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Elastic properties of triglycine sulphate

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ELASTIC PROPERTIES OF
TRIGLYCINE SULPHATE

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This was perhaps the most pleasurable part of the thesis to write (it's the last bit!) and at which stage I can express my thanks to several people who have helped or contributed unwittingly to the hopefully, successful completion of this project.

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I also would like to thank my fellow postgrads for the various useful discussions and for their friendship. Without them my time at Bath would not have been so enjoyable. I will not name names, there has been to many of you!
The properties of a number of the adiabatic elastic stiffness constants of triglycine sulphate (TGS) have been determined over the temperature range 20 to 65 °C from measurements of the ultrasonic wave velocities in selected directions. Ten out of the thirteen elastic stiffness constants have been determined, the exceptions being $c_{12}, c_{13}$ and $c_{33}$. In the region of the ferroelectric phase transition ($T_c = 49^\circ C$) anomalies are observed in the elastic stiffness constants, with that of $c_{33}$ being the most pronounced.

The temperature derivatives of the elastic stiffness constants show different characteristics in the ferroelectric phase as compared to those in the paraelectric phase. For $c_{11}, c_{33}$ and $c_{44}$ the temperature derivative magnitude is decreased in the paraelectric phase, while for $c_{13}, c_{15}, c_{35}$ and $c_{46}$ the temperature derivative changes sign and becomes positive. The magnitudes of the temperature derivatives for $c_{44}$ and $c_{22}$ are observed to be the same on both sides of the transition.

A method has been developed for obtaining the hydrostatic pressure derivatives ($\partial C_{ij}/\partial P$) of the elastic stiffness constants of a monoclinic crystal from the hydrostatic pressure dependences of the ultrasonic wave velocities. This method has been applied to investigate the properties of ($\partial C_{ij}/\partial P$) over the temperature range 20 °C to 65 °C. The pressure derivatives of the elastic stiffness
stiffness constants increase with temperature; all derivatives show an anomaly at the phase transition varying from a slight effect in $\partial c_{22}/\partial P$ to the larger change in $\partial c_{44}/\partial P$.

At room temperature all thirteen of the monoclinic elastic stiffness constants have been determined along with their pressure derivatives. The results are used to describe the elastic behaviour of TGS. Accidental pure mode directions have been found at $9.4^\circ$ and $106.5^\circ$. 
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INTRODUCTION

Triglycine sulphate \((\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4\) (abbreviated to TGS) at room temperature is a ferroelectric crystal belonging to the monoclinic system and space group \(P2_1\). Ferroelectricity is observed along the direction of the 2-fold polar axis (monoclinic b-axis). At 49 °C TGS undergoes a second-order phase transition into a paraelectric, non-piezoelectric phase. The transition temperature is pressure dependent. The phase above the transition has monoclinic symmetry and belongs to the centrosymmetrical class \(2/m\). TGS has proved to be a popular material to work with as it is a convenient model system for the study of a second order ferroelectric phase transition and perhaps more importantly good quality crystals are easily grown. It has a number of technological applications, in particular as the pyroelectric sensing element in infrared vidicon cameras.

Previous experimental work concerned with the measurement of the physical properties of TGS can clearly be split into two main groups. The first group is concerned with the measurement of the magnitude of selected physical properties over a wide temperature range (or even just at one selected temperature). The second area of work is concerned with measuring a particular property very accurately over a narrow temperature range centred on the phase transition. The experimental data is then used either to confirm the predictions made by a specific model, or in some cases
used to suggest whether a particular model provides a comprehensive enough physical picture. The present work falls into the latter category and provides the most comprehensive experimental data to date on the elastic properties of TGS over the temperature range 20 to 65 °C.

Experimentally the elastic stiffness constants have been obtained using standard pulsed ultrasonic techniques, while their pressure derivatives have been found from the pressure-induced changes in the ultrasonic wave velocities. For a monoclinic crystal, which is characterized by 13 independent elastic stiffness constants, extraction of the elastic stiffness constants and their pressure derivatives from ultrasonic velocity data is rather complex. However, procedures which can be used to obtain the elastic stiffness constants have been suggested by several workers. A method for finding the pressure derivatives is given here and is used to find them for triglycine sulphate. The second-order elastic stiffness constants of a crystal determine the slopes of the acoustic phonon dispersion curves in long wavelength limit; their hydrostatic pressure dependences provide information on the shift of the mode energies with compression.

Previously the elastic stiffness constants have been measured in both the ferroelectric (Konstantinova et al (1960), Luspin and Hauret (1977) and Tylczynski (1981) and paraelectric phases (Haussuhl and Albers (1977)). There are piezoelectric contributions to the elastic stiffness constants in the ferroelectric phase. These
have been considered in part in a Brillouin scattering determination of the elastic stiffness constants but not in the ultrasonic measurements of Konstantinova et al (1960). Haussuhl and Albers (1977) have found that calculations of the piezoelectric corrections are unsatisfactory and suggest a requirement for high precision determination of the piezoelectric and dielectric constants for TGS under accurately defined dielectric conditions. In view of this, they have restricted their work to a determination of the elastic stiffness constants in the paraelectric phase. The Brillouin scattering measurement of Luspin and Hauret (1977), which include measurements of \( c_{11}, c_{22} \) and \( c_{33} \) in both phases suggest that the piezoelectric contributions in ferroelectric TGS are not large. Hence in these present measurements of the elastic stiffness constants, piezoelectric stiffening effects have not been taken into account. Results are used to provide a comprehensive picture of the elastic behaviour and its pressure dependences in TGS on both sides of the phase transition.
CHAPTER 1
THE CRYSTALLOGRAPHIC STRUCTURE OF TGS

1.1 Introduction

Triglycine sulphate \((\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4\), usually abbreviated to TGS, at room temperature is a ferroelectric crystal belonging to the monoclinic class with space group \(P\overline{2}_1\). The polar axis lies along the direction of the two fold axis (monoclinic b axis), and the crystal is piezoelectric. TGS undergoes a ferroelectric phase transition at \(49^\circ\text{C}\); the transition temperature is pressure dependent. In the paraelectric phase TGS still possesses monoclinic symmetry but then belongs to the space group \(P2_1/m\) which has a centre of symmetry so that TGS is not piezoelectric in this phase. Detailed dielectric and thermal studies of TGS show that the ferroelectric transition is of the second order type; the deviation of the structure from the ferroelectric phase to the paraelectric phase is slight.

1.2 Reference axis for TGS

Two possible orientations for the crystallographic a and c axis have been quoted in the literature. The earliest is due to Wood and Holden (1957), who reported the following lattice constants;

\[
a = 9.15 \text{ Å} \quad b = 12.69 \text{ Å} \quad c = 5.73 \text{ Å} \quad \beta = 105^\circ 40' 20"
\]

and showed that there are two formula units per unit cell. In a later study Hoshino et al (1959) used a different selection of the a and c axis, claiming that
this simplifies the description of the crystal structure; in this axial reference frame the lattice constants are:

\[ a = 9.14 \, \text{Å}, \quad b = 12.64 \, \text{Å}, \quad c = 5.73 \, \text{Å}, \quad \beta = 110° 23' \]

The two axes are related by the transforms \( a = a' + c' \), \( b = b' \) and \( c = -c' \) where the primed axes are those used by Wood and Holden (1957). The relationship between the two axial reference forms is shown in Fig 1.1. In acoustic studies of TGS the monoclinic axis due to Wood and Holden (1957) is used by all workers.

To define a set of three orthogonal axes \((x, y, z)\), which are often more convenient than the crystallographic monoclinic axes in description of the physical properties of the crystal, the standards set out by the Institute of Radio Engineers (IRE) can be used. For a monoclinic crystal the IRE convention is that the axis of symmetry is taken to be the \( b \) axis (which is also used as the orthogonal \( y \) axis), with the smaller of the other two denoted as the \( c \) axis. The rectangular axes \( y \) and \( z \) will then coincide with \( b \) and \( c \) respectively with the \( x \) axis at an angle of 15° to the \( a \) axis in the \( ac \) plane (see fig 1.2). This orthogonal \((x, y, z)\) axial set has been used by Tylczynski (1981), Luspin and Hauret (1977).

Konstantinova et al (1960) who made the first recorded determination of the elastic constants of TGS adopted a different reference orthogonally axial set (see fig 1.3), where the \( x \) and \( y \) axis are in opposite directions to those proposed by the IRE standards. In using the orthogonal reference axis due to Konstantinova et al instead of the IRE recommended axis...
Fig 1.1  Relationship between the unit cell proposed by Wood and Holden (1957) and that of Hoshino et al (1959).
Fig 1.2 Relationship between the orthogonal axis and crystallographic axis as used by Tylczynski (1981) Luspin and Hauret (1977).

Fig 1.3 Relationship between the orthogonal axis and crystallographic axis as used by Konstantinova et al (1960).
has the effect of reversing the sign of 4 elastic constants \((c_{16}, c_{23}, c_{36}, c_{44})\).

