CHAPTER 1

INTRODUCTION

1.1 Elastic wave propagation in crystalline solids

1.1.1 Elastic waves and elastic constants

Elastic waves are always generated by mechanical vibrations of various media. They can propagate through gases, liquids and solids and these waves are the result of collective vibrations of the atoms and molecules of the medium. The vibration characteristics of the atoms and molecules of the medium are determined by the interatomic forces. The nature of these forces are different in solids, liquids and gases and thus the wave propagation characteristics are also different. In solids both transverse and longitudinal wave propagation are possible while in liquids and gases only longitudinal type of wave propagation is possible. Liquids and gases have same properties in all directions and hence the wave propagation characteristics are isotropic. Some solids like glass have isotropic properties while others like a single crystal have anisotropic properties. Study of elastic wave propagation through crystals enables one to determine their elastic properties.

Wave propagation in a medium is characterised by its velocity and attenuation. In general the waves can be generated over a wide range of frequencies and amplitudes. The dynamic properties of the medium limits the range of frequency for the propagating wave and the interatomic nonlinear interactions will limit the possible wave amplitude. For small amplitudes the interactions can be assumed to be linear.

The elastic properties of a medium is understood in terms of its response to an applied stress. Under the
application of an external force or stress the medium undergoes a deformation or gets strained. The amount of strain developed for a given stress is a characteristic of a medium and the ratio of stress to strain is the elastic constant or elastic modulus of the medium. Stress can be of two types - compressive type and shear type. Liquids and gases can be elastically compressed but not elastically sheared. Hence they have compressibility as their only elastic modulus. An isotropic solid can be compressed as well as sheared elastically hence they have fundamentally two elastic moduli identified as bulk and shear moduli. The elastic properties of a crystal is the most general case. Here in any spatial direction there can be three types of stresses; one longitudinal and two shear type perpendicular to each other. On resolving the generalised stress and strain on an orthogonal axial reference frame the stress and strain are second rank tensors and therefore require nine numbers to specify them. The stress and strain tensors may be expressed as arrays of nine numbers which represent the three components of stress and strain along the directions of the coordinate axes. The stress tensor represents a force which can be applied along any arbitrary direction of the crystal and is called a field tensor; similar is the case of strain tensor. The tensor which connects the stress and strain is the tensor of the medium and is called the matter tensor [1.1-1.2]. This tensor have definite orientation within the crystal and must conform to crystal symmetry and these are the elastic constants of the crystal. Since it links two second rank tensors, it is a tensor of the fourth rank.

Under the assumption that stress is proportional to strain with in the elastic deformation limit the generalised Hook’s Law can be expressed as

$$\sigma_{ij} \propto C_{ki}$$  \hspace{1cm} (1.01)

The constant of proportionality is the fourth rank
matter tensor. This tensor is the elastic stiffness \( c_{ijkl} \). Its inverse is the elastic compliance \( s_{ijkl} \) and connects the strain to the stress. The relations between these constants and stress and strain are

\[
\sigma_{ij} = \sum c_{ijkl} \varepsilon_{kl} \\
\varepsilon_{ij} = \sum s_{ijkl} \sigma_{kl}
\]  

(1.02)

These stiffness or elastic compliances are determined by undertaking elastic wave propagation measurements in solids. Further, these are the constants which determine the velocity of elastic waves in any direction in an anisotropic solid. \( c_{ijkl} \) and \( s_{ijkl} \) have 81 elements relating 9 stress components to 9 strain components. In the absence of rotation in the material the stress and strain tensors obey the symmetry

\[
\sigma_{ij} = \sigma_{ji} \\
\varepsilon_{ij} = \varepsilon_{ji}
\]

(1.03)

This reduces the number of independent stress and strain components from 9 to 6. The above symmetry lead to at most 36 independent elastic constants. At this point it is appropriate to introduce the more compact two suffix notation for the elastic constants, in which the tensor for the \( c_{ijkl} \) \((i, j, k, l = 1, 2, 3)\) is replaced by the matrix \( c_{ij} \) \((i, j = 1, 2, 3, 4, 5, 6)\) according to the following subscript equality:

<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 relations
\[
\begin{align*}
\text{ij} \rightarrow m = i & \quad \text{if } i = j \\
\text{ij} \rightarrow m = 9 - i - j & \quad \text{if } i \neq j
\end{align*}
\] (1.04)

It may be noted that this two suffix notation is only used for convenience and they do not transform like a second rank tensor. To transform the constants to other axes it is necessary to go back to the original tensor notation.

Considering the elastic energy of the strained crystal, further symmetry can be found in the elastic constant matrix in the form

\[
\begin{align*}
C_{ij} &= C_{ji} \\
S_{ij} &= S_{ji}
\end{align*}
\] (1.05)

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

It may be noted that the elastic constant tensor \( C_{ijkl} \) is equated to the second-order differential of the crystal potential energy function and for this reason they are sometimes referred to as second-order elastic constants. The next term in the Taylor series expansion of the crystal potential energy function gives rise to the third order elastic constants, which give a measure of the anharmonic form of the interatomic forces or their deviation from the harmonic form of an ideal Hook's law solid.

Further reduction of the number of independent elastic constants is possible when the symmetry of the crystals are considered and this number is different for the different crystal classes. When appropriate directions are chosen as axes, all crystals may be grouped on the basis of their macroscopic morphology into one of 32 crystal classes (symmetry point groups) which are subgroups among 7 crystal systems [1.3]. These 7 systems in the order of decreasing
symmetry are - Cubic, Hexagonal, Tetragonal, Trigonal, Orthorhombic, Monoclinic, and Triclinic. The crystal classes comprise the combinations of the point symmetry operations which result in distinct groupings consistent with the definition of the crystal system to which they belong. The point symmetry operations are those which operate on point in space in such a manner as to produce a symmetrically equivalent point, and by repetition of the operation, the original point is once again attained. Such point symmetry operations include, inversion, n-fold rotation, reflection, n-fold rotary inversion etc.

The following procedure can be used to determine the form of the elastic constant tensor in a crystal of specified symmetry. Given a symmetry operation \( R \) we can perform the corresponding coordinate transformation for the elastic constant tensor \( c_{ijkl} \) to obtain the transformed tensor \( c'_{ijkl} \). Since the two coordinate systems are indistinguishable due to symmetry, we require that \( c_{ijkl} = c'_{ijkl} \) for all components. This yields relations between the original tensor components. Additional relations follow by applying all symmetry operations, one after another, to each tensor component and requiring that it go into itself after the transformation. Once all relations between the tensor components are known, we can solve the whole set of equations and determine those components which must vanish and also find any relations between the nonvanishing terms.

