the $g(\omega)$ function calculated for Tl are:

$$\langle \omega^2 \rangle = 0.989 \times 10^{26} \text{ s}^{-2}$$
$$\langle \omega^4 \rangle = 1.728 \times 10^{52} \text{ s}^{-4}$$
$$\langle \omega^6 \rangle = 3.587 \times 10^{78} \text{ s}^{-6}$$

The high-temperature limit of the Debye temperature, $\theta_\infty$, that can be calculated from the relation

$$\theta_\infty = \left( \frac{\hbar}{k} \right) \left( \frac{5 \langle \omega^2 \rangle}{3} \right)^{1/2}$$

has the value 98 K for Tl. This is of the same order as $\theta_D = 96 \text{ K}$ and $\theta^M = 90.1 \text{ K}$ estimated respectively from the experimental room-temperature specific heat data and the Lindemann equation, both being reported by Gschneidner [9].

The frequency distribution function shown in figure 1 is utilized to calculate the lattice heat capacity as a function of temperature

$$C'_V(T) = \frac{3 R \sum g(\omega) \sigma(\omega, T)}{\sum g(\omega)}$$

where $\sigma(\omega, T)$ is the Einstein specific heat function and $R$ is the gas constant. The $C'_V$ values derived from eq. (2) are compared in figure 2a with those estimated from the experimental $C_p$ data of Tl [2], through the thermodynamic relation

$$C_p = C'_V + \gamma T + AC_p^2 T.$$
The quantity $A$ in the dilation term of eq. (3) has the value $2.907 \times 10^{-5}$ mole cal$^{-1}$ for TI as quoted by Gschneidner [9]. We have taken for the electronic specific heat constant $\gamma$, the value equal to $3.51 \times 10^{-4}$ cal mole$^{-1}$ K$^{-2}$ reported for TI by van der Hoeven and Keesom [1].

In figure 2b we present the plot of the equivalent Debye temperature $\theta_D(T)$ from 0 to 50 K.

3. TOE constants. — The present model contains five anharmonic parameters which enter the theoretical expressions for the pressure derivatives of the second-order elastic (SOE) constants of a hcp crystal via its TOE constants as was shown by Ramji Rao and Srinivasan [10]. A knowledge of the experimental pressure derivatives of the SOE constants, therefore, enables these anharmonic parameters to be determined; the former, however, are not available in the literature in the case of TI. We have, therefore, taken into account two anharmonic parameters $\xi$ and $\zeta$, implying the inclusion of anharmonic interactions up to second neighbours only. The parameters $\xi$ and $\zeta$ correspond respectively to the J and I atoms, the first two neighbours of the $\left(\begin{array}{l}0 \\ 1 \end{array}\right)$ atom at the origin.

In the case of TI, the J and I atoms are almost equally separated from the $\left(\begin{array}{l}0 \\ 1 \end{array}\right)$ atom and this fact makes it possible to set $\xi$ and $\zeta$ equal. The value of $\xi$ and $\zeta$ is then adjusted in a way such that the high temperature limit $\gamma_H$ of thermal expansion shows reasonable agreement with experiment.

The values of the parameters $\xi$ and $\zeta$, the calculated TOE constants and the pressure derivatives of the SOE constants of TI are collected in table II.

### Table II. Values of the third-order parameters, calculated TOE constants and the pressure derivatives of the SOE constants of TI.

<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 SOE constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle D^0/Va \rangle \xi$</td>
<td>-3.174</td>
<td>C$_{111}$</td>
<td>-7.13</td>
<td>C$_{111}$/dp</td>
</tr>
<tr>
<td>$\langle D^0/Va \rangle \zeta$</td>
<td>-3.174</td>
<td>C$_{112}$</td>
<td>-5.55</td>
<td>dC$_{11}$/dp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_{122}$</td>
<td>-5.41</td>
<td>dC$_{12}$/dp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_{133}$</td>
<td>-4.14</td>
<td>dC$_{33}$/dp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_{144}$</td>
<td>-3.36</td>
<td>C$_{44}$/dp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_{155}$</td>
<td>-2.38</td>
<td>C$_{55}$/dp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_{133}$</td>
<td>-10.36</td>
<td>C$_{33}$/dp</td>
</tr>
</tbody>
</table>

The generalized Gruneisen parameters (GPs) for the elastic waves propagating in a uniaxial crystal are given by

$$\gamma' = -\frac{\partial \ln \rho}{\partial \varepsilon}, \quad \gamma'' = -\frac{\partial \ln (\ln \rho)}{\partial \varepsilon} \quad (4)$$

where $\varepsilon$ is a uniform areal strain in the basal plane and $\varepsilon''$ is a uniform longitudinal strain parallel to the unique axis. The effective Gruneisen functions $\gamma'_j(T)$ and $\gamma''_j(T)$ obtained as the weighted averages of the GPs, can be used to explain the temperature dependence of the linear thermal expansion coefficients $\alpha_1$ and $\alpha_2$ through the equations

$$V\alpha_1 = [(S_{11} + S_{12}) \gamma'_1(T) + S_{13} \gamma'_2(T)] C_v$$

4. Thermal expansion. — The generalized Gruneisen parameters (GPs) for the elastic waves propagating in a uniaxial crystal are given by