A different orthogonal axial set (see fig 1.4) has been used by Haussuhl and Albers (1977). In their work they adopted the following axis

\[ x//a, \ y//b, \ z//a \times b \]

Early on in this work the orthogonally axis of Konstantinova et al was adopted before I was aware of the IRE recommendations. On this discovery I considered it unwise to change to the recommended orthogonal axial set as this ran the risk of introducing confusion over which axial system measurements were taken in.

1.3 The crystallographic structure

The crystal structure of TGS has been examined in detail by Hoshino et al (1959), and was later refined by Itoh and Mitsui (1973). By considering over 2,000 reflections from a scattered x-ray beam, using a fourier synthesis technique, they were able to establish the position of all the individual atoms in the unit cell and their temperature dependence. Fig 1.5 shows the structure of TGS viewed down the c axis, the hydrogen bonds are also indicated (note the axial system is that due to Hoshino et al (1959)).

Before examining the structure of TGS in general, first consider the glycine molecule, \(\text{NH}_2\text{CH}_2\text{COOH}\), which commonly crystallizes in two different forms. One is a structure in which the two carbon atoms and the two oxygen atoms are approximately coplanar, with the
Fig 1.4 Relationship between the orthogonal axis and crystallographic axis as used by Haussuhl and Albers (1977).
Crystal structure of TBS at 19°C (due to Itoh and Mitsui (1973)) viewed along the c-axis. Dashed lines show the hydrogen bonds of which those terminated at half way indicate that the mate of the bond exists in the upper or lower cells.
nitrogen atom significantly displaced out of this plane; while the other form is a structure in which all carbon, nitrogen and oxygen atoms are close to planar. In TGS, which has three glycine groups, two (designated II and III in Fig 1.5) are quasi-planar and one (designated I) is non-planar, where the nitrogen atom is displaced by 0.5 Å out of the plane. The two planar glycine molecules II and III are arranged almost perpendicular to the polar b-axis and are in mirror image positions. They are connected by a hydrogen bond between oxygen atoms (O\(_{\text{II}}\) and O\(_{\text{III}}\)) which are some 0.25 nm apart. There are other hydrogen bonds in the detailed structure (see the original papers or fig 1.5 for their probable arrangement).

It has been shown by Itoh and Mitsui (1973), that bond distances and angles in glycine I change slightly with temperature, whereas variations in glycines II and III are significant. The atomic positions of glycine I depend significantly upon temperature.

It has been shown that chemically two protons from the \(\text{H}_2\text{SO}_4\) group are more properly associated with the glycines and the compound is often written as glycine di-glycinium sulphate \((\text{NH}_2\text{CH}_2\text{COOH})(\text{NH}_3\text{CH}_2\text{COOH})_2\text{SO}_4\). The glycine I is more correctly a glycinium ion. The other proton can be thought of as the \(O_{\text{III}}-\text{H}-O_{\text{III}}\) proton and resonates between glycine II and glycine III, at least in the paraelectric phase. This suggests that glycine II and III are by nature intermediate in state between glycinium \(\text{NH}_3\text{CH}_2\text{COOH}^+\) and glycine zwitter ion \((\text{NH}_3^+\text{CH}_2\text{COO}^-)\). This
description of the glycines II and III is termed glycinium-glycine.

The only strong intermolecular bonding between the glycine I and other molecules is the hydrogen bond through H1 (see fig 1.5), if the NH$_3$ group is rotating. Glycine I is associated with the reversible dipole. It is by considering the glycine I group that the most convincing evidence is provided that the phase transition is of the order-disorder type. Above the Curie temperature the b-plane through the glycine molecules is a plane of mirror symmetry, and Itoh and Mitsui (1973) found that, if an analysis of the X-ray scattering data is commenced assuming a planar glycine I in the mirror plane, the refined structure shows that all the oxygen, carbon and nitrogen atoms occupy double-minimum sites straddling the mirror plane. In effect this means that above the curie temperature the mirror plane refers only to the average structure, with the glycine molecule undergoing a thermally activated hopping motion between equivalent potential wells on either side of the b plane. In the paraelectric phase there is no disorder with respect to the glycine II and III molecules.

Near the transition temperature a comparison of the average amplitudes of motion for the heavy atoms show that by far the greatest amplitude is for the glycine I nitrogen atom in the b-direction. This in turn has lead to the suggestion of the possibility of a driving role for the nitrogen double-well instability in the mechanism of the ferroelectric transition. Although the hydrogen
bond may still play an important part, effects of deuteration on the dielectric properties have been found to be small which suggest that this role may be less than a dominant one.

The sulphate ion which sits on the mirror plane has been shown to deviate from tetrahedral symmetry, this is to be expected since there are hydrogen bonds of unequal strength existing between the sulphate oxygens and the other atoms. The shape of the sulphate ion changes only slightly with temperature.

The transition of each atom during the polarization reversal has been investigated by many workers. It has been shown that there is a negligible shift of the sulphur atom. The three glycine groups I,II,III are all participating in the polarization reversal, but the main reversible dipole is that associated with glycine I. With reference to the model of Itoh and Mitsui (1973), it can be seen how polarization reversal takes place with respect to glycine I, and it can be easily recognized that the polarization reversal does not correspond to a simple rotation of the molecule, but to a combination of the shift of the C-CO$_2$ plane along the b-axis (accompanied by a small rotation) and a kind of isomer transformation in glycine I involving the rotation along the C-C$^\text{N}$ bond which brings N$_1$ to the opposite side of the C-CO$_2$ plane. As shown in fig 1.5 the only strong intermolecular bonding between the glycine I and other molecules is the hydrogen bond through H1, if the NH$_3$ group is rotating. Probably this fact makes the large movement of the glycine I molecule easy.
CHAPTER TWO

THE DEFINITION AND MEASUREMENT OF ELASTIC CONSTANTS

2.1 Introduction

The elastic constants of solids were introduced originally to describe the experimentally observed linear relationship between stress and strain. This relationship is known as Hooke's law (Nye, 1957, Huntington 1958)

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

(\(i,j,k,l=1,2,3\))

where \(\sigma_{ij}\) and \(\varepsilon_{kl}\) are second rank stress and strain tensors, while \(C_{ijkl}\) is a fourth rank elastic stiffness tensor. The associated elastic constants are termed second order (SOEC). It has been shown that Hooke's law is only valid for infinitesimal strains; for finite strains the relationship becomes non-linear. If one includes higher order elastic constants in the definition, the non-linear region of the stress-strain relationship observed in practice for finite strains, can be accounted for. This specification of higher order elastic constants has been investigated in detail by Murnaghan (1951) and Wallace (1972).

The elastic constants of a material are dependent on its physical state and the conditions under which they are considered. Therefore the definition of elastic constants is best expressed in thermodynamic terms. Such definition permits elastic constants of any order, whereas only SOEC are required by Hooke's law. The inclusion of higher order elastic constants are required
to describe successfully the non-linear stress-strain region observed for finite strains. The thermodynamic definition of elastic constants is described in this chapter.

2.2 Homogeneous strain

For thermodynamic calculations the crystal is considered to be a homogeneous anisotropic medium, which when subjected to a uniform stress suffers a homogeneous strain.

Consider a body occupying a space, with every particle referenced to a rectangular Cartesian frame. The position P of a particle in the unstrained state is located at \((a_1, a_2, a_3)\) with its position described by the vector \(a\). On straining the body this particle moves to a new position Q with coordinates \((x_1, x_2, x_3)\) described by the vector \(x\). The deformation of the body is known if \(x_1, x_2, x_3\) are known functions of \(a_1, a_2, a_3\)

\[
x_1 = x_1(a_1, a_2, a_3)
\]

(2.2)

It is assumed that the deformation is continuous, a neighbourhood is transferred into a neighbourhood and that the transformation is one-to-one; i.e. the functions in 2.2 are single-valued, continuous and have unique inverse for every point in the body

\[
a_i = a_i(x_1, x_2, x_3)
\]

(2.3)

As the strain is homogeneous the vectors \(a\) and \(x\) are related by a linear transform according to

\[
x_i = \sum \epsilon_{ij} a_j
\]

(2.4)

where \(\epsilon_{ij}\) is the deformation gradient from the unstrained
configuration to the strained configuration. It also follows from the definition of the transform that

$$\varepsilon_{ij} = \frac{\partial x_i}{\partial a_j}$$

2.5

The stress induced displacement from \( a \) to \( x \) is described by a displacement vector \( u \), defined by

$$u_i = x_i - a_i$$

2.6

with displacement gradients given by

$$u_{ij} = \frac{\partial u_i}{\partial a_j}$$

2.7

Differentiation of equation 2.6 with respect to \( a_j \), and comparison of the result with equation 2.5 leads to the relationship between the transformation coefficients and the displacement gradients.

$$\varepsilon_{ij} = \delta_{ij} + u_{ij}$$

2.8

where \( \delta_{ij} \) is the Kronecker delta.

Describing the strain of a body in terms of the displacement gradients \( u_{ij} \) is not satisfactory as, if the body is not deformed but undergoes a translation or rotation, the displacement gradients are non-zero and the internal energy of the body remains unaltered. A more useful strain parameter is one which is zero for a body rotation or translation.

