Chapter 2

Theory of higher order elastic constants and low temperature lattice thermal expansion

2.1 Introduction

Evidence of nonlinear elastic behaviour in a number of solids has been established in recent years by direct and indirect measurements, namely stress-strain curves showing strong deviations from Hooke’s law [1], development of higher-order harmonics in finite-amplitude wave propagating through a medium [2], and variation in ultrasonic transmission velocities with applied stress [3, 4]. In the equation of state of the solids, nonlinear elastic effects are characterized by the third and higher order elastic constants [5–9]. Thus third order elastic constants (TOEC) have been used to describe many anharmonic properties of solids [10–13]. In particular, they have been related to some features of materials undergoing structural phase transition, such as pressure dependence of second order elastic constants (SOEC) [14–20]. Thus TOEC are indispensable in the finite strain
elasticity theory of Murnaghan [21] where the variation of elastic strain is nonlinear with elastic stress.

In this chapter an introduction to the finite strain elasticity theory of Murnaghan [21] is presented. The theory behind the method of calculating the full set of SOEC and TOEC is described. The expressions for the effective SOEC of hexagonal systems based on the finite strain elasticity theory in terms of the natural state SOEC and TOEC are obtained. The basic importance of these expressions is that they enable one to fix up the first-order anharmonic parameters in the potential energy expansion of a crystal in a lattice dynamical model which are useful to study the anharmonic properties such as thermal expansion. These expressions are utilized to obtain the first order pressure derivatives of the effective SOEC of hexagonal wurtzite CdS, CdSe, CdTe, AlN, GaN, InN and SiC single crystals. A procedure to obtain the mode Grüneisen parameters and the low temperature limits of the thermal expansion coefficients from the quasi-harmonic theory of thermal expansion is described in detail for uniaxial crystals. We give also an introduction to some of the ideas and theories that are fundamental to the calculations involved in this study.

### 2.2 An introduction to the finite strain elasticity theory

Three states of a crystal are involved in the finite strain elasticity theory proposed by Murnaghan [21]. They are the natural state also called the unstrained state, where the crystal is in its natural state and has no stress applied on it. The second state is the
initial state, where a finite stress (say a hydrostatic pressure) is applied on the crystal. The third state is the final state, where an infinitesimal strain is superimposed by applying an infinitesimal stress.

Consider an elastic medium where the co-ordinates of a point are denoted by \((a_1, a_2, a_3)\), the orthonormal vectors \(e_1', e_2', e_3'\) as the basis vectors of the co-ordinate system and the \(k^{th}\) component of the stress acting on the plane \(e_i = 0\) as \(\sigma_{ik}\) where \(i\) and \(k\) are the component indices. Consider the equilibrium of a small element centered at the point \(a_i\) and bounded by the plane \(a_i + (1/2)\delta a_i\). Let \(u_i\) denote the elastic displacement at the point \(a_i\) of the body and \(\rho\) the density of this point. The equation of volume element can be derived by considering the total force acting on the volume element. If the body forces are ignored, the equations of motion for an elastic solid can be written as (the convention that repeated indices indicate summation over the indices will be followed hereafter) \([22]\).

\[
\rho \ddot{u}_i = \frac{\partial \sigma_{ik}}{\partial a_k} \tag{2.1}
\]

where the stress tensor \(\sigma_{ik}\) is given by

\[
\sigma_{ik} = \frac{\partial \phi}{\partial \epsilon_{ik}} \tag{2.2}
\]
where $\phi$ is the crystal potential and $\epsilon_{ik}$ are the components of the strain tensor given by

$$
\epsilon_{ik} = \frac{1}{2} \left( \frac{\partial u_k}{\partial a_i} + \frac{\partial u_i}{\partial a_k} \right) \quad (2.3)
$$

$\sigma_{ik}$ and $\epsilon_{ik}$ are symmetric tensors of second rank. According to Hooke’s law

$$
\sigma_{ik} = C_{iklm} \epsilon_{lm} \quad (2.4)
$$

The constants $C_{iklm}$ form a fourth rank tensor with 81 components. From Eqs. 2.2 and 2.4, we have

$$
C_{iklm} = \frac{\partial \sigma_{ik}}{\partial \epsilon_{lm}} = \frac{\partial^2 \phi}{\partial \epsilon_{lm} \partial \epsilon_{ik}} = \frac{\partial^2 \phi}{\partial \epsilon_{ik} \partial \epsilon_{lm}} = C_{lmik} \quad (2.5)
$$

Hence the elastic constants $C_{iklm}$ are multiple strain derivatives of the state functions and since the strains $\epsilon_{lm}$ are symmetric, the elastic constants possess complete Voigt symmetry. Thus,

$$
C_{iklm} = C_{kilm} = C_{ikml} = C_{lmik} \quad (2.6)
$$

These quantities are symmetric with respect to interchange of the subscripts. It will
be convenient to abbreviate the double subscript notation to the single subscript Voigt notation running from 1 to 6, according to the following scheme:

\[ 11 \rightarrow 1; \quad 22 \rightarrow 2; \quad 33 \rightarrow 3; \quad 23 \rightarrow 4; \quad 13 \rightarrow 5; \quad \text{and} \quad 12 \rightarrow 6 \quad (2.7) \]

Hence the matrix of elastic constants \( C_{iklm} \), would contain a 6 x 6 array of 36 independent quantities in the most general case. This number is, however, reduced to 21 by the requirements that the matrices be symmetric on interchange of double indices [22, 23]. The number of independent elastic constants will be further reduced by the symmetry operations of the respective crystal classes. The hexagonal wurtzite semiconductor crystals CdS, CdSe, CdTe, AlN, GaN, InN and SiC belong to the hexagonal \( p\overline{6}_3mc \) class [24], which have six independent elastic constants. The elastic constant matrix for this class of compounds is given by:

\[
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66} \\
\end{pmatrix}
\tag{2.8}
\]

In the equation of motion for an elastic medium, the forces on an element of volume, are given by the divergence of the stress field. Using Eqs. 2.3 and 2.2, the Eq. 2.1
can be written as:

$$\rho \ddot{u}_i = \frac{\partial}{\partial a_j} \left\{ C_{ijkl} \left[ \left( \frac{\partial u_k}{\partial a_l} \right) + \left( \frac{\partial u_l}{\partial a_k} \right) \right] \right\}$$ (2.9)

For an elastic plane wave, we have

$$u_k = A_k \exp \left( i \omega t - \vec{k} \cdot \vec{a} \right)$$ (2.10)

where $A_k$ are the components of the amplitude of vibration, $\omega$ is the angular frequency and $\vec{k}$ is the wave vector corresponding to the wavelength $\lambda = \frac{2\pi}{\vec{k}}$.

The resulting equations of motion from Eq. 2.9 are:

$$\left( \rho \omega^2 \delta_{im} - C_{ijkl} k_j k_l \right) u_m = 0$$ (2.11)

substituting $\vec{k} = k \hat{n}$, where $\hat{n}$ is the unit vector, we get

$$\left( T_{ijkl} n_j n_l - v^2 \delta_{im} \right) u_m = 0$$ (2.12)

where $T_{ijkl} = C_{ijkl}/\rho$ are the reduced elastic constants and $v$ is the phase velocity given by $v = \omega/k$ and $\delta_{im}$ is the Kronecker delta. The components of second rank
tensor $\Lambda$ are given by

$$\Lambda = T_{ijkl}n_jn_l$$  \hspace{1cm} (2.13)

Hence Eq. 2.12 can be written as:

$$(\Lambda - v^2) u = 0$$  \hspace{1cm} (2.14)

This shows that $u$ is the eigen vector of tensor $\Lambda$ where eigen value is $v^2$. Hence $v^2$ is the root of the equation:

$$|\Lambda - v^2| = 0$$  \hspace{1cm} (2.15)

This is the Christoffel equation. The theory of elastic waves generally reduces to finding $u$ and $v$ for all plane waves propagating in an arbitrary direction for crystals possessing different symmetries. Here, all terms in Eq. 2.12 that involve differentiation with respect to co-ordinates other than that along the propagation direction cancel out. An important fact is that the elastic constants appears as the second derivatives of elastic energy with respect to strains. Again, the stored elastic energy is only a part of the complete thermodynamic potential of the crystal, since it depends on many other variables. Also, one can introduce elastic constants as a constitutive, local relation between stress and strain for materials in which
long-range atomic forces are not important.