Table 1.1 gives the non-zero elastic constants for the various crystal systems and point groups. It can be noted at this point that an isotropic solid has only 2 independent elastic constants with the condition \( C_{11} = C_{22} = C_{33}, \ C_{12} = C_{13} = C_{23} \) and \( C_{44} = C_{55} = C_{66} \). Further, \( C_{12} = C_{11} - 2C_{44} \). The two independent constants of the isotropic solid are sometimes called Lame constants \([1.4]\) \( \lambda \) and \( \mu \), defined by
Table 1.1
The nonzero elastic constants for various crystal systems

<table>
<thead>
<tr>
<th>System</th>
<th>Number of point groups</th>
<th>Point group (Schoenflies notation)</th>
<th>Number* of $c_{ij}$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>2</td>
<td>$C_1$ and $C_1$</td>
<td>21 (a)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>3</td>
<td>$C_{2h}$, $C_s$, $C_2$</td>
<td>13 (b)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3</td>
<td>$D_{2h}$, $C_{2v}$, $D_2$</td>
<td>9 (c)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>3</td>
<td>$C_{4h}$, $S_4$, $C_4$</td>
<td>7 (d)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4</td>
<td>$D_{4h}$, $D_{2d}$, $C_{4v}$, $D_4$</td>
<td>6 (e)</td>
</tr>
<tr>
<td>Trigonal</td>
<td>2</td>
<td>$C_{31}$, $C_3$</td>
<td>7 (f)</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3</td>
<td>$D_{3d}$, $C_{3v}$, $D_3$</td>
<td>6 (g)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>7</td>
<td>$D_{6h}$, $D_{3h}$, $C_{6v}$, $D_6$, $C_{6h}$, $C_{3h}$, $C_6$</td>
<td>5 (h)</td>
</tr>
<tr>
<td>Cubic</td>
<td>5</td>
<td>$O_h$, $T_d$, $O$, $T_h$, $T$</td>
<td>3 (i)</td>
</tr>
</tbody>
</table>

*See the equalities given below
Table 1.1 continued.

(a) All 21 constants

(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) $C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}$ and $C_{66}$

(d) $C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{16} = -C_{26}, C_{33}, C_{44} = C_{55}$ and

$C_{66}$

(e) $C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}, C_{44} = C_{55}$, and $C_{66}$

(f) $C_{11} = C_{22}, C_{12,}, C_{13} = C_{23}, C_{14} = -C_{24}, -C_{15} = C_{25}, C_{33}$ and

$C_{44} = C_{55}$ also $C_{46} = 2C_{25}, C_{56} = 2C_{14}$ and $C_{66} = (1/2)(C_{11} - C_{12})$

(g) $C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{14} = -C_{24}, C_{33}$ and $C_{44} = C_{55}$

also $C_{56} = 2C_{14}$ and $C_{66} = (1/2)(C_{11} - C_{12})$

(h) $C_{11} = C_{22}, C_{12}, C_{13} = C_{23}, C_{33}$ and $C_{44} = C_{55}$ also

$C_{66} = (1/2)(C_{11} - C_{12})$

(i) $C_{11} = C_{22} = C_{33}, C_{12} = C_{13} = C_{23}$ and $C_{44} = C_{55} = C_{66}$
\[ \lambda = C_{12} \]  
\[ \mu = C_{44} \]  
(1.06)  
\\
\( \mu \) is same as the shear modulus \( G \), the bulk modulus \( B \) is defined by  
\[ B = \lambda + 2\mu/3 \]  
(1.07)  
While \( B \) and \( G \) are of fundamental importance in theories of elastic constants using atomistic approach, the constants \( C_{11} \) and \( C_{44} \) are of importance respectively in longitudinal and shear elastic wave propagation studies in isotropic solids.

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

\[
C_{1j} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\
C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\
C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66}
\end{bmatrix}
\]  
(1.08)  
\\
\[ C_{1j} = C_{j1} \]

1.1.2 Equations of motion and their general solution

The propagation of acoustic waves in elastically anisotropic solids is governed by a set of three linear equations known as the Christoffel equations. The characteristic equation relates the velocity \( v \), the direction of the wave propagation and the elastic constants of the medium. It is cubic in \( v^2 \). These equations occupy an important position in the field of crystal acoustics, and their solution is required for a wide variety of purposes [1.4-1.10]. Considerable simplification to these equations comes about
when the wave normal lies along a crystal symmetry direction. In general the secular equations for these directions factor into a term which is linear in \(v^2\) and one which is quadratic. Thus simple expressions for the velocities result, and in many cases these are easily reversed to obtain the elastic constants from the measured velocities.

Consider an anisotropic medium which shows the ideal Hook's law behavior and in which dissipative processes and nonlinear or dispersive phenomena can be neglected. A disturbance in such a medium is represented by the equation of motion for an element of the medium. This when expressed in the tensor format appears as

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

(1.09)

Where \(\rho\) is the density of the 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 made use of. This gives the wave equation in the form

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

(1.10)

We expect that in an unbounded medium this equation has basic solutions given by plane waves

\[
u_i = U_1 \exp \{i(k \cdot r - \omega t)\}
\]

(1.11)

Inserting this solution in the wave equation, we obtain, for the conditions on the wave amplitude \(U_1\)
\begin{equation}
\begin{pmatrix}
C_{ijkl} k_j k_l - \rho \omega^2 \delta_{ik}
\end{pmatrix} U_k = 0
\tag{1.12}
\end{equation}

The three homogeneous equations for \( U_i \) from the above equation are the Christoffel equations and they have a solution only if the secular equations of their coefficients 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 vector in terms of direction cosines as \( k = k(n_1, n_2, n_3) \), the secular determinant becomes

\begin{equation}
\left| \Gamma_{ik} - \rho v^2 \delta_{ik} \right| = 0
\tag{1.13}
\end{equation}

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

\begin{equation}
\Gamma_{ik} = C_{ijkl} n_j n_l
\tag{1.14}
\end{equation}

\( \Gamma \) is called the christoffel matrix and its elements depend on the direction of wave propagation and the elastic constants. \( \delta_{ik} \) has the usual meaning, that is

\begin{align}
\delta_{ik} &= 0, \text{ for } k \neq j \\
\delta_{ik} &= 1, \text{ for } k = j
\tag{1.15}
\end{align}

