5.1 Introduction

The investigation of the Grüneisen parameter is a subject of great interest (1-18), given their importance in understanding the macroscopic behaviour of solids (19-21). Thermal expansion is a direct consequence of the anharmonicity of the crystal lattice (22). Grüneisen parameters are a measure of the strength of the magneto elastic coupling (2). At low temperatures the thermal expansion coefficient of any crystal is mainly determined by the acoustic modes of the elastic waves and their dependence on the strains of the lattice. For cubic materials it is enough to consider the dependence of the frequency on the volume strain.

The recent discovery of bulk quantities of C₆₀ has raised enormous interest in this material owing to its superconducting properties (23-35). Measurements of the hydrostatic pressure derivatives of the elastic stiffness tensor components used to determine the Grüneisen parameters of the acoustic modes in the long wave length limit enable the effects of these
modes to be separated from these of optical modes and higher wave vector acoustic modes (1, 2). We give the low temperature limit of the lattice thermal expansion of $C_{60}$, $\text{Mn}_{78}\text{Pt}_{22}$ and $\text{Fe}_{72}\text{Pt}_{28}$. In these compounds the thermal expansion coefficient $\alpha$ at low temperatures is governed by the generalised Grüneisen parameters $\gamma_j(\theta, \phi)$. Using the generalised Grüneisen functions, the low temperature limit of the Grüneisen parameter $\gamma_L$ is calculated (36-37). The procedure to calculate the low temperature limit of the Grüneisen Parameter is given below.

5.2 Procedure to Obtain the Low Temperature Limit of the Lattice Thermal Expansion

The low temperature limit of the Grüneisen parameter $\gamma_L \{\text{Gp}\}$ depends on the generalised Grüneisen parameters $\gamma_j(\theta, \phi)$ of the acoustic modes propagating in different directions in the crystal lattice. A method of calculation of the generalised Grüneisen parameters $\gamma_j(\theta, \phi)$ for cubic compounds $C_{60}$, $\text{Mn}_{78}\text{Pt}_{22}$ and $\text{Fe}_{72}\text{Pt}_{28}$ from their higher order elastic constants is presented.

A medium is homogeneously strained when the components of the strain tensor $n_{ij}$ do not vary from point to point, in the medium. Let the co-ordinates of the lattice point in the strained state be $X_i (i = 1, 2, 3)$. When the lattice is given infinitesimal displacements $u_i$ from the strained state, the resulting state is referred by the co-ordinates $x_i = X_i + u_i$.
the equation of motion is

$$\rho \ddot{x}_i = \frac{\partial}{\partial x_i} \tau_{kl}$$  \hspace{1cm} (5.1)

where \(\rho\) is the density in the strained state and \(\tau_{kl}\) is the stress tensor. The condition of equilibrium requires that the stress tensor be symmetric, i.e.,

$$\tau_{jk} = \tau_{kj}$$  \hspace{1cm} (5.2)

We have for the Jacobian \(J\)

$$\frac{\partial}{\partial x_k} \left( \frac{1}{J} \frac{\partial x_k}{\partial \alpha_p} \right) = 0$$  \hspace{1cm} (5.3)

Using equations (5.1) and (5.2), Thurston and Brugger (38) arrive at the following wave equation in a homogeneously strained lattice in terms of the displacements \(u_i\).

$$\rho_0 \ddot{u}_i = A_{\text{ijkl}} \frac{\partial^2 u_k}{\partial \alpha_p \partial \alpha_m}$$  \hspace{1cm} (5.4)

where \(J\) in equation (5.3) is defined as

$$J = \text{Det} \left( \frac{\partial X_i}{\partial a_j} \right)$$  \hspace{1cm} (5.5)

with \(a_i\) (\(i = 1, 2, 3\)) being the position co-ordinates of a lattice point in the unstrained state. In equation (5.4), \(\rho_0\) is the density of the crystal before deformation and

$$A_{\text{ijkl}} \delta_{ik} t_{pm} + \frac{\partial X_j}{\partial a_q} \frac{\partial X_k}{\partial a_l} \left( \frac{\partial t_{pm}}{\partial \eta_{mi}} \right)$$  \hspace{1cm} (5.6)
where \( i_{mn} = \left( \frac{\partial U}{\partial \eta_{pm}} \right) \) \( n \) (5.7)