2.3 Calculation of the second and third order elastic constants by the method of homogeneous deformation

When a crystal undergoes deformation, the elastic energy between the particles is stored as potential energy, called the strain energy. The potential energy $\phi$ of the crystal is presumed to be an analytical function of position of the atoms due to interactions among them in a given configuration. The potential energy per unit cell $\phi$ can be expanded using Taylor expansion involving displacements $R_i$ as:

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \cdots$$  \hspace{1cm} (2.16)

where $\phi_0$ is the static potential energy of the crystal which is a constant and

$$\phi_1 = \sum_{I,\mu} \phi_i \left( \begin{array}{c} I \\ \mu \end{array} \right) R_i \left( \begin{array}{c} I \\ \mu \end{array} \right)$$  \hspace{1cm} (2.17)
where \( R_i \left( \begin{array}{c} I \\ \mu \end{array} \right) \) is the i-cartesian component of \( R \left( \begin{array}{c} I \\ \mu \end{array} \right) \), and \( R \left( \begin{array}{c} I \\ \mu \end{array} \right) \) is the displacement of the \( \mu^{th} \) atom in the \( I^{th} \) unit cell.

\[
\phi_i \left( \begin{array}{c} I' \\ \mu \end{array} \right) = \left[ \frac{\partial \phi}{\partial R_i(I_{\mu})} \right]_0
\] (2.18)

\[
\phi_2 = \frac{1}{2!} \sum_{I, \mu} \phi_{ij} \left( \begin{array}{c} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_i \left( \begin{array}{c} I \\ \mu \end{array} \right) R_j \left( \begin{array}{c} I' \\ \mu' \end{array} \right)
\] (2.19)

where \( R \left( \begin{array}{c} I' \\ \mu' \end{array} \right) \) is the displacement of the \( \mu'^{th} \) atom in the \( I'^{th} \) cell. The subscript zero means that the derivatives have to be evaluated in the equilibrium configuration. Here \( \phi \) holds both the translational symmetry of the lattice and the conditions of atomic equilibrium.

\[
\phi_{ij} \left( \begin{array}{c} I \\ \mu \\ I' \\ \mu' \end{array} \right) = \left[ \frac{\partial^2 \phi}{\partial R_i(I_{\mu}) \partial R_j(I'_{\mu'})} \right]_0
\] (2.20)

\( \phi_3 \) is a homogeneous function of third degree in strains which involves coefficients of the type \( C_{ijk} \) in Voigts’ notation as third order elastic constants. In the case of hexagonal wurtzite symmetry with space group P6_3mc, there are ten independent
third order elastic constants.

\[ \phi_3 = \frac{1}{3!} \sum_{I, \mu} \phi_{ijk} \left( \begin{array}{ccc} I & I' & I'' \\ \mu & \mu' & \mu'' \end{array} \right) R_i \left( \begin{array}{c} I \\ \mu \end{array} \right) R_j \left( \begin{array}{c} I' \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I'' \\ \mu'' \end{array} \right) \] (2.21)

\[ \phi_{ijk} \left( \begin{array}{ccc} I & I' & I'' \\ \mu & \mu' & \mu'' \end{array} \right) = \left[ \frac{\partial^3 \phi}{\partial R_i^{(I)}(\mu) \partial R_j^{(I')}(\mu') \partial R_k^{(I'')}(\mu'')} \right]_0 \] (2.22)

Here \( R \left( \begin{array}{c} I'' \\ \mu'' \end{array} \right) \) is the displacement of the \( \mu'' \)th atom in the \( I'' \)th cell. The subscript zero in Eq. 2.20 and Eq. 2.22 means that the derivatives have to be evaluated in the equilibrium configuration. Under equilibrium conditions, the contribution to the potential energy per unit cell is only from \( \phi_2 \) and \( \phi_3 \), which are the second- and third order terms, as \( \phi_1 = 0 \) at equilibrium. Therefore the change in potential energy is:

\[ \Delta \phi = \phi - \phi_0 = k_2 \sum \left[ \Delta R^2 \left( \begin{array}{cc} I & I' \\ \mu & \mu' \end{array} \right) \right]^2 + k_3 \sum \left[ \Delta R^2 \left( \begin{array}{cc} I & I' \\ \mu & \mu' \end{array} \right) \right]^3 \] (2.23)

where, \( k_2 = \frac{1}{2} \sum_{I, \mu, I', \mu'} \phi_{ij} \left( \begin{array}{cc} I & I' \\ \mu & \mu' \end{array} \right) \) (2.24)
is the second order parameter characterising the two body interactions between pair of atoms \( (\mu) \) and \( (\mu') \) and

\[ k_3 = \frac{1}{6} \sum \phi_{ijk} \begin{pmatrix} I & I' & I'' \\ \mu & \mu' & \mu'' \end{pmatrix} \tag{2.25} \]

is the corresponding third order parameter.

Also, \( \Delta R \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} = R' \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} - R \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} \tag{2.26} \)

where \( R \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} \) is the vector distance between atom \( \mu \) in the cell \( I \) and atom \( \mu' \) in the cell \( I' \) in the unstrained state. \( R' \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} \) refers to the corresponding vector distance in the strained state. Thus when a lattice is homogeneously deformed, the components of the inter atomic vectors are transformed as

\[ R_i' \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} = R_i \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} + \sum_j \epsilon_{ij} R_j \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} \tag{2.27} \]

\[ + w_i \left( 1 - \delta_{\mu \mu'} \right) \]
\( \epsilon_{ij} \) is the deformation parameter related to the macroscopic Lagrangian strains \( \eta_{ij} \) by

\[
2\eta_{ij} = \epsilon_{ij} + \epsilon_{ji} + \sum_{k=1}^{3} \epsilon_{ik}\epsilon_{kj}
\]  
(2.28)

\( w_i \) are the components of the internal displacement of the sublattice \( \mu \) relative to the sublattice \( \mu' \), and can be replaced by the relative internal displacement \( \bar{w}_i \),

\[
\bar{w}_i(\mu, \mu') = w_i(\mu, \mu') + \sum_j \epsilon_{ij}w_j(\mu, \mu')
\]  
(2.29)

In terms of Lagrangian strains \( \eta_{ij} \) and internal displacements \( \bar{w}_i(\mu, \mu') \) the energy is invariant towards rigid rotations of the lattice. By minimizing the strain energy with respect to the internal displacements, we obtain \( \bar{w}_i(\mu, \mu') \) in terms of the Lagrangian strain parameters to the first order in \( \eta_{ij} \) as,

\[
\bar{w}_i(\mu, \mu') = -4k_2 \sum_{jkl} \eta_{jl}D_{jkl}M_{ik}^{-1}
\]  
(2.30)
where $M_{ik}^{-1}$ is the inverse of the matrix $M_{ik}$

\[
M_{ik} = \begin{bmatrix}
M_{xx} & M_{xy} & M_{xz} \\
M_{yx} & M_{yy} & M_{yz} \\
M_{zx} & M_{zy} & M_{zz}
\end{bmatrix}
\]

(2.31a)

\[
= 4k^2 \sum_{I, I'} R_i \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} R_k \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix}
\]

(2.31b)

and

\[
[D_{jkl}] = \sum_{I, I', I''} R_j \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} R_k \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix} R_l \begin{pmatrix} I & I' \\ \mu & \mu' \end{pmatrix}
\]

(2.32)

Eq. 2.30 on expansion and simplification becomes:

\[
\bar{w}_i (\mu, \mu') = -4k^2 \left[ \eta_{xx} \left( D_{xxx} M_{zi}^{-1} + D_{xyy} M_{yi}^{-1} + D_{xxz} M_{zi}^{-1} \right) + \right.
\]

\[
\eta_{yy} \left( D_{gyy} M_{yi}^{-1} + D_{gyy} M_{yi}^{-1} + D_{yyz} M_{zi}^{-1} \right) + \right.
\]

\[
\eta_{zz} \left( D_{zzz} M_{zi}^{-1} + D_{zzz} M_{zi}^{-1} + D_{zzz} M_{zi}^{-1} \right) + \right.
\]

\[
2\eta_{xy} \left( D_{xyy} M_{yi}^{-1} + D_{yyx} M_{yi}^{-1} + D_{xyz} M_{zi}^{-1} \right) + \right.
\]

\[
2\eta_{yz} \left( D_{xyz} M_{zi}^{-1} + D_{xyz} M_{zi}^{-1} + D_{yzz} M_{zi}^{-1} \right) + \right.
\]

\[
2\eta_{xz} \left( D_{xyz} M_{zi}^{-1} + D_{xyz} M_{zi}^{-1} + D_{yzz} M_{zi}^{-1} \right) \]