This strain parameter is obtained by considering the change in distance between any two points in the body. In the unstrained state consider an infinitesimal line element \( dS_0 \), connecting the point \( P(a_1, a_2, a_3) \) to a neighbouring point \( P'(a_1 + da_1, a_2 + da_2, a_3 + da_3) \). The square
of the length \( dS_0 \) at PP' in the unstrained configuration is given by

\[ dS_0^2 = da_1 + da_2 + da_3 \quad (2.9) \]

On straining, the points P and P' are deformed to \( Q(x_1, x_2, x_3) \) and \( Q'(x_1+dx_1, x_2+dx_2, x_3+dx_3) \) respectively, the square of the length \( dS \) of the new element QQ' is

\[ dS^2 = dx_1^2 + dx_2^2 + dx_3^2 \quad (2.10) \]

on differentiating Eq's 2.2 and 2.3

\[ dx_1 = \frac{\partial x_1}{\partial a_j} da_j \quad (2.11) \quad da_j = \frac{\partial a_j}{\partial x_3} dx_3 \quad (2.12) \]

introducing the Kronecker delta \( \delta_{ij} \), 2.9 can be rewritten using 2.11

\[ dS_0^2 = \delta_{ij} da_j da_3 = \delta_{ij} \frac{\partial a_i}{\partial a_3} \frac{\partial a_j}{\partial a_m} dx_1 dx_m \quad (2.13) \]

and similarly for 2.10 using 2.12

\[ dS^2 = \delta_{ij} dx_1 dx_3 = \delta_{ij} \frac{\partial x_4}{\partial a_3} \frac{\partial x_4}{\partial a_m} da_1 da_m \quad (2.14) \]

The difference between the squares of the length elements may be written after several changes in the suffixes for dummy indices either as

\[ dS^2 - dS_0^2 = (\delta_{ij} - \delta_{ij}) \frac{\partial x_4}{\partial a_3} \frac{\partial x_4}{\partial a_m} da_1 da_m \quad (2.15) \]

or

\[ dS^2 - dS_0^2 = (\delta_{ij} - \delta_{ij}) \frac{\partial a_1}{\partial x_3} \frac{\partial a_m}{\partial x_3} dx_1 dx_3 \quad (2.16) \]
The following strain tensors can be defined

\[ \eta_{ij} = \frac{1}{2} \left( \frac{\partial x_m}{\partial a_i} \frac{\partial x_m}{\partial a_j} - \delta_{ij} \right) = \frac{1}{2} \left( \epsilon_{ms} \epsilon_{ms} - \delta_{ij} \right) \]  \hspace{1cm} (2.17)

\[ \epsilon_{ij} = \frac{1}{2} \left( \frac{\partial x_m}{\partial a_i} \frac{\partial x_m}{\partial a_j} \right) \]  \hspace{1cm} (2.18)

so that

\[ dS^2 - dS_0^2 = 2 \eta_{ij} da_i da_j \]  \hspace{1cm} (2.19)

\[ dS^2 - dS_0^2 = 2 \epsilon_{ij} dx_i dx_j \]  \hspace{1cm} (2.20)

where \( \eta_{ij} \) are the elements of the Lagrangian strain (measured in the initial coordinate system), and \( \epsilon_{ij} \) are the elements of the Eulerian strain, measured in the strained coordinate system.

The tensors \( \eta \) with components \( \eta_{ij} \) is symmetric. From 2.17 it can be seen that if \( \eta_{ij} = 0 \), then \( \epsilon_{ij} \) represents a body rotation only. In this way the strained state of a crystal may be completely specified in terms of the initial unstrained state and either the transformation coefficients \( \epsilon_{ij} \) or the displacement gradients \( u_{ij} \).
2.3 Thermodynamic definition of elastic constants

In the following consideration, to simplify matters, it is assumed that there are no other contributions to thermodynamic potentials, including those which arise from magnetic and electric fields.

Brugger (1964) introduced the thermodynamic definitions for higher order elasticity by using the combined first and second laws of thermodynamics i.e.

\[ dU = TdS - dW \] 2.21

The work \( dW \), is that done by the crystal in changing the configuration from \( \mathbf{a} \) to \( \mathbf{a} + \Delta \mathbf{a} \) against an applied stress \( \mathbf{r} \).

The applied stress is represented by the thermodynamic stress tensor \( r_{ij} \) which is analogous to \( \mathbf{r}_{ij} \) used in Hooke's law.

If the surface of the crystal in the initial unstrained configuration \( \mathbf{a} \) is \( s \), with a surface element denoted by \( ds \), the \( i \)'th component of force on \( ds \), due to the applied stress is given by

\[ f_i = \sum_j r_{ij} ds_j \] 2.22

The displacement gradients corresponding to the strain \( \Delta \mathbf{a} \) is \( \Delta \mathbf{u}_{ij} \), the displacement of \( ds \) in the \( i \) direction is

\[ \Delta a_i = \sum_k \Delta u_{ik} \] 2.23

The work done by the crystal against the stress applied to \( ds \) is

\[ - \int f_i \Delta a_i = - \int \sum_j r_{ij} ds_j \Delta u_{ik} \] 2.24

Note that the customary convention is that positive stresses are directed outward from the crystal surface. The total work done by the crystal is the integral of this expression over the surface \( s \). This surface integral
is transformed to a volume integral by Gauss’s theorem and becomes

$$\Delta W = \int_{S} \sum_{i,j} \Gamma_{i,j} \Delta u_{i,j} \, ds = - \int_{V} \sum_{i,j} \Gamma_{i,j} \Delta u_{i,j} \, dV = - \sum_{i,j} \Gamma_{i,j} \Delta u_{i,j} \, V(a) \quad 2.25$$

since $\Gamma_{i,j}$ and $\Delta u_{i,j}$ are constants.

Finally, since $\Gamma_{i,j}$ is symmetric, the anti-symmetric part of $\Delta u_{i,j}$ gives no contribution to the $\Sigma_{i,j}$ in 2.25, so $\Delta u_{i,j}$ may be replaced by $\Delta \eta_{i,j}$ to a first order approximation. Writing the work 2.25 in differential form gives

$$dW = - \sum_{i,j} \Gamma_{i,j} \, d\eta_{i,j} \quad 2.26$$

If the case of unit mass is considered and $\rho_0$ is the density of the unstrained solid, then rewriting 2.26

$$dW = -(1/\rho_0) \sum_{i,j} \Gamma_{i,j} \, d\eta_{i,j} \quad 2.27$$

From the first and second laws of thermodynamics (2.1)

$$dU = T \, dS + (1/\rho_0) \sum_{i,j} \Gamma_{i,j} \, d\eta_{i,j} \quad 2.28$$

and for the Helmholtz free energy

$$dF = (1/\rho_0) \sum_{i,j} \Gamma_{i,j} \, d\eta_{i,j} - BD $$

In a similar way Brugger (1964) obtained the following potentials for the enthalpy $H$ and Gibbs free energy

$$dH = T \, dS - (1/\rho_0) \sum_{i,j} \eta_{i,j} \, d\Gamma_{i,j} \quad 2.30$$

$$dG = -BD - (1/\rho_0) \sum_{i,j} \eta_{i,j} \, d\Gamma_{i,j} \quad 2.31$$

The potentials and all extensive variables are taken per unit mass and all the above are summed over repeated indices $i$ and $j$. The thermodynamic tensors $\Gamma_{i,j}$ are given by

$$\Gamma_{i,j} = \rho_0 \left( \frac{\partial U}{\partial \eta_{i,j}} \right)_{\eta,\eta} = \rho_0 \left( \frac{\partial F}{\partial \eta_{i,j}} \right)_{T,\eta} \quad 2.32$$
The subscript \( \eta' \) means that all other components of \( \eta_{ij} \) are held constant while differentiating with respect to \( \eta_{ij} \).

The state functions \( U \) and \( F \) must remain unchanged if the body is translated or rotated, without deformation. This rotational invariance suggests that \( U \) and \( F \) depend on the strained configuration \( x \) only through the initial configuration \( a \) and the rotational-independent strains \( \eta_{ij} \). Therefore, the functional dependence may be written:

\[
U(x,S) = U(a,\eta_{ij},S) \tag{2.33}
\]

and

\[
F(x,T) = F(a,\eta_{ij},T) \tag{2.34}
\]

As the strains involved are small, it is possible to express the strain dependence of the thermodynamic potentials in the form of a Taylor series expansion about the state of zero strain. For example

\[
U(S) = U(S,\eta) - U(S,0) = \left( \frac{\partial U(S,\eta)}{\partial \eta_{ij}} \right)_{\eta = 0} \eta_{ij} + \tag{2.35}
\]

\[
\left( \frac{1}{2} \right) \left( \frac{\partial^2 U(S,\eta)}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{\eta = 0} \eta_{ij} \eta_{kl} + \left( \frac{1}{6} \right) \left( \frac{\partial^3 U(S,\eta)}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right)_{\eta = 0} \eta_{ij} \eta_{kl} \eta_{mn}
\]

but for an unstrained crystal in thermodynamic equilibrium

\[
\left( \frac{\partial U(S,\eta)}{\partial \eta_{ij}} \right)_{\eta = 0} = 1/\rho_{ij} \eta_{ij} = 0 \tag{2.36}
\]

As elastic coefficients of order \( n \) (\( n > 2 \)) are defined thermodynamically as the \( n \)'th partial derivatives of the appropriate thermodynamic potential with respect to the Lagrangian strains, evaluated at zero strain (or with respect to the tensions, evaluated at zero tension).The
energy density can be written as

\[ \rho \mathcal{U}(\mathbf{q}) = \left( \frac{1}{2} \right) \epsilon_{ij} \eta_{ij} + \left( \frac{1}{6} \right) \epsilon_{ijk} \eta_{ijk} + \frac{2}{3} \eta \]

where

\[ \epsilon_{ij} = \rho \left( \frac{\partial \mathcal{U}(\mathbf{q})}{\partial \eta_{ij}} \right)_{\eta=0} \]

and

\[ \epsilon_{ijk} = \rho \left( \frac{\partial \mathcal{U}(\mathbf{q})}{\partial \eta_{ijk}} \right)_{\eta=0} \]

The first two terms in the above energy expansion are the second order and third order adiabatic elastic constants respectively.