The 'bar' denotes that the quantities have to be evaluated in the homogeneously strained state of the lattice. \( \delta_{ik} \) is the Kronecker delta symbol and \( \eta \)'s are the Lagrangian strains. \( U \) is the internal energy of the lattice, which is a function of entropy \( S \) and Lagrangian strain components \( \eta_{ij} \). \( U \) can be expanded in powers of the strain parameters about the unstrained state as

\[
U = U_0 + \frac{1}{2} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{3} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} + \ldots \] (5.8)

The linear term in strain is absent because the unstrained state is one where \( U \) is minimum. \( C_{ijkl} \) and \( C_{ijklmn} \) are the second-and third-order elastic constants defined as

\[
C_{ijkl} = \left[ \frac{\partial^2 U}{\partial \eta_i \partial \eta_{kl}} \right]_{0, S} \] (5.9)

\[
C_{ijklmn} = \left[ \frac{\partial^3 U}{\partial \eta_i \partial \eta_{kl} \partial \eta_{mn}} \right]_{0, S} \] (5.10)

Here, the derivatives are to be evaluated at equilibrium configuration and at constant entropy. The elements of the position co-ordinates \( dx_i \) are related to \( da \), by the equation (39)
where $\varepsilon_{ij}$ are deformation parameters.

Using equations (5.8) and (5.11), we get $A^{s}_{jk,pm}$ in equation (5.6) to the first order in $\varepsilon_{jk}$ as

$$A^{s}_{jk,pm} = C_{pj,mk} + \sum_{rs} \left( C_{pj,rs} V_{pm,r} \delta_{j,k} \right) \varepsilon_{rs}$$

$$+ \sum_{q} C_{pq,mk} \varepsilon_{j,q} \sum_{q} C_{pj,mq} \varepsilon_{k,q}$$  \hspace{1cm} (5.12)

The plane wave solution in strained co-ordinate is

$$u_j = u_j^0 \exp \{ i \omega (t - \frac{n_i X_j}{W}) \}$$  \hspace{1cm} (5.13)

where $W$ is the actual velocity of the wave in the strained state and $\omega$ the frequency of the wave in the strained state. $n_i$ are the direction cosines of wave propagation and $t$ is the time. $u_j$, the displacements in equation (5.13) can be expressed as

$$u_j = u_j^0 \exp \{ i \omega (t - \frac{N_i a_i}{v}) \}$$  \hspace{1cm} (5.14)

where $v$ is the natural velocity and $N_i$ are the direction cosines of the wave in the unstrained state. Let $\lambda_0$ be the wavelength of a given wave in the
unstrained state travelling along a direction having direction cosines \( N \).

After deformation, the wavelength of the elastic wave changes to \( \lambda \) and the wave propagation direction also is changed and the corresponding direction cosines are \( n \). The frequency of the wave changes from \( \omega_0 \) to \( \omega \). In the unstrained state, the actual velocity \( W_0 \) in the direction \( N \) is

\[
W_0 = \frac{\omega_0 \lambda}{2\pi}
\]  

(5.15)

In the strained state, the actual velocity \( W \) of the wave is

\[
W = \frac{\omega \lambda}{2\pi}
\]

(5.16)

and the natural velocity of the wave is

\[
v = \frac{\omega \lambda_0}{2\pi}
\]

(5.17)

The ratio \( \frac{\omega}{\omega_0} \) directly gives \( \frac{v}{W_0} \) without involving the changes in the dimensions.

Substituting (5.14) in (5.4), we get

\[
\rho_0 v^2 u_i^0 = \sum_{pmn} A_{ik,pm}^s N_p N_m u_k^0
\]

(5.18)

The three linear homogeneous equations (5.18) corresponding to \( j = 1, 2, 3 \) can be solved only if

\[
\text{Det} \left| \rho_0 V^{-1} \delta_{ik} - \sum_{pmn} A_{ik,pm}^s N_p N_m \right| = 0
\]

(5.19)

where \( D_{jk} = \sum_{pmn} A_{jk,pm}^s N_p N_m \) 

