Chapter 1

Ultrasonic measurements of elastic constants of single crystals- An analysis

This Chapter contains a brief introduction to the theory of elastic wave propagation through anisotropic media. Expressions for the velocity of propagation of ultrasonic waves along different symmetry directions are derived from Christoffel equations for crystals of orthorhombic, tetragonal, trigonal and hexagonal symmetries. The necessary theory and details of investigation of phase transition using ultrasonic technique are outlined. Various other elastic constants such as Young's modulus, linear compressibility, Bulk modulus, Volume compressibility and Poisson's ratio are also discussed briefly.
Ultrasonic measurements of elastic constants of single crystals- An analysis

1.1 Introduction

In science and technology elastic properties of solids have considerable significance. Their measurement yields valuable information regarding the forces operative between the atoms or ions in a solid. This information is of fundamental importance in interpreting and understanding the nature of bonding in the solid state, because the elastic properties describe the mechanical behaviour of materials. When a material is subjected to a stress it will get strained. Within the elastic limit, strain varies linearly with the applied stress. The proportionality constant relating the stress and strain in the elastic limit is the elastic constant or elastic modulus. The common elastic moduli are the Young’s modulus (E), Bulk modulus (K), Shear modulus (G) and Poisson’s ratio (σ). In addition to the above elastic constants there is longitudinal modulus and transverse modulus that could be determined from the velocity of propagation of longitudinal wave and transverse wave through a solid. The number of elastic constants for anisotropic solids like crystals having anisotropy have been discussed by various workers like Huntington [1.1], Nye [1.2], Federov [1.3], Musgrave [1.4] and others, whereas the use of physical acoustics to study the properties of solids has been discussed by Mason [1.5].

1.1.1 Elastic properties of Crystalline Solids

The elastic constant determination by measuring the velocity of sound in crystals is a standard method. The use of high frequency acoustic waves leads to precise results compared to the static methods. The elastic constants are tensors, which measure the crystal property.

The elastic constants of crystals link the structure of the lattice with its macroscopic behaviour [1.6,1.7]. The elastic constants enable one to determine
the properties like compressibility ($K_v$), anisotropy parameter ($\lambda$), Debye temperature ($\theta_D$) and Gruneisen parameter ($\gamma$) and other related thermodynamic parameters of the crystal. All these properties are structure dependent and are also related to the inter atomic forces or potentials in the solids.

The mathematical theory of elasticity relates on stress and strain in the interior of the solid [1.16]. The state of strain in the solid at any given point can be expressed by resolving the displacement of an elementary volume originally located at some point along three mutually perpendicular directions and differentiating these components, thus obtaining the nine components of strain tensor. Likewise the state of stress, which the volume element is subjected to could be resolved into interactive forces acting along each of the three coordinate axes. Thus there are three types of stresses, viz., one longitudinal and two of shear, perpendicular to each other. There are nine components of stress-strain proportionality relationship and would involve ($9 \times 9$) or 81 elastic constants.

Writing the nine components of the strain tensor as

\[ \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 \varepsilon_5 \varepsilon_6 \varepsilon_7 \varepsilon_8 \varepsilon_9 \]  

(1.1)

And likewise the nine components of the stress tensor as

\[
\begin{bmatrix}
\sigma_{xx} & \sigma_{yx} & \sigma_{yz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{yz} & \sigma_{zy} & \sigma_{zz}
\end{bmatrix}
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{bmatrix}
\]

(1.2)

Stress tensor and strain tensor are expressed in the general form as (matrix notation)

\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \]  

(1.3)

The stress tensor and strain tensor are second rank tensors. Hence the
constant of proportionality is a fourth rank tensor. This tensor is referred to as the elastic stiffness tensor $C_{ijkl}$, and the inverse is the elastic compliance tensor $S_{ijkl}$ and connects the strain to the stress. The relation of these constants to stress and strain is

$$\varepsilon_{ij} = S_{ijkl} \sigma_{kl}$$  \hspace{1cm} (1.4)

The stiffness constants and elastic compliances are determined by elastic wave propagation measurements in solids [1,2,1.15,1.17,1.18]. Further, these constants determine the velocity of elastic waves in any direction in an anisotropic solid. $C_{ijkl}$ and $S_{ijkl}$ have 81 elements relating 9 strain components and 9 stress components. In the absence of rotation in the material the stress and strain tensors obey the symmetry

$$\sigma_{ij} = \sigma_{ji} \quad \text{and} \quad \varepsilon_{ij} = \varepsilon_{ji}$$  \hspace{1cm} (1.5)

The well-known Law of Reciprocity enables one to interchange the direction of force and displacement without change in the constant of proportionality. Thus the number 81 is reduced to 45 constants. Thus 45 constants are required to describe the elastic behaviour of triclinic crystal. On the basis of Cauchy's assumption and by the application of the Reciprocity relationship, the number of constants reduces to 21 for a triclinic crystal. The reduction in the strain component from 9 to 6 may be summarized by the statement that the elastic strain can be separated into pure strains and rotations and latter can be ignored. A correct and complete theory of elasticity has necessarily to take all the nine components of the stress and strain tensors into consideration.

At this point it is appropriate to introduce the more compact two suffix notation for the elastic constant, in which the tensor for the $C_{ijkl}$ \hspace{1cm} (ijkl = 1,2,3...) is replaced by the matrix
\[ C_{ij} = [1,2,3,4,5,6] \]

According to the following subscript equality relationship

<table>
<thead>
<tr>
<th>Tensor notation</th>
<th>11</th>
<th>22</th>
<th>33</th>
<th>23,32</th>
<th>31,13</th>
<th>12,21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix notation</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

The matrix notation is also called Voigt notation and is easily obtained from the relation

\[
\begin{align*}
  i j &\rightarrow m = i & \text{if} & i = j \\
  i j &\rightarrow m = 9-i-j & \text{if} & i \neq j
\end{align*}
\] (1.6)

It may be noted that two-suffix notation cannot be used to transform the constants to other axes and it is necessary to go back to the original tensor notation. Considering the elastic energy of the strained crystal, further symmetry can be identified in the elastic constant matrix in the form

\[
\begin{align*}
  C_{ij} &= C_{ji} \\
  S_{ij} &= S_{ji}
\end{align*}
\] (1.7)

This introduces another 15 equalities in the elastic constants and reduces the maximum number of independent constants to 21.

Further reduction of the number of independent elastic constants is possible, when the symmetry of the crystals is considered and this number is different for the different crystal classes. When suitable directions are chosen as axes, crystal may be grouped on the basis of its macroscopic morphology into one of 32 crystal classes (point group symmetry) which forms a sub group among 7 crystal systems [1.9]. The crystal classes comprise of the combination of the point symmetry operations such as inversion, n-fold rotation, reflection etc.
A symmetry operation is a transformation performed on the body which leaves it unchanged or invariant. The study of symmetry elements enable one to classify crystals. The basic crystal systems in the order of decreasing symmetry are described in the following Table 1.1 [1.9,1.36]. The following procedure can be used to determine the form of elastic constant in a crystal of specified symmetry. Given a symmetry operation $R$ one can perform the corresponding co-ordinate transformation for the elastic constant tensor $C_{ijkl}$ to obtain the transformed tensor $C'_{ijkl}$. Since the two co-ordinate systems are indistinguishable due to symmetry, one requires that $C_{ijkl} = C'_{ijkl}$ for all components. This yields relation between the original tensor components. Additional relations follow by applying all symmetry operation, one after another to each tensor component and requiring that it goes into itself after the transformation. If all the relations between the tensor components are known, one can solve the whole set of equations and determine those components which must vanish and also find any relation between the non-vanishing tensor. Table 1.2 gives the non-zero elastic constants for the various crystal systems [1.3,1.36].

Isotropic solid has only two independent elastic constants with the condition

$$
C_{11} = C_{12} = C_{13} \\
C_{11} = C_{12} = C_{22} \\
C_{44} = C_{55} = C_{66} \quad \text{further} \quad C_{12} = C_{11} - 2C_{44}
$$

(1.8)
Table 1.1 Crystal Systems, axial lengths and interaxial angles

<table>
<thead>
<tr>
<th>sl.no</th>
<th>Crystal systems</th>
<th>Axial length a, b, c</th>
<th>Interaxial angles α, β, γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cubic</td>
<td>a = b = c</td>
<td>α = β = γ = 90</td>
</tr>
<tr>
<td>2</td>
<td>Hexagonal</td>
<td>a = b ≠ c</td>
<td>α = β = 90, γ = 120</td>
</tr>
<tr>
<td>3</td>
<td>Tetragonal</td>
<td>a = b ≠ c</td>
<td>α = β = γ = 90</td>
</tr>
<tr>
<td>4</td>
<td>Trigonal</td>
<td>a = b ≠ c</td>
<td>α = β = γ = 90</td>
</tr>
<tr>
<td>5</td>
<td>Orthorhombic</td>
<td>a ≠ b ≠ c</td>
<td>α = β = 90 = γ</td>
</tr>
<tr>
<td>6</td>
<td>Monoclinic</td>
<td>a ≠ b ≠ c</td>
<td>α = β ≠ 90 ≠ γ</td>
</tr>
<tr>
<td>7</td>
<td>Triclinic</td>
<td>a ≠ b ≠ c</td>
<td>α ≠ β ≠ 90 ≠ γ</td>
</tr>
</tbody>
</table>

The two independent constants of the isotropic solid are called Lame constants \([1.4]\). \(λ\) and \(μ\) are defined by
\[
λ = C_{12}, \quad μ = C_{44} \tag{1.9}
\]

\(μ\) is same as shear modulus \(G\), the bulk modulus \(B\) is defined by
\[
B = λ + \frac{2μ}{3} \tag{1.10}
\]

The elastic constant matrix \(C_{ij}\) for the most general case, that is for a triclinic crystal is given below:

\[
C_{ij} = C_{ji} \tag{1.11}
\]
Table 1.2 Elastic constants for various crystal systems

<table>
<thead>
<tr>
<th>Systems</th>
<th>No. of Point groups</th>
<th>No. of Cij’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>2</td>
<td>C1 and C2</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>3</td>
<td>C2h, Cc, C2</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3</td>
<td>D2h, C2v, D2</td>
</tr>
<tr>
<td>Tetragonal I</td>
<td>3</td>
<td>C4h, S4, C4</td>
</tr>
<tr>
<td>Tetragonal II</td>
<td>4</td>
<td>D4h, D2d, C4v, D4</td>
</tr>
<tr>
<td>Trigonal I</td>
<td>2</td>
<td>C31, C3</td>
</tr>
<tr>
<td>Trigonal II</td>
<td>3</td>
<td>C3d, C3v, D3</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>7</td>
<td>D6h, D3h, C6v, D6</td>
</tr>
<tr>
<td>Cubic</td>
<td>5</td>
<td>O_h, O, T_d, T_h, T</td>
</tr>
</tbody>
</table>

(a) All 21 elements
(b) C_{11}, C_{12}, C_{13}, C_{15}, C_{22}, C_{23}, C_{25}, C_{33}, C_{35}, C_{44}, C_{46}, C_{55} and C_{66}
(c) C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{25}, C_{33}, C_{35}, C_{44}, C_{46}, C_{55} and C_{66}
(d) C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55}, C_{16} = C_{26} and C_{66}
(e) C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55} and C_{66}
(f) C_{11} = C_{12}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55}, C_{14} = -C_{24}, C_{15} = -C_{25} and C_{66}
also C_{46} = 2 C_{25}, C_{56} = 2 C_{14}, C_{66} = \frac{1}{2} (C_{11} - C_{12})
(g) C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55}, C_{14} = -C_{24}
also C_{56} = 2 C_{14}, C_{66} = \frac{1}{2} (C_{11} - C_{12})
(h) C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55} and C_{66} = \frac{1}{2} (C_{11} - C_{12})
(i) C_{11} = C_{22} = C_{33}, C_{12} = C_{13} = C_{23}, C_{44} = C_{55} = C_{66}

1.1.2 Equations of motion and their solution

The propagation of acoustic waves in an anisotropic medium is governed by three linear equations known as 'Christoffel equations'. The characteristic
equation relates the velocity \( v \), direction of the waves, and elastic constant of the medium. The equations occupy an important position in the field of crystal acoustics, and their solution is used for a wide variety of purposes [1.3-1.10].