If a similar approach is adopted with the expression for Helmholtz free energy the expressions for the isothermal elastic constants are obtained

\[ \epsilon_{ij} = \rho \left( \frac{\partial \mathcal{F}(\mathbf{q})}{\partial \eta_{ij}} \right)_{\eta=0} \]

\[ \epsilon_{ijk} = \rho \left( \frac{\partial \mathcal{F}(\mathbf{q})}{\partial \eta_{ijk}} \right)_{\eta=0} \]

The form of these expansions is similar to that for potential energy in terms of interatomic displacement, and thus it is ultimately possible to relate the elastic constants to the interatomic forces in a solid.

Since the strains and the thermodynamic tensions are symmetric i.e., \( \eta_{ij} = \eta_{ji} \) and \( \eta_{ijk} = \eta_{ikj} \), only six of each set of nine variables are independent, and it is customary to use the Voigt notation:

11 = 12 = 22 = 23 = 13 = 33 = 1 = 21 = 12, 23 = 32

By convention, in the contracted notation the strain \( \eta_{ij} \) is written as \( \eta_{ij} \). The magnitudes of the \( \eta_{ij} \) are related to
the magnitudes of the \( \eta_{ij} \) by
\[
\eta_{ij} = \frac{1}{2} (1 + \delta_{ij}) \eta_i
\]

Also by Brugger (1964)
\[
\gamma_{ij} = \gamma_i
\]

where lower case subscripts run from 1 to 3 and capital subscripts run from 1 to 6.

Applying this contracted notation to the elastic constants gives
\[
C_{ij} = C_{ijkl}
\]

In the reduced notation the thermodynamic potential becomes
\[
C_{ij} = \rho_0 \left( \frac{\delta^2 U}{\delta \eta_i \delta \eta_j} \right) s, \eta = 0
\]
\[
C_{ijkl} = \rho_0 \left( \frac{\delta^2 U}{\delta \eta_i \delta \eta_j \delta \eta_k} \right) s, \eta = 0
\]

The potentials \( U, F, H \) and \( \Theta \) are extensive properties of the system \( s \), and so their n'th partial derivatives are independent of the order of differentiation; i.e., the strain energy must be independent of the path by which the state of strain is attained. Thus all permutations of the contracted suffixes lead to the same constants, so for second order
\[
C_{ij} = C_{ji}
\]

and third order
\[
C_{ijkl} = C_{iklj} = C_{kjil} = C_{klij} = C_{ijlk} = C_{ijlk}
\]

The maximum numbers of independent SOEC and TOEC are 21 and 56 respectively. These numbers are further reduced by crystal symmetry. Brugger (1965a) lists the
independent SOEC and TOEC for all of the crystallographic systems. For a crystal of monoclinic symmetry there are 13 second order elastic constants and 32 third order elastic constants. These are

\[ C_{11}, C_{12}, C_{13}, C_{15}, C_{22}, C_{23}, C_{25}, C_{33}, C_{35}, C_{44}, C_{46}, C_{55}, C_{66} \]

and

\[ C_{111}, C_{112}, C_{113}, C_{115}, C_{122}, C_{123}, C_{125}, C_{133}, C_{155}, C_{144}, C_{146}, C_{166}, C_{222}, C_{233}, C_{235}, C_{244}, C_{246}, C_{266}, C_{255}, C_{333}, C_{335}, C_{344}, C_{346}, C_{366}, C_{355}, C_{444}, C_{446}, C_{466}, C_{555}, C_{666} \]

2.4 Propagation of elastic waves in crystals

The SOEC of a crystal are determined from measurements of the velocity of ultrasonic waves propagating in that crystal. The wave motion is assumed to be adiabatic and to cause only infinitesimal displacements of volume elements in the crystal.

The equation of motion comes from the fundamental law of dynamics: force equals mass times acceleration. It can be shown that the force exerted on a unit volume of a stressed material is

\[ f = \frac{\partial \sigma_{ij}}{\partial a_{ij}} \]

When the effect of gravity and any other forces on the body are neglected, this force gives rise to an
\text{acceleration along the } i^{th} \text{ axis for a unit volume of mass } \rho_0.\\

\[ \rho_0 \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{1i}}{\partial a_j} \quad 2.48 \]

From equations 2.8 and 2.17 the Lagrangian strain parameter is

\[ \eta_{1j} = (u_{1j} + u_{ji} + u_{ki}u_{kj}) \quad 2.49 \]

but as \( u_{1j} \) are infinitesimal strains, \( u_{ki}u_{kj} \) are second order infinitesimal, and in a first order approximation can be ignored. This leads to the usual infinitesimal strain definition

\[ \epsilon_{1j} = \frac{(u_{1j} + u_{ji})}{2} \quad 2.50 \]

\[ \epsilon_{1j} = \frac{1}{2} \left( \frac{\partial u_j}{\partial a_j} + \frac{\partial u_j}{\partial a_k} \right) \quad 2.51 \]

by differentiating 2.1 with respect to \( a \), and comparing with 2.48, the equation of motion is obtained as

\[ \rho_0 \frac{\partial^2 u_i}{\partial t^2} = c_{1jk} \frac{\partial \sigma_{1j}}{\partial a_j} \quad 2.53 \]

Assuming a plane wave solution, travelling in the direction of a unit vector \( \mathbf{N} \), where \( u_0 \) is the particle displacement amplitude, then the particle displacement vector \( \mathbf{u} \) at any point can be described by

\[ \mathbf{u} = u_0 \exp \left( i(wt - k\mathbf{N} \cdot \mathbf{a}) \right) \quad 2.54 \]

Substituting 2.54 into 2.53 and carrying out the differentiation

\[ \rho V^2 u_i = c_{1jk} N_j N_k u_i \quad 2.55 \]

Introducing the second rank tensor

\[ \Gamma_{1j} = c_{1jk} N_j N_k \quad 2.56 \]

This is known as Christoffel equation. Rewriting 2.55
\[ \gamma_{11} u_1 = \rho v^2 u_1 \quad \text{2.57} \]

The velocities and particle polarization of those plane waves which propagate along a direction \( \mathbf{N} \) in a crystal with elastic stiffness tensor \( c_{ijkl} \) are obtained by searching for the eigenvalues and eigenvectors of the tensor \( \gamma_{11} \). For a given propagation direction, there are three roots of the equation

\[ \gamma_{11} - \rho v^2 \delta_{11} = 0 \quad \text{2.58} \]

Each velocity obtained is related to an eigenvector which defines the particle displacement direction (i.e., the wave polarization). Since the eigenvalues must be real and positive, there are generally three waves propagating in the same direction with different velocities and mutually orthogonal polarizations. The particle displacement vector \( \mathbf{u} \) is generally not parallel or perpendicular to the polarization direction \( \mathbf{N} \).

A pure mode occurs when the particle displacement vector \( \mathbf{u} \) is parallel (for longitudinal modes) or perpendicular (for shear modes) to the wave propagation direction \( \mathbf{N} \). If all three waves propagating in a direction \( \mathbf{N} \) are pure, the direction is referred to as being a pure mode one. Brugger (1965a) investigated the necessary conditions for a pure mode direction to occur for most of the crystal classes. This was achieved by identifying the conditions necessary for the longitudinal mode to be pure \( (\mathbf{u} \cdot \mathbf{N} = 0) \). As the wave solutions are orthogonal, it automatically implies that the two shear modes are also pure and hence a pure mode direction is identified. Brugger (1965a) found that the number of pure
mode directions is dependent on the crystal symmetry. Pure mode directions are important as in these directions the energy flux vector is perpendicular to the plane wavefronts. When this occurs maximum energy is transferred from the transducer to the mode under measurement.

In monoclinic crystals there are very few pure mode directions (see Fig 2.1) only one of which, denoted as $\beta$, is directly determined by crystal symmetry. This occurs along the two fold symmetry axis (Y direction). Any other pure mode directions present are a function of the elastic stiffness of the material, not on crystal symmetry; these are termed accidental pure mode directions. It can be shown that there are two accidental pure mode directions which can be designated by $\alpha$ and $\gamma$ in the XZ plane. Also in this plane for all directions the $\gamma$ polarized shear is a pure mode. Other accidental pure mode directions may occur in monoclinic crystals, but these lie off any of the axial planes and are of little experimental use.