(5.20)
giving the natural velocities for any direction of wave propagation. The
generalised Grüneisen parameters $\gamma_j(\theta, \phi)$ for the $j^{th}$ acoustic mode
propagating in the direction $(\theta, \phi)$ can be defined as

$$\gamma_j(\theta, \phi) = -\frac{\partial \log v_j(\theta, \phi)}{\partial \log V}$$ (5.21)

where $V$ is the molar volume of the crystal. $v_j(\theta, \phi)$ is the natural velocity of
the $j^{th}$ acoustic mode propagating in the direction $(\theta, \phi)$ when the lattice is
homogeneously strained by a uniform volume strain $\varepsilon = d \log V$. When a
cubic crystal subjected to a hydrostatic pressure it will experience a uniform
volume strain $\varepsilon$ and we have $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \left(\frac{\varepsilon}{3}\right)$. The other components of $\varepsilon_{ij}$ vanish. Expanding (5.20) using (5.12) for this class of crystals with the
non-vanishing terms

$$D_{xx} = \left[C_{11}N_x^2 + \left(N_y^2 + N_z^2\right)C_{44}\right] + \frac{\varepsilon}{3}\left[(C_{111} + 2C_{112} + 3C_{11} + 2C_{12})N_x^2 + (2C_{155} + C_{144} + 2C_{12} + C_{11})N_y^2 + (2C_{155} + C_{144} + 2C_{12} + C_{11})N_z^2\right]$$

$$D_{yy} = \left[C_{44}N_y^2 + C_{11}N_x^2 + C_{44}N_z^2\right] + \frac{\varepsilon}{3}\left[(2C_{155} + C_{111} + 2C_{144} + 2C_{12} + C_{11})N_x^2 + (2C_{155} + C_{144} + 2C_{12} + C_{11})N_y^2 + (C_{144} + 2C_{155} + 2C_{12} + 3C_{11})N_z^2\right]$$

$$D_{zz} = \left[C_{44}N_z^2 + C_{11}N_x^2 + C_{44}N_y^2\right] + \frac{\varepsilon}{3}\left[(2C_{155} + C_{144} + C_{11} + 2C_{12} + 2C_{144})N_x^2 + (C_{144} + 2C_{155} + 2C_{12} + 3C_{11})N_y^2 + (2C_{155} + 2C_{12} + C_{11} + 3C_{11})N_z^2\right]$$
Putting $p_0 v^2 = X$, the determinantal equation (5.19) can be expanded to give the cubic equation

$$X^3 - AX^2 + BX - C = 0 \quad (5.23)$$

where $A = \sum_i D_i$

$$B = \begin{vmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{vmatrix} + \begin{vmatrix} D_{yx} & D_{yz} \\ D_{zy} & D_{zz} \end{vmatrix} + \begin{vmatrix} D_{xz} & D_{zx} \\ D_{zr} & D_{zz} \end{vmatrix}$$

$$C = \begin{vmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{vmatrix} \quad (5.24)$$

The coefficients $A$, $B$ and $C$ are functions of $\epsilon$. In the unstrained state, i.e. when $\epsilon$ is zero, their values are $\overline{A}$, $\overline{B}$ and $\overline{C}$ and the roots of the equation are $\overline{X}_1$, $\overline{X}_2$ and $\overline{X}_3$. Differentiating equation (5.23) with respect to $\epsilon$ and using the definition

$$\gamma_j(0, \phi) = \frac{1}{2} \frac{\partial \log X_j}{\partial \epsilon}, \text{ we have}$$

$$\gamma = -\frac{1}{2X_j} \left[ \frac{\overline{X}_j \frac{\partial}{\partial \epsilon} (A + B) - \frac{\partial}{\partial \epsilon} (AB - C^2)}{2\overline{X}_j - (\overline{A} + \overline{B})} \right] \quad (5.25)$$
The derivatives of A, B and C are to be evaluated at equilibrium configuration. The low temperature limits of the effective Grüneisen parameter can be calculated using the individual generalised Grüneisen parameters of the acoustic modes. In the class of crystals discussed here, the acoustic wave velocities and the generalised Grüneisen parameters depends only on θ and not on the azimuth φ, where (θ, φ) gives the direction of wave propagation. At very low temperatures where only acoustic modes of long wavelength are predominant the low temperature limit of the Grüneisen parameter is calculated using

\[ \gamma_L(0) = \frac{\int \sum_{j=1}^{3} \gamma_j(\theta) v_j^{-3}(\theta) \, d\Omega}{\int \sum_{j=1}^{3} v_j^{-3}(\theta) \, d\Omega} \] (5.26)