Consider an anisotropic medium, which obeys ideal Hooke’s law, and in which body forces, body torques, dissipative processes, and non-linear or dissipative phenomena can be neglected. A disturbance in such a medium is represented by a set of position and time dependent particle displacements \( U[x,t] \) which are related by the equations

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{ij}}{\partial x_j}
\]

(1.12)

where \( \rho \) is the density of medium. To obtain the wave equation the right hand side of this equation is written in terms of the deformation components of \( U_i \). For this the relation between stress and strain is used. This gives the wave equation in the form

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l}
\]

(1.13)

The \( C_{ijkl} \) is the second order elastic constant. A plane monochromatic wave

\[
U_i = U_0 \exp[i(k.r - \omega t)]
\]

is a solution of the above equation, where \( U_0 \) is the amplitude, \( k = k_i \) is the wave vector and \( '\omega' \) is the frequency, satisfying the condition

\[
[C_{ijkl} k_j k_l - \rho \omega^2 \delta_{ik}]_k = 0
\]

(1.14)

The three homogeneous equations for \( U_i \) from the above equation have a solution only if the secular equation of their co-efficients is satisfied.
This requirement leads to the familiar form of a determinantal equation for the propagation velocity \( v = \omega / k \). If we write the propagation velocity in terms of direction cosines as \( k = k [ n_1, n_2, n_3 ] \) the secular determinant becomes

\[
\left| \Gamma_{ik} - \rho v^2 \delta_{ik} \right| = 0
\]

(1.15)

Where the coefficients \( \Gamma_{ik} \) are defined by

\[
\Gamma_{ik} = C_{ijkl} n_j n_l
\]

(1.16)

\[\text{Figure 1.1 Schematic representation of the components of stress acting on a volume.}\]

\( \Gamma_{ik} \) is called Christoffel matrix and its elements depend on the direction of wave propagation and the elastic constant. The Equation [1.13] is a cubic equation for \( \rho v^2 \), which has three roots with respect to interchange of \( k \) and \( i \). The requirement for crystal stability ensures that \( \Gamma_{ik} \) is a positive definite matrix and hence the three eigen values are positive.

\[
\delta_{ik} = 0 \quad \text{for} \quad k \neq j
\]

\[
\delta_{ik} = 1 \quad \text{for} \quad k = j
\]

(1.17)
The expanded form of this determinantal equation is

\[
\begin{vmatrix}
\Gamma_{11} - \rho \nu^2 & \Gamma_{12} & \Gamma_{13} \\
\Gamma_{12} & \Gamma_{22} - \rho \nu^2 & \Gamma_{23} \\
\Gamma_{13} & \Gamma_{23} & \Gamma_{33} - \rho \nu^2
\end{vmatrix} = 0
\] (1.18)

Using the contracted Voigt notation for the elastic constants, the Christoffel coefficients are in the most general case are given in Table 1.3. On evaluating the determinant and equating it to zero, one gets the secular equation. This is a cubic equation in $\nu^2$ and hence it has three solutions and three different velocities are associated with it. Thus for a given direction there are three waves propagating with different velocities. The fastest of the three is the longitudinal wave or quasi-longitudinal wave. The other two are fast and slow transverse waves or quasi-transverse waves. The waves are purely longitudinal or purely transverse only in the pure mode directions in the crystal and the directions are usually the symmetry axes or symmetry planes in the crystal [1.39, 1.40]. The three values of $\rho \nu^2$ are the eigen values of the matrix $\Gamma_{ik}$ and corresponding solutions for the displacement vector $U_k$ are the eigen vectors. While eigen values give the three velocities. The corresponding eigen vectors give the direction of particle motion or the polarization direction of the wave.

Table 1.3 The Christoffel Coefficients

<table>
<thead>
<tr>
<th>$\Gamma_i$</th>
<th>$n_1^2$</th>
<th>$n_2^2$</th>
<th>$n_3^2$</th>
<th>$2n_1n_3$</th>
<th>$2n_3n_1$</th>
<th>$2n_1n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{11}$</td>
<td>$C_{11}$</td>
<td>$C_{66}$</td>
<td>$C_{55}$</td>
<td>$C_{56}$</td>
<td>$C_{15}$</td>
<td>$C_{16}$</td>
</tr>
<tr>
<td>$\Gamma_{22}$</td>
<td>$C_{66}$</td>
<td>$C_{22}$</td>
<td>$C_{44}$</td>
<td>$C_{24}$</td>
<td>$C_{46}$</td>
<td>$C_{26}$</td>
</tr>
<tr>
<td>$\Gamma_{33}$</td>
<td>$C_{55}$</td>
<td>$C_{44}$</td>
<td>$C_{33}$</td>
<td>$C_{34}$</td>
<td>$C_{35}$</td>
<td>$C_{45}$</td>
</tr>
<tr>
<td>$\Gamma_{23} = \Gamma_{23}$</td>
<td>$C_{56}$</td>
<td>$C_{24}$</td>
<td>$C_{34}$</td>
<td>$\frac{1}{2}[C_{23}+C_{44}]$</td>
<td>$\frac{1}{2}[C_{23}+C_{44}]$</td>
<td>$\frac{1}{2}[C_{23}+C_{44}]$</td>
</tr>
<tr>
<td>$\Gamma_{31} = \Gamma_{13}$</td>
<td>$C_{15}$</td>
<td>$C_{46}$</td>
<td>$C_{35}$</td>
<td>$\frac{1}{2}[C_{36}+C_{45}]$</td>
<td>$\frac{1}{2}[C_{36}+C_{45}]$</td>
<td>$\frac{1}{2}[C_{36}+C_{45}]$</td>
</tr>
<tr>
<td>$\Gamma_{21} = \Gamma_{12}$</td>
<td>$C_{16}$</td>
<td>$C_{26}$</td>
<td>$C_{45}$</td>
<td>$\frac{1}{2}[C_{25}+C_{66}]$</td>
<td>$\frac{1}{2}[C_{25}+C_{66}]$</td>
<td>$\frac{1}{2}[C_{25}+C_{66}]$</td>
</tr>
</tbody>
</table>
1.2 Ultrasonic wave propagation in single crystals

1.2.1 Orthorhombic

From the general expression for elastic waves propagation presented in the above section, one can deduce equations for higher symmetry crystals \([1.43]\). This is due to the fact that several elastic constants are zero for the higher symmetry crystals as it was shown in Table 1.1. Further simplification occurs when symmetry direction or planes are chosen as propagation direction so that one or two of the direction cosines \(n_1, n_2, n_3\) are equal to zero. For the orthorhombic crystal, for all point groups the nonzero elastic constants are \(C_{11}, C_{12}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}\). When other constants in the Christoffel matrix are zero, the coefficient of Christoffel matrix \(\Gamma_{ik}\) can be written as

\[
\begin{align*}
\Gamma_{11} &= C_{11}n_1^2 + C_{66}n_2^2 + C_{55}n_3^2 \\
\Gamma_{22} &= C_{66}n_1^2 + C_{22}n_2^2 + C_{44}n_3^2 \\
\Gamma_{33} &= C_{55}n_1^2 + C_{44}n_2^2 + C_{33}n_3^2 \\
\Gamma_{12} &= \Gamma_{21} = (C_{12} + C_{66})n_1n_2 \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{55})n_1n_3 \\
\Gamma_{23} &= \Gamma_{32} = 0 \\
\Gamma_{11} &= \Gamma_{22} = \Gamma_{33} = 0 \\
\Gamma_{12} &= \Gamma_{21} = (C_{12} + C_{66})n_1n_2
\end{align*}
\] (1.19)

Now consider wave propagation in the x- y plane which means \(n_3 = 0\). The \(\Gamma_{ik}\) coefficients now become

\[
\begin{align*}
\Gamma_{11} &= C_{11}n_1^2 + C_{66}n_2^2 \\
\Gamma_{22} &= C_{66}n_1^2 + C_{22}n_2^2 \\
\Gamma_{33} &= C_{55}n_1^2 + C_{44}n_2^2 \\
\Gamma_{12} &= \Gamma_{21} = (C_{12} + C_{66})n_1n_2 \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{55})n_1n_3 \\
\Gamma_{23} &= \Gamma_{32} = 0 \\
\Gamma_{11} &= \Gamma_{22} = \Gamma_{33} = 0 \\
\Gamma_{12} &= \Gamma_{21} = (C_{12} + C_{66})n_1n_2
\end{align*}
\] (1.20)
The determinantal equation can be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho v^2 & \Gamma_{12} & 0 \\
\Gamma_{12} & \Gamma_{22} - \rho v^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho v^2
\end{vmatrix} = 0
\]  

(1.21)

On expansion we get

\[
(\Gamma_{11} - \rho v^2) (\Gamma_{22} - \rho v^2) (\Gamma_{33} - \rho v^2) - \Gamma_{12}^2 (\Gamma_{13} - \rho v^2) = 0
\]

(1.22)

\[
(\Gamma_{33} - \rho v^2) [\rho^2 v^4 - \rho v^2 (\Gamma_{11} + \Gamma_{22}) + (\Gamma_{11} \Gamma_{22} - \Gamma_{12}^2)] = 0
\]

i.e. \( \Gamma_{33} = \rho v_0^2 \)  

(1.23)

and the quadratic equation gives the roots as

\[
2\rho v_1^2 = (\Gamma_{11} + \Gamma_{22}) + [((\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11} \Gamma_{22} - \Gamma_{12}^2)]^{1/2}
\]

and

\[
2\rho v_2^2 = (\Gamma_{11} + \Gamma_{22}) - [((\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11} \Gamma_{22} - \Gamma_{12}^2)]^{1/2}
\]

(1.24)

\( v_0 \) is a pure shear wave with polarization in the z-direction, \( v_1 \) is a quasi longitudinal wave and \( v_2 \) is a quasi shear wave.

In the x-y plane, the velocities are calculated in terms of elastic constants and direction cosines as

\[
\rho v_0^2 = C_{55} n_1^2 + C_{44} n_2^2
\]

(1.25)

\[
2\rho v_1^2 = (C_{11} n_1^2 + C_{22} n_2^2 + C_{66}) +
[(C_{11} n_1^2 + C_{22} n_2^2 + C_{66})^2 - 4(C_{11} n_1^2 + C_{66} n_2^2)]^{1/2}
\]

(1.26)

\[
2\rho v_2^2 = (C_{11} n_1^2 + C_{22} n_2^2 + C_{66}) -
[(C_{11} n_1^2 + C_{22} n_2^2 + C_{66})^2 - 4(C_{11} n_1^2 + C_{66} n_2^2)]^{1/2}
\]

(1.27)
These equations are obeyed by the normalized direction cosines

\[ n_1^2 + n_2^2 + n_3^2 = 1 \]  

(1.28)

Consider propagation in x-z plane, which means \( n_2 = 0 \), and the coefficients are then obtained as

\[ \Gamma_{11} = C_{11} n_1^2 + C_{55} n_3^2 \]

\[ \Gamma_{22} = C_{66} n_1^2 + C_{44} n_3^2 \]

\[ \Gamma_{33} = C_{55} n_1^2 + C_{33} n_3^2 \]

\[ \Gamma_{23} = \Gamma_{32} = 0 \]

\[ \Gamma_{12} = \Gamma_{21} = 0 \]

\[ \Gamma_{13} = \Gamma_{31} = (C_{13} + C_{55}) n_3 n_1 \]  

(1.29)

The characteristic equation is then given by

\[ (\Gamma_{22} - \rho v^2) \left[ \rho^2 v^4 - \rho v^2 (\Gamma_{11} + \Gamma_{33}) + (\Gamma_{11} \Gamma_{33} - \Gamma_{13}^2) \right] = 0 \]  

(1.30)

Then

\[ \rho v_0^2 = \Gamma_{22} \]  

(1.31)

The roots of quadratic equation are given by

\[ 2 \rho \nu_1^2 = (\Gamma_{11} + \Gamma_{33}) + [(\Gamma_{11} + \Gamma_{33})^2 - 4(\Gamma_{11} \Gamma_{33} - \Gamma_{13}^2)]^{1/2} \]

\[ 2 \rho \nu_2^2 = (\Gamma_{11} + \Gamma_{33}) - [(\Gamma_{11} + \Gamma_{33})^2 - 4(\Gamma_{11} \Gamma_{33} - \Gamma_{13}^2)]^{1/2} \]  

(1.32)

On substituting the values of \( \Gamma \) for x-z planes, the velocities are obtained in terms of the elastic constants and direction cosines as

\[ \rho v_0^2 = C_{66} n_1^2 + C_{44} n_3^2 \]

\[ 2 \rho \nu_1^2 = (C_{11} n_1^2 + C_{55} n_3^2) + [(C_{11} n_1^2 + C_{33} n_3^2 + C_{55})^2 - 4 (C_{11} n_1^2 + C_{55} n_3^2)]^{1/2} \]

\[ (C_{55} n_1^2 + C_{33} n_3^2) - (C_{13} + C_{55}) n_1^2 n_3^2 \]  

(1.34)
Consider the propagation in the y-z plane, which means that \( n_1 = 0 \), the coefficients are then obtained as

\[
\begin{align*}
\Gamma_{11} &= C_{66} n_2^2 + C_{55} n_3^2 \\
\Gamma_{22} &= C_{22} n_2^2 + C_{44} n_3^2 \\
\Gamma_{33} &= C_{44} n_2^2 + C_{55} n_3^2 \\
\Gamma_{13} &= \Gamma_{32} = 0 \\
\Gamma_{12} &= \Gamma_{21} = 0 \\
\end{align*}
\]  

(1.36)

The characteristic equation is given by

\[
(\Gamma_{11} - \rho v^2) [\rho^2 v^4 - \rho v^2 (\Gamma_{22} + \Gamma_{33}) + (\Gamma_{22} \Gamma_{33} - \Gamma_{23}^2)] = 0
\]

(1.37)

Then \( \Gamma_{11} = \rho v_0^2 \)

(1.38)

The quadratic equation provides two roots as

\[
2 \rho v_1^2 = (\Gamma_{22} + \Gamma_{33}) + [(\Gamma_{22} + \Gamma_{33})^2 - 4(\Gamma_{22} \Gamma_{33} - \Gamma_{23}^2)]^{1/2}
\]

(1.39)

On substituting values of \( \Gamma \) for the y-z plane in the above three equations, the velocities are obtained in terms of the elastic constants and direction cosines as
Thus one gets three sets of equations corresponding to three orthogonal symmetry
planes of the crystal.

Now consider the propagation along the symmetry axis of the crystal. Then x, y, z direction for the orthorhombic system corresponds to a, b, and c directions of the crystal or they are the [001], [010] and [001] directions.

For propagation in x-direction, the corresponding direction cosines are
\( n_1 = 1, n_2 = 0, n_3 = 0 \). In this case the coefficients reduce to

\[
\begin{align*}
\Gamma_{11} &= C'_{11}, \Gamma_{33} = 0 \\
\Gamma_{22} &= C'_{66}, \Gamma_{13} = 0 \\
\Gamma_{33} &= C'_{55}, \Gamma_{12} = 0
\end{align*}
\] (1.43)

The off diagonal elements are all zero and the characteristic equation is

\[
(\Gamma_{11} - \rho \nu^2)(\Gamma_{22} - \rho \nu^2)(\Gamma_{33} - \rho \nu^2) = 0
\] (1.44)

Which gives the solutions as
\[ \rho v_0^2 = \Gamma_{11} = C_{55} \]
\[ \rho v_1^2 = \Gamma_{22} = C_{22} \]
\[ \rho v_2^2 = \Gamma_{33} = C_{33} \] (1.45)

Then the three pure modes will be, \( v_0 \) longitudinal, \( v_1 \) transverse with \( y \) polarization and \( v_2 \) transverse with \( z \) polarization.