The expanded form of this determinantal equation is

\begin{equation}
\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
\tag{1.16}
\end{equation}
Using the contracted Voigt notation for the elastic constants, the Christoffel coefficients are, in the most general case given by

$$\Gamma_{11} = c_{11} n_1^2 + c_{66} n_2^2 + c_{55} n_3^2 + 2c_{56} n_2 n_3 + 2c_{15} n_3 n_1 + 2c_{16} n_1 n_2$$

$$\Gamma_{22} = c_{66} n_1^2 + c_{22} n_2^2 + c_{44} n_3^2 + 2c_{24} n_2 n_3 + 2c_{46} n_3 n_1 + 2c_{26} n_1 n_2$$

$$\Gamma_{33} = c_{55} n_1^2 + c_{44} n_2^2 + c_{33} n_3^2 + 2c_{34} n_2 n_3 + 2c_{35} n_3 n_1 + 2c_{45} n_1 n_2$$

$$\Gamma_{23} = \Gamma_{32} = c_{56} n_1^2 + c_{24} n_2^2 + c_{34} n_3^2 + (c_{23} + c_{44}) n_2 n_3 + (c_{36} + c_{45}) n_3 n_1 + (c_{25} + c_{46}) n_1 n_2$$

$$\Gamma_{13} = \Gamma_{31} = c_{15} n_1^2 + c_{46} n_2^2 + c_{35} n_3^2 + (c_{36} + c_{45}) n_2 n_3 + (c_{13} + c_{55}) n_3 n_1 + (c_{14} + c_{56}) n_1 n_2$$

$$\Gamma_{12} = \Gamma_{21} = c_{16} n_1^2 + c_{26} n_2^2 + c_{45} n_3^2 + (c_{25} + c_{46}) n_2 n_3 + (c_{14} + c_{56}) n_3 n_1 + (c_{12} + c_{66}) n_1 n_2$$

(1.17)

On evaluating the determinant and equating it to zero we get the secular equation. This is a cubic equation in $v^2$ and hence it has three solutions and three different velocities are associated with it. Thus in 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 the 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 these directions are usually the symmetry directions or symmetry planes in the crystal. The three values of $\rho v^2$ are the eigenvalues of the matrix $\Gamma_{ik}$, and the corresponding solutions for the displacement vector $U_k$ are the eigenvectors. While eigenvalues give the three velocities the corresponding eigenvectors give the direction of particle motion or the polarisation direction of the wave.

1.2 Wave propagation in orthorhombic and hexagonal systems

1.2.1 Orthorhombic

In the above section the general expressions for elastic wave propagation in crystals have been presented. The general equations are formidably large when applied to specific crystal systems. While the full equations are necessary for the triclinic crystal much simplified equations can be obtained for higher symmetry crystals. 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 directions or planes are chosen as propagation directions so that one or two of the direction cosines $n_1$, $n_2$, or $n_3$ are equal to zero. The simplest expressions are those for cubic crystals and are available in textbooks [1.11]. Since ultrasonic measurements have been performed on orthorhombic and hexagonal crystals in the work presented in this thesis, the necessary equations are derived for these crystals in the following paragraphs.

For the orthorhombic crystals of all point groups the
nonzero elastic constants are \( C_{11} \), \( C_{22} \), \( C_{33} \), \( C_{44} \), \( C_{55} \), \( C_{66} \), \( C_{12} \), \( C_{13} \), and \( C_{23} \). All other constants in the general matrix are zero. Retaining only the terms that contain nonzero elements the coefficients of the Christoffel matrix \( \Gamma_{ik} \) can be written as

\[
\Gamma_{11} = C_{11} n_1^2 + C_{66} n_2^2 + C_{55} n_3^2 \\
\Gamma_{22} = C_{66} n_1^2 + C_{22} n_2^2 + C_{44} n_3^2 \\
\Gamma_{33} = C_{55} n_1^2 + C_{44} n_2^2 + C_{33} n_3^2 \\
\Gamma_{23} = \Gamma_{32} = (C_{23} + C_{44}) n_2 n_3 \\
\Gamma_{13} = \Gamma_{31} = (C_{13} + C_{55}) n_3 n_1 \\
\Gamma_{12} = \Gamma_{21} = (C_{12} + C_{66}) n_1 n_2
\]  

(1.18)

None of the off diagonal terms of \( \Gamma_{ik} \) are still not equal to zero which means that the characteristic equation cannot be factored and single term equations cannot be written for the velocity.

Now, consider wave propagation in the x-y plane, which means \( n_3 = 0 \). The \( \Gamma \) coefficients now becomes

\[
\Gamma_{11} = C_{11} n_1^2 + C_{66} n_2^2 \\
\Gamma_{22} = C_{66} n_1^2 + C_{22} n_2^2 \\
\Gamma_{33} = C_{55} n_1^2 + C_{44} n_2^2 \\
\Gamma_{23} = \Gamma_{32} = 0 \\
\Gamma_{13} = \Gamma_{31} = 0 \\
\Gamma_{12} = \Gamma_{21} = (C_{12} + C_{66}) n_1 n_2
\]  

(1.19)

The determinantal equation can now be written as
Expanding the determinant, we get

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

(1.20)

or

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

(1.21)

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

\[
\rho \nu_0^2 = \Gamma_{33}
\]

(1.22)

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

\[
2\rho \nu_1^2 = (\Gamma_{11} + \Gamma_{22}) + \left[ (\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11} \Gamma_{22} - \Gamma_{12}^2) \right]^{1/2}
\]

(1.23)

and

\[
2\rho \nu_2^2 = (\Gamma_{11} + \Gamma_{22}) - \left[ (\Gamma_{11} + \Gamma_{22})^2 - 4(\Gamma_{11} \Gamma_{22} - \Gamma_{12}^2) \right]^{1/2}
\]

(1.24)

\( \nu_0 \) is a pure shear wave with polarisation in the z direction, \( \nu_1 \) is a quasilongitudinal wave and \( \nu_2 \) is a quasishear wave.

On substituting the values of \( \Gamma \) for the x-y plane in above three equations, the velocities are obtained in terms of the elastic constants and the direction cosines, as
\[ \rho v^2_0 = C_{55} n_1^2 + C_{44} n_2^2 \quad (1.25) \]

\[ 2 \rho v^2_1 = (C_{11} n_1^2 + C_{22} n_2^2 + C_{66}) + \left[ (C_{11} n_1^2 + C_{22} n_2^2 + C_{66})^2 - 4((C_{11} n_1^2 + C_{66} n_2^2)(C_{66} n_1^2 + C_{22} n_2^2) - (C_{12} + C_{66})^2 n_1^2 n_2^2 \right]^{1/2} \quad (1.26) \]

\[ 2 \rho v^2_2 = (C_{11} n_1^2 + C_{22} n_2^2 + C_{66}) - \left[ (C_{11} n_1^2 + C_{22} n_2^2 + C_{66})^2 - 4((C_{11} n_1^2 + C_{66} n_2^2)(C_{66} n_1^2 + C_{22} n_2^2) - (C_{12} + C_{66})^2 n_1^2 n_2^2 \right]^{1/2} \quad (1.27) \]

Use is made of the relation,

\[ n_1^2 + n_2^2 + n_3^2 = 1 \quad (1.28) \]

which is obeyed by the normalised direction cosines.