Here, \( v_j(\theta) \) is the velocity of the long wavelength acoustic modes of polarisation index \( j \) and \( \Omega \) is the solid angle. The low temperature limits \( \gamma_L(0) \) in equation (5.26) is evaluated using the generalised Grüneisen parameters of the acoustic modes by numerical integration. Since the solid angle of the cone of semi-vertical angle \( \theta \) is proportional to \( \sin \theta \), the value \( \gamma_j X_j^{-\frac{3}{2}} \) and \( X_j^{-\frac{3}{2}} \) at any angle \( \theta \) is multiplied by \( \sin \theta \) and the sum \( \sum \gamma_j X_j^{-\frac{3}{2}} \sin \theta \) over all \( \theta \) values is taken to be proportional to \( \int \gamma_j X_j^{-\frac{3}{2}} \, d\Omega \). Thus the low temperature limits \( \gamma_L(0) \) is obtained as

\[ \gamma_L(0) = \frac{\sum_{j} \left( \sum_{i} \gamma_j X_i^{-\frac{3}{2}} \right) \sin \theta_j}{\sum_{j} \left( \sum_{i} X_i^{-\frac{3}{2}} \right) \sin \theta_j} \] (5.27)
The lattice thermal expansion coefficient at various temperatures can be expressed in terms of the effective Grüneisen parameter $\gamma_L$ as follows:

$$V\alpha = \left[(S_{11} + 2S_{12}) \gamma_L \right]C_v$$

$$= \gamma^{Br} C_v \chi_{iso}$$

(5.28)

Here, $S_{ij}$ are the elastic compliance coefficients, $V$ is the molar volume, $\chi_{iso}$ is the isothermal compressibility and $C_v$ is the specific heat at constant volume. From equation (5.28) we may calculate the Brugger gammas $\gamma^{Br}$ at low temperature as

$$\gamma^{Br} = \left[(S_{11} + 2S_{12}) \gamma_L \right] \chi_{iso}^{-1}$$

(5.29)

where

$$S_{11} = \frac{2C_{11} - C_{12}^2}{(C_{12} - C_{11})(2C_{12}^2 - C_{11}(C_{11} + C_{12}))}$$

$$S_{12} = \frac{C_{12}^2 - C_{12}C_{11}}{(C_{12} - C_{11})(2C_{12}^2 - C_{11}(C_{11} + C_{12}))}$$

$$\chi_{iso} = 3\left[S_{11} + 2S_{12}\right]$$

(5.30)

where $C_{ij}$ are the second-order elastic constants. The low temperature limit of the volume Grüneisen parameter $\gamma_L$ is then obtained by

$$\gamma_1 = 3 \gamma^{Br}$$

(5.31)
5.3 Low Temperature Limit of the Lattice Thermal Expansion of C\textsubscript{60}

In C\textsubscript{60}, the acoustic wave velocities and the Grüneisen parameters depend only on $\theta$ and not on $\phi$, where $(\theta, \phi)$ gives the direction of wave propagation in polar co-ordinates (40). The second- and third-order elastic constants of C\textsubscript{60} given in Table 2.1 in Section 2.3 of Chapter 2 and in Table 3.2 in Section 3.3 of Chapter 3 respectively are used to obtain the generalised Grüneisen parameters $\gamma_j(\theta)$ of the acoustic modes using the equations (5.25). The results of the wave velocities obtained from equation (5.23) and the generalised Grüneisen parameters for the corresponding elastic wave velocities at different angles $\theta$ for C\textsubscript{60} are summarised in Table 5.1. The low temperature limit $\gamma_L$ for C\textsubscript{60} is obtained from equations (5.27) by numerical integration procedure using the data given in Table 5.1. Since the solid angle of the cone of semi-vertical angle is proportional to $\sin \theta$, the values of $\gamma_jX_j \gamma^2$ have been multiplied by $\sin \theta$ and have been summed over all values of $\theta$. Thus the low temperature limit $\gamma_L$ has been evaluated using equations (5.27) for C\textsubscript{60} and is given in Table 5.2. The elastic compliances $S_{11}$ and $S_{12}$ and isothermal compressibility $\chi_{iso}$ are evaluated using equation (5.30). These values of $S_{ij}$ and $\chi_{iso}$ along with the value of $\gamma_L$ given in Table 5.2 are substituted in equation (5.29) to calculate the Brugger gammas $\gamma^{Br}$. The value thus obtained for $\gamma_L$ is presented in Table 5.2. The low temperature volume lattice thermal expansion $\gamma_L$ for C\textsubscript{60} is obtained from equation (5.31) by substituting the value
of Burger gamma $\gamma^{Br}$ from Table 5.2. The value of $\gamma$, thus obtained is given in Table 5.2 along with experimental values.