For propagation in \( y \)-direction, the corresponding direction cosines are \( n_1 = 0 \), \( n_2 = 1 \), \( n_3 = 0 \). Then the coefficients reduce to

\[ \Gamma_{11} = C_{66}, \Gamma_{23} = 0 \]
\[ \Gamma_{23} = C_{23}, \Gamma_{13} = 0 \]
\[ \Gamma_{33} = C_{44}, \Gamma_{12} = 0 \] (1.46)

The characteristic equation readily factorises to give the solutions

\[ \rho v_0^2 = \Gamma_{11} = C_{66} \]
\[ \rho v_1^2 = \Gamma_{22} = C_{22} \]
\[ \rho v_2^2 = \Gamma_{33} = C_{44} \] (1.47)

\( v_0 \) is transverse with \( x \)-polarization \( v_1 \) is longitudinal \( v_2 \) is transverse with \( z \)-polarization.

For propagation in \( z \) direction the corresponding direction cosines are \( n_1 = 0 \), \( n_2 = 0 \), \( n_3 = 1 \). In this case the coefficients reduce to

\[ \Gamma_{11} = C_{55}, \Gamma_{23} = 0 \]
\[ \Gamma_{22} = C_{44}, \Gamma_{13} = 0 \]
\[ \Gamma_{33} = C_{33}, \Gamma_{12} = 0 \] (1.48)

The characteristic equation readily factorises to give the solutions

\[ \rho v_0^2 = \Gamma_{11} = C_{55} \]
\[ \rho v_1^2 = \Gamma_{22} = C_{44} \]
\[ \rho v_2^2 = \Gamma_{33} = C_{33} \] (1.49)
These are also pure modes with $v_0$, transverse with $x$-polarization, $v_1$, transverse with $y$-polarization and $v_2$, longitudinal.

The elastic constant $C_{12}$ can be calculated by measuring the velocity perpendicular to the $a$-$b$ plane. Here the angle is measured from the $a$-axis. Then

$$C_{12} = f_{ab} = \left\{ \frac{1}{c^2 s^2} [(s^2 C_{11} + s^2 C_{66} - \rho v^2) (c^2 C_{66} + s^2 C_{22} - \rho v^2)] \right\}^{\frac{1}{2}} - C_{66} \quad (1.50)$$

The elastic constant $C_{23}$ is measured by propagating the sound wave with the velocity normal to the $b$-$c$ plane. The angle is measured from the $b$-axis. Then

$$C_{23} = f_{bc} = \left\{ \frac{1}{c^2 s^2} [(c^2 C_{22} + s^2 C_{44} - \rho v^2) (c^2 C_{44} + s^2 C_{33} - \rho v^2)] \right\}^{\frac{1}{2}} - C_{44} \quad (1.51)$$

The elastic constant $C_{13}$ can be measured by propagating the waves perpendicular to the $a$-$c$ plane where angle $\theta$ is measured from the $c$-axis.

$$C_{13} = f_{ac} = \left\{ \frac{1}{c^2 s^2} [(s^2 C_{11} + c^2 C_{55} - \rho v^2) (s^2 C_{55} + c^2 C_{33} - \rho v^2)] \right\}^{\frac{1}{2}} - C_{55} \quad (1.52)$$

Where $s = \sin \theta$, $c = \cos \theta$ and $v$ is the velocity of propagation of respective mode.

### 1.2.2 Tetragonal Type I (Point group (4, 4/m))

Tetragonal crystals have a four-fold axis of symmetry. The non-zero elastic constants [1.2] of tetragonal type-1 crystals are $C_{11} = C_{22}, C_{12} = C_{23}, C_{16} = - C_{26}, C_{33}$, $C_{44} = C_{55}$, and $C_{66}$. Retaining only the terms that contain non-zero elements, the coefficients of the Christoffel matrix $\Gamma_{ik}$ can be written as
Now consider the wave propagation in the x-y plane, the corresponding direction cosines are, \( n_3 = 0 \). In this case the coefficients reduce to

\[
\begin{align*}
\Gamma_{11} &= C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2 \\
\Gamma_{22} &= C_{66}n_1^2 + C_{11}n_2^2 + C_{44}n_3^2 \\
\Gamma_{33} &= C_{44}n_1^2 + C_{44}n_2^2 + C_{33}n_3^2 \\
\Gamma_{23} &= \Gamma_{32} = 0 \\
\Gamma_{13} &= \Gamma_{31} = 0 \\
\Gamma_{12} &= \Gamma_{21} = (C_{12} + C_{66})n_1n_2 + C_{16}n_1^2 \\
\end{align*}
\]  
(1.53)

Then the determinantal equation can be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho v^2 & \Gamma_{12} & 0 \\
\Gamma_{12} & \Gamma_{22} - \rho v^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho v^2 \\
\end{vmatrix} = 0
\]  
(1.55)

Which can be expanded as

\[
(\Gamma_{33} - \rho v^2)[(\Gamma_{11} - \rho v^2)(\Gamma_{22} - \rho v^2) - \Gamma_{12}^2] = 0
\]

\[
(\Gamma_{33} - \rho v^2)[\rho^2v^4 - \rho v^2(\Gamma_{11} + \Gamma_{22}) + (\Gamma_{22} - \Gamma_{11} - \Gamma_{12}^2)] = 0
\]  
(1.56)
The factor, which is linear in $\rho v^2$, yields the root

$$
\Gamma_{33} = \rho v_0^2 = C_{44}(n_1^2 + n_2^2) \tag{1.57}
$$

The factor, which is quadratic in $\rho v^2$, provides the other two roots

$$
2\rho v_1^2 = (\Gamma_{11} + \Gamma_{22}) + [(\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11}\Gamma_{22} - \Gamma_{12}^2)]^{1/2} \quad \text{and}
$$

$$
2\rho v_2^2 = (\Gamma_{11} + \Gamma_{22}) - [(\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11}\Gamma_{22} - \Gamma_{12}^2)]^{1/2} \tag{1.58}
$$

or

$$
2\rho v_1^2 = (C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2) + (C_{66}n_1^2 + C_{11}n_2^2)
$$

$$
+ \{(C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2) + (C_{66}n_1^2 + C_{11}n_2^2)\}^2
$$

$$
- 4[(C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2)(C_{66}n_1^2 + C_{11}n_2^2) - (C_{16}n_1^2 + (C_{12} + C_{66})n_1n_2)^2]^{1/2} \tag{1.59}
$$

$$
2\rho v_2^2 = (C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2) + (C_{66}n_1^2 + C_{11}n_2^2)
$$

$$
- \{(C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2) + (C_{66}n_1^2 + C_{11}n_2^2)\}^2
$$

$$
- 4[(C_{11}n_1^2 + C_{66}n_2^2 + 2C_{16}n_1n_2)(C_{66}n_1^2 + C_{11}n_2^2) - (C_{16}n_1^2 + (C_{12} + C_{66})n_1n_2)^2]^{1/2} \tag{1.60}
$$

on solving

$$
C_{12} = -\frac{1}{s c}\{(C_{11}s^2 + C_{66}s^2 + 2C_{16}s^2) - \rho v^2)((C_{66}s^2 + C_{11}s^2) - \rho v^2)]^{1/2} - (C_{66}s + C_{11}s^2)\} \tag{1.61}
$$

Where $s = \sin \theta$, $c = \cos \theta$ and $\theta$ is measured from the $a$-axis.

For the $x$-$z$ plane $n_2 = 0$, and the coefficients now become

$$
\Gamma_{11} = C_{11}n_1^2 + C_{44}n_3^2
$$

$$
\Gamma_{22} = C_{66}n_1^2 + C_{44}n_3^2
$$

$$
\Gamma_{33} = C_{44}n_1^2 + C_{33}n_3^2
$$
\[ \Gamma_{23} = \Gamma_{32} = 0 \]

\[ \Gamma_{13} = \Gamma_{31} = (C_{13} + C_{44})n_1n_3 \]

\[ \Gamma_{12} = \Gamma_{21} = C_{16}n_1^2 \]

Then the determinantal equation can be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho \nu^2 & \Gamma_{12} & \Gamma_{13} \\
\Gamma_{12} & \Gamma_{22} - \rho \nu^2 & 0 \\
\Gamma_{13} & 0 & \Gamma_{33} - \rho \nu^2
\end{vmatrix} = 0
\]  

(1.63)

Which can be expanded as

\[
(\Gamma_{33} - \rho \nu^2) (\Gamma_{11} - \rho \nu^2) (\Gamma_{22} - \rho \nu^2) - \Gamma_{12}^2 (\Gamma_{33} - \rho \nu^2) - \Gamma_{13}^2 (\Gamma_{22} - \rho \nu^2) = 0
\]

(1.64)

Which yields a cubic equation in \( \nu = \rho \nu^3 \)

\[ m^3 - m^2 A + mB - C = 0 \]  

(1.65)

in terms of elastic constants and direction sines and cosines

\[ m^3 - m^2 [(C_{33} + 2C_{44})c^2 + (C_{11} + C_{44} + C_{66})s^2] \\
\quad + m[(s^4 (2C_{66}C_{11} + C_{11}C_{66}) + s^2 c^2 (C_{66}C_{44} + C_{44}C_{11} + 2C_{44}^2 + C_{33}C_{11} + C_{33}) \\
\qquad c^4 (C_{44}^2 + 2C_{44}C_{33}) - s^4 C_{16}^2 + (C_{13} + C_{44})^2 s^2 c^2] \\
\quad - [s^4 C_{11}C_{66}C_{44} + c^4 C_{33}C_{44} + c^2 s^4 (C_{44}^2 (C_{11} + C_{66}) + C_{11}C_{22}C_{66}) \\
\qquad + s^2 c^4 ((C_{44}C_{11}C_{33} + C_{33}C_{66}) + C_{44}) - (C_{44}s^2 + C_{33}c^2)C_{16}^2 s^4 \\
\qquad + (C_{66}s^2 + C_{44}c^2) (C_{13} + C_{44})^2 c^2 s^2] ] \]

(1.66)

On solving, the value of \( m \) can be determined. Where

\[ A = a + b + c, B = ab + bc + ac - l^2, \]

\[ C = abc - cl^2, D = m - b \]  

(1.67)
And from this the elastic stiffness constant $C_{13}$ can be evaluated as

$$C_{13} = \frac{1}{sc} \left[ \frac{m^3 - m^2 A + m B + C}{D} \right]^{1/2} - C_{44} \quad (1.68)$$

$$a = C_{11} s^2 + C_{44} e^2, \quad b = C_{66} s^2 + C_{44} e^2,$$

$$c = C_{44} s^2 + C_{33} e^2,$$

$$l = C_{16} s^2, m = \rho v^2 \quad (1.69)$$

Now consider the wave propagation in the $y$-$z$ plane, the corresponding direction cosines are, $n_1 = 0$. In this case the coefficients reduce to

$$\Gamma_{11} = C_{44} n_3^2 + C_{66} n_2^2$$

$$\Gamma_{22} = C_{33} n_2^2 + C_{44} n_3^2 \quad (1.70)$$

$$\Gamma_{33} = C_{44} n_3^2 + C_{33} n_3^2$$

Consider the wave propagation in the $x$ direction. The corresponding direction cosines are $n_1 = 1, n_2 = 0, n_3 = 0$. In this case the coefficients reduce to

$$\Gamma_{23} = \Gamma_{32} = 0$$

$$\Gamma_{13} = \Gamma_{31} = 0$$

$$\Gamma_{12} = \Gamma_{21} = 0 \quad (1.71)$$

Then the determinantal equation can be written as

$$\begin{vmatrix}
\Gamma_{11} - \rho v^2 & 0 & 0 \\
0 & \Gamma_{22} - \rho v^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho v^2 
\end{vmatrix} = 0 \quad (1.72)$$
Which can be expanded as

\[(\Gamma_{11} - \rho \nu^2)[(\Gamma_{22} - \rho \nu^2)(\Gamma_{33} - \rho \nu^2)] = 0\]

\[(\Gamma_{11} - \rho \nu^2)[\rho^2 \nu^4 - \rho \nu^2(\Gamma_{33} + \Gamma_{22}) + (\Gamma_{22} + \Gamma_{33})] = 0\]  

(1.73)

The factor, which is linear in \(\rho \nu^2\), yields the root

\[\Gamma_{11} = \rho \nu_0^2 = C_{66}n_2^2 + C_{44}n_3^2\]  

(1.74)

The factor, which is quadratic in \(\rho \nu^2\), provides the other two roots

\[2\rho \nu_1^2 = (\Gamma_{33} + \Gamma_{22}) + [(\Gamma_{33} + \Gamma_{22})^2 - 4(\Gamma_{33}, \Gamma_{22})]^{1/2}\] and

\[2\rho \nu_2^2 = (\Gamma_{33} + \Gamma_{22}) - [(\Gamma_{33} + \Gamma_{22})^2 - 4(\Gamma_{33}, \Gamma_{22})]^{1/2}\]  

(1.75)

\[2\rho \nu_1^2 = (C_{11}n_2^2 + C_{33}n_3^2 + C_{44}) +

\left\{[(C_{11}n_2^2 + C_{33}n_3^2 + C_{44})^2 - 4(C_{11}n_2^2 + C_{44})n_3^2](C_{44}n_2^2 + C_{33}n_3^2)\right\}^{1/2}\]  

(1.76)

\[2\rho \nu_2^2 = (C_{11}n_2^2 + C_{33}n_3^2 + C_{44}) -

\left\{[(C_{11}n_2^2 + C_{33}n_3^2 + C_{44})^2 - 4(C_{11}n_2^2 + C_{44})n_3^2](C_{44}n_2^2 + C_{33}n_3^2)\right\}^{1/2}\]  

(1.77)

\[\Gamma_{11} = C_{11}, \quad \Gamma_{23} = \Gamma_{32} = 0\]

\[\Gamma_{22} = C_{66}, \quad \Gamma_{13} = \Gamma_{31} = 0\]

\[\Gamma_{33} = C_{44}, \quad \Gamma_{12} = C_{16}\]  

(1.78)

Then the determinantal equation can be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho \nu^2 & \Gamma_{12} & 0 \\
\Gamma_{12} & \Gamma_{22} - \rho \nu^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho \nu^2
\end{vmatrix} = 0\]  

(1.79)
(Γ₃₃ − ρν²)[(Γ₁₁ − ρν²)(Γ₂₂ − ρν²) − Γ₁₂²] = 0

(Γ₃₃ − ρν²)[ρ²ν² − ρν²(Γ₁₁ + Γ₂₂) + (Γ₂₂Γ₁₁ − Γ₁₂²)] = 0

2ρν₁² = (Γ₁₁ + Γ₂₂) + [(Γ₁₁ + Γ₂₂)² − 4(Γ₁₁Γ₂₂ − Γ₁₂²)]² and

2ρν₂² = (Γ₁₁ + Γ₂₂) − [(Γ₁₁ + Γ₂₂)² − 4(Γ₁₁Γ₂₂ − Γ₁₂²)]²

in terms elastic constants

2ρν₁² = (C₁₁ + C₆₆) + [(C₁₁ + C₆₆)² − 4(C₁₁C₆₆ − C₁₆²)]²

2ρν₂² = (C₁₁ + C₆₆) − [(C₁₁ + C₆₆)² − 4(C₁₁C₆₆ − C₁₆²)]²

On solving

C₁₆ = \frac{1}{2} \left[ (ρν₁² − ρν₂²) − (C₁₁ + C₆₆)² \right]^{\frac{1}{2}}

v₀ is the shear mode polarized normal to the z, ν₁ is a longitudinal wave and ν₂ is the shear mode polarized normal to the y.