In general the waves propagated are quasi-pure modes, for these the energy flux vector is not perpendicular to the plane wavefronts. Ideally one would use pure modes if at all possible, so that no energy is lost from the transducer in exciting modes which are not under measurement with the subsequent energy loss. Unfortunately it is not usually possible with monoclinic crystals to use pure modes as practically every mode is quasi-pure.
Fig 2.1 Pure mode directions for monoclinic crystal. $\beta$ lies along the two fold $y$ axis. $\alpha$ and $\gamma$ lie in the $xz$ plane.
Expressions linking the wave velocities and elastic stiffness for monoclinic crystals are listed in table 2.1. The evaluation procedure used to obtain the elastic constants is rather lengthy; an example is discussed in chapter four.

2.5 Hydrostatic pressure derivatives of "effective" SOEC

Thurston and Brugger (1963) defined a "natural velocity" \( W = \frac{l_0}{t} \), where \( l_0 \) is the path length of the wave in the unstressed crystal and \( t \) is the measured experimentally measured transit time over the distance \( l_0 \). The product \( \rho_0 W^2 \) being the measure of elastic stiffness in that direction.

The quantity \( (\rho_0 W^2)_{p=0} \) does not represent the actual pressure derivative of the SOEC as no correction has been applied to account for the increase in pressure altering the sample path length and density. Using a relationship developed by Thurston (1965) the pressure derivatives can be calculated, without the need to calculate the path length and density for each data point used. The equation is

\[
\left[ (\rho_0 V^2) - (\rho_0 W^2) \right]_{p=0} = \rho_0 W_0^2 \left( S_{Kii}^{T} - 2N_k N_m S_{Kii}^{T} \right)_{p=0}
\]

Here \( W_0 \) is the natural velocity, defined as the path length at zero pressure divided by the transit time at pressure \( p \). The quantity in parentheses on the right is the volume compressibility minus twice the linear compressibility in the direction \( N \). The volume compressibility component corresponds to the effects of changes of density and the linear compressibility part to
the pressure induced change in path length. It is the isothermal compliance coefficients which appear in 2.59 because the pressure derivatives are measured at constant temperature. The advantage of using the natural velocity is that \((P_0W^3)_{P=0}\) is directly related to the initial slope and intercept of the measured frequency versus pressure graph.

\[(P_0W^3)_{P=0} = 2P_0V^2f'/f_0\]  

Combining 2.59 and 2.60

\[(P_0W^3)_{P=0} = \frac{\partial C^{2U}}{\partial P} _{P=0} = P_0V^2(2f'/f_0 + \lambda^T - 2N_xN_y\dot{\lambda}_{x_11})\]  

where \(\lambda^T\) is the volume compressibility, \(f'\) is the gradient of the least square line of a plot of frequency versus pressure and \(f_0\) is the intercept at zero pressure.

From Nye (1957) the volume compressibility is

\[\lambda = S_{11} + S_{12} + S_{13} \pm 2(S_{11} + S_{12} + S_{13})\]  

and the linear compressibility by

\[\beta = (S_{11} + S_{12} + S_{13})l_1 + (S_{12} + S_{22} + S_{23})l_2 + (S_{13} + S_{23} + S_{33})l_3 + (S_{16} + S_{26} + S_{36})l_3 l_1\]  

Strictly equation 2.61 is only true for modes where the pressure derivative of the particle displacement vector \(u\) and the propagation direction \(N\) are zero. These conditions are only true for the longitudinal mode propagating in the Y direction. As the errors in excluding this effect are small in comparison with the experimental error to a first order approximation they can be ignored and equation 2.61 used for all mode directions.
CHAPTER THREE
EXPERIMENTAL METHODS

3.1 Introduction

To obtain the SOEC and the associated pressure derivatives of a solid, it is usual to measure the transit time of an ultrasonic wave through the solid and the change of this transit time with pressure.

Prominent names in the early development of pulsed ultrasonic techniques are Huntington (1947), Mason and McSkimin (1947), Arenberg (1950), Roderick and Truell (1952), May (1958) and Papadakis (1964, 1966, 1967). Several variations of the basic technique have been described in the literature, the simple pulsed-echo method remains the most common type: a suitable equipment can easily be constructed from commercially available apparatus.

In this work the ultrasonic wave measurements were made using a single ended pulse echo method in which a transducer is bonded onto a sample which has flat and parallel faces. A radio frequency tone burst of 1 to 2 microseconds duration is applied to the transducer, which excites mechanical stress waves at the sample surface. Then stress waves propagate through the bulk and are reflected at the opposite face. This echo, and subsequent impinging echoes are detected by the same transducer which produces an electrical voltage in proportion to the amplitude of the stress wave. This voltage, after amplification, can be used to display the echoes on an oscilloscope from which the attenuation and the transit
time of propagation of the stress waves through the solid can be determined.

This chapter describes the pulse echo overlap technique used to measure the transit time of ultrasonic waves in TGS samples and the equipment used to stress hydrostatically these samples. The temperature dependences of the hydrostatic pressure derivatives of wave velocity for several directions have also been investigated. The method by which the temperature of the hydrostatic pressure cell was measured, varied and controlled is also described here.

3.2 Sample preparation

Large crystals of TGS can be grown from water solutions prepared by reacting an aqueous glycine solution with the correct amount of sulphuric acid. A suitable crystal growth rate can be achieved by slow evaporation of the solvent at constant temperature or by slowly lowering the temperature at constant supersaturation. The habit of the crystals obtained depends on the growth procedure and is generally quite complex owing to the presence of many faces in this material. Further details of the habits of TGS can be obtained by referring to Furuhata (1970), Konstantinova et al (1960) and Mitsui et al (1976). TGS crystals have a pronounced cleavage plane parallel to [010] direction, thus crystal plates orientated perpendicular to this polar axis can easily be obtained by cleavage of larger crystals without needing to know the directions of the
monoclinic a and c axes. The crystals used in this work were kindly provided by Dr R.J. Jones of R.S.R.E. Malvern.

Orientation of a monoclinic crystal by X-Ray methods alone can be rather difficult. With carefully grown crystals, where pronounced faces are present, the crystal morphology (see Fig 3.1) can be used to assist in the identification of the crystallographic axis. The TGS crystal used in this work was orientated by first identifying the two fold symmetry axes using the X-Ray back reflection Laue technique, then the a and c axes were identified by reference to the crystal morphology (Konstantinova et al (1960) corresponding to our crystal.

As shown in chapter 4, for monoclinic crystals it is possible to obtain all the SQEC's by propagating ultrasonic waves along six crystallographic directions, namely [001], [010], [100], [101], [110] and [011]. This required four rectangular parallelepipeds to be cut (with a diamond wheel) of dimensions about 1 cm x 1 cm x 1 cm, one with faces perpendicular to the [001], [010] and [100] directions and the other three such that they had a pair of faces perpendicular to the [101], [011] and [110] directions respectively. Faces were polished flat and parallel on a cast-iron plate, first with aloxite and water for a few seconds and finished with 14 μm diamond paste. The parallelism between the faces was checked by making several measurements at different points on the surface using a micrometer; parallelism was found to be
Fig 3.1 The Mythology of TGS viewed down -b axis. The crystallographic axes being due to Wood and Holden (1957) and the reference orthogonal axis due to Konstantinova et al (1960).
better than $10^{-3}$ radians.

Transducers are effectively phase sensitive devices, which places narrow tolerance upon the parallelism of the sample faces. For example if the phase of the wavefront striking the transducer is positive on one half and negative on the other due to path difference, then the net response of the transducer would be zero.

### 3.3 Transducers

The generation and detection of the ultrasonic waves was accomplished by the use of a gold plated piezoelectric quartz transducer with a diameter of 6 mm, attached by a bonding medium to one of the sample faces (see fig 3.2). The fundamental frequency of the transducers used in this work was 10 MHz. The resonant frequency of the transducer is determined by its thickness, the fundamental frequency is given by

$$ d = \frac{\lambda}{2} $$

where $d$ is the thickness and $\lambda$ is the wavelength of the stress wave in quartz at the resonant frequency. For longitudinal modes the transducer thickness is 0.29 mm and for shear modes 0.19 mm.

The transducer acts as a piston source and generates a wave which is essentially plane and has a width equal to the diameter of the piston up to a distance ($r$) given by

$$ r = \frac{a^2}{\lambda} $$

where $a$ is the radius of the vibrating piston. The size of the transducer was chosen such that the vibrations were plane in nature but not large enough when it is
Fig 3.2 Schematic representation of sample bond and transducer which has gold plated electrodes with a guard ring.
compared with the crystal cross section to risk side-wall reflections (Waterman 1959).

This work required the generation of longitudinal and shear modes of vibration in TGS crystals. For longitudinal modes X-cut quartz transducers are employed, while Y-cut transducers were used for shear modes. The transducers were obtained commercially from Gooch and Housego Ltd, Ilminster, England.