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

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

The characteristic equation is then given by,

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

(1.30)

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

15
\[ \rho v_0^2 = \Gamma_{22} \]  

(1.31)

and the factor which is quadratic in \( \rho v^2 \) provides the other two roots

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

(1.32)

and

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

(1.33)

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

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

(1.34)

\[ 2\rho v_1^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{55}) + [(C_{11} n_1^2 + C_{33} n_3^2 + C_{55})^2 - 4((C_{11} n_1^2 + C_{55} n_3^2) (C_{55} n_1^2 + C_{33} n_3^2) - (C_{13} + C_{55})^2 n_1^2 n_3^2)]^{1/2} \]

(1.35)

\[ 2\rho v_2^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{55}) - [(C_{11} n_1^2 + C_{33} n_3^2 + C_{55})^2 - 4((C_{11} n_1^2 + C_{55} n_3^2) (C_{55} n_1^2 + C_{33} n_3^2) - (C_{13} + C_{55})^2 n_1^2 n_3^2)]^{1/2} \]

(1.36)

Consider propagation in the y-z plane, which means that \( n_1 = 0 \), the coefficients are then obtained as,
\[ \Gamma_{11} = C_{66} n_2^2 + C_{55} n_3^2 \]  
\[ \Gamma_{22} = C_{22} n_2^2 + C_{44} n_3^2 \]  
\[ \Gamma_{33} = C_{44} n_2^2 + C_{33} n_3^2 \]  
\[ \Gamma_{23} = \Gamma_{32} = (C_{23} + C_{44}) n_2 n_3 \]  
\[ \Gamma_{13} = \Gamma_{31} = 0 \]  
\[ \Gamma_{12} = \Gamma_{21} = 0 \]  

(1.37)

The characteristic equation is then given by,

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

(1.38)

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

\[ \rho v_0^2 = \Gamma_{11} \]  

(1.39)

and the factor which is quadratic in \( \rho v^2 \) provides the other two roots

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

(1.40)

and

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

(1.41)

On substituting values of \( \Gamma \) for the y-z plane in above three equations, the velocities are obtained in terms of the elastic constants and the direction cosines, as

\[ \rho v_0^2 = C_{66} n_2^2 + C_{55} n_3^2 \]  

(1.42)

\[ 2\rho v_1^2 = (C_{22} n_2^2 + C_{33} n_3^2 + C_{44}) + \left[ (C_{22} n_2^2 + C_{33} n_3^2 + C_{44})^2 - 4((C_{22} n_2^2 + C_{44} n_3^2)(C_{44} n_2^2 + C_{33} n_3^2)) \right]^{1/2} \]  

(1.43)
\[ 2\rho v^2 = (C_{22} n_2^2 + C_{33} n_3^2 + C_{44}) - [(C_{22} n_2^2 + C_{33} n_3^2 + C_{44})^2 - 4((C_{22} n_2^2 + C_{44} n_3^2)(C_{44} n_2^2 + C_{33} n_3^2) - (C_{23} + C_{44})^2 n_2^2 n_3^2)^{1/2}] \]  

(1.44)

The above analysis for wave propagation in orthorhombic crystals have provided us three set of equations corresponding to the three orthogonal symmetry planes of the crystal. As a general observation it can be seen that when the wave propagation is in a symmetry plane there is always a pure shear mode which is polarised normal to the plane. These equations can be used to compute the velocities in any direction in these symmetry planes if the elastic constants are known.

Now consider the propagation along the symmetry axis of the crystal. These directions are the x, y, and z directions for the orthorhombic system and it corresponds to the a, b, and c directions of the crystal or they are the [100], [010] and [001] directions.

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

\[
\Gamma_{11} = C_{11} \quad \Gamma_{23} = 0 \\
\Gamma_{22} = C_{66} \quad \Gamma_{13} = 0 \\
\Gamma_{33} = C_{55} \quad \Gamma_{12} = 0
\]

(1.45)

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

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

(1.46)
which readily factors to give the solutions,

\[ \rho v_0^2 = C_{11}, \quad \rho v_1^2 = C_{66} \quad \text{and} \quad \rho v_2^2 = C_{55} \quad (1.47) \]

These are pure mode waves, \( v_0 \) is longitudinal, \( v_1 \) is transverse with y polarisation and \( v_2 \) is transverse with z polarisation.

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

\[
\begin{align*}
\Gamma_{11} &= C_{66} & \Gamma_{23} &= 0 \\
\Gamma_{22} &= C_{22} & \Gamma_{13} &= 0 \\
\Gamma_{33} &= C_{44} & \Gamma_{12} &= 0
\end{align*}
\quad (1.48)
\]

The characteristic equation readily factors to give the solutions,

\[ \rho v_0^2 = C_{66}, \quad \rho v_1^2 = C_{22} \quad \text{and} \quad \rho v_2^2 = C_{44} \quad (1.49) \]

These are also pure mode waves, \( v_0 \) is transverse with x polarisation, \( v_1 \) is longitudinal and \( v_2 \) is transverse with z polarisation.

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

\[
\begin{align*}
\Gamma_{11} &= C_{55} & \Gamma_{23} &= 0 \\
\Gamma_{22} &= C_{44} & \Gamma_{13} &= 0 \\
\Gamma_{33} &= C_{33} & \Gamma_{12} &= 0
\end{align*}
\quad (1.50)
\]

The characteristic equation readily factors to give the solutions,

\[ \rho v_0^2 = C_{55}, \quad \rho v_1^2 = C_{44} \quad \text{and} \quad \rho v_2^2 = C_{33} \quad (1.51) \]
These are also pure mode waves, $v_0$ is transverse with $x$ polarisation, $v_1$ is transverse with $y$ polarisation and $v_2$ is longitudinal.

1.2.2 Hexagonal

Hexagonal crystals are having a six fold axis of symmetry. The nonzero elastic constants of hexagonal crystals are

$$C_{11} = C_{22}, \quad C_{13} = C_{23}, \quad C_{33} \quad \text{and} \quad C_{44} = C_{55}$$

Also, $C_{66} = (1/2)(C_{11} - C_{12})$ or $C_{12} = C_{11} - 2C_{66}$

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

$$\begin{align*}
\Gamma_{11} &= C_{11} n_1^2 + C_{66} n_2^2 + C_{44} n_3^2 \\
\Gamma_{22} &= C_{66} n_1^2 + C_{11} n_2^2 + C_{44} n_3^2 \\
\Gamma_{33} &= C_{44} n_1^2 + C_{44} n_2^2 + C_{33} n_3^2 \\
\Gamma_{23} &= \Gamma_{32} = (C_{13} + C_{44}) n_2 n_3 \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{44}) n_3 n_1 \\
\Gamma_{12} &= \Gamma_{21} = (C_{11} - C_{66}) n_1 n_2
\end{align*}$$

(1.52)