**Table 5.1 Generalised Grüneisen parameter for elastic waves propagating at different angles $\theta$ for the crystal axis in the C$_{60}$ system**

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\gamma_1$</th>
<th>$\rho_0v_1^2$</th>
<th>$\gamma_2$</th>
<th>$\rho_0v_2^2$</th>
<th>$\gamma_3$</th>
<th>$\rho_0v_3^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.32</td>
<td>14.9</td>
<td>3.35</td>
<td>6.2</td>
<td>3.35</td>
<td>6.2</td>
</tr>
<tr>
<td>5</td>
<td>3.33</td>
<td>15.0</td>
<td>3.27</td>
<td>6.2</td>
<td>3.34</td>
<td>6.1</td>
</tr>
<tr>
<td>15</td>
<td>3.36</td>
<td>15.4</td>
<td>2.65</td>
<td>6.2</td>
<td>3.25</td>
<td>5.6</td>
</tr>
<tr>
<td>25</td>
<td>3.40</td>
<td>16.0</td>
<td>1.70</td>
<td>6.2</td>
<td>3.12</td>
<td>5.0</td>
</tr>
<tr>
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<td>3.00</td>
<td>4.5</td>
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<tr>
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<td>6.2</td>
<td>2.95</td>
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</tr>
<tr>
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<td>3.42</td>
<td>16.5</td>
<td>0.87</td>
<td>6.2</td>
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<tr>
<td>65</td>
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<td>6.2</td>
<td>3.12</td>
<td>5.0</td>
</tr>
<tr>
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<td>3.36</td>
<td>15.4</td>
<td>2.65</td>
<td>6.2</td>
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<td>5.6</td>
</tr>
<tr>
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<td>6.2</td>
<td>3.34</td>
<td>6.1</td>
</tr>
<tr>
<td>90</td>
<td>3.32</td>
<td>14.9</td>
<td>3.35</td>
<td>6.2</td>
<td>3.35</td>
<td>6.2</td>
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</table>
Table 5.2 The values of the Grüneisen parameters $\gamma^Br$ and $\gamma_L$ for C$_{60}$

<table>
<thead>
<tr>
<th></th>
<th>$\gamma^Br$</th>
<th>$\gamma_L$</th>
<th>Rao and Venkatesh (6)</th>
<th>White (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>0.94</td>
<td>2.8</td>
<td>3.3</td>
<td>3</td>
</tr>
</tbody>
</table>

The variation of the generalised Grüneisen parameters $\gamma_1(\theta)$ at different angles $\theta$ for the crystal C$_{60}$ are shown in Fig. 5.1.

Fig. 5.1 Variation of the generalised Grüneisen parameters $\gamma_j(\theta)$ as a function of angle $\theta$ of the C$_{60}$ system.
The variation of $\rho_0 V^2$ at different angles $\theta$ for the crystal $C_{60}$ are shown in Fig. 5.2.

Fig. 5.2 Variation of $\rho_0 V^2$ as a function of angle $\theta$ for $C_{60}$.
5.4 Low Temperature Limit of the Lattice Thermal Expansion of Mn$_{78}$Pt$_{22}$