3.4 Bonding materials and procedure

To attach the transducer to the sample, a bonding medium is required. The bonding medium will couple the acoustic energy from the transducer into the sample. The principle of making a good bond is based on the minimum loss of the acoustic energy converted by a transducer. For a bond to meet these requirements, the bond thickness should be small compared to the acoustic wavelength (this avoids losses due to reflection). It should also be uniform, and more importantly, it should not damage or react with either the sample surface or the transducer. A viscoelastic resin, Dow Resin 276-v9 (Dow - Corning Corp) meets these requirements and was used exclusively as a bonding medium. It was found that the bond resisted attack from the castor oil used as the pressure transmitting medium in the hydrostatic pressure bomb and remained usable for 4 to 5 days at least. For general information on bonding agents which can be used see Bateman (1966) or Farley (1973).
The essential procedure for bonding is to form a uniform thin bond between the transducer and sample without damaging either since the quartz transducer is fragile. The shear transducers have to be bonded with the polarization vector parallel to that of the ultrasonic waves required. The procedure for bonding the transducer to the sample was to ensure first that the faces of the transducer and sample were free from grease and dust by cleaning with acetone. A small amount of the bonding medium was placed on to the sample face. As the resin used has a high viscosity at room temperature, it was warmed using a hair-dryer to approximately 40° C; then the transducer was placed onto the resin and by gently rotating the transducer (use of a Q tip was efficacious) a thin film (2 to 3 µm) bond was produced. After the bond had cooled, any excess bonding material which had been extruded from the bond was removed. At the end of the experimental run, the transducers were easily removed by warming the sample and gently sliding off the transducer from the sample face.

3.5 Pulse echo overlap system

A pulse echo overlap system was used to measure the wave transit times and their temperature and pressure derivatives of TGS. This equipment is based on the development of a system first proposed by May (1958) and Papadakis (1964, 1966, 1967) and was constructed using commercially obtainable equipment from the Matec Corporation of America. A schematic diagram of the pulse
echo overlap system is shown in Fig 3.3. An accuracy of better than 1 part in $10^4$ can be obtained using this equipment.

In the pulse echo overlap system used the pulse modulator and receiver (Matec model 6600) generate a tone burst containing 10 MHz cycles, which are at the resonant frequency of the transducer. The tone burst is generated at a rate derived from the high resolution frequency source (0.5Hz to 50 Mhz, Matec model 110) which has been divided by a factor of 100 or 1000 by the frequency divider, (Matec Model 122B and referred to as the divided sync line). The division ratio is chosen such that the repetition rate does not exceed 1000 Hz. If the x axis of the oscilloscope is triggered from the divided sync line, and the output from the transducer (after amplification) is connected to the Y input of the oscilloscope, the whole echo train can be displayed on the oscilloscope screen (see fig 3.4). The repetition rate of the r.f pulse generator is low enough to ensure that all echoes have decayed before the next tone burst is applied. By using the video output from the Matec pulse modulator and receiver, the rectified echoes can be coupled via an exponential generator (Matec model 1204B) to the oscilloscope so that attenuation can be measured manually.

By using the dual delay strobe generator (Matec model 122B), which produces two time variable square wave pulses, delayed from the divided sync pulse, which when linked to the Z modulation of the oscilloscope enable
Fig 3.3 Schematic Diagram of the Pulse Echo Overlap Apparatus.
Fig 3.4 Schematic diagram of the echo train as viewed on an oscilloscope.

Fig 3.5 Schematic representation of two successive overlapped echoes as seen on an oscilloscope.
intensification of any two chosen sections of the echo train. By decreasing the oscilloscope brightness, it is then possible to eliminate all echoes but the two intensified ones. If the oscilloscope is now triggered from the master sync line, and the time between each sync pulse corresponds to the transit time, then the result is an illusion of the two intensified echoes superimposed on the display (see Fig 3.5), provided that the time base sweep of the oscilloscope is set to roughly the echo width. By careful adjustment of the high resolution frequency source, cycle-to-cycle matching can be obtained. The echo transit time is then given by the reciprocal of the oscillator frequency. The frequency is measured on a racal 9913 frequency counter. The typical repetition frequency is of the order 80 to 300Khz.

3.6 Hydrostatic pressure system

The pressure system used in this work is of the simple piston and cylinder type, using castor oil (for low pressure) as the pressure transmitting fluid.

A schematic diagram of this pressure system is shown in Fig 3.6. It consists of a cylinder and two pistons made from EN26 nickel alloy carbon steel. The dimensions of the cylinder are, diameter 127 mm, height 115 mm with a 25.4 mm bore. There are two pistons; the lower piston rests on the base of the pressure rig with the sample holder and the manganin coil gauge mounted on it. Electrical connections to the transducer, manganin coil and the thermocouple are made into the pressure bomb.
Fig 3.6 Schematic diagram of the hydrostatic pressure cell.
through beryllium - copper (2.0 to 2.5% Be, 0.3%Co, remainder Cu) plugs in ceramic insulators lapped into conical holes at the top of the lower piston. The top of the press drives down onto the top piston. Sealing between the pistons and the internal cylinder walls is achieved by using nylon delta rings and nylon O-rings on each piston. These seals were found to be satisfactory for pressures up to 2 Kbar and temperatures in the range 10°C to 70°C. The hydraulic press employed was built by Bishop Lifting Services (Bristol, England) and is capable of supplying 50 tons. To satisfy safety requirements, the press and the pressure cell are contained within a 7mm thick steel cabinet.

The normal operational procedure was to seal the bomb and lightly pressurize the system (to about 0.2 Kbar) to test for leaks and to set the bond on the transducer. The system was then left to regain thermal equilibrium. This point was found to be particularly important when temperature runs were commenced because when the press made contact with the upper piston the heat loss mechanism altered (the mass of the press was then in thermal contact and acted as an extra heat sink) and resulted in a change of bomb temperature. After the system had regained thermal equilibrium, data acquisition commenced by pressurizing the system in steps of 0.2 Kbar. Changes in pressure caused the temperature in the pressure cell to alter. On average it took fifteen minutes for the system to return to its equilibrium temperature, at which time measurements of the pressure
and echo transit time were taken.

An important point to realize is that in some cases the change of the ultrasonic wave transit time due to a pressure increase of 0.2 Kbar is comparable to that obtained if the sample temperature changes by a few tenths of a degree C; therefore for most modes it was necessary to keep the sample temperature stable during the course of the experiment.

During the course of the experiment, the data obtained was entered into a CBM 30XX series microcomputer (PET), running a programme hydroplot. This programme allowed, amongst other features the conversion of the resistance of the manganin coil to a pressure reading and permitted a low resolution plot of the data on the microcomputer's VDU. The data obtained could be saved on tape and transferred to another microcomputer, which was connected to a Philip's intelligent plotter, printer and disk drives. By using a programme HP ADV a plot and hardcopy of the data could be obtained. The data could be stored on floppy disc for further analysis.

3.7 Measurement of hydrostatic pressure

The measurement of the hydrostatic pressure within the pressure cell can be obtained by two methods. The first method which can be used provides an immediate but an approximately measurement of pressure. This is achieved by using the hydraulic pressure gauge situated on the pressure line between the pump and the press intensifier. When the reading of this gauge is multiplied by the
intensification factor of the intensifier and divided by the area of the piston, the result being the pressure inside the pressure cell.

The second method of pressure measurement used is based on the change of electrical resistance of a manganin wire with applied hydrostatic pressure. Manganin is an alloy, consisting of a face centred cubic solution of manganese in copper with an addition of nickel. The pressure properties of manganin were first reported by Lisell (1903), and the alloy was first used as a pressure gauge by Bridgman (1911) and its use has become widespread since.

Manganin has several advantages for use as a pressure gauge, the principle advantages being (i) high sensitivity of resistance with pressure, (ii) low drift of the wire resistance with time or past history (Boren et al 1965) and a low hysteresis, (iii) a high degree of uniformity between coils prepared from the same batch of wire (providing they have undergone the Bridgman (1940) cycle), and (iv) a linear response with pressure.

It has been shown from static measurements that the change in manganin resistance with pressure is not far from linear up to approximately 150 Kbar (Montgomery (1963)); shock wave techniques have indicated that this behaviour extends up to 300 Kbar (Fuller (1962)). However manganin is known to be very sensitive to shear stress, and even in hydrostatic usage, the slightest strains can change its pressure coefficient by several percent.
Various values for the pressure coefficient for manganin wire have been quoted in the literature ranging from $2.1 \times 10^{-3}$ to $2.5 \times 10^{-3}$ Kbar$^{-1}$. Most of the recent work (Samara and Giardini (1964), S. Kume et al (1980), Wang (1967) indicates a value near $2.4 \times 10^{-3}$ Kbar (to 2 significant figures) which is used in this work.