(2.33)
\[ \bar{w}_x (\mu, \mu') = -4k_2 \left[ \eta_{xx} \left( D_{xxx}M_{xx}^{-1} + D_{xxy}M_{yx}^{-1} + D_{xxz}M_{zx}^{-1} \right) \right. \\
\left. + \eta_{yy} \left( D_{yyy}M_{yx}^{-1} + D_{ygy}M_{gy}^{-1} + D_{ygz}M_{gz}^{-1} \right) + \eta_{zz} \left( D_{zzz}M_{zx}^{-1} + D_{zzy}M_{zy}^{-1} + D_{zzg}M_{gz}^{-1} \right) + 2\eta_{xy} \left( D_{xxy}M_{yx}^{-1} + D_{yyx}M_{yy}^{-1} + D_{xyz}M_{zy}^{-1} \right) + 2\eta_{xz} \left( D_{xxz}M_{zx}^{-1} + D_{zzx}M_{zx}^{-1} + D_{zzg}M_{gz}^{-1} \right) + 2\eta_{yz} \left( D_{yzy}M_{zy}^{-1} + D_{yyz}M_{yz}^{-1} + D_{yzz}M_{yz}^{-1} \right) \right] \tag{2.34} \]

\[ \bar{w}_y (\mu, \mu') = -4k_2 \left[ \eta_{xx} \left( D_{xxx}M_{xy}^{-1} + D_{xxy}M_{yx}^{-1} + D_{xxz}M_{zy}^{-1} \right) \right. \\
\left. + \eta_{yy} \left( D_{yyy}M_{yx}^{-1} + D_{ygy}M_{gy}^{-1} + D_{ygz}M_{gy}^{-1} \right) + \eta_{zz} \left( D_{zzz}M_{zy}^{-1} + D_{zzy}M_{zy}^{-1} + D_{zzg}M_{gz}^{-1} \right) + 2\eta_{xy} \left( D_{xxy}M_{yx}^{-1} + D_{yyx}M_{yy}^{-1} + D_{xyz}M_{zy}^{-1} \right) + 2\eta_{xz} \left( D_{xxz}M_{zy}^{-1} + D_{zzx}M_{zy}^{-1} + D_{zzg}M_{gz}^{-1} \right) + 2\eta_{yz} \left( D_{yzy}M_{zy}^{-1} + D_{yyz}M_{yz}^{-1} + D_{yzz}M_{yz}^{-1} \right) \right] \tag{2.35} \]

\[ \bar{w}_z (\mu, \mu') = -4k_2 \left[ \eta_{xx} \left( D_{xxx}M_{xz}^{-1} + D_{xxy}M_{yz}^{-1} + D_{xxz}M_{zz}^{-1} \right) \right. \\
\left. + \eta_{yy} \left( D_{yyy}M_{yz}^{-1} + D_{ygy}M_{yz}^{-1} + D_{ygz}M_{gy}^{-1} \right) + \eta_{zz} \left( D_{zzz}M_{zz}^{-1} + D_{zzy}M_{zy}^{-1} + D_{zzg}M_{gz}^{-1} \right) + 2\eta_{xy} \left( D_{xxy}M_{yx}^{-1} + D_{yyx}M_{yy}^{-1} + D_{xyz}M_{zy}^{-1} \right) + 2\eta_{xz} \left( D_{xxz}M_{zy}^{-1} + D_{zzx}M_{zy}^{-1} + D_{zzg}M_{gz}^{-1} \right) \right] \]
\[
\begin{align*}
\eta_{xz} \left( D_{xxz} M_{xx}^{-1} + D_{gxx} M_{yz}^{-1} + D_{xzz} M_{zz}^{-1} \right) \\
\eta_{yz} \left( D_{xyz} M_{xx}^{-1} + D_{gyz} M_{yz}^{-1} + D_{yzz} M_{zz}^{-1} \right)
\end{align*}
\]

(2.36)

The evaluation has been done for the four nearest neighbours of to obtain \( \bar{w}_x (\mu, \mu') \), \( \bar{w}_y (\mu, \mu') \) and \( \bar{w}_z (\mu, \mu') \). Substituting for \( \Delta R \left( \begin{array}{c} I \\ I' \\ \mu \\ \mu' \end{array} \right) \) from Eq. 2.27, in Eq. 2.23, and making use of Eqs. 2.28, 2.29, 2.30, 2.31, 2.32, 2.33, 2.34, 2.35, 2.36 we get:

\[
\Delta \phi = 4k_2 \sum_{I, I'} \sum_{\mu, \mu'} \left[ \sum_{ijkl} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_j \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_k \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_l \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) \eta_{ij} \eta_{kl} \\
+ \sum_{ij} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_j \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) \bar{w}_ix \left( \mu, \mu' \right) \bar{w}_j \left( \mu, \mu' \right) \\
+ 2 \sum_{ijk} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_j \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_k \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) \bar{w}_k \left( \mu, \mu' \right) \eta_{ij} \\
+ \sum_{ij} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_j \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) \bar{w}_2^2 \left( \mu, \mu' \right) \eta_{ij} \\
+ \sum_{ij} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \bar{w}_2^2 \left( \mu, \mu' \right) \right] \\
+ 8k_3 \sum_{I, I'} 5 \sum_{ijklmn} R_i \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right) R_j \left( \begin{array}{cc} I \\ \mu \\ I' \\ \mu' \end{array} \right)
\]

\]
\[ R_k \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_l \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) R_m \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_n \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) \eta_{ij} \eta_{kl} \eta_{mn} \]

\[ + \sum_{ijk} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \bar{w}_j \left( \mu, \mu' \right) \]

\[ \bar{w}_k \left( \mu, \mu' \right) + 3 \sum_{ijklm} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) R_l \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) \eta_{kl} \]

\[ R_j \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) R_m \left( \begin{array}{c} I' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \]

\[ \bar{w}_j \left( \mu, \mu' \right) \eta_{kl} + 3 \sum_{ijklmn} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \\ \mu \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \]

\[ \bar{w}_j \left( \mu, \mu' \right) \eta_{kl} + 3 \sum_{ijklmn} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \]

\[ R_j \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) R_m \left( \begin{array}{c} I' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \]

\[ \bar{w}_j \left( \mu, \mu' \right) \bar{w}_m \left( \mu, \mu' \right) \eta_{ij} \eta_{kl} + 3 \sum_{ijklmn} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) \bar{w}_i \left( \mu, \mu' \right) \]

\[ \bar{w}_j \left( \mu, \mu' \right) \bar{w}_m \left( \mu, \mu' \right) + 3 \sum_{ijkl} R_i \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) R_j \left( \begin{array}{c} I' \end{array} \right) R_k \left( \begin{array}{c} I' \end{array} \right) R_l \left( \begin{array}{c} I' \end{array} \right) \]

\[ R_k \left( \begin{array}{c} I \\ \mu \\ \mu' \end{array} \right) \bar{w}_k \left( \mu, \mu' \right) \bar{w}_i \left( \mu, \mu' \right) \eta_{ij} \]

\[ (2.37) \]
\[
= 4k_2 \sum_{\mu, \mu'} \left\{ R_x^4 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{xx}^2 + R_y^4 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{yy}^2 + R_z^4 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{zz}^2 \right. \\
+ 2 \left[ R_x^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{xx} \eta_{yy} + R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_z^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{yy} \eta_{zz} \right] \\
+ R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_z^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{yy}^2 + 4 \left[ R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_z^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \eta_{xy}^2 \right] \\
+ R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_z^2 \left( \mu, \mu' \right) + R_y^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_x^2 \left( \mu, \mu' \right) + R_z^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \right. \\
\bar{w}_x^2 \left( \mu, \mu' \right) + 2 \left[ R_x \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_y \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_x \left( \mu, \mu' \right) \bar{w}_y \left( \mu, \mu' \right) \right. \\
+ R_x \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_z \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_x \left( \mu, \mu' \right) \bar{w}_z \left( \mu, \mu' \right) + R_y \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \right. \\
+ R_x \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_y \left( \mu, \mu' \right) \bar{w}_z \left( \mu, \mu' \right) + R_x^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_z \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) \bar{w}_y \left( \mu, \mu' \right) \bar{w}_z \left( \mu, \mu' \right) + R_x^2 \left( \frac{I}{\mu} \frac{I'}{\mu'} \right) R_x \left( \frac{I}{\mu} \frac{I'}{\mu'} \right)
\[\bar{w}_z(\mu, \mu') \eta_{xx} + R_y^2(\mu, \mu') R_z(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{yy} \]

\[+ R_z(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{xx} + 4 R_x(\mu, \mu') R_y(\mu, \mu') \]

\[R_z(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{xy} + R_x(\mu, \mu') R_z^2(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{xz}\]

\[+ R_y(\mu, \mu') R_z^2(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{yz} + \left[ \bar{w}_x^2(\mu, \mu') \right] \]

\[+ 2 \bar{w}_x(\mu, \mu') \bar{w}_y(\mu, \mu') + 2 \bar{w}_x(\mu, \mu') \bar{w}_z(\mu, \mu') + \bar{w}_y^2(\mu, \mu') \]