The low temperature limit of the lattice thermal expansion of cubic Mn$_{78}$Pt$_{22}$ depends on the generalised Grüneisen parameters $\gamma_j(\theta)$ for the elastic waves propagating in the crystal. The calculated values of second-order and third-order elastic constants of Mn$_{78}$Pt$_{22}$ given in Table 2.2 in Section 2.4 of Chapter 2 and in Table 3.4 in Section 3.4 of Chapter 3 respectively are used to evaluate the generalised Grüneisen parameters $\gamma_j(\theta)$ for the acoustic modes from equations (5.25). The results of the wave velocities obtained from equation (5.23) and the generalised Grüneisen parameters for elastic waves propagating at different angles $\theta$ in Mn$_{78}$Pt$_{22}$ obtained are given in Table 5.3. The low temperature limits $\gamma_L$ is obtained from equations (5.27) by numerical integration procedure using the data given in Table 5.3. Since the solid angle of the cone of semi-vertical angle is proportional to $\sin \theta$, the values of $\gamma_j X_j^{-\gamma_j}$ has been multiplied by $\sin \theta$ and have been summed over all values of $\theta$. Thus the low temperature limits $\gamma_L$ has been evaluated for Mn$_{78}$Pt$_{22}$ using equations (5.27) and are presented in Table 5.4. The elastic compliances $S_y$ and isothermal compressibility $\chi_{iso}$ for Mn$_{78}$Pt$_{22}$ is calculated using equation (5.30). The values of $S_{11}$, $S_{12}$, $\chi_{iso}$, and $\gamma_L$ are substituted in equation (5.29) to obtain the Brugger gamma $\gamma^{Br}$. The value of Brugger
gamma thus obtained for Mn\(_{78}\)Pt\(_{22}\) is given in Table 5.4. The low
temperature volume lattice thermal expansion \(\gamma_L\) for Mn\(_{78}\)Pt\(_{22}\) is obtained
from equation (5.31) by substituting the value of Brugger gamma \(\gamma^{Br}\)
given in Table 5.4. The value of \(\gamma_L\) thus obtained is presented in Table
5.4 along with the calculated value of Saunders et al. (40).

Table 5.3 Generalised Grüneisen parameter for elastic waves propagating at
different angles \(\theta\) to the crystal axis in the Mn\(_{78}\)Pt\(_{22}\) system

<table>
<thead>
<tr>
<th>(\theta)</th>
<th>(\gamma_1)</th>
<th>(\rho_0v_1^2)</th>
<th>(\gamma_2)</th>
<th>(\rho_0v_2^2)</th>
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Table 5.4 The values of the Grüneisen parameters $\gamma^B$ and $\gamma_L$ for Mn$_{78}$Pt$_{22}$

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<tr>
<th>$\gamma^B$</th>
<th>$\gamma_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>Present work</td>
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<tr>
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</table>

The variation of the generalised Grüneisen parameters $\gamma_i(\theta)$ at different angles $\theta$ for the crystal Mn$_{78}$Pt$_{22}$ are shown in Figure 5.2.

Fig. 5.3 Variation of the generalised Grüneisen parameters $\gamma_i(\theta)$ as a function of angle $\theta$ of the Mn$_{78}$Pt$_{22}$ system.
The variation of $\rho_0 V^2$ for different angles $\theta$ to the alloy Mn$_{78}$Pt$_{22}$ are shown in Fig. 5.4.

Fig. 5.4 Variation of $\rho_0 V^2$ as a function of the angles $\theta$ for Mn$_{78}$Pt$_{22}$. 
5.5 Low Temperature Limit of the Lattice Thermal Expansion of Fe$_{72}$Pt$_{28}$

The low temperature limit of the lattice thermal expansion in Fe$_{72}$Pt$_{28}$ depends on the generalised Grüneisen parameters for the acoustic modes propagating in the crystal. The calculated values of second-order and third-order elastic constants of Fe$_{72}$Pt$_{28}$ given in Table 2.3 in Section 2.5 of Chapter 2 and in Table 3.6 in Section 3.5 of Chapter 3 respectively are used to evaluate the generalised Grüneisen parameters $\gamma_j(\theta)$ for the acoustic modes using equation (5.25). The values of wave velocities obtained from equation (5.23) and the generalised Grüneisen parameters for elastic waves propagating at different angles $\theta$ in Fe$_{72}$Pt$_{28}$ obtained are given in Table 5.5. The low temperature limit $\gamma_L$ is determined by numerical integration procedure using the data given in Table 5.5 from equation (5.26). Since the solid angle of the cone of semi-vertical angle is proportional to $\sin \theta$, the value of $\gamma_j X_j X'_j$ has been multiplied by $\sin \theta$ and is summed over all values of $\theta$. Thus the low temperature limit $\gamma_L$ has been evaluated for Fe$_{72}$Pt$_{28}$ using equations (5.27) and is given in Table 5.6. The calculated values of elastic compliances $S_{11}$ and $S_{12}$ and the isothermal compressibility $\chi_{iso}$ from equation (5.30) are substituted in equation (5.29) to get the Brugger gamma $\gamma^{br}_L$. The value of Brugger gamma $\gamma^{br}_L$ thus obtained for Fe$_{72}$Pt$_{28}$ is presented in Table 5.6. The low temperature volume lattice thermal expansion $\gamma_L$ for Fe$_{72}$Pt$_{28}$ is obtained
from equation (5.31) by substituting the values of Brugger gamma $\gamma_f^*$ given in Table 5.6. The value of $\gamma_L$ thus obtained is given in Table 5.6, along with available experimental results.