Consider the wave propagation in the y direction. The corresponding direction cosines are n₁ = 0, n₂ = 1, n₃ = 0. In this case the coefficients reduce to

Γ₁₁ = C₆₆ \quad Γ₂₂ = C₂₂ = C₁₁ \quad Γ₃₃ = C₄₄

Γ₂₃ = 0 \quad Γ₁₃ = 0 \quad Γ₁₂ = 0

The characteristic equation readily factorises to give the solution

(Γ₁₁ − ρν²)(Γ₂₂ − ρν²)(Γ₃₃ − ρν²) = 0
Consider the wave propagation in the z direction. The corresponding direction cosines are $n_1 = 0$, $n_2 = 0$, $n_3 = 1$. In this case the coefficients reduce to

$$\begin{align*}
\Gamma_{33} &= C_{33} \\
\Gamma_{11} &= C_{44} = C_{55} \\
\Gamma_{23} &= 0 \\
\Gamma_{13} &= 0 \\
\Gamma_{12} &= 0
\end{align*} \quad (1.88)$$

Then

$$(\Gamma_{11} - \rho v^2)(\Gamma_{22} - \rho v^2)(\Gamma_{33} - \rho v^2) = 0 \quad (1.89)$$

$\rho v_0^2 = \Gamma_{11} = C_{44}$

$\rho v_1^2 = \Gamma_{22} = C_{44}$

$\rho v_2^2 = \Gamma_{33} = C_{33} \quad (1.90)$

Here $v_0$ is the shear mode polarized in the y direction, $v_1$ is also the shear mode polarized in the x-direction and $v_2$ is the longitudinal mode.

**1.2.3 Trigonal (Rhombohedral) type-II**

Trigonal crystals are having three-fold axis of symmetry and having three mirror planes [1.8]. The non zero elastic constants of trigonal type-II crystals are $C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{14} = \frac{1}{2} C_{24}, C_{33}$ and $C_{44} = C_{55}$ also $C_{56} = 2, C_{14}$ and $C_{66} = \frac{1}{2} (C_{11}, C_{12})$

Retaining only the terms that contain non zero elements, the coefficients of Christoffel matrix $\Gamma_{ik}$ can be written as

$$\rho v_0^2 = \Gamma_{11} = C_{44}$$

$$\rho v_1^2 = \Gamma_{22} = C_{44}$$

$$\rho v_2^2 = \Gamma_{33} = C_{33}$$
The $z$-axis gives pure mode [1.8]. In addition to this, there is pure mode axis in the base plane, perpendicular to any of the three mirror planes. There are additional pure mode axes lying in the mirror planes. With these two axes, live of the $C_{ij}$'s can be determined[1.8]. The sixth elastic constant $C_{13}$ can be found by propagating a wave in a mirror plane at 45° with the $z$-axis and the base plane[1.8]. Then from this direction the sixth elastic constant can be determined. Propagation in the $z$-direction or in the three fold symmetry axis $n_1 = 0, n_2 = 0, n_3 = 1$

The coefficients reduce to

\[
\begin{align*}
\Gamma_{11} &= C_{44} \Gamma_{22} = \Gamma_{33} = 0 \\
\Gamma_{22} &= C_{44} \Gamma_{13} = \Gamma_{31} = 0 \\
\Gamma_{33} &= C_{33} \Gamma_{12} = 0
\end{align*}
\]  

(1.92)

Then the determinantal equations can be written as

\[
\begin{bmatrix}
\Gamma_{11} - \rho v^2 & 0 & 0 \\
0 & \Gamma_{22} - \rho v^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho v^2
\end{bmatrix} = 0
\]  

(1.93)
This can be expanded as
\[(\Gamma_{11} - \rho v^2)(\Gamma_{22} - \rho v^2)(\Gamma_{33} - \rho v^2) = 0\]  
(1.94)

Which gives the solutions as
\[
\begin{align*}
\rho v_0^2 &= \Gamma_{11} = C_{44} \\
\rho v_1^2 &= \Gamma_{22} = C_{44} \\
\rho v_2^2 &= \Gamma_{33} = C_{33}
\end{align*}
\]  
(1.95)

Where \(v_2\) is the pure longitudinal mode, \(v_1\) and \(v_0\) are pure transverse modes.

For propagation in base plane normal to mirror plane i.e., in the x-direction \(n_1 = 1, \ n_2 = n_3 = 0\). Then the Christoffel matrix \(\Gamma_{ik}\) can be written as

\[
\begin{align*}
\Gamma_{11} &= C_{11}, \Gamma_{23} = \Gamma_{32} = C_{56} \\
\Gamma_{22} &= C_{66}, \Gamma_{13} = \Gamma_{31} = 0 \\
\Gamma_{33} &= C_{44}, \Gamma_{12} = 0
\end{align*}
\]  
(1.96)

Then the determinant can be written as
\[
\begin{vmatrix}
\Gamma_{11} - \rho v^2 & 0 & 0 \\
0 & \Gamma_{22} - \rho v^2 & \Gamma_{23} \\
0 & \Gamma_{33} & \Gamma_{33} - \rho v^2
\end{vmatrix} = 0
\]  
(1.97)

Which can be expanded as
\[
(\Gamma_{11} - \rho v^2)[(\Gamma_{22} - \rho v^2) (\Gamma_{33} - \rho v^2) - \Gamma_{23}^2] = 0
\]  
(1.98)

\[
\rho v_0^2 = \Gamma_{11} = C_{11}
\]  
(1.99)

The factor, which is linear in \(\rho v^2\) is
\[
(\Gamma_{11} - \rho v^2) \left[ \rho^2 v^4 - \rho v^2 (\Gamma_{22} + \Gamma_{33}) + (\Gamma_{22} \Gamma_{33} - \Gamma_{23}^2) \right] = 0
\]  
(1.100)
The factor, which is quadratic in $\rho v^2$, provides the two roots

$$2\rho v_1^2 = (\Gamma_{22} + \Gamma_{33}) + [(\Gamma_{22} + \Gamma_{33})^2 - 4(\Gamma_{33}\Gamma_{22} - \Gamma_{23}^2)]^{1/2}$$

and

$$2\rho v_2^2 = (\Gamma_{22} + \Gamma_{33}) - [(\Gamma_{22} + \Gamma_{33})^2 - 4(\Gamma_{33}\Gamma_{22} - \Gamma_{23}^2)]^{1/2}$$

(1.101)

The sign and magnitude of $C_{14}$ can be determined from Equation [1.101]

$$2\rho v_1^2 - (C_{66} + C_{44}) = \frac{I}{2} \left[(C_{66} + C_{44})^2 - 4(C_{66}C_{44} - C_{14}^2)\right]^{1/2}$$

(1.102)

$$C_{14} = \frac{1}{2} \left[2\rho v_1^2 - (C_{66} + C_{44})\right] - (C_{66} - C_{44})^2 \left[2\rho v_1^2 - (C_{66} + C_{44})\right]^{1/2}$$

(1.103)

From Equation [1.101]

$$\rho v_1^2 + \rho v_2^2 = [C_{66} + C_{44}] = C_{44} + \frac{1}{2}[C_{11} - C_{12}]$$

(1.104)

$$C_{12} = C_{44} + 2C_{44} - 2[\rho v_1^2 + \rho v_2^2]$$

(1.105)

$v_0$ is pure longitudinal mode $v_1$ is transverse mode polarized normal to $z$-axis $v_2$ is also a transverse polarized normal to $y$-axis

The sixth elastic constant $C_{13}$ can be found by propagating a wave in a mirror plane at $45^\circ$ with the $z$-axis and the base plane.

$$\Gamma_{11} = C_{11}n_1^2 + C_{44}n_3^2$$

$$\Gamma_{22} = C_{66}n_1^2 + C_{44}n_3^2$$

$$\Gamma_{33} = C_{44}n_1^2 + C_{33}n_3^2$$

$$\Gamma_{23} = \Gamma_{32} = C_{14}n_1^2$$

$$\Gamma_{13} = \Gamma_{31} = (C_{13} + C_{44})n_1n_3$$

(1.106)

$$\Gamma_{12} = \Gamma_{21} = 2C_{14}n_1n_3$$
Then the determinantal equation can be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho v^2 & \Gamma_{12} & \Gamma_{13} \\
\Gamma_{12} & \Gamma_{22} - \rho v^2 & \Gamma_{23} \\
\Gamma_{13} & \Gamma_{23} & \Gamma_{33} - \rho v^2
\end{vmatrix} = 0
\] (1.107)

Which can be expanded as

\[
[ (\Gamma_{33} - \rho v^2) (\Gamma_{11} - \rho v^2) (\Gamma_{22} - \rho v^2) - \\
\Gamma_{13}^2 - \Gamma_{12} (\Gamma_{33} - \rho v^2) - \Gamma_{13}^2 + \Gamma_{13} (\Gamma_{22} - \rho v^2) ] = 0
\] (1.108)

which yields a cubic equation in \( m = \rho v^2 \)

Let

\[
\begin{align*}
\Gamma_{11} &= C_{11} n_1^2 + C_{44} n_3^2 = a \\
\Gamma_{22} &= C_{66} n_1^2 + C_{44} n_3^2 = b \\
\Gamma_{33} &= C_{44} n_1^2 + C_{33} n_3^2 = c \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{44}) n_1 n_3 = n \\
\Gamma_{12} &= \Gamma_{21} = 2 C_{14} n_1 n_3 = l
\end{align*}
\] (1.109)

\( \rho v^2 = m \)

where \( n_1 = 0, n_2 = 1/\sqrt{2}, n_3 = 1/\sqrt{2} \)

\[
(a - m)[(b - m)(c - m) - n^2] - l^2 (c - m) + 2 \ln^2 - n^2 (b - m) = 0
\] (1.110)

\[
m^3 - m^2 (a + b + c) + m(ab + bc + ac - l^2) = abc - n^2 (a - b - 2l) - cl^2
\]

Let

\[
\begin{align*}
a + b + c &= A \\
ab + bc + ac - l^2 &= B \\
abc - cl^2 &= C \\
(a - b - 2l) &= D
\end{align*}
\] (1.111)
Then \[ m^3 - m^2 A + mB = C - n^2 D \] (1.112)

\[ n^2 = \frac{[C - (m^3 - m^2 A + mB)]}{D} \]

But \[ n = (C_{13} + C_{44}) n_3 n_1 \]

Therefore \[ C_{13} = \frac{1}{n_3 n_1} \left\{ \frac{[C - (m^3 - m^2 A + mB)]}{D} \right\}^{\frac{1}{2}} - C_{44} \] (1.113)

where \( n_3 = \cos \theta \quad n_1 = \sin \theta \quad \) and \( \theta \) is measured from c axis. Here velocity is in quasi-longitudinal mode

Now consider the wave propagation in the y-z plane, the corresponding direction cosines is \( n_1 = 0 \). In this case the coefficients reduce to

\[ \Gamma_{11} = C_{66} n_2^2 + C_{44} n_3^2 + 2C_{68} n_2 n_3 \]

\[ \Gamma_{22} = C_{11} n_2^2 + C_{44} n_3^2 \]

\[ \Gamma_{33} = C_{44} n_1^2 + C_{44} n_3^2 \]

\[ \Gamma_{23} = \Gamma_{32} = (C_{13} + C_{44}) n_2 n_3 \]

\[ \Gamma_{13} = \Gamma_{31} = 0 \]

\[ \Gamma_{12} = \Gamma_{21} = 0 \] (1.114)