\[+ 2 \bar{w}_y(\mu, \mu') \bar{w}_x(\mu, \mu') + \bar{w}_y^2(\mu, \mu') \left[ R_x(\mu, \mu') \bar{w}_z(\mu, \mu') \right] \]

\[+ R_y(\mu, \mu') \bar{w}_y(\mu, \mu') + \bar{w}_z(\mu, \mu') \bar{w}_y(\mu, \mu') \left[ R_x(\mu, \mu') \bar{w}_z(\mu, \mu') \right] + \bar{w}_x^2(\mu, \mu') \]

\[+ 2 \bar{w}_x(\mu, \mu') \bar{w}_y(\mu, \mu') + 2 \bar{w}_x(\mu, \mu') \bar{w}_z(\mu, \mu') + \bar{w}_y^2(\mu, \mu') \]

\[+ 2 \bar{w}_y(\mu, \mu') \bar{w}_z(\mu, \mu') + \bar{w}_y^2(\mu, \mu') \left[ R^2_x(\mu, \mu') \eta_{xx} \right] \]
\[\begin{align*}
+ & 2R_x \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{xy} + 2R_x \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_z \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{xz} \\
+ & R_y \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{yy} + 2R_y \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_z \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{yz} + R_y \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{zz} \\
+ & 8k_3 \left\{ R_x^6 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{xx}^3 + R_y^6 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{yy}^3 + R_z^6 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \eta_{zz}^3 \right\} \\
+ & 3 \left[ R_x^4 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \left( \eta_{xx}^2 \eta_{yy} + 4\eta_{xx} \eta_{yy}^2 \right) \right] \\
+ & 3 \left[ R_x^4 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \left( \eta_{xx}^2 \eta_{zy} + 2/3 \eta_{xx} \eta_{zy} + 4\eta_{xx} \eta_{zz}^2 \right) \right] \\
+ & 3 \left[ R_x^4 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \left( \eta_{xx} \eta_{yy}^2 + 4\eta_{yy} \eta_{zy}^2 \right) \right] \\
+ & 6 \left[ R_x^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_z^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \right] \left( \eta_{xx} \eta_{yy} \eta_{zz} + 2\eta_{xx} \eta_{yz}^2 \right) \\
+ & 2\eta_{zz} \eta_{xy}^2 + 8\eta_{xy} \eta_{xz} \eta_{yz} + 2\eta_{yy} \eta_{zx}^2 \right) + 3 \left[ R_x^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) R_y^2 \left( I_{\mu \mu'} I'_{\mu \mu'} \right) \right]
\end{align*}\]
\[
\left( \eta_{xx} \eta_{zz}^2 + 4 \eta_{zz} \eta_{xz}^2 \right) + 3 \left[ R_y^4 \left( I_{\mu}^I \mu' \right) R_z^2 \left( I_{\mu}^I \mu' \right) \right]
\]

\[
\left( \eta_{yy} \eta_{zz}^2 + 4 \eta_{yy} \eta_{yz}^2 \right) + 2 \left[ R_y^2 \left( I_{\mu}^I \mu' \right) R_z^2 \left( I_{\mu}^I \mu' \right) \right]
\]

\[
\left( 6 \eta_{zz} \eta_{yz}^2 + \eta_{zz} \eta_{yy} \right) + R_x^3 \left( I_{\mu}^I \mu' \right) \bar{w}_x^3 \left( \mu, \mu' \right) + R_y^3 \left( I_{\mu}^I \mu' \right)
\]

\[
\bar{w}_y^3 \left( \mu, \mu' \right) + R_z^3 \left( I_{\mu}^I \mu' \right) \bar{w}_z^3 \left( \mu, \mu' \right) + 3 R_x^2 \left( I_{\mu}^I \mu' \right) \left[ R_y \left( I_{\mu}^I \mu' \right) \right]
\]

\[
\bar{w}_x^2 \left( \mu, \mu' \right) \bar{w}_y \left( \mu, \mu' \right) + R_z \left( I_{\mu}^I \mu' \right) \bar{w}_x^2 \left( I_{\mu}^I \mu' \right) \bar{w}_z \left( I_{\mu}^I \mu' \right) \left[ 4 R_y \left( I_{\mu}^I \mu' \right) \right]
\]

\[
\bar{w}_y \left( \mu, \mu' \right) + 5 R_x \left( I_{\mu}^I \mu' \right) \bar{w}_z \left( \mu, \mu' \right) \left[ 3 R_x \left( I_{\mu}^I \mu' \right) R_z^2 \left( I_{\mu}^I \mu' \right) \right]
\]

\[
\bar{w}_x \left( \mu, \mu' \right) \bar{w}_y^2 \left( \mu, \mu' \right) + 3 R_y \left( I_{\mu}^I \mu' \right) R_z \left( I_{\mu}^I \mu' \right) \left[ R_y \left( I_{\mu}^I \mu' \right) \right]
\]
\[ \bar{w}_y^2(\mu, \mu') \bar{w}_z(\mu, \mu') + R_z(I_{\mu} I'_{\mu'}) \bar{w}_y(\mu, \mu') \bar{w}_z^2(\mu, \mu') \right] \}

\[ + 3R_3^2(I_{\mu} I'_{\mu'}) R_y^2(I_{\mu} I'_{\mu'}) \left[ \bar{w}_x(\mu, \mu') \left( 2\eta_{xy}^2 + 3\eta_{xy} \eta_{yy} + \eta_{xx} \eta_{yy} \right) \right] \]

\[ \bar{w}_y(\mu, \mu') \left( \eta_{xx} \eta_{yy} + 3\eta_{xy}^2 \right) + R_y^2(I_{\mu} I'_{\mu'}) \left[ \bar{w}_x(\mu, \mu') \left( 2\eta_{xy}^2 + 3\eta_{xy} \eta_{yy} + \eta_{xx} \eta_{yy} \right) \right] \]

\[ + R_x^2(I_{\mu} I'_{\mu'}) R_y^2(I_{\mu} I'_{\mu'}) \left[ \bar{w}_x(\mu, \mu') \left( 2\eta_{xy}^2 + \eta_{xx} \eta_{yy} \right) \right. \]

\[ + 2\eta_{xy} \eta_{yy} + 4\eta_{xy} \eta_{xz} + 2\eta_{xy} \eta_{yz} + \eta_{xz} \eta_{yy} \right) + \bar{w}_y(\mu, \mu') \left( 3\eta_{xy}^2 \right. \]

\[ + 2\eta_{xy} \eta_{xz} + 5\eta_{xy} \eta_{yz} + 2\eta_{yy} \eta_{xz} + \bar{w}_z(\mu, \mu') \left( 3\eta_{xy} \eta_{xz} + \eta_{xy} \eta_{yz} \right) \]

\[ + 2\eta_{yz} \eta_{xz} \right] + R_x^2(I_{\mu} I'_{\mu'}) R_z^2(I_{\mu} I'_{\mu'}) \left[ \bar{w}_x(\mu, \mu') \left( 2\eta_{xz}^2 + 2\eta_{xx} \eta_{xz} \right) \right. \]

\[ + \eta_{xx} \eta_{zz} \right) + \bar{w}_z(\mu, \mu') \left( \eta_{xx} \eta_{xz} + 2\eta_{xz}^2 + 3\eta_{xy} \eta_{zz} \right) \right] + R_y^2(I_{\mu} I'_{\mu'}) \]
\[ R_y \left( I \mu I' \mu' \right) R_z^2 \left( I \mu I' \mu' \right) \left[ \tilde{w}_x (\mu, \mu') \left( 2\eta^2_{xx} + 2\eta_{xx} \eta_{yz} + \eta_{xz} \eta_{zz} \right) \right. \]
\[ + 4\eta_{xy} \eta_{xz} + \eta_{xy} \eta_{zz} + 3\eta_{zz} \eta_{yz} \right) + \tilde{w}_y (\mu, \mu') \left( 2\eta_{xy} \eta_{xz} + \eta_{xy} \eta_{zz} \right) \]
\[ + 2\eta_{xx} \eta_{yz} + \tilde{w}_z (\mu, \mu') \left( 3\eta_{xy} \eta_{xz} + 2\eta^2_{xz} + 4\eta_{xz} \eta_{yz} + 4\eta_{xy} \eta_{zz} \right) \right] \]
\[ + R_z^2 \left( I \mu I' \mu' \right) R_z^3 \left( I \mu I' \mu' \right) \left[ \tilde{w}_x (\mu, \mu') \left( 3\eta_{xx} \eta_{xy} + 2\eta^2_{xz} + \eta_{xz} \eta_{zz} \right) \right] + R^4_x \left( I \mu I' \mu' \right) \]
\[ R_y \left( I \mu I' \mu' \right) \left[ \tilde{w}_x (\mu, \mu') \left( \eta^2_{xx} + 3\eta_{xx} \eta_{xy} + \eta_{xy} \eta_{zz} \right) + \tilde{w}_y (\mu, \mu') \eta_{xy} \eta_{zz} \right] \]
\[ + R_z^2 \left( I \mu I' \mu' \right) R_y \left( I \mu I' \mu' \right) R_z \left( I \mu I' \mu' \right) \left[ \tilde{w}_x (\mu, \mu') \left( 3\eta_{xx} \eta_{xy} + 3\eta_{xx} \eta_{xz} \right) \right. \]
\[ + 2\eta_{xx} \eta_{yz} + 4\eta_{xy} \eta_{xz} \right) + \tilde{w}_y (\mu, \mu') \left( \eta_{xy} \eta_{xz} + 2\eta_{xy} \eta_{zz} \right) + \tilde{w}_z (\mu, \mu') \left( \eta_{xx} \eta_{xz} + 3\eta_{xy} \eta_{xz} \right) \]
\[ + R_z^2 \left( I \mu I' \mu' \right) R_z \left( I \mu I' \mu' \right) \left[ \tilde{w}_x (\mu, \mu') \eta^2_{xx} \right. \]
\[ + 3\eta_{xx}\eta_{zz} + \bar{w}_x(\mu, \mu')\eta_{xx}\eta_{zz} \] 