**Table 5.5** Generalized Grüneisen parameter for elastic waves propagating at different angles $\theta$ to the crystal axis in the Fe$_{23}$Pt$_{38}$ system

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\gamma_1$</th>
<th>$\rho_0v_1^2$</th>
<th>$\gamma_2$</th>
<th>$\rho_0v_2^2$</th>
<th>$\gamma_3$</th>
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<tbody>
<tr>
<td>0</td>
<td>-6.02</td>
<td>144.0</td>
<td>-6.76</td>
<td>59.5</td>
<td>5.63</td>
<td>59.5</td>
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<td>59.5</td>
<td>5.62</td>
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<td>148.9</td>
<td>-5.61</td>
<td>59.5</td>
<td>5.57</td>
<td>54.6</td>
</tr>
<tr>
<td>25</td>
<td>-6.11</td>
<td>154.8</td>
<td>-4.07</td>
<td>59.5</td>
<td>5.51</td>
<td>48.7</td>
</tr>
<tr>
<td>35</td>
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<td>159.5</td>
<td>-2.72</td>
<td>59.5</td>
<td>5.47</td>
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<td>45</td>
<td>-6.15</td>
<td>161.2</td>
<td>-2.19</td>
<td>59.5</td>
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<td>55</td>
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<td>159.5</td>
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<td>-6.76</td>
<td>59.5</td>
<td>5.63</td>
<td>59.5</td>
</tr>
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</table>
Table 5.6  The values of the Grüneisen parameters $\gamma^{Br}$ and $\gamma_L$ for Fe$_{72}$Pt$_{28}$

<table>
<thead>
<tr>
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<th>$\gamma^{Br}$</th>
<th>$\gamma_L$</th>
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</thead>
<tbody>
<tr>
<td>Present work</td>
<td>-0.19</td>
<td>-0.57</td>
</tr>
<tr>
<td>Present work</td>
<td></td>
<td>-0.6</td>
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<tr>
<td>Manosa et. al. (37)</td>
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</tbody>
</table>

The variation of the Generalised Grüneisen parameters $\gamma_j(\theta)$ at different angles $\theta$ for the crystal Fe$_{72}$Pt$_{28}$ are shown in Figure 5.3.

**Fig. 5.5**  Variation of the generalised Grüneisen parameters $\gamma_j(\theta)$ as a function of angle $\theta$ of the Fe$_{72}$Pt$_{28}$ system
The variation of $\rho_0V^2$ at different angles $\theta$ for the alloy Fe$_{72}$Pt$_{28}$ is shown in Fig. 5.6.

Fig. 5.6  Variation of $\rho_0V^2$ as a function of angle $\theta$ for Fe$_{72}$Pt$_{28}$. 
5.6 Results and Discussion

The low temperature limit of the Grüneisen parameters obtained in the present work for the cubic compounds $C_{60}$, $Mn_{78}Pt_{22}$ and $Fe_{72}Pt_{28}$ have been compared with available experimental results. An important feature of the Grüneisen parameter in $C_{60}$ is that all the mode gammas are positive. Figure 5.1 shows the variation of generalised Grüneisen parameters $\gamma_i(\theta)$ as a function of angle $\theta$ for $C_{60}$. The acoustic mode of Grüneisen parameter $\gamma_1$ assumes a minimum value of 3.32 at both angles $\theta = 0^\circ$ and $90^\circ$. It has a maximum value of 3.43 at $\theta = 45^\circ$. While the acoustic mode $\gamma_2$ assumes a minimum value of 0.54, at $\theta = 45^\circ$ and a maximum value of 3.35 at both the angles $\theta = 0$ and $90^\circ$. 3.35 is the maximum value of $\gamma_3$ obtained both at $\theta = 0$ and $90^\circ$ and has a minimum of 2.95 obtained at $\theta = 45^\circ$. It is seen that the transverse acoustic modes and longitudinal acoustic modes are equal in the case of this cubic crystal $C_{60}$.