Then the determinantal equation be written as

\[
\begin{vmatrix}
\Gamma_{11} - \rho \nu^2 & 0 & 0 \\
0 & \Gamma_{22} - \rho \nu^2 & \Gamma_{23} \\
0 & \Gamma_{32} & \Gamma_{33} - \rho \nu^2
\end{vmatrix} = 0
\] (1.115)
Which can be expanded as

\[(\Gamma_{11} - \rho \nu^2) [ (\Gamma_{33} - \rho \nu^2) (\Gamma_{22} - \rho \nu^2) - \Gamma_{23}^2 ] = 0\]

\[(\Gamma_{11} - \rho \nu^2) \left[ \rho^2 \nu^4 - \rho \nu^2 (\Gamma_{33} + \Gamma_{22}) + (\Gamma_{22} \Gamma_{33} - \Gamma_{23}^2) \right] = 0\]

\[2\rho \nu_1^2 = (\Gamma_{33} + \Gamma_{22}) + [(\Gamma_{33} + \Gamma_{22})^2 - 4(\Gamma_{33} \Gamma_{22} - \Gamma_{23}^2)]^{1/2}\]

and

\[2\rho \nu_2^2 = (\Gamma_{33} + \Gamma_{22}) - [(\Gamma_{33} + \Gamma_{22})^2 - 4(\Gamma_{33} \Gamma_{22} - \Gamma_{23}^2)]^{1/2}\]

\[\rho \nu_0^2 = C_{66} n_2^2 + C_{44} n_3^2 + 2C_{56} n_2 n_3\]  \hspace{1cm} (1.116)

\[2\rho \nu_1^2 = (C_{11} n_2^2 + C_{44} n_3^2 + C_{44}) + [(C_{11} n_2^2 + C_{44} n_3^2 + C_{44})^2 - 4(C_{11} n_2^2 + C_{44} n_3^2 + C_{44}) n_2^2 n_3^2]^{1/2}\]  \hspace{1cm} (1.117)

\[2\rho \nu_2^2 = (C_{11} n_2^2 + C_{44} n_3^2 + C_{44}) - [(C_{11} n_2^2 + C_{44} n_3^2 + C_{44})^2 - 4(C_{11} n_2^2 + C_{44} n_3^2 + C_{44}) n_2^2 n_3^2]^{1/2}\]  \hspace{1cm} (1.118)

where \(n_3 = \cos \theta\), \(n_2 = \sin \theta\), and \(\theta\) is measured from the c-axis. Here \(\nu_0\), velocity in quasi-longitudinal mode, \(\nu_1\) and \(\nu_2\) are the velocities in quasi-transverse modes.

### 1.2.4 Hexagonal

For the hexagonal crystal the nonzero elastic constants are \(C_{11} = C_{22}\), \(C_{13}, C_{44} = C_{55}, C_{12}, C_{13} = C_{23}\) and \(C_{66} = \frac{1}{2} [C_{11} - C_{12}]\). All other constants in the Christoffel matrix are zero. The coefficients of Christoffel matrix \(\Gamma_{ik}\) can be written as

\[\Gamma_{11} = C_{31} n_1^2 + C_{66} n_2^2 + C_{44} n_3^2\]

\[\Gamma_{22} = C_{66} n_1^2 + C_{11} n_2^2 + C_{44} n_3^2\]

\[\Gamma_{33} = C_{44} n_1^2 + C_{44} n_2^2 + C_{33} n_3^2\]

\[\Gamma_{23} = \Gamma_{32} = (C_{44} + C_{13}) n_3 n_3\]

\[\Gamma_{13} = \Gamma_{31} = (C_{13} + C_{44}) n_3 n_1\]

\[\Gamma_{12} = \Gamma_{21} = (C_{11} - C_{66}) n_1 n_2\]  \hspace{1cm} (1.119)
Now consider the wave propagation in the x-y plane which means $n_3 = 0$ the $\Gamma_{ik}$ coefficients now become

$$
\Gamma_{11} = C_{11}n_1^2 + C_{66}n_2^2 \\
\Gamma_{22} = C_{66}n_1^2 + C_{11}n_2^2 \\
\Gamma_{33} = C_{44}n_1^2 + C_{44}n_2^2 \\
\Gamma_{23} = \Gamma_{32} = 0 \\
\Gamma_{13} = \Gamma_{31} = 0 \\
\Gamma_{12} = \Gamma_{21} = (C_{11} - C_{66})n_1n_2
$$

The determinantal equation can be written as

$$
\begin{vmatrix}
\Gamma_{11} - \rho v^2 & \Gamma_{12} & 0 \\
\Gamma_{12} & \Gamma_{22} - \rho v^2 & 0 \\
0 & 0 & \Gamma_{33} - \rho v^2
\end{vmatrix} = 0
$$

(1.121)

On expansion one will get

$$(\Gamma_{11} - \rho v^2)(\Gamma_{22} - \rho v^2)(\Gamma_{33} - \rho v^2) - \Gamma_{12}^2(\Gamma_{33} - \rho v^2) = 0$$

(1.122)

$$(\Gamma_{33} - \rho v^2)[\rho^2 v^4 - \rho v^2(\Gamma_{11} + \Gamma_{22}) + (\Gamma_{11}\Gamma_{22} - \Gamma_{12}^2)] = 0$$

i.e., $\Gamma_{33} = \rho v^2$

(1.123)

And the quadratic equation gives the roots as

$$2\rho v_1^2 = (\Gamma_{11} + \Gamma_{22}) + [(\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11}\Gamma_{22} - \Gamma_{12}^2)]^{1/2}$$

and

$$2\rho v_2^2 = (\Gamma_{11} + \Gamma_{22}) - [(\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11}\Gamma_{22} - \Gamma_{12}^2)]^{1/2}$$

(1.124)
On substitution of the \( \Gamma \) values for the \( x\)-\( y \) plane in the above solution for hexagonal crystal, considerable algebraic simplification occurs and very simple solutions are obtained as

\[
\begin{align*}
\rho v_o^2 &= C_{44} \\
\rho v_1^2 &= C_{11} \\
\rho v_2^2 &= C_{66}
\end{align*}
\]  
(1.125)

The above results showed that the velocity is independent of the direction in this plane and that all modes are pure. \( v_o \) is a shear mode polarized parallel to \( z \)-axis, \( v_1 \) is a longitudinal mode and \( v_2 \) is a shear mode polarized normal to \( z \)-axis. The above relations are valid for the directions \( x \), \( y \) or any direction in the plane.

Consider propagation in \( x\)-\( z \) plane, which means \( n_2 = 0 \). The coefficients are then obtained as

\[
\begin{align*}
\Gamma_{11} &= C_{11} n_1^2 + C_{44} n_3^2 \\
\Gamma_{22} &= C_{66} n_1^2 + C_{44} n_3^2 \\
\Gamma_{33} &= C_{44} n_1^2 + C_{33} n_3^2 \\
\Gamma_{23} &= \Gamma_{32} = 0 \\
\Gamma_{12} &= \Gamma_{21} = 0 \\
\Gamma_{13} &= \Gamma_{31} = (C_{15} + C_{44}) n_3 n_1
\end{align*}
\]  
(1.126)

The characteristic equation is then given by

\[
(\Gamma_{22} - \rho v^2) [\rho^2 v^4 - \rho v^2 (\Gamma_{11} + \Gamma_{33}) + (\Gamma_{11} - \Gamma_{33} - \Gamma_{13}^2)] = 0
\]  
(1.127)

Then the linear part gives one root and the quadratic part gives two roots. Then

\[
\rho v_o^2 = \Gamma_{22}
\]  
(1.128)
The roots of quadratic equation are given by

\[ 2 \rho v_1^2 = (\Gamma_{11} + \Gamma_{33}) + [(\Gamma_{11} + \Gamma_{33})^2 - 4(\Gamma_{11} \Gamma_{33} - \Gamma_{13}^2)]^{1/2} \]

\[ 2 \rho v_2^2 = (\Gamma_{11} + \Gamma_{33}) - [(\Gamma_{11} + \Gamma_{33})^2 - 4(\Gamma_{11} \Gamma_{33} - \Gamma_{13}^2)]^{1/2} \]

On substituting the values of \( \Gamma \) for \( x-z \) planes, the velocities are obtained in terms of the elastic constants and direction cosines as

\[ \rho v_0^2 = C_{66} n_1^2 + C_{44} n_3^2 \]  \hspace{1cm} (1.130)

\[ 2 \rho v_1^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{44}) + [(C_{11} n_1^2 + C_{33} n_3^2 + C_{44})^2 - 4 (C_{11} n_1^2 + C_{44} n_3^2)] \]

\[ (C_{44} n_1^2 + C_{33} n_3^2) - (C_{13} + C_{44})^2 n_1^2 n_3^2 \] \(1/2\)  \hspace{1cm} (1.131)

\[ 2 \rho v_2^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{44}) - [(C_{11} n_1^2 + C_{33} n_3^2 + C_{44})^2 - 4 (C_{11} n_1^2 + C_{44} n_3^2)] \]

\[ (C_{44} n_1^2 + C_{33} n_3^2) - (C_{13} + C_{44})^2 n_1^2 n_3^2 \] \(1/2\)  \hspace{1cm} (1.132)

\( v_0 \) is a pure shear mode polarized normal to the plane, \( v_1 \) is a quasi longitudinal wave and \( v_2 \) is a quasi shear wave. It can be seen that these expressions are rotationally invariant for rotations about the \( z \)-axis. Hence same expressions are valid for the \( y-z \) plane also.

For propagation in \( x \)-direction, the corresponding direction cosines are \( n_1 = 1 \), \( n_2 = 0 \), \( n_3 = 0 \). In this case the coefficients reduce to

\[ \Gamma_{11} = C_{11}, \quad \Gamma_{23} = \Gamma_{32} = 0 \]

\[ \Gamma_{22} = C_{66}, \quad \Gamma_{13} = \Gamma_{31} = 0 \]

\[ \Gamma_{33} = C_{44}, \quad \Gamma_{12} = 0 \]  \hspace{1cm} (1.133)

The off diagonal elements are all zero and the characteristic equation is

\[ (\Gamma_{11} - \rho v^2) (\Gamma_{22} - \rho v^2) (\Gamma_{33} - \rho v^2) = 0 \]  \hspace{1cm} (1.134)
\[ \rho v_0^2 = \Gamma_{33} = C_{44} \]

This gives the solutions as

\[ \rho v_1^2 = \Gamma_{11} = C_{33} \]
\[ \rho v_2^2 = \Gamma_{22} = C_{66} \]  

Then the pure mode waves are \( v_0 \) transverse mode polarized parallel to \( z \) axis, \( v_1 \) is longitudinal and \( v_2 \) is transverse mode polarized normal to \( z \).

For symmetry direction along the \( z \) axis the above expressions [1.130-1.132] can be simplified by putting \( n_1 = 0 \) and \( n_3 = 1 \). This gives

\[ \rho v_0^2 = \Gamma_{33} = C_{44} \]

i.e.

\[ \rho v_1^2 = \Gamma_{11} = C_{33} \]
\[ \rho v_2^2 = \Gamma_{22} = C_{44} \]  

\( v_1 \) is a longitudinal modes, \( v_0 \) and \( v_2 \) are shear modes polarized normal to \( z \) axis and are degenerate since the two transverse velocities are identical in the \( z \) direction of the hexagonal crystal. Then the \( z \)-axis is an acoustic axis of the crystal.

From Equations [1.131,1.132] The elastic constant \( C_{13} \) can be measured by propagating the waves perpendicular to \( a-c \) plane where angle \( \theta \) is measured from \( c \)-axis.

Let

\[ \Gamma_{11} = a \quad \Gamma_{33} = b \quad \Gamma_{13} = c \quad \rho v^2 = m \]

\[ m^2 - m(a + b) + ab = c \quad \text{or} \quad (a - m)(b - m) = c = (C_{13} + C_{44})s^2C^2 \]

\[ C_{13} = f_{ac} = \left\{ \frac{1}{c^2 s^2} \left[ (s^2 C_{11} + c^2 C_{55} - \rho v^3)(s^2 C_{44} + c^2 C_{33} - \rho v^2) \right] \right\}^{1/2} - C_{44} \]  

where \( s = \sin \theta \quad c = \cos \theta \) and \( v \) is the velocity of propagation of respective mode.
1.3 Measurements of elastic constants by Ultrasonic methods

The elastic stiffness constants can be obtained by measuring ultrasonic velocity and density of the material. Thus by measuring the acoustic wave velocity in specified direction, one can measure the elastic constants of the crystal. Obtaining elastic constants for low symmetry crystal is very difficult. If eigen values represent the mode of vibration neither parallel nor perpendicular to the propagation direction, such modes are known as quasi-longitudinal or quasi shear mode. For such modes velocity cannot be related directly to single elastic constant. Further, great care is required in orienting, cutting and polishing the crystal exactly in the pure mode direction. Then measurements can be performed along that direction. Any small deviation from the required direction will bring contributions from several other constants. In ultrasonic experiments the three different modes in any given direction can be obtained by choosing [X-cut] transducer for the longitudinal and the [Y-cut] transducer for the two transverse modes.

1.3.1 Density measurement

Density is an essential parameter in the determination of elastic constant. The accuracy of the density determination by hydrostatic weighing depends on the weight in air \( W_a \), weight in liquid \( W_l \) and density of the liquid \( \rho_l \). Then error in density can be calculated \[1.41\]. For the highest precision one must use big samples and the immersion liquid must be with a density as close as possible to that of the material to be measured. Then error can be kept small.

1.3.2 Elastic constant measurements in orthorhombic crystal

In Orthorhombic crystal, the crystallographic directions a, b, c are pure mode directions. All the three velocities measured along these directions are related to single elastic constant only. Measurement in this direction will isolate all the diagonal constants \( C_{11}, C_{22}, C_{33}, C_{44}, C_{55} \) and \( C_{66} \) in the elastic constant matrix.
To find the off diagonal constant quasi-longitudinal waves in various symmetry planes x-y, x-z, and y-z can be used. The off diagonal constants $C_{12}$, $C_{13}$ and $C_{23}$ appear in combination with other constants. The corresponding relationships are explained in Section 1.2.1. When propagation direction is to be specified for cutting the crystal or to measure the direction of propagation, it is convenient to express the direction in a plane, in terms of angle from a, b, c than in terms of direction cosines. The direction cosines are obtained as the sine and cosines function of this angle. The convention adopted for this work is illustrated in Figure 1.2. The sound velocity-elastic moduli relationship of the orthorhombic system have been tabulated in the Table 1.4.