\[ + R_x(I_\mu I'_\mu)R^z_g(I_\mu I'_\mu) \]

\[ \left[ \bar{w}_x(\mu, \mu')\eta_{yy}\eta_{xy} + \bar{w}_y(\mu, \mu')(3\eta_{xy}\eta_{yy} + \eta_{yy}^2) \right] + R_x(I_\mu I'_\mu) \]

\[ R^3_y(I_\mu I'_\mu)R_z(I_\mu I'_\mu) \left[ \bar{w}_x(\mu, \mu')(\eta_{xy}\eta_{yy} + 2\eta_{xy}\eta_{yz} + \eta_{xx}\eta_{yy}) \right] 

\[ + \bar{w}_y(\mu, \mu')(3\eta_{xy}\eta_{yy} + 5\eta_{xy}\eta_{yz} + 2\eta_{yy}\eta_{zz} + 3\eta_{yy}\eta_{yz}) \]

\[ + \bar{w}_z(\mu, \mu')(\eta_{xx}\eta_{yz} + 2\eta_{yz}\eta_{xy} + \eta_{yy}\eta_{yz}) \] 

\[ + R_y(I_\mu I'_\mu)R^2_g(I_\mu I'_\mu) \]

\[ R^2_z(I_\mu I'_\mu) \left[ \bar{w}_x(\mu, \mu')(2\eta_{xy}\eta_{yz} + \eta_{xx}\eta_{zz} + \eta_{xz}\eta_{yy} + 3\eta_{xx}\eta_{yz}) \right] \]

\[ + \bar{w}_y(\mu, \mu')(5\eta_{xy}\eta_{yz} + \eta_{xy}\eta_{zz} + 2\eta_{yy}\eta_{xx} + \eta_{yy}\eta_{zz} + 2\eta_{zz}\eta_{yy}) \]

\[ + 2\eta_{yz}^3 + \bar{w}_z(\mu, \mu')(\eta_{xz}\eta_{yy} + 4\eta_{zz}\eta_{yz} + 2\eta_{yz}\eta_{xy} + 2\eta_{yz}^2) \]

\[ + \eta_{zz}\eta_{yy} \right] + R_x(I_\mu I'_\mu)R_y(I_\mu I'_\mu)R^3_z(I_\mu I'_\mu) \left[ \bar{w}_x(\mu, \mu') \right. \]

\[ \left( \eta_{xy}\eta_{zz} + 3\eta_{xz}\eta_{yz} + \eta_{zz}\eta_{zz} \right) + \bar{w}_y(\mu, \mu')(\eta_{xy}\eta_{zz} + 2\eta_{xz}\eta_{yz} \]
\[ + \eta_{yz} \eta_{zz} \right] + \bar{w}_z(\mu, \mu') \left( 4\eta_{xz} \eta_{yz} + 3\eta_{xz} \eta_{zz} + 3\eta_{yz} \eta_{zz} \right) + R_x \left( I, I' \right) \]

\[ R_z^1 \left( I, I' \right) \bar{w}_x(\mu, \mu') \eta_{xx} \eta_{zz} + \bar{w}_z(\mu, \mu') \left( 3\eta_{xz} \eta_{zz} + \eta_{zz}^2 \right) \]

\[ R_z^1 \left( I, I' \right) R_z \left( I, I' \right) \bar{w}_x(\mu, \mu') \left( \eta_{yy}^2 + 3\eta_{yy} \eta_{yz} \right) + \bar{w}_z(\mu, \mu') \]

\[ \eta_{yy} \eta_{yz} \right] + R_y^3 \left( I, I' \right) R_z^2 \left( I, I' \right) \left[ \bar{w}_y(\mu, \mu') \left( 3\eta_{yy} \eta_{yz} + \eta_{xy} \eta_{yz} \right) \right] + R_y^2 \left( I, I' \right) \]

\[ R_z^2 \left( I, I' \right) \left[ \bar{w}_y(\mu, \mu') \left( \eta_{yy} \eta_{yz} + 2\eta_{yz}^2 + \eta_{yz} \eta_{xz} \right) + \bar{w}_z(\mu, \mu') \right] \]

\[ \left( 2\eta_{yz}^2 + 3\eta_{yz}^2 + \eta_{zz} \eta_{yy} \right) \right] + R_y \left( I, I' \right) R_z^4 \left( I, I' \right) \left[ \bar{w}_y(\mu, \mu') \right] \]

\[ \left( \eta_{yz} \eta_{zz} + \bar{w}_z(\mu, \mu') \left( 3\eta_{yz} \eta_{xz} + \eta_{zz}^2 \right) \right] + R_x^5 \left( I, I' \right) \bar{w}_x(\mu, \mu') \eta_{xx}^2 \]
+ R^5_y\left( I_{\mu}^I I_{\mu'}^I \right) \bar{w}_y(\mu, \mu') \eta_{yy}^2 + R^5_z\left( I_{\mu}^I I_{\mu'}^I \right) \bar{w}_z(\mu, \mu') \eta_{zz}^2 \\
+ 3 \left\{ R^2_x\left( I_{\mu}^I I_{\mu'}^I \right) R^2_y\left( I_{\mu}^I I_{\mu'}^I \right) \left[ \bar{w}_x^2(\mu, \mu') \eta_{yy} + 4 \bar{w}_x(\mu, \mu') \right] \\
+ R^2_z\left( I_{\mu}^I I_{\mu'}^I \right) R^2_x\left( I_{\mu}^I I_{\mu'}^I \right) \left[ \bar{w}_x^2(\mu, \mu') \eta_{zz} + 4 \bar{w}_x(\mu, \mu') + \bar{w}_z(\mu, \mu') \eta_{xz} \right] \\
+ \bar{w}_z^2(\mu, \mu') \eta_{zz} + 4 \bar{w}_z(\mu, \mu') \bar{w}_z(\mu, \mu') \eta_{xz} + \bar{w}_z^2(\mu, \mu') \eta_{zz} \right\} \\
+ \eta_{yy} + R^3_x\left( I_{\mu}^I I_{\mu'}^I \right) R^3_z\left( I_{\mu}^I I_{\mu'}^I \right) \eta_{zz} + \bar{w}_z^2(\mu, \mu') R^4_x\left( I_{\mu}^I I_{\mu'}^I \right) \eta_{xx} \\
+ \bar{w}_y^2(\mu, \mu') R^4_y\left( I_{\mu}^I I_{\mu'}^I \right) \eta_{yy} + \bar{w}_z^2(\mu, \mu') R^4_z\left( I_{\mu}^I I_{\mu'}^I \right) \eta_{zz} \right\} } \quad (2.38)

The position coordinates of the four nearest neighbours of the atoms in the unit
cell of the hexagonal wurtzite phase are used. Summations in Eq. 2.38 are done separately for each atom.