Now consider wave propagation in the $x$-$y$ plane, which means $n_3 = 0$. The coefficients now become

$$\begin{align*}
\Gamma_{11} &= C_{11} n_1^2 + C_{66} n_2^2 \\
\Gamma_{22} &= C_{66} n_1^2 + C_{11} n_2^2 \\
\Gamma_{33} &= C_{44} n_1^2 + C_{44} n_2^2 \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{44}) n_3 n_1 \\
\Gamma_{12} &= \Gamma_{21} = (C_{11} - C_{66}) n_1 n_2
\end{align*}$$

(1.53)
The characteristic equation is,
\[
( \Gamma_{33} - \rho v^2 ) \left[ \rho^2 v^4 - \rho v^2 \left( \Gamma_{11} + \Gamma_{22} \right) + \Gamma_{11} \Gamma_{22} - \Gamma_{12}^2 \right] = 0
\]  
(1.54)

The factor which is linear in $\rho v^2$ yields the root
\[
\rho v_0^2 = \Gamma_{33}
\]  
(1.55)

and the factor which is quadratic in $\rho v^2$ provides the other two roots
\[
2\rho v_1^2 = ( \Gamma_{11} + \Gamma_{22} ) + \left[ ( \Gamma_{11} + \Gamma_{22} )^2 - 4( \Gamma_{11} \Gamma_{22} - \Gamma_{12}^2 ) \right]^{1/2}
\]  
(1.56)

and
\[
2\rho v_2^2 = ( \Gamma_{11} + \Gamma_{22} ) - \left[ ( \Gamma_{11} + \Gamma_{22} )^2 - 4( \Gamma_{11} \Gamma_{22} - \Gamma_{12}^2 ) \right]^{1/2}
\]  
(1.57)

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,

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

\[
\rho v_1^2 = C_{11}
\]  
(1.58)

\[
\rho v_2^2 = C_{66}
\]

The above result shows that the velocity is independent of the direction in this plane and that all modes are pure. $v_0$ is a shear mode polarised parallel to z axis, $v_1$ is a longitudinal mode and $v_2$ is a shear mode polarised normal to z axis. The above relations are valid for the directions x, y or any direction in the plane.

Consider propagation in the x-z plane, which means that $n_z = 0$, the coefficients are then obtained as,
\[
\begin{align*}
\Gamma_{11} &= C_{11} n_1^2 + C_{44} n_3^2 \\
\Gamma_{22} &= C_{66} n_1^2 + C_{44} n_3^2 \\
\Gamma_{33} &= C_{44} n_1^2 + C_{33} n_3^2 \\
\Gamma_{23} &= \Gamma_{32} = 0 \\
\Gamma_{13} &= \Gamma_{31} = (C_{13} + C_{44}) n_3 n_1 \\
\Gamma_{12} &= \Gamma_{21} = 0
\end{align*}
\]

The characteristic equation is then given by,
\[
(\Gamma_{22} - \rho v^2) \left[ \rho^2 v^4 - \rho v(\Gamma_{11} + \Gamma_{33}) + \Gamma_{11} \Gamma_{33} - \Gamma_{13}^2 \right] = 0
\]

The linear part gives one root and the quadratic part gives the other two roots. On substituting the \( \Gamma \) values and simplifying the following expressions are obtained for the three velocities,

\[
\rho v_0^2 = C_{66} n_1^2 + C_{44} n_3^2 \\
2\rho v_1^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{44}) + [(C_{11} n_1^2 + C_{33} n_3^2 + C_{44})^2 - 4((C_{11} n_1^2 + C_{44} n_3^2)(C_{44} n_1^2 + C_{33} n_3^2)) \]^{1/2}

\]

\[
2\rho v_2^2 = (C_{11} n_1^2 + C_{33} n_3^2 + C_{44}) - [(C_{11} n_1^2 + C_{33} n_3^2 + C_{44})^2 - 4((C_{11} n_1^2 + C_{44} n_3^2)(C_{44} n_1^2 + C_{33} n_3^2)) \]^{1/2}

\]

\( v_0 \) is a pure shear mode polarised normal to the plane, \( v_1 \) is a quasilongitudinal wave and \( v_2 \) is a quasishear wave. It can be seen that these expressions are rotationally invariant for rotations about the \( z \) axis. Hence the same expressions are valid for the \( y-z \) plane or any meridian plane.

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

\[
\begin{align*}
\rho v_0^2 &= C_{44} \\
\rho v_1^2 &= C_{33} \\
\rho v_2^2 &= C_{44}
\end{align*}
\]

(1.64)

\( v_1 \) is a longitudinal mode, \( v_0 \) and \( v_2 \) are shear modes polarised normal to the z-axis and they are degenerate. Since two transverse velocities are identical the z direction of the Hexagonal crystal is an acoustic axis of the crystal.

1.3 Ultrasonic velocity measurements to determine the elastic constants.

1.3.1 General remarks

In the last section we have found that the propagation velocity of acoustic waves in a crystal is related to the elastic constants, density of the crystal and the propagation direction. Thus by measuring the acoustic wave velocities along defined directions it is possible to deduct the elastic constants of the crystal. Although the velocity measurements are straight forward, obtaining the elastic constants from the experimental data can be very tedious, especially for low symmetry crystals. Only for certain simple directions, which occur more frequently for high symmetry crystals, will a sound wave be pure longitudinal or pure transverse [1.12]. In general, the eigenvectors which specify the modes of vibration are neither parallel nor perpendicular to the propagation direction. For such quasilongitudinal and quasishear modes it is not possible to relate the measured velocity directly to a single constant. For general directions the measured velocity can depend on as many as 21 elastic constants (triclinic) which obviously, leads to complications in reducing the data.
[1.13]. It can be noted that only for cubic crystals it is possible to obtain all elastic constants from measurements of pure longitudinal or pure transverse waves. For all other symmetries, some of the elastic constants must be determined from measurements of quasilongitudinal and/or quasitransverse waves.

Further, great care is required in orienting, cutting and polishing the crystal exactly in the pure mode directions when measurements are to be performed along these directions. Any small deviation from the required direction will bring in contributions from several other constants and special misorientation correction techniques [1.14] are to be applied to correct the data.

Fortunately in ultrasonic experiments the three different modes in any given direction can be separately excited by choosing the transducers for longitudinal and transverse waves and by rotating the transverse mode transducer the polarisation can be selected in the desired direction. This facility simplifies the otherwise difficult problem of selecting the correct expression for the desired mode of propagation.

1.3.2. Elastic constant measurements on orthorhombic crystals

In the previous section we have derived the expressions for the velocity of elastic waves in various symmetry directions and symmetry planes in the orthorhombic crystal. For the measurement of elastic constants, these expressions are to be reversed. As we have seen for the orthorhombic crystals the crystallographic directions a, b, and c are pure mode directions. All the three velocities measured in each of these directions are related to single elastic constants only. Measurements in these directions 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 constants the quasilongitudinal 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 when measurements are done in these symmetry planes. The necessary expressions for computing the elastic constants from the measured velocities are obtained by reversing the equations for the velocities obtained earlier in previous section. These reversed relations are summarised in Table 1.2. When the 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 the angle from a crystallographic axis like a, b, or c, than in terms of the direction cosines. The direction cosines are then obtained as the sine and cosine functions of this angle. The convention adopted in this work for this is illustrated in figure 1.1.