Table 1.4: Sound velocity- Elastic moduli relations for the orthorhombic system

<table>
<thead>
<tr>
<th>No</th>
<th>Mode</th>
<th>Direction of propagation</th>
<th>Direction of Polarisation</th>
<th>Formula for Elastic moduli</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L</td>
<td>a</td>
<td>a</td>
<td>$C_{11} = \rho V_{1}^2$</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>a</td>
<td>b</td>
<td>$C_{66} = \rho V_{2}^2$</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>a</td>
<td>c</td>
<td>$C_{15} = \rho V_{3}^2$</td>
</tr>
<tr>
<td>4</td>
<td>L</td>
<td>b</td>
<td>b</td>
<td>$C_{22} = \rho V_{4}^2$</td>
</tr>
<tr>
<td>5</td>
<td>T</td>
<td>b</td>
<td>a</td>
<td>$C_{66} = \rho V_{5}^2$</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>b</td>
<td>c</td>
<td>$C_{44} = \rho V_{6}^2$</td>
</tr>
<tr>
<td>7</td>
<td>L</td>
<td>c</td>
<td>c</td>
<td>$C_{33} = \rho V_{7}^2$</td>
</tr>
<tr>
<td>8</td>
<td>T</td>
<td>c</td>
<td>a</td>
<td>$C_{55} = \rho V_{8}^2$</td>
</tr>
<tr>
<td>9</td>
<td>T</td>
<td>c</td>
<td>b</td>
<td>$C_{44} = \rho V_{9}^2$</td>
</tr>
<tr>
<td>10</td>
<td>QL</td>
<td>a-b plane</td>
<td>a</td>
<td>$C_{12} = \rho V_{10}^2$</td>
</tr>
<tr>
<td>11</td>
<td>QT</td>
<td>a-b plane</td>
<td>c</td>
<td>$C_{33} = \rho V_{11}^2$</td>
</tr>
<tr>
<td>12</td>
<td>T</td>
<td>a-b plane</td>
<td>c</td>
<td>$C_{55} = \rho V_{12}^2$</td>
</tr>
<tr>
<td>13</td>
<td>QL</td>
<td>b-c plane</td>
<td>a</td>
<td>$C_{23} = \rho V_{13}^2$</td>
</tr>
<tr>
<td>14</td>
<td>QT</td>
<td>b-c plane</td>
<td>a</td>
<td>$C_{33} = \rho V_{14}^2$</td>
</tr>
<tr>
<td>15</td>
<td>T</td>
<td>b-c plane</td>
<td>a</td>
<td>$C_{44} = \rho V_{15}^2$</td>
</tr>
<tr>
<td>16</td>
<td>QL</td>
<td>a-c plane</td>
<td>b</td>
<td>$C_{66} = \rho V_{16}^2$</td>
</tr>
<tr>
<td>17</td>
<td>QT</td>
<td>a-c plane</td>
<td>b</td>
<td>$C_{11} = \rho V_{17}^2$</td>
</tr>
<tr>
<td>18</td>
<td>T</td>
<td>a-c plane</td>
<td>b</td>
<td>$C_{44} = \rho V_{18}^2$</td>
</tr>
</tbody>
</table>

The abbreviations used have the following meaning L-longitudinal, T-Transverse, QL-Quasi-longitudinal, QT-Quasi-transverse, S-sine and C-cosine
of angle $\theta$ from respective axis, $\rho$- density, $V$-velocity of propagation of respective mode, $a$, $b$, $c$ crystallographic axes

$$C_{12} = f_{12} = \left\{ \frac{1}{c^2 s^2} \left[ (s^2 C_{11} + s^2 C_{66} - \rho \nu_{10}^2)(c^2 C_{66} + s^2 C_{22} - \rho \nu_{10}^2) \right] \right\}^{1/2} - C_{66} \quad (1.138)$$

$$C_{23} = f_{23} = \left\{ \frac{1}{c^2 s^2} \left[ (c^2 C_{22} + s^2 C_{44} - \rho \nu_{32}^2)(c^2 C_{44} + s^2 C_{33} - \rho \nu_{32}^2) \right] \right\}^{1/2} - C_{44} \quad (1.139)$$

$$C_{13} = f_{13} = \left\{ \frac{1}{c^2 s^2} \left[ (s^2 C_{11} + c^2 C_{55} - \rho \nu_{61}^2)(s^2 C_{55} + c^2 C_{33} - \rho \nu_{61}^2) \right] \right\}^{1/2} - C_{55} \quad (1.140)$$

Eighteen such mode velocity measurements are possible. But twelve mode velocity measurements are sufficient to evaluate the nine-second order elastic stiffness constant with cross checks possible on some of the values.

$$n_1 = \cos \theta; \: n_2 = \sin \theta \quad \text{a-b plane} \: \quad n_2 = \cos \theta; \: n_3 = \sin \theta \quad \text{b-c plane} \: \quad n_3 = \cos \theta; \: n_1 = \sin \theta \quad \text{a-c plane}$$

*Figure 1.2 Direction cosines to rotation angle conversion scheme in symmetry plane*

1.3.3 Elastic constant measurements of Tetragonal crystal

In Section 1.2.2 the relation connecting propagation velocity and elastic constant have been derived for tetragonal crystal. The diagonal constants $C_{11} = C_{22}, \: C_{33}, \: C_{44} = C_{55}$ and $C_{66}$ can be obtained by measuring velocities in the symmetry direction $a$ and $c$. The measurement in the $b$- direction gives the same
information as in the a-direction due to rotational invariance of velocity. For finding $C_{16}$ the transverse velocity measurement in a-direction with polarization in c-direction can be used, $C_{16}$ can then be computed by using Equation 1.141 after substituting the values of $C_{11}$ and $C_{66}$. The independent off diagonal constant $C_{12}$ is obtained by measuring velocity of the quasi longitudinal wave in the a-b plane provided the constant $C_{11}$, $C_{16}$ and $C_{66}$ are known (Eq 1.142). The seventh off diagonal constant $C_{13}$ is deduced by measuring velocity of the quasi longitudinal wave in the a-c plane provided the constants $C_{11}$, $C_{33}$, $C_{44}$, $C_{66}$ and $C_{16}$ are known (Eq 1.143). All the measuring relations required for elastic constant measurement of tetragonal crystal are listed in the Table 1.5

Table 1.5: Sound velocity-Elastic moduli relations for the Tetragonal system

<table>
<thead>
<tr>
<th>No</th>
<th>Mode</th>
<th>Direction of Propagation</th>
<th>Direction of Polarisation</th>
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<tr>
<td>1</td>
<td>L</td>
<td>a</td>
<td>a</td>
<td>$C_{11} = C_{22} = \rho V_1^2$</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>a</td>
<td>b</td>
<td>$C_{66} = \rho V_2^2$</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>a</td>
<td>c</td>
<td>$C_{55} = C_{44} = \rho V_3^2$</td>
</tr>
<tr>
<td>4</td>
<td>T</td>
<td>a</td>
<td>c</td>
<td>$C_{16} = f_1(V_4)$</td>
</tr>
<tr>
<td>5</td>
<td>L</td>
<td>c</td>
<td>c</td>
<td>$C_{33} = \rho V_5^2$</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>c</td>
<td>a</td>
<td>$C_{44} = C_{55} = \rho V_6^2$</td>
</tr>
<tr>
<td>7</td>
<td>T</td>
<td>c</td>
<td>b</td>
<td>$C_{44} = C_{55} = \rho V_7^2$</td>
</tr>
<tr>
<td>8</td>
<td>QL</td>
<td>a-b plane</td>
<td>(\perp c)</td>
<td>$C_{12} = f_{ab}$</td>
</tr>
<tr>
<td>9</td>
<td>QT</td>
<td>a-b plane</td>
<td>(\perp c)</td>
<td>$C_{12} = f_{ab}$</td>
</tr>
<tr>
<td>10</td>
<td>T</td>
<td>a-b plane</td>
<td>b</td>
<td>$C_{44}$</td>
</tr>
<tr>
<td>11</td>
<td>QL</td>
<td>a-c plane</td>
<td>(\perp b)</td>
<td>$C_{13} = C_{23} = f_{ac}$</td>
</tr>
<tr>
<td>12</td>
<td>QT</td>
<td>a-c plane</td>
<td>(\perp b)</td>
<td>$C_{13} = C_{23} = f_{ac}$</td>
</tr>
</tbody>
</table>
Where

\[ f_{i}(V_{4}) = C_{16} = \frac{1}{2} \left[ \left( C_{11} - \rho v_{4}^{2} \right) - \left( C_{11} + C_{66} \right) \right]^{1/2} \]  

(1.141)

\[ f_{ab} = C_{12} = \frac{1}{s_{c}} \left[ \left( \left( C_{11} s^{2} + C_{66} \rho v_{6}^{2} \right) - \rho v_{6}^{2} \right) \left( \left( C_{66} \rho v_{6}^{2} + C_{11} \rho v_{6}^{2} \right) - \rho v_{6}^{2} \right) \right]^{1/2} - \left( C_{66} \rho v_{6}^{2} + C_{66}^{2} \right) \]  

(1.142)

\[ f_{ac} = C_{13} = \frac{1}{s_{c}} \left[ \frac{m^{1/2} - m^{1/2} A + mB + C}{D} \right]^{1/2} - C_{44} \]  

(1.143)

where

\[ A = a + b + c, \quad B = ab + bc + ac - 1^{2}, \]
\[ C = abc - c^{2}, \quad D = m - b \]

\[ a = C_{11} s^{2} + C_{33} c^{2}, \quad b = C_{66} s^{2} + C_{44} c^{2}, \]
\[ c = C_{44} s^{2} + C_{33} c^{2}, \]
\[ l = C_{16} s^{2}, \quad m = \rho v_{11}^{2} \]  

(1.144)

Twelve such mode velocity measurements are possible. But seven mode velocity measurements are sufficient to evaluate the seven-second order elastic stiffness constants with cross checks possible on some of the values.

### 1.3.4 Elastic constant measurements of Trigonal crystal

A Rhombohedral crystal has three-fold axis of symmetry and three mirror planes [1.8]. In Section 1.3.3 the expression for the velocity of elastic waves in different symmetry directions are derived. It is found that \( C_{11} = C_{22}, C_{33}, C_{44} = C_{55}, C_{12} \) and \( C_{14} \) can be obtained by measuring the velocity in \( c \)-direction (three fold symmetry axis) and any one of the three axes in the base plane normal
to a mirror plane and the third pure mode axis in the $m_1$ plane. The sixth elastic constant $C_{13} = C_{23}$ can be found by velocity measurement of quasi-longitudinal wave in a mirror plane at $45^0$ with c-axis. The elastic constant $C_{66}$ can be obtained by knowing $C_{11}$ and $C_{12}$ by the relation

$$C_{66} = \frac{1}{2}[C_{11} - C_{12}]$$  \hspace{1cm} (1.145)

**Figure 1.3** Symmetry axis and mirror planes of Trigonal crystals

Trigonal has one axis with three fold symmetry and three mirror planes $m_1, m_2, m_3$ as indicated in Figure 1.3. The sound velocity- elastic moduli relations for the trigonal system are presented in the Table 1.6.

**Table 1.6 Sound velocity- Elastic moduli relations for the Trigonal (Rhombohedral) system**

<table>
<thead>
<tr>
<th>No</th>
<th>Mode</th>
<th>Direction of Propagation</th>
<th>Direction of Polarisation</th>
<th>Formula for Elastic moduli</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L</td>
<td>Along base Plane $\perp$ mirror plane</td>
<td>a</td>
<td>$C_{11} = C_{22} = \rho V_1^2$</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>Do</td>
<td>c</td>
<td>$C_{14} = f_a (V_2)$</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>Do</td>
<td>b and c</td>
<td>$C_{12} = f_a' (V_2, V_3)$</td>
</tr>
<tr>
<td>4</td>
<td>L</td>
<td>Along three fold symmetry axis</td>
<td>c</td>
<td>$C_{33} = \rho V_3^2$</td>
</tr>
<tr>
<td>5</td>
<td>L</td>
<td>Do</td>
<td>a</td>
<td>$C_{44} = C_{55} = \rho V_5^2$</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>Do</td>
<td>b</td>
<td>$C_{44} = C_{55} = \rho V_6^2$</td>
</tr>
<tr>
<td>7</td>
<td>QL</td>
<td>Along the mirror plane $45^0$ to C axes ($\theta = 45^0$)</td>
<td>$\perp b$</td>
<td>$C_{12} = C_{23} = f_m (V_3)$</td>
</tr>
<tr>
<td>8</td>
<td>QL</td>
<td>Do</td>
<td>$\perp b$</td>
<td>$C_{14} = f_m'$</td>
</tr>
<tr>
<td>9</td>
<td>QT</td>
<td>Do</td>
<td>b</td>
<td>$C_{44} c^2 + C_{11} s^2 = \rho V_6^2$</td>
</tr>
</tbody>
</table>
where

\[ f_a = C_{14} = \frac{1}{2} \left\{ \left( \frac{2 \rho v_2^2 - (C_{66} + C_{44})}{2} - (C_{66} - C_{44}) \right)^{\frac{1}{2}} \right\} \]  

(1.146)

\[ f_a' = C_{12} = C_{11} + 2C_{44} - 2 \left( \rho v_1^2 + \rho v_2^2 \right) \]  

(1.147)

\[ f_{m} = C_{13} = \frac{1}{\sin \theta \cos \theta} \left\{ \left[ \frac{C - (m^2 - m^2 A + mB)}{D} \right] \right\}^{\frac{1}{2}} - C_{44} \]  

(1.148)

where

\[ \alpha + b + c = A \]
\[ ab + bc + ac - l^2 = B \]
\[ abc - cl^2 = C \]
\[ (a - b - 2l) = D \]

\[ a = C_{11} \sin \theta^2 + C_{44} \cos \theta^2 \]
\[ b = C_{66} \sin \theta^2 + C_{44} \cos \theta^2 \]
\[ n = (C_{13} + C_{44}) \sin \theta \cos \theta \]  

(1.150)

\[ l = 2C_{14} \sin \theta \cos \theta \]
\[ m = \rho v_7^2 \]

Nine such mode velocity measurements are possible. But five mode velocity measurements are sufficient to evaluate the six-second order elastic stiffness constants with cross checks possible on some of the values.