The lattice energy density $U$ from the continuum model approximation $[22]$ is given by:

$$U = U_0 + \frac{1}{2} \sum_{ij,kl} C_{ij,kl} \eta_{ij} \eta_{kl} + \frac{1}{6} \sum_{ij,kl, mn} C_{ij,kl,mn} \eta_{ij} \eta_{kl} \eta_{mn} + \cdots$$

(2.39)

where $U_0$ is the lattice energy density in the unstrained state, $C_{ij,kl}$ and $C_{ij,kl,mn}$ are the second order and third elastic constants.

$$C_{ij,kl} = \left[ \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right]_{o,s}$$

(2.40a)

$$C_{ij,kl,mn} = \left[ \frac{\partial^3 U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right]_{o,s}$$

(2.40b)

The subscript $o$ stands for the equilibrium configuration and $S$, the entropy of the system. The value of second order potential parameter, $k_2$ and third order potential parameter, $k_3$ are evaluated by assuming a central potential of the type:

$$\phi(r) = -\frac{a}{r^m} + \frac{b}{r^n}$$

(2.41)

Here $a$ and $b$ are constants and $r$ is the interatomic distance. The exponent $m$ corresponds to the long range electrostatic interaction and $n$ corresponds to Born exponent, the repulsive exponent in the central potential.
2.4 Pressure derivatives of the second order elastic constants using finite strain elasticity theory

Expressions for the pressure derivatives of the SOEC of hexagonal system are derived using Murnaghan’s [21] finite strain elasticity theory. For such a class of system there are six independent SOEC and ten independent TOEC. Consider a hexagonal lattice under a hydrostatic pressure $p$. Let $r_i$ be the coordinates of a material point in the natural state and $R_i$ the coordinates of the same material point after applying the pressure. The Jacobian of transformation after the application of pressure is,

$$J = \left| \frac{\partial R_i}{\partial r_i} \right| = \begin{vmatrix} (1 - \nu) & 0 & 0 \\ 0 & (1 - \nu) & 0 \\ 0 & 0 & (1 - \mu) \end{vmatrix}$$

Every line element perpendicular and parallel to the hexagonal axis is reduced by a factor $\nu$ and $\mu$. If $\eta_{xx} = \eta_{yy} = \eta$ and $\eta_{zz} = \zeta$ are the Lagrangian strain parameters, then

$$(1 - \nu)^2 = 1 + 2\eta \quad \text{(2.43a)}$$
$$(1 - \mu)^2 = 1 + 2\zeta \quad \text{(2.43b)}$$
The densities $\rho_0$ and $\rho$ corresponding to the natural and deformed states are related to the Jacobian, $J$ as:

$$\frac{\rho}{\rho_0} = \frac{1}{\det|J|} \quad (2.44)$$

Now if an infinitesimal strain is superimposed on the deformed state, the coordinates of the particle become:

$$r_i = R_i + \sum_j \mu_{ij} R_j \quad (2.45)$$

where $\mu_{ij}$ are the infinitesimal strain parameters. The Lagrangian strain parameters $\eta$ and $\zeta$ and $\mu_{ij}$ from the expression:

$$\eta_{ij} = \frac{1}{2} \sum_p \left( \frac{\partial R_p}{\partial r_i} \frac{\partial R_p}{\partial r_j} - \delta_{ij} \right) \quad (2.46)$$

where $\delta_{ij}$ is the Kronecker delta. The stress tensor $\tau_{ij}$ is given by Murnaghan [21] as:

$$\tau_{ij} = \frac{\rho}{\rho_0} \sum_{pq} \left( \frac{\partial R_i}{\partial r_p} \frac{\partial U}{\partial \eta_{pq}} \frac{\partial R_j}{\partial r_q} - \delta_{ij} \right) \quad (2.47)$$

where $U$, is the strain energy density given by Eq. 2.48 as:

$$U = U_0 + \frac{1}{2} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{6} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} \quad (2.48)$$
Comparing Eq. 2.47 with the expression:

\[ \tau_{ij} = -p\delta_{ij} + \sum_{pq} C'_{ij,pq}\eta_{pq} \]

the effective SOEC \( C'_{ij,pq} \) can be obtained to the first order in strains \( \eta \) and \( \zeta \) as:

\[ C'_{11} = C_{11} + \eta(4C_{11} + 2C_{12} + C_{111} + C_{112}) + \zeta(-C_{11} + 2C_{13} + C_{113}) \]  

(2.50a)

\[ C'_{12} = C_{12} + \eta(2C_{12} + C_{111} + 2C_{112} - C_{222}) + \zeta(-C_{12} + C_{123}) \]  

(2.50b)

\[ C'_{13} = C_{13} + \eta(C_{113} + C_{131}) + \zeta(C_{13} + C_{133}) \]  

(2.50c)

\[ C'_{33} = C_{33} + \eta(4C_{13} - 2C_{33} + 2C_{133}) + \zeta(5C_{33} + C_{333}) \]  

(2.50d)

\[ C'_{44} = C_{44} + \eta(1/2(C_{11} + C_{12}) + C_{13} + C_{14} + C_{155}) + \]  

\( \zeta(1/2(C_{13} + C_{33}) + C_{44} + C_{344}) \)  

(2.50e)

\[ C'_{66} = C_{66} + \eta(2C_{11} - 1/2(C_{112} - C_{222})) + \]  

\( \zeta(C_{13} - C_{66} + 1/2(C_{133} - C_{123})) \)  

(2.50f)

The Lagrangian parameters obtained in terms of hydrostatic pressure are:

\[ \eta = \frac{(C_{13} - C_{33})}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p, \quad \zeta = \frac{2C_{13} - C_{11} - C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p \]  

(2.51)

The pressure derivative \( \left( \frac{dC'_{13}}{dp} \right) \) is obtained by multiplying the coefficients of \( \eta \) and \( \zeta \) in the expressions for \( C_{ij} \) in Eqs. 2.50.
2.5 Quasiharmonic theory of thermal expansion of uniaxial crystals

The low temperature limits of the effective Grüneisen functions $\bar{\gamma}_\perp$ and $\bar{\gamma}_\parallel$ of a uniaxial crystal depend on the generalised Grüneisen parameters (GPs) $\gamma''_i (\theta, \phi)$ and $\gamma'_i (\theta, \phi)$ of the acoustic modes propagating in different directions in the crystal. In this section a method of calculation of these GPs from the third order elastic constants is presented.

Let the position coordinates of a material particle in the unstrained or natural state be $a_i$ $(i=1,2,3)$. Let the coordinates of the material particle in the strained state be $x_i$ $(i=1,2,3)$. Consider two material particles located at $a_i$ and $a_i + da_i$. Let their coordinates in the deformed state be $x_i$ and $x_i + dx_i$. The elements $dx_i$ are related to $da_i$ by the equation,

$$dx_i = \frac{\partial x_i}{\partial a_j} da_j$$  \hspace{1cm} (2.52)

$$= \sum_{j=1}^{3} (\delta_{ij} + \epsilon_{ij}) da_j$$

$\delta_{ij}$ is the Kronecker delta and $\epsilon_{ij}$ are the deformation parameters. The Jacobian of the transformation,

$$J = Det \left( \frac{\partial x_i}{\partial a_j} \right)$$  \hspace{1cm} (2.53)
is taken to be positive for all real transformations. If $dV_a$ is a volume element in the natural state and $dV_x$ its volume after deformation,

$$\frac{dV_x}{dV_a} = \frac{\rho_0}{\rho} = J$$  \hspace{1cm} (2.54)

where $\rho_0$ and $\rho$ are the densities in the natural and deformed states respectively. The square of the length of arc from $a_i$ to $a_i + da_i$ be $dS_0$ in the unstrained state and $dS$ in the strained state. Then

$$dS^2 - dS_0^2 = dx_i dx_i - da_i da_i$$  \hspace{1cm} (2.55)

$$= \left( \frac{dx_i}{da_j}, \frac{dx_j}{da_k} - \delta_{jk} \right) da_j da_k$$

$$= 2\eta_{jk} da_j da_k$$

where $\eta_{jk}$ are the Lagrangian strain components. They are symmetric with respect to an interchange of the indices $j$ and $k$. In terms of $\epsilon_{jk}$,

$$\eta_{jk} = \frac{1}{2} \left( \epsilon_{jk} + \epsilon_{kj} + \sum_i \epsilon_{ij} \epsilon_{ik} \right)$$  \hspace{1cm} (2.56)

The internal energy function $U(S, \eta_{jk})$ for the material is a function of the entropy and the Lagrangian strain components. $U$ can be expanded in powers of the strain parameters about the undeformed state by substituting Eq. 2.40a and Eq. 2.40b in Eq. 2.48,

$$U = U_0 + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{0,S} \eta_{ij} \eta_{kl} + \frac{1}{6} \left( \frac{\partial^3 U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right)_{0,S} \eta_{ij} \eta_{kl} \eta_{mn}$$  \hspace{1cm} (2.57)
The linear term is absent because the natural state is one where $U$ is a minimum.