1.3.3 Elastic constant measurements on hexagonal crystals

In section 1.2.2 we have derived the relations connecting the elastic constants to the propagation velocity for hexagonal crystals. We find that all the diagonal constants, $C_{11} = C_{22}$, $C_{33}$, $C_{44} = C_{55}$ and $C_{66}$ can be obtained by measuring the velocities in the symmetry directions a and c. The measurement in the b direction gives the same information as in the a direction due to the rotational invariance of velocity in the a-b plane of a hexagonal crystal. The number of nonzero elastic constants of Orthorhombic and Hexagonal systems are the same. But for orthorhombic all the 9 constants are independent while for Hexagonal only 5 are independent as listed in Table 1.1. Once $C_{11}$ and $C_{66}$ are known the off diagonal constant $C_{12}$ can be calculated using the relation,
Figure 1.1

Direction cosines to rotation angle conversion scheme in symmetry planes a-c, b-c and a-b.
Table 1.2

Sound velocity - Elastic moduli relations for the Orthorhombic system

<table>
<thead>
<tr>
<th>No.</th>
<th>Mode</th>
<th>Direction of particle motion</th>
<th>Formula for elastic moduli</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
</tr>
</tbody>
</table>

**Propagation along a - axis**

1. L  a  \( C_{11} = \rho v^2 \)
2. T  b  \( C_{66} = \rho v^2 \)
3. T  c  \( C_{55} = \rho v^2 \)

**Propagation along b - axis**

4. L  b  \( C_{22} = \rho v^2 \)
5. T  a  \( C_{66} = \rho v^2 \)
6. T  c  \( C_{44} = \rho v^2 \)

**Propagation along c - axis**

7. L  c  \( C_{33} = \rho v^2 \)
8. T  a  \( C_{55} = \rho v^2 \)
9. T  b  \( C_{44} = \rho v^2 \)
Table 1.2 continued

<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
</table>

**Propagation in a-b plane, angle measured from a-axis**

10. QL \ perpendicular \ c \quad C_{12} = f_{ab}

11. QT \ perpendicular \ c \quad C_{12} = \text{similar to } f_{ab}

12. T \ c \quad \rho v^2 = c^2 C_{55} + s^2 C_{44}

**Propagation in b-c plane, angle measured from b-axis**

13. QL \ perpendicular \ a \quad C_{23} = f_{bc}

14. QT \ perpendicular \ a \quad C_{23} = \text{similar to } f_{bc}

15. T \ a \quad \rho v^2 = c^2 C_{66} + s^2 C_{55}

**Propagation in a-c plane, angle measured from c-axis**

16. QL \ perpendicular \ b \quad C_{13} = f_{ac}

17. QT \ perpendicular \ b \quad C_{13} = \text{similar to } f_{ac}

18. T \ b \quad \rho v^2 = s^2 C_{66} + c^2 C_{44}
Table 1.2 continued

The abbreviations used have the following meanings:
L - Longitudinal, T - Transverse, QL - Quasi-longitudinal, QT - Quasi-transverse, s = sine and c = cosine of angle θ from the respective axis, ρ = density, v = velocity of propagation of respective mode. a, b, c - Crystallographic axis. $f_{ab}$, $f_{bc}$ and $f_{ac}$ are defined as,

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

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

$$f_{ac} = \left[ \frac{\left( s^2 C_{11} + c^2 C_{55} - \rho v^2 \right) \left( s^2 C_{55} + c^2 C_{33} - \rho v^2 \right)}{c^2 s^2} \right]^{\frac{1}{2}} - C_{55}. $$
The only independent off diagonal constant $C_{13}$ which is also equal to $C_{23}$ can be obtained by velocity measurement of the quasilongitudinal wave in the a-c plane, provided the constants $C_{11}$, $C_{33}$ and $C_{44}$ are known. The form of the reversed expression obtained is similar to the orthorhombic system. All the necessary relations required for elastic constant measurement of Hexagonal crystals are listed in Table 1.3. The abbreviations used in the table carry the same meanings as that defined in Table 1.2.

1.4 Investigation of structural phase transitions using ultrasonics

1.4.1 Structural phase transitions: An overview

The change of structure during a phase transition in a solid can occur in two quite distinct ways [1.15]. In the first type the atoms of the solid reconstruct to a new lattice like graphite transforming to diamond or like an amorphous solid changing to a crystalline form. These reconstructive transitions are often slow recrystallization process and are not symmetry related. In the second type the regular lattice is only slightly distorted without disrupting the linkage of the network. This can occur as a result of small displacements in the lattice position of single atoms or molecular units, or due to the ordering of atoms or molecules among various equivalent positions. These type of transitions are symmetry related. The term structural phase transition (SPT) is sometimes used, in a narrow sense, to describe the second type only. Since two different mechanisms are there for the second type of SPT or the distortive SPT, they can be classified as
Table 1.3

Sound velocity - Elastic moduli relations for Hexagonal system

<table>
<thead>
<tr>
<th>No.</th>
<th>Mode</th>
<th>Direction of particle motion</th>
<th>Formula for elastic moduli</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pro-Eagation along a-axis</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>L</td>
<td>a</td>
<td>$C_{11} = C_{22} = \rho v^2$</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>b</td>
<td>$C_{66} = \rho v^2$</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>c</td>
<td>$C_{44} = C_{55} = \rho v^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pro-Eagation along c-axis</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>L</td>
<td>c</td>
<td>$C_{33} = \rho v^2$</td>
</tr>
<tr>
<td>5</td>
<td>T</td>
<td>a</td>
<td>$C_{44} = C_{55} = \rho v^2$</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>b</td>
<td>$C_{44} = C_{55} = \rho v^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Propagation in a-c plane, angle $\theta$ measured from c-axis</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>QL</td>
<td>l b</td>
<td>$C_{13} = C_{23} = f_{ac}$</td>
</tr>
<tr>
<td>8</td>
<td>QT</td>
<td>l b</td>
<td>$C_{13} = C_{23} = \text{similar to } f_{ac}$</td>
</tr>
<tr>
<td>9</td>
<td>T</td>
<td>b</td>
<td>$\rho v^2 = s^2 C_{66} + c^2 C_{44}$</td>
</tr>
</tbody>
</table>

where $f_{ac}$ is defined as,

$$f_{ac} = \left[ \frac{\left(S^2 C_{11} + C^2 C_{44} - \rho v^2\right)\left(S^2 C_{44} + C^2 C_{33} - \rho v^2\right)}{S^2 C_{66} + c^2 s^2 C_{44}} \right]^{1/2} - C_{44}$$
displacive type and order-disorder type.