1.3.5 Elastic constant measurements in Hexagonal crystal

In Section 1.2.4 the expressions connecting acoustic wave velocity and elastic constants of hexagonal crystals are derived. The diagonal constants
\( C_{11} = C_{22}, C_{33}, C_{44} = C_{55} \) and \( C_{66} \) can be obtained by measuring the velocity in the symmetry directions \( a \) and \( c \). From \( C_{11} \) and \( C_{66} \) one can calculate \( C_{12} \) by using relation

\[
C_{12} = C_{11} - 2C_{66}
\]  

(1.151)

The off-diagonal constant \( C_{13} = C_{23} \) can be obtained by velocity measurement of quasi-longitudinal wave in the \( a-c \) plane provided the constants \( C_{11}, C_{33}, \) and \( C_{44} \) are known. The necessary relations are listed in the Table 1.7

<table>
<thead>
<tr>
<th>No</th>
<th>Mode</th>
<th>Direction of Propagation</th>
<th>Direction of Polarisation</th>
<th>Formula for Elastic moduli</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L</td>
<td>a</td>
<td>A</td>
<td>( C_{11} = C_{22} = \rho V_1^2 )</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>a</td>
<td>B</td>
<td>( C_{66} = \rho V_2^2 )</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>a</td>
<td>C</td>
<td>( C_{44} = C_{55} = \rho V_3^2 )</td>
</tr>
<tr>
<td>4</td>
<td>L</td>
<td>c</td>
<td>C</td>
<td>( C_{33} = \rho V_4^2 )</td>
</tr>
<tr>
<td>5</td>
<td>L</td>
<td>c</td>
<td>A</td>
<td>( C_{44} = C_{55} = \rho V_5^2 )</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>c</td>
<td>B</td>
<td>( C_{44} = C_{55} = \rho V_6^2 )</td>
</tr>
<tr>
<td>7</td>
<td>QL</td>
<td>a-c plane</td>
<td>( \perp b )</td>
<td>( C_{13} = C_{23} = f_{ac} (V_1) )</td>
</tr>
<tr>
<td>8</td>
<td>QT</td>
<td>a-c plane</td>
<td>( \perp b )</td>
<td>( C_{13} = C_{23} = f_{ac} )</td>
</tr>
<tr>
<td>9</td>
<td>T</td>
<td>a-c plane</td>
<td>B</td>
<td>( C_{44}s^2 + C_{66}s^2 - \rho V_9^2 )</td>
</tr>
</tbody>
</table>

where

\[
C_{13} = f_{ac} (V_1) = \left[ \frac{1}{c^2 s^2} \left( (s^2 C_{11} + e^2 C_{55} - \rho V_7^2) (s^2 C_{44} + e^2 C_{33} - \rho V_7^2) \right) \right]^{\frac{1}{2}} - C_{44}
\]

(1.152)
Nine such mode velocity measurements are possible. But five mode velocity measurements are sufficient to evaluate the five-second order elastic stiffness constants with cross checks possible on some of the values.

1.4 Other related elastic properties

The elastic parameters like, Elastic compliance constants, Linear compressibility, Volume compressibility, Poisson's ratios and Bulk modulus can be determined from the Elastic stiffness constants. The anisotropy in elastic wave propagation and elastic properties have been demonstrated by plotting two-dimensional surfaces of Phase velocity, Slowness or Inverse of phase velocity, Young's modulus and Linear compressibility along a-b, b-c, and a-c planes.

1.4.1 Young's modulus

No single surface can represent the elastic behaviour of a crystal completely. A surface that is useful in practice is one that shows the variation of Young's modulus with direction. If a material is under a stress the Young's modulus \[ E \] in the direction of stress can be defined as the ratio of longitudinal stress to longitudinal strain. Let the uniaxial stress be applied along the \( OX_1 \) (arbitrary direction)

\[
\text{Then } \quad \text{the strain is } \quad \varepsilon_{11} = S_{1111} \sigma_{11} \\
\text{Youngs modulus } \quad E = \sigma_{11} / \varepsilon_{11} = 1 / S_{1111}
\]

\( S'_{1111} \) can be expressed in terms of the compliances \( S_{ij} \) referred to the basic symmetry axes using the transformation law

\[
S'_{1111} = a_1 a_1' a_{1k} a_{1l} S_{ijkl} = 1 / E
\]

Here \( a_{ij} \) relates the arbitrary direction \( OX_1' \) to the symmetry axis \( OX_i \). Inserting appropriate components of the compliance tensor and making use of the relation between the \( a_{ij} \)'s, one can derive the expression for the Young's modulus of a crystal for any arbitrary direction defined by the direction cosines \( n_1, n_2, \) and \( n_3 \) as
Orthorhombic system

\[ E^{-1} = \frac{1}{n_1^4 S_{11}} + \frac{2n_2^2}{n_2^4} S_{12} + \frac{2n_1^2 n_2^2 S_{22}}{n_2^4} + n_2^4 S_{33} + n_2^2 S_{23} + 2n_2^2 n_3^2 S_{23} + n_3^4 S_{33} + n_2^2 n_3^2 S_{44} + n_1^2 n_3^2 S_{55} + n_1^2 n_2^2 S_{66} \]  
\[ (1.155) \]

Tetragonal type I

\[ E^{-1} = S_{11}[n_1^4 + n_2^4] + S_{33} n_3^4 + \left(2 S_{12} + S_{66}\right) n_1^2 n_2^2 + n_3^2 \left[1 - n_3^2\right][2 S_{13} + S_{44}] + 2 S_{15} n_1 n_3 \left[n_1^2 - n_2^2\right] \]  
\[ (1.156) \]

Trigonal type II

\[ E^{-1} = [1 - n_3^2] S_{11} + S_{33} n_3^4 + \left(2 S_{12} + S_{66}\right) n_1^2 n_2^2 + n_3^2 \left[1 - n_3^2\right][2 S_{13} + S_{44}] + 2 n_1 n_3 \left[3 n_1^2 - n_2^2\right] S_{14} \]  
\[ (1.157) \]

Hexagonal

\[ E^{-1} = [1 - n_3^2]^2 S_{11} + n_1^4 S_{33} + n_3^2 \left[1 - n_3^2\right][2 S_{13} + S_{44}] \]  
\[ (1.158) \]

In an anisotropic crystal, Young’s modulus will be different in different directions and hence, the anisotropy in the Young’s modulus can be illustrated by plotting Young’s modulus value for various directions in the symmetry planes a-b, b-c and a-c so as to get sections of the Young’s modulus surface lying in these planes.

1.4.2 Linear compressibility

The linear compressibility of a crystal is the relative decrease in the length of any imaginary line in a crystal when it is subjected to unit hydrostatic pressure. In general, it varies with direction [1.2,1.3] under pressure P. The sketch of a line in the direction of unit vector n, is
\[ \varepsilon'_{ij} n_i n_j = -P S_{ijkl} n_i n_j \]

So linear compressibility

\[ \beta = S_{ijkl} n_i n_j \]  \hspace{1cm} (1.159)

Retaining only the components of the compliance matrix the expression for \( \beta \) for different crystal systems are as follows.

**Orthorhombic**

\[ \beta = [S_{11} + S_{12} + S_{13}] n_1^2 + [S_{12} + S_{22} + S_{23}] n_2^2 + [S_{13} + S_{23} + S_{33}] n_3^2 \]  \hspace{1cm} (1.160)

**Tetragonal type I**

\[ \beta = [S_{11} + S_{12} + S_{13}] - [S_{11} + S_{12} - S_{13} - S_{33}] n_3^2 \]  \hspace{1cm} (1.161)

**Trigonal type II**

\[ \beta = [S_{11} + S_{12} + S_{13}] - [S_{11} + S_{12} - S_{13} - S_{33}] n_3^2 \]  \hspace{1cm} (1.162)

**Hexagonal**

\[ \beta = [S_{11} + S_{12} + S_{13}] - [S_{11} + S_{12} - S_{13} - S_{33}] n_3^2 \]  \hspace{1cm} (1.163)

Thus the linear compressibility in the optically uniaxial system is rotationally symmetrical about the unique axis.

**1.4.3 Volume compressibility and Bulk modulus**

The volume compressibility can be defined as the proportional decrease in volume of a crystal when subjected to unit hydrostatic pressure.

We have

\[ \varepsilon'_{ij} = S_{ijkl} \sigma_{kl} \]

put \( \sigma_{kl} = -P \delta_{kl} \).

Then \( \varepsilon_{ij} = -S_{ijkl} P \delta_{kl} = -P S_{ijkl} \).

For the dilation \( \Delta \) we have

\[ \Delta = \varepsilon_{ii} = -P S_{ikk} \]
And so volume compressibility

\[ \Delta P = S_{iikk}. \]  

(1.164)

In the matrix notation, Volume compressibility for different crystals is as follows [1.2,1.3]

**Orthorhombic**

\[ S_{iik} = [S_{11} + S_{22} + S_{33}] + 2[S_{12} + S_{23} + S_{13}] \]  

(1.165)

**Tetragonal type I**

\[ S_{iik} = S_{33} + 2[S_{11} + S_{12} + 2S_{13}] \]  

(1.166)

**Trigonal type II**

\[ S_{iik} = S_{33} + 2[S_{11} + S_{12} + 2S_{13}] \]  

(1.167)

**Hexagonal**

\[ S_{iik} = S_{33} + 2[S_{11} + S_{12} + 2S_{13}] \]  

(1.168)

1.4.4 Bulk modulus

Bulk modulus is defined as the reciprocal of Volume compressibility.

\[ K = \frac{1}{S_{iikk}} \]  

(1.169)

1.4.5 Poisson’s ratio

Poisson’s ratio is defined as the ratio of lateral contraction to the longitudinal extension. When stress is applied uniaxially to the crystal, being elastically anisotropic produces lateral contraction different in magnitude in different directions [1.3,1.4]. The general Equation [1.42] for Poisson’s ratio for an anisotropic media is given by

\[ \nu_{hk} = -S_{hk} / S_{kk} \]
**Orthorhombic**

Consider longitudinal stress in the a- [100] direction in an orthorhombic crystal.

Longitudinal strain in the a direction is given by

\[ \varepsilon_{11} = S_{1111} \sigma_{11} + S_{1112} \sigma_{12} + S_{1113} \sigma_{13} + S_{1121} \sigma_{21} + S_{1122} \sigma_{22} + S_{1123} \sigma_{23} + S_{1131} \sigma_{31} + S_{1132} \sigma_{32} + S_{1133} \sigma_{33} \]  

Here \( \sigma_{11} \neq 0 \) and all other \( \sigma_{ij} = 0 \) then

\[ \varepsilon_{11} = S_{1111} \sigma_{11} \]

Lateral strains in the b [010]- direction and c [001]- direction are given by

\[ \varepsilon_{22} = S_{2211} \sigma_{11} \]

\[ \varepsilon_{33} = S_{3311} \sigma_{11} \]

Usually \( \varepsilon_{22} \) and \( \varepsilon_{33} \) are contractions and hence Poisson’s ratios can be defined as

\[ v_{12} = -\varepsilon_{22} / \varepsilon_{11} = -S_{2211} / S_{1111} = -S_{21} / S_{11} \]

\[ v_{31} = -\varepsilon_{33} / \varepsilon_{11} = -S_{3311} / S_{1111} = -S_{31} / S_{11} \]  

Similarly equations for Poisson’s ratios can be derived when uniaxial stress is applied along b – and c- directions.

\[ v_{12} = -\varepsilon_{11} / \varepsilon_{22} = -S_{112} / S_{22} \]

\[ v_{32} = -\varepsilon_{33} / \varepsilon_{22} = -S_{23} / S_{22} \]

\[ v_{13} = -\varepsilon_{11} / \varepsilon_{33} = -S_{13} / S_{33} \]

\[ v_{23} = -\varepsilon_{22} / \varepsilon_{33} = -S_{23} / S_{33} \]

Thus there are six values for Poisson’s ratios in orthorhombic crystal [1.3].
Tetragonal

For Tetragonal crystal there are four values for Poisson’s ratio in different directions [1.3]

\[ \nu_{12} = -\varepsilon_{11} / \varepsilon_{21} = -S_{12} / S_{22} \]  \hspace{1cm} (1.172)

\[ \nu_{21} = -\varepsilon_{22} / \varepsilon_{11} = -S_{21} / S_{11} \]

\[ \nu_{13} = -\varepsilon_{11} / \varepsilon_{33} = -S_{13} / S_{33} \]

\[ \nu_{31} = -\varepsilon_{33} / \varepsilon_{11} = -S_{31} / S_{11} \]

Trigonal

This system also possesses four values for Poisson's ratio [1.3]. They are

\[ \nu_{12} = -\varepsilon_{11} / \varepsilon_{21} = -S_{12} / S_{22} \]  \hspace{1cm} (1.173)

\[ \nu_{21} = -\varepsilon_{22} / \varepsilon_{11} = -S_{21} / S_{11} \]

\[ \nu_{13} = -\varepsilon_{11} / \varepsilon_{33} = -S_{13} / S_{33} \]

\[ \nu_{31} = -\varepsilon_{33} / \varepsilon_{11} = -S_{31} / S_{11} \]

Hexagonal

There are only two values for Poisson’s ratio for this system [1.3]

\[ \nu_{13} = -\varepsilon_{11} / \varepsilon_{33} = -S_{13} / S_{33} \]  \hspace{1cm} (1.174)

\[ \nu_{31} = -\varepsilon_{33} / \varepsilon_{11} = -S_{31} / S_{11} \]
1.5 Acoustic wave fronts in crystalline solids

Sound waves radiate spherically from a point source in the atmosphere. Vibrational waves in a solid medium exhibit a similar behaviour [1.12,1.14,1.34]. Due to ordering of atoms into a lattice structure and the directional bonding between atoms, a crystal exhibits significant anisotropy in its elastic properties. Consequently, the wave front of vibrational energy radiating from a point disturbance with in the crystal is far from sphericity.