Rao and Venkatesh (6) have estimated the Grüneisen parameter using the elastic constants of $C_{60}$. Rao and Venkatesh (6) also calculated the second Grüneisen parameters $\gamma_L$ as 3.3, which is given in Table 5.2. White et. al. (9) calculated the over all Grüneisen parameter as 3, using the relationship between the frequency of the mode $\omega$ and the volume $V$, using the relation

$$\gamma = -\frac{\partial \log \omega}{\partial \log V}.$$  

The result obtained in the present work for the low
temperature limit of lattice thermal expansion for cubic $C_{60}$ is $\gamma_L = 2.8$, which is in good agreement with the results obtained by Rao and Venkatesh (6) and White et al. (9). For $C_{60}$ we observe that at low temperatures the $C_{60}$ molecules show a high degree of anharmonicity. This causes the deviation in $\gamma_L$ from zero and can be interpreted as a direct measure of the anharmonicity. The high degree of anharmonicity in $C_{60}$ shows that $C_{60}$ molecules have an incompressible hard core.

Fig. 5.3 shows the variation of generalised Grüneisen parameters $\gamma_j(\theta)$ as a function of $\theta$ for the cubic crystal $\text{Mn}_7\text{Pt}_{22}$. The acoustic mode $\gamma_1$ assumes a minimum value of 5.19 both at the angles $\theta = 0^\circ$ and $90^\circ$ and a maximum value of 5.51 at $\theta = 45^\circ$. While $\gamma_2$ has a maximum value of 4.3 which occurs both at the angles $\theta = 0^\circ$ and $90^\circ$. $-0.72$ is the minimum value of $\gamma_2$ in the antiferromagnetic alloy $\text{Mn}_7\text{Pt}_{22}$ at an angle $\theta = 45^\circ$. The acoustic modes of $\gamma_3$ of the cubic crystal $\text{Mn}_7\text{Pt}_{22}$ are negative. The minimum value of $\gamma_3$ for $\text{Mn}_7\text{Pt}_{22}$ is $-4.3$ which occurs at both the angles $0^\circ$ and $90^\circ$ and a maximum value $-2.71$ which occurs at $45^\circ$. The negative value of the mode $\gamma_1$ shows negative thermal expansion of the invar compound $\text{Mn}_7\text{Pt}_{22}$.

Saunders et al. (40) obtained the Grüneisen parameter $\gamma_L$ of the antiferromagnetic cubic alloy $\text{Mn}_7\text{Pt}_{22}$ as 1.35. The low temperature limit of
the Grüneisen parameter $\gamma$, in the present work is 1.5, which agrees with the results obtained by Saunders et. al. (40).

Fig. 5.5 gives the plot of the variation of generalised Grüneisen parameters $\gamma_i (\theta)$ as a function of $\theta$ for the ferromagnetic alloy Fe$_{72}$Pt$_{28}$. The value of the acoustic mode $\gamma_1$ attains a minimum value of $-6.15$ at $\theta = 45^0$ and a maximum value is $-6.02$ both at $\theta = 0^0$ and $90^0$. The acoustic mode $\gamma_2$ of the cubic Fe$_{72}$Pt$_{28}$ also has a minimum value $-6.76$ which occurs at $\theta = 0^0$ and $90^0$ and a maximum value $-2.19$ which occurs at $45^0$. The negative values of the acoustic modes of the cubic compound Fe$_{72}$Pt$_{28}$ predicts a negative thermal expansion for this compound. The maximum value of $\gamma_1$ of Fe$_{72}$Pt$_{28}$ is $5.63$ which occurs at both at $\theta = 0^0$ and $90^0$. While the minimum value is $5.45$ that occur at angle $45^0$. Manosa et. al. (37) have determined the acoustic mode Grüneisen parameter for the ferromagnetic invar alloy Fe$_{72}$Pt$_{28}$ as $-0.60$. The present value of the low temperature lattice thermal expansion of Fe$_{72}$Pt$_{28}$ is $-0.57$.

The Grüneisen parameter plays a significant role in the studies of the contributions of the lattice vibrations since it is a measure of the vibrational anharmonicity. The value of the Grüneisen parameter for C$_{60}$ and Mn$_{78}$Pt$_{22}$ are positive, while the corresponding value for Fe$_{72}$Pt$_{28}$ is negative.
References


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