The pressure $P$ within the pressure cell is given by

$$P = \frac{\Delta R}{R_{\text{atm}}} \times \frac{2.4 \times 10^{-3}}{\text{Kbar}}$$

where $R(p)$ is the coil resistance at a pressure $P$, and

$$\frac{\Delta R}{R_{\text{atm}}} = \frac{R(p) - R_{\text{atm}}}{R_{\text{atm}}}$$

Basically the pressure sensor used in this work consisted of a length of insulated manganin wire wound non-inductively onto a PTFE core. The coil was then subjected to the Bridgman (1940) cycle of seasoning, which involved heating the coil to 140 °C for 8 hours and then quenching in liquid nitrogen (-196 °C) for two hours. The Bridgman cycle was repeated several times. The final stage of the seasoning of the coil was to pressurize the gauge to the maximum operating pressure obtainable by the equipment (8.5 Kbar) for several hours. This had the effect of establishing the pressure coefficient of resistance (Bridgman 1911).

The gauge used in this work had a resistance of approximately 50 ohms at atmospheric pressure, the resistance being measured by a digital multimeter with a sensitivites of $10^{-3}$ ohm in 100 ohms. A pressure change of 0.2 Kbar corresponded to a change in coil resistance of $0.024 \omega$, which permitted the pressure to be measured to an accuracy of 0.01 Kbar. Manganin does not have
a zero temperature coefficient of resistance (Decker et al. 1972). This means that all readings of pressure must be taken at the same temperature so that resistance changes due to the applied pressure are not significantly offset by variations in the coil temperature. Although the value of the temperature coefficient is dependent on temperature, it has been shown to increase with temperature. At the maximum temperature used of 65 °C a change of 1 °C causes a temperature induced change in resistance of 0.0017 A; this would correspond to a pressure change of 0.014 Kbar, which corresponds to the limit of resolution of the multimeter. In practice using a temperature controller stability can be obtained of 0.1 °C, so the errors due to temperature fluctuation are negligible.

It has been shown by Wang (1967), Adams, Goranson and Gibson (1937), Michels and Lenssen (1934) and Bridgman (1940a,b) that the pressure coefficient of manganin is independent of temperature at pressures below 10 Kbar up to about 120 °C, whereupon the pressure coefficient starts to increase with temperature. So if the gauge is operated at the same temperature, and \( R_{\text{atm}} \) has been measured at the operational temperature, the pressure in the chamber can be measured accurately at elevated temperatures.
3.8 Temperature controller

In this work ultrasonic measurements were made in the temperature range from room temperature to 65 °C. The temperature of the pressure cell was increased by passing an electric current through a cylindrical heating element clamped onto the external walls of the pressure cylinder. Initially the temperature was controlled using a Eurotherm Ether mini 17-90B relay controller. The sensing element for the controller was a NiCr/NiAl thermocouple sandwiched between the heater element and the external walls of the pressure cylinder. The power supplied to the heater was controlled by a simple on-off operation of the relay (the power to the heater element being supplied via a variac). It was found that although the temperature at the external cylinder wall was held constant to a few degrees C, damping by the thermal mass of the system resulted in the sample temperature at the centre of the cylinder remaining constant to within 1 °C. As the temperature induced change of the ultrasonic wave velocity was greater than the contribution from the induced pressure change, this gave unsatisfactory experimental results: a different approach was required.

An alternative controller (see fig 3.7) was constructed based on the three term controller principle. The heart of this temperature controlling system was an Oxford Instrument three term controller EA 2349. This was originally designed to use a carbon film resistance thermometer as its temperature sensing element, but was modified to accept the 1 mV per deg °C output from a
Fig 3.7 Schematic diagram of the pressure system temperature control.
digitron digital thermometer as its temperature sensing input (a NiCr/NiAl thermocouple connected to the digitron acted as the temperature sensing element). The advantage of using the output from the digitron was two fold: (i) the temperature compensating network inherent in the instrument could be utilized, (ii) the low noise amplifiers of the digitron could be used to amplify the small thermocouple voltage to a usable level. The Oxford controller was unable to supply enough power to drive the heating element directly so an interface unit was constructed to enable the controller heater output to control a 0 to 90 Volt DC power supply which was connected to the heater element. The use of the three term controller system permitted the pressure cell temperature to be held stable to within 0.1 °C.

When pressure runs were carried out at elevated temperatures, it generally took 3 to 4 hours for the pressure cell to reach and stabilize at the selected temperature starting from room temperature. It was usual practice to connect the whole controller system to a timer so that it switched on five hours before the experiment was due to begin. The hydrostatic experiment itself was performed in the usual way; after increasing the pressure the temperature was left to return to its equilibrium value before an echo transit time measurement was made. It was observed that during a pressure run the temperature of the pressure cell would gently drift downwards when pressure increased and upwards when pressure was decreased. This effect could be negated by
increasing or decreasing the controller set temperature as appropriate. It is probably due to the piston being pushed further into the pressure cylinder and increasing the heat loss path to the press, but as the controller's thermocouple is situated on the outside of the pressure cylinder walls, the controller is unable to compensate for this.

3.9 Experimental errors and their correction

There are several sources of experimental error which can affect the overall accuracy of an elastic constant measurement. These are discussed below; the principle source of error is due to the accuracy with which the ultrasonic transit time and the relative changes in velocities can be measured.

(i) Measurement of sample dimensions

In all cases the sample dimensions were measured using a micro 2000 micrometer which has an accuracy of 0.002 mm. Several measurements were made at different points on the samples faces and the mean of these measurements was taken as the sample length. It can be shown that the error in velocity measurement \( \delta V \) due to an error in measurement of sample length \( \delta l \) is given by \( \delta V = \frac{\delta l}{t} \) where \( \delta l \) is the error in measurement of the sample length and \( t \) is the measured transit time. Substituting typical numbers shows that this can give an error in velocity of approximately 0.5 ms\(^{-1}\) which corresponds to a percentage error of about 0.02%.

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(ii) Transit time errors

The largest source of error in the determination of the SOEC arises from the measurement of the ultrasonic wave transit time. The largest component of this error being due to the delay in transit time caused by multiple internal reflections within the quartz transducer. Altman and Beyer (1976) considered a typical pulse incident on the transducer/sample boundary, which would be partially transmitted into the transducer and reflected back into the sample. The portion transmitted into the transducer will undergo multiple reflections inside the transducer; each time the waves hits the sample/transducer interface a wave will be transmitted into the sample, which is an image of the incident pulse (reduced in amplitude due to the reflections) and delayed by a time $1/\omega_0$ for each reflection it has undergone in the transducer. Therefore the resulting pulse consists of a superposition of pulses of ever-diminishing amplitude whose "peak" is shifted by a time of $1/\omega_0$ for each reflection in the transducer. The resulting reflected pulse is both lengthened and delayed with respect to a pulse which is totally reflected from the front surface in the absence of a transducer.

The delay due to this effect can be estimated by reference to calculations made by Kittinger (1977) which relate the estimated echo delay $t$ (in units of the reciprocal fundamental transducer frequency) to the acoustic reflection coefficient $r$ at the sample-transducer boundary. This reflection coefficient
is defined as

\[ \gamma = \frac{\rho_2 c_2 - \rho_1 c_1}{\rho_2 c_2 + \rho_1 c_1} \]

where \( \rho_1 \) is the density and \( c \) is the velocity of sound; the subscripts 1 denotes the sample, and 2 denotes the transducer medium. The quantity \( \rho c \) is the acoustic impedance. The corresponding echo delay time \( \delta t \) can be found from Kittinger's experimental curve; the corrected ultrasonic wave transit time \( t_r \) is given by \( t_r = t_m - \delta t \), where \( t_m \) is the measured transit time. This correction was of the order of a few percent, a programme "TRANS-CORR" (Brassington 1982) being used to make it.

These corrections do not take into account the effect of the gold plated electrodes on the transducer or the resin bond between the transducer and sample. Kittinger (1977) considers their contribution to the echo delay time to be small.

(iii) Diffraction and non-parallelism

The transducer can be regarded as a piston source producing plane ultrasonic waves. However some radiated energy may still be lost from the sides of the cylindrical region of acoustic flux because the transducer is finite in extent and has a diffraction field. Errors in transit time measurement can occur from these diffraction effects especially at low frequencies when small transducers are used. This effect has been investigated by Truell et al (1959) at various
frequencies. They came to the conclusion that when the ultrasonic wave is propagated along directions which have 2 or 4-fold symmetry, the transit time error due to diffraction is of the order 0.01%, providing the crystal orientation is accurate to within 0.5° and the area of the transducer is smaller than the sample.

A related source of error in the transit time is due to non-parallelism of the sample faces, which results in the transducer receiving different phases of the wave across its surface. This effect has been investigated by Truell (1954). It can be reduced to negligible proportions by ensuring the faces of each sample are parallel to 10⁻³ radians.

(iv) Errors due to temperature fluctuations

In most materials the velocity of sound and hence the SOEC are temperature dependent; therefore when measuring relative velocity changes due to applied hydrostatic pressure, the temperature must be maintained at a constant value. For the case of TGS, whose pressure coefficients are small, a change of 0.4°C corresponds to a pressure induced change of 0.2 Kbars. During the course of the experiment the temperature of the sample in the hydrostatic pressure cell was monitored by a thermocouple mounted in close proximity to it. Temperature control was stable to be within 0.1 °C.
CHAPTER 4
EVALUATION OF ELASTIC CONSTANTS

4.1 Introduction

The determination of the elastic properties of an anisotropic medium by a dynamic method requires the measurement of the velocities of elastic waves in several non-equivalent directions in the medium. From the measured values of the elastic wave velocities certain combinations of the elastic constants can be obtained with the aid of the Christoffel determinant. Aleksandrov (1958) showed that for a monoclinic crystal measurements of the ultrasonic wave velocities in six directions, namely [001], [010], [100], [101], [110] and [011] referenced to the orthogonal axis frame, sufficient experimental data can be obtained to enable the thirteen elastic constants to be determined. Only for certain directions are the velocities related to the elastic constants of the crystal by simple relationships.