$$\gamma' = -\frac{\partial \ln \rho}{\partial \varepsilon}, \quad \gamma'' = -\frac{\partial \ln (\ln \rho)}{\partial \varepsilon} \quad (4)$$

where $\varepsilon$ is a uniform areal strain in the basal plane and $\varepsilon''$ is a uniform longitudinal strain parallel to the unique axis. The effective Gruneisen functions $\gamma'_j(T)$ and $\gamma''_j(T)$ obtained as the weighted averages of the GPs, can be used to explain the temperature dependence of the linear thermal expansion coefficients $\alpha_1$ and $\alpha_2$ through the equations

$$V\alpha_1 = [(S_{11} + S_{12}) \gamma'_1(T) + S_{13} \gamma'_2(T)] C_v$$

where $S_{ij}$ are the elastic compliance coefficients, $V$ is the molar volume and $\chi$ is the isothermal compressibility; $\gamma''_1$ and $\gamma''_2$ are the average Gruneisen functions used by Brugger and Fritz [11]. At very low temperatures, the acoustic modes are predominant and the low-temperature limits of $\gamma'_1(T)$ and $\gamma''_1(T)$, denoted respectively by $\gamma'_1(-3)$ and $\gamma''_1(-3)$, become

$$\gamma'_1(-3) = 3 \sum_{j=1}^3 \int \gamma_j'(\theta, \varphi) V_j^{-3}(\theta, \varphi) d\Omega \int \frac{3}{\sum_{j=1}^3} V_j^{-3}(\theta, \varphi) d\Omega$$

$$\gamma''_1(-3) = 3 \sum_{j=1}^3 \int \gamma_j''(\theta, \varphi) V_j^{-3}(\theta, \varphi) d\Omega \int \frac{3}{\sum_{j=1}^3} V_j^{-3}(\theta, \varphi) d\Omega . \quad (6)$$

Here $V_j(\theta, \varphi)$ is the wave velocity of the acoustic wave of polarisation index $j$ propagating in the direction $(\theta, \varphi); \gamma_j'(\theta, \varphi)$ and $\gamma_j''(\theta, \varphi)$ are the GPs for the acoustic mode. The values of $\gamma'_1(-3)$ and $\gamma''_1(-3)$ calculated for TI following a procedure proposed by Ramji Rao and Srinivasan [12] are 3.45 and -0.55 respectively. The low-temperature limit of the lattice volume thermal expansion derived from

$$\gamma = 2 \gamma''_1(-3) + \gamma''_1(-3) \quad (7)$$

has the value 2.38 for TI, which is comparable to the value 2.36 deduced from the experimental thermal expansion data of TI around 7.5 K obtained by Meyerhoff and Smith [13]. It may be mentioned that the experimental value contains the electronic contribution as well besides the lattice contribution, whereas our calculated value refers to the lattice part only.

Blackman's [14] procedure has been utilized to study the temperature dependence of $\gamma'_1(T)$ and $\gamma''_1(T)$.
are calculated for 484 points evenly distributed over 1/24th volume of the Brillouin zone using a program written for the computer IBM 370/155. For each frequency interval of width
\[ \Delta \omega = 0.03 \times 10^{13} \text{ Hz}, \]
the individual GPs \( \gamma' \) and \( \gamma'' \) are determined and their average values \( \overline{\gamma}' \) and \( \overline{\gamma}'' \) are obtained. In figure 3, we have shown the computer plots of \( \overline{\gamma}'(\omega) \) and \( \overline{\gamma}''(\omega) \), their low-frequency values tending to their respective low-temperature limits 3.45 and \(-0.55\). The following equations then yield \( \overline{\gamma}'_1(T) \) and \( \overline{\gamma}''_1(T) \):

\[
\overline{\gamma}'_1(T) = \int_0^{\omega_{\text{max}}} \overline{\gamma}'(\omega) g(\omega) \sigma(\omega, T) \, d\omega / \int_0^{\omega_{\text{max}}} g(\omega) \sigma(\omega, T) \, d\omega,
\]
\[
\overline{\gamma}''_1(T) = \int_0^{\omega_{\text{max}}} \overline{\gamma}''(\omega) g(\omega) \sigma(\omega, T) \, d\omega / \int_0^{\omega_{\text{max}}} g(\omega) \sigma(\omega, T) \, d\omega.
\]  

These, in turn, enable us to calculate \( \overline{\gamma}'_1(B) \) and \( \overline{\gamma}''_1(B) \) through the eqs. (5), and thus the volume Grüneisen function is known finally from

\[ \overline{\gamma}_1(T) = 2 \overline{\gamma}'_1(T) + \overline{\gamma}''_1(T) \]  

at any temperature \( T \). The variation of \( \overline{\gamma}_1(T) \) with temperature is shown in figure 4. The high-temperature limit of \( \gamma_1(T) \), i.e., \( \gamma_1 \) turns out to be 2.01 which compares well with the value 2.28 estimated from the experimental thermal expansion data at 273 K for TI reported by Meyerhoff and Smith [13]. A similar value (= 2.27) is also quoted by Gschneidner [9].