Following Brugger [25] we define the elastic constants of different orders referred to the natural state:

\[
C^{S}_{ij,kl} = \left( \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{o,s} \tag{2.58a}
\]

\[
C^{S}_{ij,kl,mn} = \left( \frac{\partial^3 U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right)_{o,s} \tag{2.58b}
\]

These are the adiabatic elastic constants of second and third orders respectively. They are tensors of fourth and sixth ranks. The number of independent nonvanishing SOE and TOE constants for different crystal systems are tabulated by Bhagavantam [23]. Starting from the free energy $F(T, \eta_{rs})$, one can define isothermal elastic constants as derivatives of $F$ with respect to $\eta_{rs}$. Following Murnaghan [21], the expression for stress:

\[
\tau_{jk} = \frac{1}{J} \left( \frac{\partial U}{\partial \eta_{pq}} \right)_{S} \frac{\partial x_{k}}{\partial a_{p}} \frac{\partial x_{j}}{\partial a_{q}} \tag{2.59}
\]

The stress tensor $\tau_{jk}$ is referred to the deformed state of the medium. The conditions for equilibrium require that the stress tensor be symmetric, i.e

\[
\tau_{jk} = \tau_{kj} \tag{2.60}
\]

A medium is said to be homogeneously deformed if the components of the strain tensor $\eta_{pq}$ do not vary from point to point in the medium. The homogeneously deformed state is called the initial state and the coordinates in this state are referred to by $X_i$. When the particles are given infinitesimal displacements $u_i$ from this
state, the resulting state, called the final state, is referred to by the coordinates \( x_i = X_i + u_i \). The equation of motion is,

\[
\rho \ddot{x}_j = \frac{\partial}{\partial x_k} \tau_{kj}
\]  

(2.61)

using the expression Eq. 2.60 and the result

\[
\frac{\partial}{\partial x_k} \left( \frac{1}{J} \frac{\partial x_k}{\partial a_p} \right) = 0
\]  

(2.62)

The wave equation in terms of the displacement \( u_i \) obtained by Thurston and Brugger [26] is:

\[
\rho_0 \ddot{u}_j = A_{jk,pm}^S \frac{\partial^2 u_k}{\partial a_p \partial a_m}
\]  

(2.63)

For a homogeneously strained medium

\[
\tilde{A}_{jk,pm}^S = \delta_{jk} \tilde{\tau}_{pm} + \frac{\partial X_j}{\partial a_q} \frac{\partial X_k}{\partial a_i} \left( \frac{\partial \tilde{\tau}_{pq}}{\partial \eta_{mi}} \right)
\]  

(2.64)

where \( \tilde{\tau}_{pm} = \left( \frac{\partial \tilde{U}}{\partial \eta_{pm}} \right)_S \). The tilde denotes that the quantities have to be evaluated in the homogeneously strained state of the medium. Using Eqs. 2.52 and 2.57 for \( U \) we get \( \tilde{A}_{jk,pm}^S \) to the first order in \( \epsilon_{jk} \) as:

\[
\tilde{A}_{jk,pm}^S = C_{pj,mk}^S + (C_{pj,mk,rs} + C_{pm,rs} \delta_{jk}) \epsilon_{rs} + C_{pq,mk} \epsilon_{jq} + C_{pj,ma} \epsilon_{kq}
\]  

(2.65)
Substituting the plane wave solution in Eq. 2.63, the solution in the deformed coordinates is:

\[ u_j = u_j^0 \exp(i \omega \left( t - \frac{n_i X_i}{W} \right)) \]  

(2.66)

where \( W \) is the actual velocity of the wave in the deformed state and \( n_i \) are the direction cosines of wave propagation. However, it is more advantageous to write the displacements as:

\[ u_j = u_j^0 \exp(i \omega \left( t - \frac{N_i a_i}{V} \right)) \]  

(2.67)

where \( V \) is called the natural velocity and \( N_i \) are the direction cosines of the wave in the undeformed state. Let \( \lambda_0 \) be the wavelength of a given wave in the undeformed state traveling along a direction having direction cosines \( N_i \). After the deformation the wavelength of the wave changes to \( \lambda \) and the wave propagation direction is also changed. The direction cosines are now \( n_i \). The frequency of the wave changes from \( \omega_0 \) to \( \omega \). In the unstrained state the velocity \( W_0 \) in the direction \( \vec{N} \) is:

\[ W_0 = \frac{\omega_0 \lambda_0}{2\pi} \]  

(2.68)

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

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

(2.69)
and the natural velocity of the wave is

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

(2.70)
i.e. the ratio \( \frac{\omega}{\omega_0} \) directly gives \( \frac{V}{V_0} \) without involving the changes in the dimensions of the specimen. Substituting Eq. 2.67 in Eq. 2.63

\[ \rho_0 V^2 u_0^j = \tilde{A}^S_{jk,pm} N_p N_m u_k^0 \]  

(2.71)

These three linear homogeneous equations corresponding to \( j = 1,2,3 \) can have nontrivial solutions if and only if

\[ |\rho_0 V^2 \delta_{jk} - \tilde{A}^S_{jk,pm} N_p N_m| = 0 \]  

(2.72)

Thus, giving the three natural velocities for any direction of wave propagation. The Grüneisen parameters (GPs) \( \gamma_{j}''(\theta,\phi) \) and \( \gamma_{j}'(\theta,\phi) \) for the \( j^{th} \) acoustic mode propagating in the direction \((\theta,\phi)\) are,

\[ \gamma_{j}' = \frac{\partial \ln \omega(\tilde{q}_i,j)}{\partial \ln a} = -\frac{\partial \ln V_1(\theta,\phi)}{\partial \ln a}, \]  

(2.73)

\[ \gamma_{j}'' = \frac{\partial \ln \omega(\tilde{q}_i,j)}{\partial \ln c} = -\frac{\partial \ln V_1(\theta,\phi)}{\partial \ln c} \]  

(2.74)

\( V_1(\theta,\phi) \) is the natural velocity of the \( j^{th} \) acoustic mode propagating in the direction \((\theta,\phi)\), referred to the unique axis as the z-axis when the medium is homogeneously deformed by:
1. a uniform longitudinal strain $\varepsilon'' = d \ln c$ along the unique axis, or

2. a uniform areal strain $\varepsilon' = d \ln a$ in the plane perpendicular to the unique axis.

The direction cosines are $N_x = \sin \theta \cos \phi$, $N_y = \sin \theta \sin \phi$ and $N_z = \cos \theta$.

To the first order in $\varepsilon_{ij}$, the uniform longitudinal strain $\varepsilon''$ corresponds to $\varepsilon_{33}$ and the uniform areal strain $\varepsilon'$ is equivalent to $\varepsilon_{11} = \varepsilon_{22} = \frac{1}{2} \varepsilon'$. The rest of the $\varepsilon_{ij}$ are zero.

The expression

$$D_{jk} = \tilde{A}_{jk,pm}^S N_p N_m$$

under the strain $\varepsilon''$ and $\varepsilon'$ for the hexagonal system taking into account the nonvanishing SOEC and TOEC on expansion gives:

$$D_{xx} = \left[ C_{11} N_x^2 + \frac{1}{2} (C_{11} - C_{12}) N_y^2 + C_{44} N_z^2 \right] + \frac{\varepsilon'}{2} \left( \left( C_{11} + C_{12} \right) \frac{\varepsilon'}{2} \left( \frac{1}{2} (C_{222} - C_{112}) + 2C_{11} \right) N_y^2 + (C_{155}) \right) + (C_{113} + 3C_{123}) N_x^2 + C_{144} + 2C_{44} + 2C_{13} N_x^2 \right] + \frac{\varepsilon''}{2} \left( \left( C_{111} + C_{112} + 3C_{11} + C_{12} \right) N_y^2 + \left( C_{344} + C_{333} \right) N_z^2 \right)$$

$$D_{yy} = \left[ \frac{1}{2} \left( C_{11} - C_{12} \right) N_x^2 + C_{11} N_y^2 + C_{44} N_z^2 \right] + \frac{\varepsilon'}{2} \left( \frac{1}{2} (C_{222} + C_{112}) \right) + (2C_{11}) N_x^2 \right] + \frac{\varepsilon'}{2} \left( \left( C_{111} + C_{112} + 3C_{11} + C_{12} \right) N_y^2 + (C_{144} + C_{155}) \right)$$
\[ D_{zz} = \left[ C_{44} \left( N_x^2 + N_y^2 \right) + C_{33} N_z^2 \right] + \frac{\epsilon'}{2} \left[ (C_{155} + C_{144} + C_{11} + C_{12}) \left( N_x^2 + N_y^2 \right) \right] + \frac{\epsilon''}{2} \left[ (C_{344} + C_{13} + 2C_{44}) \left( N_x^2 + N_y^2 \right) \right] + \frac{\epsilon'''}{2} \left[ (C_{333} + 3C_{33}) N_z^2 \right] \]

\[ (2.78) \]