The shape of a vibrational wave front depends on the particular elastic fourth rank tensor of the medium that relates the second rank tensor of stress and strain. In contrast, electromagnetic waves in an isotropic medium are typically generated by a second rank tensor leading to elliptical wave fronts.

1.5.1 Vibrational waves

The vibrational properties of solids that involve the motion of atomic nuclei impact nearly every aspect of condensed matter physics. At frequency in the mega hertz range vibrational waves are known as ultrasound. At frequency in the Giga Hertz or Tera Hertz range it is described as packet of energy or phonons. Active phonons govern the thermal properties of solids. Continuum elastic theory describes the elastic wave properties in an anisotropic medium accurately in terms of elastic constants and mass density since wavelength of elastic waves is long compared to the atomic spacing.

Quantum mechanics asserts energy of a wave with frequency \( \omega \) to a zero point contribution of \( \frac{1}{2} \hbar \omega \) plus an integral number of quanta with energy \( \hbar \omega \) known as phonons. A quantum statistical treatment of phonons provides the basis for understanding the thermal properties of non-metallic solid, such as its specific heat and thermal conductivity. Unlike photons, the phonons can possess longitudinal polarisation. The propagation reflects the anisotropies if the elastic medium and dispersion relation \( \omega(k) \) contains both 'acoustic' and 'optic' branches. Optical modes occur when there is more than one atom per unit cell in the crystal.
1.5.2 Anisotropy in phase velocity

Consider only the acoustic phonons when frequency ranges from 0 to $10^{12}$ Hz in most solids [1.34]. The wave equation for an anisotropic medium has plane wave solution of the usual form

$$U = U_0 \mathbf{e} \cos (\mathbf{k} \cdot \mathbf{r} - \omega t / v),$$  \hspace{1cm} (1.175)

where $U$ represents the local displacement of the atoms from their equilibrium position and $\mathbf{e}$ is the unit polarisation vector. These waves have linear dispersion relation $\omega = v \mathbf{k}$, but the plane velocity $v$ depends on the direction of $\mathbf{k}$. For a given $\mathbf{k}$ there are three possible acoustic waves with the above form. One longitudinal $\mathbf{e} \cdot \mathbf{k}$ and two transverse $\mathbf{e} \times \mathbf{k}$ possessing orthogonal polarisation vector and distinct phase velocities. For an anisotropic medium, waves are actually quasi-longitudinal or quasi transverse because their polarisation vectors are not exactly parallel or perpendicular to $\mathbf{k}$.

These curves have quite a lot of practical applications. The nonspherical shape of the acoustic wave front, governed by the elastic anisotropy of the medium, gives the direction dependent bonds between atoms. In addition, the ability to measure the attenuation of ultrasound as a continuous function of angle may provide information about the coupling of acoustic waves to electron and defects in crystals. Also it gives unique information about the bonding and homogeneity of composite structure.

1.5.3 Slowness curve

The slowness is the inverse of phase velocity, ie, $1/v = \mathbf{k} / w$. The shape of the slowness curve is governed by the elastic tensor $C_{ijkl}$. The phase velocity $v$ is an eigen value of Christoffel equation

$$[\Gamma_{ik} - \rho v^2] \delta_{ik} = 0 \hspace{1cm} (1.176)$$

If the velocities are calculated using the corresponding elastic constants for different values of angle $\theta$ in the range from 0 to 360 degrees with some small
steps of $1^\circ$, then the resulting velocities can be plotted to get a phase velocity surface for the corresponding plane. For plotting the curve on an $x$-$y$ plane of the paper, one has to convert the velocity angle $\theta$ to the $x$- and $y$- co-ordinates. If $\theta$ is measured from the $x$-axis of the graph, then $x$- and $y$- co-ordinates are given by

$$x = v \cos \theta, \quad y = v \sin \theta$$

and if $\theta$ is measured from $y$ axis of the graph then

$$x = v \sin \theta \quad \text{and} \quad y = v \cos \theta$$

Similar procedure can be used to plot surface plots in $x$-$z$ and $y$-$z$ planes. From the above plots, velocity or inverse velocity in any direction or in any symmetry plane can be easily found out by measuring the length of the straight line drawn from the centre to the curve at the required angle from the symmetry axis.

1.6 Structural Phase Transition

The phase transitions in solids are accompanied by interesting changes in many of material properties [1.19]. Measurement of any sensitive property across the phase transition provides a means of investigating the transition. Changes in properties at the phase transition are often of technological interest. Five properties are often subjected to examination, viz. elastic, magnetic, electrical, thermal and dielectric properties. Of these, the present study considered the elastic properties in detail.

The change of structure during phase transition in a solid occurs in two ways. In the first case, atoms of a solid reconstruct into a new lattice. In the second case, the regular lattice is only slightly distorted without disrupting the linkage of networks. Second case is due to small displacement in the lattice position of atoms or ordering of atoms among various equivalent positions. These transitions are symmetry related. The term structural phase transition [SPT] is used to describe the second type only. This distortive SPT can be classified into displacive type and order-disorder type [1.35].
A crystal has six independent elastic degrees of freedom, out of which only three are acoustic modes. If one of the acoustic modes is soft, the transition is Ferro elastic SPT. In ultrasonic measurement the order parameter couples linearly with strain. Here elastic constants vanish at the second order phase transition. When order parameter couples quadratically to strain, reduction of elastic constant occurs near $T_c$. They can be used to determine the phase diagram as a function of external applied parameter. Experimentally one can determine second order phase transition. Near second order phase transition the crystal becomes 'soft' with respect to the order parameter.

The Para-Ferro and Piezo-Ferro electric transitions depend on symmetry of excited state and order parameter. If the $\mathbf{i} \mathbf{o} \mathbf{i}$ site possesses a centre of symmetry and $\chi$ lacks inversion symmetry, the coupling between the states is allowed. This is Para-ferroelectric transition. If a lattice does not have inversion symmetry and linear coupling is allowed then it is piezo-ferroelectric transition. In ferroelastic case, the centre of symmetry is preserved across the phase transition. Ferroelastic materials are characterised by the existence of spontaneous strain. The symmetry properties of ferroelastic are different from those of ferroelectrics. In particular, a soft mode related to a ferroelastic transition would be Raman active on both sides of the transition. Hence they give an opportunity to study the soft mode by light scattering through the phase transition.

1.6.1 Investigation of phase transition using ultrasonics

Ultrasonics is an accurate, convenient and a very popular tool for investigating phase transition in solids. When distortive phase transition occurs in the crystal, the acoustic modes are affected. This will change elastic constant and ultrasonic velocity at the transition temperature. In case where the strain is linearly coupled with the order parameter, the ultrasonic velocity can directly probe the order parameter and its static and dynamic response. Another tool for investigating elastic properties near phase transition is Brillouin scattering. While ultrasonic measurements are done in the frequency range of 10-100 MHz using large sample sizes, the Brillouin scattering technique probes the acoustic modes
in the GHz region of frequency and requires only small sample sizes. The precision of measurement is much higher for ultrasonic than for Brillouin scattering.

1.6. 2 Landau Theory for a Second Order Phase Transition

Phase transitions in condensed matter can be basically be interpreted within the scope of thermo dynamical principles, while for critical regions precise knowledge of transition mechanism is essential. Structural phase transition in crystals is complex. In nature, there are various types of phase transitions, which Ehrenfest [1.24,1.35] classified in terms of a derivative, viz. the thermo dynamical potential exhibiting a discontinuous change at T_c. Among others, the second order phase transition is characterised as a continuous change of Gibbs potential that has attracted many investigations since it is closely related with the lattice stability.

Landau formulated a theory of continuous phase transitions in binary systems. In his theory, a single thermo dynamical variable called the order parameter emerges at T_c, signifying the ordered phase below T_c by a non-zero value. The theory proposed the variation of the Gibbs potential near T_c, which is expressed by an infinite power series of the order parameter, implying that ordering is essentially a non-linear process.

In the Landau theory [1.24], the free energy of the system is written in terms of the order parameter as

\[ F(Q, T) = F_0(T) + \frac{1}{2} a(T) Q^2 + \frac{1}{4} b Q^4 + ... \]  \hspace{1cm} (1.177)

Here 'a' is temperature dependent near T_o as

\[ a = a' (T-T_o) \]  \hspace{1cm} (1.178)

The strain 'e' gives the elastic energy contribution \( \frac{1}{2} C_0 e^2 \) with the background elastic constant \( C_0 \) taken at zero order parameter. Due to the coupling
of the strain to the ordering quantity, an interaction energy density $F_{\text{int}}$ has to be added, which is phenomenologically expanded in powers of $e$ and $Q$ as

$$F_{\text{int}} = g e Q + h e Q + i e^2 Q + ...$$

(1.179)

To keep the discussion simple we consider here only one component of $e$ and $Q$ which is the bilinear interaction term. Actually it is the symmetry, which decides which coefficients in the expansion (1.179) are different from zero. The expansion of free energy would now appear as,

$$F(Q,T) = F_o(T) + \frac{1}{2} a(T) Q^2 + \frac{1}{4} b Q^4 + ... + \frac{1}{2} c_o e^2 + g e Q$$

(1.180)

The ordering quantity plays the role of an internal degree of freedom. It can move more or less freely under the action of forces exerted by the ultrasonic strain field and described by $F_{\text{int}}$. The ordering quantity responds to these forces and reacts back on the elastic system. This results in a change in the elastic stiffness and in general it decreases. Therefore the most important information about the SPT is obtained from the temperature dependence of the elastic functions.

In the case of bilinear coupling, $F_{\text{int}} = g e Q$ and these forces are proportional to the strain alone. There are no other forces and so

$$\frac{\partial F}{\partial Q} = g e + (\frac{\partial^2 F}{\partial Q^2}) e \delta Q = g e + \delta Q / \chi_o = 0$$

(1.181)

and the order parameter can in general follow the varying strain: $\delta Q = -\chi_o g e$. Its response is determined by the unnormalised order parameter susceptibility $\chi_o$. The changing ordering quantity $\delta Q$ in turn, adds a contribution to the stress $\sigma$ acting within the sound wave as

$$\sigma = g \delta Q + C_o e = C_o e - g^2 e \chi$$

(1.182)

The result is a diminished elastic stiffness, which in the static limit is equal to

$$C_T = C_o - g^2 \chi_Q = C_o \{T-T_o - g^2/a'C_o\} / T-T_o$$

(1.183)
In the above expression \( T_0 = T_0^* \) is, in the case of continuous transition, the transition temperature for zero strain (clamped state), in the absence of strain interaction (1.69) and in the free state (zero stress),

\[
T^* = T_0 + g^2/a'C_0
\]

(1.184)

is the transition temperature. For discontinuous transitions \( T_0 \) denotes the lower stability limit. If this bilinear coupling prevails, the elastic stiffness probes directly the order parameter susceptibility. This is the case not only for the static or low frequency response, but also for the general dynamic response throughout the whole frequency range. The imaginary part of \( \chi_\Omega^e \) is the source for the critical ultrasonic attenuation. In many cases the order parameter response can be described by a relaxation process. This results in the dispersion of elastic constant and is described in terms of relaxation process. Then

\[
C_T(\omega) - C_T(\omega = 0) = \frac{g^2 \chi_\Omega^e(0) \tau^2 \omega^2}{1 + \omega^2 \tau^2}
\]

(1.185)

i.e., there is bilinear coupling between strain and order parameter and an attenuation \( \alpha(\omega) = g^2 \alpha_\Omega^e(0) \omega^2 \tau / 2 \rho v_x^3 (1 + \omega^2 \tau^2) \)

(1.186)

for \( \omega \tau >> 1 \) then \( C_T - C_0 = g^2 \chi_\Omega^e(0) \)

(1.187)

which according to (1.73), is the background elastic function \( C_0 \).

In the above discussions we have considered only the bilinear coupling of the order parameter and strain. But there are several phase transitions in which this is not the case. In some systems the coupling is linear in strain but quadratic in order parameter. In some other case coupling is linear in order parameter but quadratic in strain. More complex non-linear coupling type also can be there. Landau theory can be extended to these cases and different types of elastic response functions can be obtained. On the other hand, the experimentally obtained elastic response functions can be fitted to the theoretically predicted...
curves to identify the type of coupling in the system under investigation. Landau
theory is a mean field theory and in its simplest form it neglects the fluctuations
of the ordering quantity and close to the critical region its application is rather
limited.

1.7 Summary and Conclusions

In the investigation of the anisotropy in elastic properties of a crystal, ultrasonics has a prominent role to play. It enables one to determine all elastic
stiffness constants, compliance constants, Poisson’s ratios, volume compressibility
and bulk modulus of a material. It also helps to demonstrate the anisotropy by
plotting phase velocity, slowness curves, Young’s modulus plots, linear
compressibility plots along a-b, a-c and b-c planes. They also help one to
understand more about phonon amplification and helps to interpret various
phenomena associated with ultrasonic wave propagation, thermal conductivity,
phonon transport etc.

Ultrasonics has proved to be a good and sensitive tool for investigating
phase transition in crystals and also it can be used for solving the structural
controversy that exist in crystals.
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