The symmetry of a crystal normally undergoes a change when a SPT takes place. For a large class of systems this change consists in the loss of a part of symmetry elements by a crystal under its transformation from the higher to the lower temperature phase. In this the symmetry group of the new (less symmetrical) phase is a subgroup of the old (more symmetrical) phase.

In the study of phase transitions the order parameter is a crucial quantity. The simplest way to define the order parameter is as a variable that characterizes the magnitude of these atomic displacements or the degree of their ordering, which just represent the change in the crystal undergoing phase transition. Many diverse changes takes place in a crystal during phase transition and in general, several order parameters are to be considered to describe them. But in many cases a dominant role is played by a single order parameter. The order parameter is the starting quantity in the Landau theory of Phase transition [1.16] which has provided the most formidable and successful theoretical formulation for Phase transitions. The basic formula of the Landau theory is the expression for the thermodynamic potential considered as a function of the order parameter as outlined below.

The Landau free energy expansion can be written as

$$ F = F_0 + A Q^2 + B Q^4 + \text{higher order terms} \quad (1.66) $$

where $F_0$ contains all other degrees of freedom of the system, $Q = Q(T)$ is the order parameter and $A = \alpha (T - T_c)$. $\alpha$ and $B$ can be viewed as nearly temperature independent near $T_c$. The order parameter $Q(T)$ is assumed to have only one dimension. Upon minimization of the free energy with respect to the order parameter, one finds a second order transition at $T_c$ when $B > 0$ with the order parameter varying continuously as
$Q^2 \propto (T - T_c)$. With $B < 0$ a first order transition results with a discontinuous jump of the order parameter.

In displacive type SPT the atoms in the distorted phase are slightly displaced away from their equilibrium positions of the high temperature phase. This then led to the suggestion by Cochran [1.17] and Anderson [1.18] and earlier but largely unnoticed comments by others (Raman and Nedungadi [1.19] and Saksena [1.20]) that these phase transitions might be the result of an instability of the crystal against a particular normal mode of vibration of the high temperature phase. Since this suggestion, there have been numerous measurements of the so-called soft modes associated with SPT and for the displacive SPT their existence is well established. It can be seen that a mode of finite frequency exists even above $T_c$ and tends to freeze out on approaching $T_c$ from above. In order-disorder type SPT the ordering process of the atomic groups cannot be described in terms of small displacements from equilibrium positions. Consequently in these order-disorder systems soft mode ideas are less useful than in displacive systems.

The modes of the crystal, characterized by a dispersion relationship $\omega(q)$, of a crystal, are collective excitations and extend over the whole wave vector space $q$ of the Brillouin zone. At a displacive transition the freezing out of the soft mode produces the lattice found on the low temperature side of the transition. For $T < T_c$, the soft mode frequency $\omega_s(q)$ has a minimum at some wave vector in $q$ space. This minimum is most often found at the zone center $q = 0$ or at particular points of the Brillouin zone boundary $q_b$. Accordingly they are termed zone center and zone boundary transitions. In zone boundary transitions the unit cell gets doubled (or subject to even higher multiplication) in the low temperature phase because the point $q_b$ gets "folded into" the zone center. These cases have been termed earlier by Gränicher and Müller [1.21] as
ferro and antiferrodistortive transitions. In cell multiplying zone boundary transitions if the multiplying factor n is a rational multiple of a particular Brillouin zone boundary wave vector \( q_b \), then the transition is called commensurate. If, however, n is an irrational number the transitions are called incommensurate [1.22]. Some of the recent studies in SPT are aimed towards an understanding of this interesting class of incommensurate transitions.

In a zone center or ferrodistortive SPT the macroscopic quantities may couple linearly to the order parameter. If the spontaneous electric polarization \( P_s \) couple linearly with the order parameter then the corresponding transition is called a Ferroelectric Transition. On the other hand if the spontaneous strain \( X_s \) couple linearly with order parameter then the corresponding transition is called Ferroelastic Transition. In zone boundary transitions the macroscopic properties cannot couple linearly with the order parameter.

1.4.2 Probing SPT using ultrasonics

Ultrasonics is an accurate, convenient and a very popular tool for investigating phase transitions in solids. When a distortive phase transition is taking place in the crystal the acoustic modes of vibration in the crystal are directly or indirectly affected. This will in turn reflect as changes in the elastic constants of the crystal near the transition temperature which in turn affects the ultrasonic velocity which is being measured. In cases where the strain is linearly coupled with the order parameter, the ultrasonic measurements of velocity and attenuation can directly probe the order parameter and its static and dynamic response. Ultrasonic measurements can always be related somehow to the ordering quantity because there exists always some kind of coupling between the strain and the order parameter. A
complimentary tool for investigating elastic properties near phase transitions is Brillouin scattering. While ultrasonic measurements are done usually in the frequency range of 10 to 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, however, much higher for ultrasonics than for Brillouin scattering.

In the next section a brief discussion is given on how the elastic response function can be related to the relevant processes occurring at a SPT, in the frame work of Landau theory of phase transition [1.16, 1.23-1.27].

1.4.3 Theoretical analysis

In the Landau theory the free energy of the system is written in terms of the order parameter as [1.25],

\[ F(Q,T) = F_0(T) + \frac{1}{2} a(T)Q^2 + \frac{1}{4} bQ^4 + \ldots \]  

(1.67)

with \( a \) as temperature dependent near \( T_0 \) as,

\[ a = a'(T - T_0) \]  

(1.68)

The strain \( e \) gives an elastic energy contribution \( \frac{1}{2}c_0e^2 \) 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,

\[ F_{\text{int}} = geQ + heQ^2 + ie^2Q + \ldots \]  

(1.69)

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 (1.69) is different from zero. The expansion of the free energy would now appear as,
\[ F(Q,T) = F_0(T) + \frac{1}{2} a(T)Q^2 + \frac{1}{4} bQ^4 + \cdots + \frac{1}{2} c_0 e^2 + g e Q \] (1.70)

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. The result is a change, in general a decrease, in the elastic stiffness. Therefore the most important information about the SPT is obtained from the temperature dependence of the elastic functions.