\[ D_{xy} = \left[ \frac{1}{2} (C_{11} + C_{12}) N_x N_y \right] + \frac{\epsilon'}{2} \left[ \left( C_{111} + \frac{3}{2} C_{112} - \frac{1}{2} C_{222} + C_{11} + C_{12} \right) N_x N_y \right] + \frac{\epsilon''}{2} \left[ \left( C_{113} + C_{123} \right) N_x N_y \right] \]

\[ (2.79) \]

\[ D_{xz} = \left[ (C_{13} + C_{44}) N_x N_z \right] + \frac{\epsilon'}{2} \left[ \left( C_{113} + C_{123} + C_{155} + C_{144} + C_{13} + C_{44} \right) N_x N_z \right] + \frac{\epsilon''}{2} \left[ \left( C_{133} + C_{344} + C_{13} + C_{44} \right) N_x N_y \right] \]

\[ (2.80) \]

\[ D_{yz} = \left[ (C_{13} + C_{44}) N_y N_z \right] + \frac{\epsilon'}{2} \left[ \left( C_{113} + C_{123} + C_{144} + C_{155} + C_{13} + C_{44} \right) N_y N_z \right] + \frac{\epsilon''}{2} \left[ \left( C_{133} + C_{344} + C_{13} + C_{44} \right) N_y N_z \right] \]

\[ (2.81) \]
Putting $\rho_0 V^2 = X$, the determinantal equation can be expanded to give the cubic equation

$$X^3 - AX^2 + BX - C = 0$$

(2.82)

where $A = \sum_i D_{ii}$

$$B = \begin{bmatrix} D_{xx} & D_{xy} \\ D_{xy} & D_{yy} \end{bmatrix} + \begin{bmatrix} D_{yy} & D_{yz} \\ D_{yz} & D_{zz} \end{bmatrix} + \begin{bmatrix} D_{zz} & D_{xz} \\ D_{xz} & D_{xx} \end{bmatrix}$$

(2.83)

$$C = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{bmatrix}$$

(2.84)

The $A$, $B$, $C$ are functions of $\epsilon'$ and $\epsilon''$. When $\epsilon'$ and $\epsilon''$ are zero, their values are $\bar{A}$, $\bar{B}$ and $\bar{C}$ and the roots of the equation are $\bar{X}_1$, $\bar{X}_2$ and $\bar{X}_3$. Differentiating Eq. 2.82, with respect to $\epsilon'$ and using the definition,

$$\gamma'_{j}(\theta, \phi) = \frac{1}{2} \frac{\partial \log X_j}{\partial \epsilon'}$$

(2.85)

we have

$$\gamma'_j = -\frac{1}{2X_j} \left( \frac{\partial X_j}{\partial \epsilon'} \right) = -\frac{1}{2X_j} \left[ \frac{X_j^2 \left( \frac{\partial A}{\partial \epsilon'} \right)_0 - X_j \left( \frac{\partial B}{\partial \epsilon'} \right)_0 + \left( \frac{\partial C}{\partial \epsilon'} \right)_0}{3X_j^2 - 2AX_j + B} \right]$$

(2.86)
Similarly, differentiating Eq. 2.82, with respect to $\epsilon''$ and using the definition,

$$
\gamma''_{j}(\theta, \phi) = \frac{1}{2} \frac{\partial \log X_j}{\partial \epsilon''}
$$

we have,

$$
\gamma''_{j} = -\frac{1}{2X_j} \left( \frac{\partial X_j}{\partial \epsilon''} \right) = -\frac{1}{2X_j} \left[ \frac{X_j^2 \left( \frac{\partial A}{\partial \epsilon''} \right)_0 - X_j \left( \frac{\partial B}{\partial \epsilon''} \right)_0 + \left( \frac{\partial C}{\partial \epsilon''} \right)_0}{3X_j^2 - 2AX_j + B} \right]
$$

(2.88)

The derivatives of $A$, $B$ and $C$ are to be evaluated at equilibrium configuration. The low temperature limits of the effective Grüneisen functions can be calculated using the individual GPs of the acoustic modes. In the uniaxial crystals the acoustic wave velocities and the GPs depend only on $\theta$ and not on the azimuth $\phi$, where $(\theta, \phi)$ gives the direction of wave propagation for these elastic waves. At very low temperatures where only acoustic modes of long wavelength are predominant the low temperature limits of Grüneisen function are calculated using:

$$
\bar{\gamma}_\perp = \frac{\sum_{j=1}^{3} \int \bar{\gamma}'_{j}(\theta, \phi)V_j^{-3}(\theta)d\Omega}{\sum_{j=1}^{3} \int V_j^{-3}(\theta, \phi)d\Omega}
$$

(2.89)

$$
\bar{\gamma}_\parallel = \frac{\sum_{j=1}^{3} \int \bar{\gamma}''_{j}(\theta, \phi)V_j^{-3}(\theta, \phi)d\Omega}{\sum_{j=1}^{3} \int V_j^{-3}(\theta, \phi)d\Omega}
$$

(2.90)

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 \( \bar{\gamma}_\perp \) and \( \bar{\gamma}_\parallel \) in Eq. 2.89 and 2.90 are evaluated using the GPs 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 values \( \gamma'_j X_j^{-3/2} \), \( \gamma''_j X_j^{-3/2} \) and \( X_j^{-3/2} \) at any angle \( \theta \) is multiplied by \( \sin \theta \) and the sum \( \sum \gamma'_j X_j^{-3/2} \sin \theta \) over all \( \theta \) values is taken to be proportional to \( \int \gamma'_j X_j^{-3/2} d\Omega \).

Thus the low temperature limits \( \bar{\gamma}_\perp \) and \( \bar{\gamma}_\parallel \) are obtained as

\[
\bar{\gamma}_\perp = \frac{\sum_n \left( \sum_{i=1}^3 \gamma'_i X_i^{-3/2} \right) \sin \theta d\Omega}{\sum_n \left( \sum_{i=1}^3 X_i^{-3/2} \right) \sin \theta d\Omega}, \quad \bar{\gamma}_\parallel = \frac{\sum_n \left( \sum_{i=1}^3 \int \gamma''_i X_i^{-3/2} \right) \sin \theta d\Omega}{\sum_n \left( \sum_{i=1}^3 \int X_i^{-3/2} \right) \sin \theta d\Omega}
\] (2.91)

The lattice thermal expansion coefficients at various temperatures can be expressed in terms of the effective Grüneisen functions \( \bar{\gamma}_\perp \) and \( \bar{\gamma}_\parallel \) as follows

\[
V \alpha_\perp = \left[ (S_{11} + S_{12}) \bar{\gamma}_\perp + S_{13} \bar{\gamma}_\parallel \right] C_V = \gamma^{Br}_\perp C_V \chi_{iso}
\]

\[
V \alpha_\parallel = \left[ (2S_{13}) \bar{\gamma}_\perp + S_{33} \bar{\gamma}_\parallel \right] C_V = \gamma^{Br}_\parallel C_V \chi_{iso}
\] (2.92)

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 Eq.2.92, we can calculate the Brugger gammas \( \bar{\gamma}^{Br}_\perp \) and \( \bar{\gamma}^{Br}_\parallel \) as:

\[
\bar{\gamma}^{Br}_\perp = \frac{(S_{11} + S_{12}) \bar{\gamma}_\perp + S_{13} \bar{\gamma}_\parallel}{\chi_{iso}}, \quad \bar{\gamma}^{Br}_\parallel = \frac{2S_{13} \bar{\gamma}_\perp + S_{33} \bar{\gamma}_\parallel}{\chi_{iso}}
\] (2.93)
Where, $S_{ij}$ is the elastic compliance and $\chi_{iso}$ is the isothermal compressibility.

\[
S_{11} = \frac{C_{11} C_{33} - C_{13}^2}{(C_{12} - C_{11}) 2C_{13}^2 - C_{33} (C_{11} + C_{12})} \tag{2.94}
\]

\[
S_{33} = \frac{C_{11} + C_{12}}{C_{33} (C_{11} + C_{12}) - 2C_{13}^2} \tag{2.95}
\]

\[
S_{12} = \frac{C_{13}^2 - C_{12} C_{33}}{C_{13}} \tag{2.96}
\]

\[
S_{13} = \frac{C_{13}}{2C_{13}^2 - C_{33} (C_{11} + C_{12})} \tag{2.97}
\]

$\chi_{iso} = 2 [S_{11} + S_{12} + S_{13}] + 2S_{13} + S_{33}$

where $C_{ij}$ are the SOEC. The low temperature limit of volume Grüneisen function is then obtained as,

\[
\bar{\gamma}_{\text{L}} = 2\bar{\gamma}_{\perp}^{Br} + \bar{\gamma}_{\parallel}^{Br} \tag{2.98}
\]

In the present work we have calculated the GPs for different values of $\theta$ at intervals of $5^\circ$ in the wave direction and integration is carried over $\theta$ from 0 to $90^\circ$. 
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