5. Variation of lattice parameters with pressure. — Thurston’s [7] extrapolation formula for the principal stretches \( \lambda_i \) \((i = 1, 2, 3)\), which is consistent with linear pressure dependence of the bulk modulus reads

\[ \lambda_i = \left[ \frac{B_i}{B_0} \right]^{\frac{B_0}{\lambda_i(B_0)}} \exp \left[ \left( a_i + B_0 \frac{Y_{i0}}{B_0} \right) P \right]. \]

For a hexagonal crystal \( \lambda_1 = \lambda_2 = \lambda_\perp \) and \( \lambda_3 = \lambda_\parallel \) so that eq. (10) splits into

\[ \lambda_\perp = \left( a/a_0 \right) \left[ \frac{B_0}{B_0} \right] \exp \left[ \left( a_\perp + B_0 \frac{Y_{\perp0}}{B_0} \right) P \right] \]

and

\[ \lambda_\parallel = \left( c/c_0 \right) \left[ \frac{B_0}{B_0} \right] \exp \left[ \left( a_\parallel + B_0 \frac{Y_{\parallel0}}{B_0} \right) P \right]. \]

In eqs. (11), \( (a_0, c_0) \) and \( (a, c) \) denote the lattice parameters at pressures zero and \( p \) respectively. \( B \) is the bulk modulus at pressure \( p \), \( B_0 \) and \( B_0' \) are the bulk modulus and its pressure derivative at zero pressure. The parameters in eqs. (11) are given by the same expressions as in Thurston’s [7] paper. From eqs. (11), the volume ratio is seen to be

\[ \left( V/V_0 \right) = \lambda_\parallel^2 \lambda_\perp = (1 + P B_0/B_0)^{-1} \]  

![Fig. 3. — \( \overline{\gamma}(\omega) \) and \( \overline{\gamma}'(\omega) \) versus \( \omega \) for thallium.](image)

![Fig. 4. — \( \overline{\gamma}_1(T) \) versus \( T \) for thallium.](image)
which is the same as Murnaghan's eq. [15]. The calculated TOE constants of Tl have been used in
eqs. (11) and (12) to evaluate \(a_l/a_0\), \(c/c_0\) and \(V/V_0\) for Tl at different pressures up to 35 kbar and the results are compared in figure 5, with the experimental data of Worlton and Beyerlein [3] and of Vaidya and Kennedy [4]. The agreement between theory and experiment is excellent for \(a_l/a_0\) and is reasonably good in the case of \(c/c_0\) and \(V/V_0\), the maximum discrepancy being within 0.8 % only.

![Variation of V/V0, a/ao, and c/co of thallium with hydrostatic pressure. Experimental values indicated by closed circles are taken from reference [3] and those denoted by open circles are taken from reference [4].](image)

The calculated values of \(a_1\), \(a\parallel\), \(Y_{\perp0}\), \(Y_{\parallel0}\) and those of \(B_0\) and \(B'0\) are noted below:

\[
\begin{align*}
a_1 & = -1.017 \text{ Mbar}^{-1} \quad a\parallel = -0.778 \text{ Mbar}^{-1} \\
Y_{\perp0} & = 8.804 \text{ Mbar}^{-2} \quad Y_{\parallel0} = -0.828 \text{ Mbar}^{-2} \\
B_0 & = 0.357 \text{ Mbar} \quad B'0 = 2.06
\end{align*}
\]

6. Discussion. — From figures 2a and b we notice that the calculated lattice heat capacity and the equivalent Debye temperature computed from it show reasonably good agreement with the correspond-
ing experimental values. The maximum discrepancy between theory and experiment is within 5 % and this may be due partly to the assumption that \(A\), the constant used in estimating the thermodynamic correction is independent of temperature, and partly to the rather large uncertainty involved in the experimental determination of \(\gamma\), the electronic specific heat constant. The present model may therefore, be said to provide us with a good, reliable distribution function for thallium.

The TOE constants \(C_{111}, C_{222}\) and \(C_{333}\) are all small and the fact that they are nearly equal, implies higher-order elastic isotropy in this metal. The good agreement between the experimental and theoretically computed compression curves speaks well for our calculated TOE constants. As regards the thermal expansion, we find that both the high-and low-temperature limits are comparable to the experimental data.

On the whole we have shown how the present model, fitted to the limited amount of experimental data available and with reasonable simplifying assumptions, is able to provide valuable information about the anisotropic thermal expansion and TOE constants of a complex metal like Tl.

Since Tl can occur in each of the three most common structures of elemental metals, namely, hcp, bcc and fcc, it would be of considerable interest to compare the presently calculated results for the hcp phase with those for the bcc or the fcc phase. The present authors have recently developed the relevant theoretical expressions for a bcc crystal [16] using Keating's approach [6] and applied them to several bcc metals. However, similar calculations for the bcc phase of Tl could not be performed as the experimental data on the second-order elastic constants or the lattice dynamics is available neither for the bcc phase (at about 510 K) nor for the fcc phase (at about 36 kbar) of Tl [17].

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References