In the case of bilinear coupling, \( F_{\text{int}} = geQ \), these forces are proportional to the strain only. There are no other forces and so

\[
\frac{\delta F}{\delta Q} = ge + \left( \frac{\partial^2 F}{\partial Q^2} \right) e \quad \frac{\delta Q}{\chi_0} = ge + \frac{\delta Q}{\chi_0} = 0, \quad (1.71)
\]

and the order parameter can in general follow the applied varying strain: \( \delta Q = -\chi_0 ge \). Its response is determined by the unnormalized order parameter susceptibility \( \chi_0 \). The moving ordering quantity \( \delta Q \) in turn adds a contribution to the stress \( \sigma \) acting within the sound wave as

\[
\sigma = \frac{\delta F}{\delta e} = c_0 e + g \delta Q = (c_0 - g^2 \chi_0) e. \quad (1.72)
\]

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

\[
c_T = c_0 - g^2 \chi_0 = c_0 \frac{T - T_0 - g^2/a' c_0}{T - T_0} \quad (1.73)
\]

In the above expression \( T_0 = T_0^e \) is, in the case of continuous transition, the transition temperature for zero strain

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(clamped state), in the absence of strain interaction \((1.69)\). In the free state (zero stress),
\[
T^\sigma = T_0 + g^2/a'c_0
\]
(1.74)
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 \(\chi_e^e\) 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 a dispersion for the real part of the elastic constant given by

\[
c_\tau(\omega) - c_\tau(\omega = 0) = g^2\chi_e^e (0) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (1.75)
\]
and an attenuation
\[
\alpha(\omega) = \frac{g^2\chi_e^e (0) \omega \tau}{2\rho v_s^3 (1 + \omega^2 \tau^2)}. \quad (1.76)
\]
For \(\omega \tau \gg 1\), \(c_\tau(\omega)\) approaches \(c_\tau(\omega = 0) + g^2\chi_e^e (0)\) which is, according to \((1.73)\), the background elastic function \(c_0\).

Summarizing the analysis of bilinear coupling of strain and order parameter, we expect an elastic instability \(c_\tau \to 0\) can occur at \(T^\sigma\) and an ultrasonic attenuation increases as \(T\) tends towards \(T_0^\sigma\). The limit \(\omega \tau = 1\) is practically not reached in ultrasonic experiments at structural transitions, but Brillouin scattering can show dispersive effects.

In the above discussion 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 systems coupling is linear in order parameter but quadratic in strain. More complex type of nonlinear couplings 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.

1.5 Phase transitions in mixed sulphate crystals

The crystals in which we have conducted investigations belong to the family of crystals with the general formula [1.28],

\[ M^I M^{II} B X_4 \]

where

- \( M^I = \text{Li or Na} \)
- \( M^{II} = \text{Na, K, Rb, NH}_4, \text{Cs or N}_2\text{H}_5 \)
- \( B X_4 = \text{BeF}_4, \text{SO}_4 \text{ or SeO}_4 \)

The members of this family like, LiKSO_4, LiNaSO_4, LiNaSeO_4 and LiRbSO_4 are isostructural and are all pyroelectric and belong to the hexagonal crystal system. These, in terms of the classification of Chung and Hahn [1.29], can be regarded as the proper derivatives of the tridymite structure (space group Pm3 (T_h)). Compounds with larger \( M^{II} \) ions in this family are generally orthorhombic and are said to belong to the improper derivatives of the tridymite structure. The
orthorhombic Lithium Ammonium Sulphate (LiNH\textsubscript{4}SO\textsubscript{4}) and Lithium Hydrazinium Sulphate (LiN\textsubscript{2}H\textsubscript{5}SO\textsubscript{4}) are examples of the later class.

Sulphate crystals, in general, have very interesting physical properties. Many of them undergo a series of phase transitions as the temperature is varied. Some of these undergo ferroelectric transitions, while some others undergo ferroelastic transitions and some of them exhibit both these types of transitions. The object of this work has been to investigate phase transitions in these interesting materials using ultrasonic technique selecting a few representative members from this family.

From this family of mixed crystals we have selected three sulphate crystals for our investigations. They are Lithium Hydrazinium Sulphate (LHS), Lithium Ammonium Sulphate (LAS) and Lithium Potassium Sulphate (LKS). At room temperature, both LHS and LAS belong to the space group C\textsubscript{2v} and point group C\textsubscript{2v} while LKS belong to the space group C\textsubscript{6} and point group C\textsubscript{6}.

LKS is one of the most extensively studied member of the family. Above and below room temperature it shows an interesting sequence of phase transitions. Despite extensive studies a definite picture of the mechanisms responsible for the phase transitions is still lacking [1.30]. There have been several investigations on the elastic properties of this crystal but surprisingly the complete set of the elastic constants of this crystal are not yet reported. A controversy regarding an above room temperature phase transition is not well resolved which we chose to investigate. From a material application point of view, LKS has been identified as one of the most interesting electro-optic materials, since it has an electro optic coefficient more than three times that of quartz and can withstand temperatures up to 400°C [1.31].

LAS is a fairly well investigated crystal. Below and
above room temperature LAS goes through several phase transitions. While its high temperature phase transition is well studied the investigations on the low temperature transition are few [1.32]. On the high temperature side LAS undergoes a ferroelectric phase transition near 460 K and has orthorhombic structure at room temperature. It further undergoes a ferroelastic phase transition near 284 K. Recently a weak second order phase transition has been identified near 256 K in dielectric and Raman studies [1.33]. There are uncertainties about the polar character of the phase below 284 K. The elastic properties at phase transition near 460 K have been investigated by ultrasonic and Brillouin scattering technique; but near 284 K only Brillouin data is available. The elastic data near the 256 K transition has not been reported. The absolute values of the elastic constants at room temperature, reported from one ultrasonic work [1.34] and several Brillouin experiments shows wide variation in values. Hence an accurate determination of the complete set of elastic constants of this crystal is required. The applications of LAS is in a way limited due to its highly fragile nature. Even the thermal gradient due to the frictional heat generated while polishing the crystal can crack it. LAS is a nonlinear optic material and it can find application as a second harmonic generator in laser systems.

The LHS is not a very widely investigated crystal when compared to LAS or LKS. At room temperature it exhibits [1.35] ferroelectric like hysteresis loops but other studies [1.36] indicate no ferroelectricity in this crystal. It has highly temperature dependent one dimensional protonic conductivity along the c direction. Several structural, electrical, thermal, and spectroscopic investigations have been reported on this crystal but its elastic properties have not yet been probed. There are no reports on the measurement of elastic constants of this crystal and hence a measurement
of the complete set of elastic constants is required. Even though this crystal shows a ferroelectric like behavior, the dielectric studies do not carry any signature of a ferroelectric phase transition. Similarly no specific heat anomalies have been found, indicative of phase transitions in this crystal. But there are anomalies in the thermal expansion coefficients above and below room temperature [1.37], and temperature variation of NMR spectrum also supports a weak high temperature phase transition without giving definite transition temperature [1.38]. Since ultrasonics is a very sensitive technique an ultrasonic investigation is appropriate here to probe for the weak phase transitions suspected in this crystal both at high and low temperatures. The highly temperature dependent c-axis protonic conductivity, high dielectric constant and ferroelectric like hysteresis loops of this crystal are not well explained, even though these properties make it a very interesting sample from a scientific point of view.
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