This chapter describes in detail the evaluation procedure used (taking as an example the experimental data obtained in this work for TGS at 20°C) to obtain the elastic constants and their associated pressure derivatives.
4.2 Determination of the elastic constants

The propagation of an ultrasonic wave through an anisotropic medium is described by the Christoffel equation:

\[ [\mathbf{r}_{ij} - \rho v^2 \delta_{ij}] [u_j] = 0 \]  

where \( \rho \) is the density of the medium, \( v \) is the ultrasonic wave velocity, \( u_j \) is the particle displacement vector and \( \delta_{ij} \) is the Kronecker delta. The elements of the Christoffel matrix \( \mathbf{r}_{ij} \) are

\[
\begin{align*}
\mathbf{r}_{11} &= c_{11}l_n^2 + c_{66}l_y^2 + c_{33}l_z^2 + 2c_{13}l_zl_n \\
\mathbf{r}_{12} &= (c_{46} + c_{25})l_yl_z + (c_{12} + c_{66})l_nl_z \\
\mathbf{r}_{13} &= c_{13}l_n^2 + c_{46}l_y^2 + c_{33}l_z^2 + (c_{13} + c_{66})l_zl_n \\
\mathbf{r}_{22} &= c_{66}l_n^2 + c_{22}l_y^2 + c_{44}l_z^2 + 2c_{46}l_zl_n \\
\mathbf{r}_{23} &= (c_{44} + c_{23})l_yl_z + (c_{26} + c_{46})l_nl_z \\
\mathbf{r}_{33} &= c_{33}l_n^2 + c_{44}l_y^2 + c_{33}l_z^2 + 2c_{33}l_zl_n
\end{align*}
\]

where \( l_n, l_y, l_z \) are components of a unit vector in the direction of wave propagation. The condition for a non-zero solution of the Christoffel equation is given by:

\[ \det[\mathbf{r}_{ij} - \rho v^2 \delta_{ij}] = 0 \]

For each propagation direction three solutions are obtained to the Christoffel equation corresponding to a longitudinal mode and two transverse modes. Each solution of 4.2 yields the phase velocity of the ultrasonic wave expressed in terms of the medium’s elastic constants and density but contains no information on the type of vibrational mode it belongs to. To identify which vibrational mode the solution refers to, it is necessary to substitute the solution into 4.1 and by examination of
the expressions for the particle displacement vectors, the mode of vibration can be identified.

The appropriate solutions to the Christoffel equation have been given by many workers (Luspin and Hauret 1977, Kameyama et al. 1973); those for the [001], [010], [100], and [101] directions and are reproduced in table 4.1. No solutions for the [110] and [011] directions have been reported in the literature. The solutions for these directions require the extraction of roots from a complex third order algebraic equation; the resultant expression for each root would be rather lengthy. On the evaluation of 4.2 for the four directions [001], [010], [100] and [101], one root can easily be identified. The remaining two roots are obtained by the solution of a quadratic equation. In a procedure to obtain the elastic constants it is more useful to use relationships between roots and coefficients of the remaining quadratic equation than to solve uniquely for each root. These relationships are given below:

for the [100] direction

\[ \rho V_2^2 = c_{11} \]  
\[ \rho V_1^2 + \rho V_3^2 = c_{11} + c_{66} \]  
\[ \rho V_1^2 \rho V_3^2 = c_{11} c_{66} - c_{16}^2 \]

for the [010] direction

\[ \rho V_3^2 = c_{22} \]  
\[ \rho V_2^2 + \rho V_6^2 = c_{44} + c_{66} \]  
\[ \rho V_2^2 \rho V_6^2 = c_{66} c_{44} - c_{46}^2 \]
Table 4.1 Ultrasonic wave velocity and elastic stiffness constant relationships for a monoclinic crystal.

<table>
<thead>
<tr>
<th>Mode symbol</th>
<th>Direction of wave propagation</th>
<th>Polarisation vector</th>
<th>Relationship between elastic constant and wave velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁</td>
<td>[100]</td>
<td>[100]</td>
<td>( \rho v₁^2 = [C_{11} + C_{55} + \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2}] / 2 )</td>
</tr>
<tr>
<td>v₂</td>
<td>[100]</td>
<td>[010]</td>
<td>( \rho v₂^2 = C_{66} )</td>
</tr>
<tr>
<td>v₃</td>
<td>[100]</td>
<td>[001]</td>
<td>( \rho v₃^2 = [C_{11} + C_{55} - \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2}] / 2 )</td>
</tr>
<tr>
<td>v₄</td>
<td>[010]</td>
<td>[100]</td>
<td>( \rho v₄^2 = [C_{44} + C_{66} + \sqrt{(C_{44} - C_{66})^2 + 4C_{46}^2}] / 2 )</td>
</tr>
<tr>
<td>v₅</td>
<td>[010]</td>
<td>[010]</td>
<td>( \rho v₅^2 = C_{22} )</td>
</tr>
<tr>
<td>v₆</td>
<td>[010]</td>
<td>[001]</td>
<td>( \rho v₆^2 = [C_{44} + C_{66} - \sqrt{(C_{44} - C_{66})^2 + 4C_{46}^2}] / 2 )</td>
</tr>
<tr>
<td>v₇</td>
<td>[001]</td>
<td>[100]</td>
<td>( \rho v₇^2 = [C_{33} + C_{55} + \sqrt{(C_{33} - C_{55})^2 + 4C_{35}^2}] / 2 )</td>
</tr>
<tr>
<td>v₈</td>
<td>[001]</td>
<td>[010]</td>
<td>( \rho v₈^2 = C_{44} )</td>
</tr>
<tr>
<td>v₉</td>
<td>[001]</td>
<td>[001]</td>
<td>( \rho v₉^2 = [C_{33} + C_{55} - \sqrt{(C_{33} - C_{55})^2 + 4C_{35}^2}] / 2 )</td>
</tr>
<tr>
<td>v₁₀</td>
<td>[101]</td>
<td>[101]</td>
<td>( \rho v₁₀^2 = [(C_{11} + C_{33})^3 + 2(C_{15} + C_{35} + C_{55})]^2 / 4 )</td>
</tr>
<tr>
<td>v₁₁</td>
<td>[101]</td>
<td>[010]</td>
<td>( \rho v₁₁^2 = [C_{66} + C_{44} + C_{46}] )</td>
</tr>
<tr>
<td>v₁₂</td>
<td>[101]</td>
<td>[101]</td>
<td>( \rho v₁₂^2 = [(C_{11} + C_{33})^3 + 2(C_{15} + C_{35} + C_{55})] + \sqrt{4(C_{11} + C_{33} + C_{55} + C_{35} + C_{33} + C_{55})^2} / 4 )</td>
</tr>
<tr>
<td>v₁₃</td>
<td>[110]</td>
<td>[110]</td>
<td>( v₁₃ ) to ( v₁₈ ) obtained as a root of third order algebraic equations including known stiffness constants. The resulting equations are extensive.</td>
</tr>
<tr>
<td>v₁₄</td>
<td>[110]</td>
<td>[001]</td>
<td></td>
</tr>
<tr>
<td>v₁₅</td>
<td>[110]</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>v₁₆</td>
<td>[011]</td>
<td>[011]</td>
<td></td>
</tr>
<tr>
<td>v₁₇</td>
<td>[011]</td>
<td>[011]</td>
<td></td>
</tr>
<tr>
<td>v₁₈</td>
<td>[011]</td>
<td>[100]</td>
<td></td>
</tr>
</tbody>
</table>
for the [001] direction

\[ \rho V_{0}^2 = c_{44} \] 4.9
\[ \rho V_{7}^2 + \rho V_{9}^2 = c_{33} + c_{33} \] 4.10
\[ \rho V_{7}^2 \rho V_{9}^2 = c_{33} c_{33} - c_{33}^2 \] 4.11

and for the [101] direction

\[ \rho V_{11}^2 = (c_{44} + c_{66} + 2c_{46})/2 \] 4.12
\[ \rho V_{10}^2 + \rho V_{12}^2 = (c_{11} + c_{33} + 2(c_{13} + c_{33} + c_{66})) / 2 \] 4.13
\[ \rho V_{10}^2 \rho V_{12}^2 = ((c_{11} + c_{33} + 2c_{13})(c_{66} + c_{33} + c_{66})) - (c_{13} + c_{33} + c_{13} + c_{66})^2 \] 4.14

An additional relationship (equation 4.15) was obtained by substituting equations 4.4 and 4.10 into equation 4.13. This substitution has the effect of replacing three elastic constants \( c_{11}, c_{33} \) and \( c_{66} \) in terms of experimental measured velocities:

\[ c_{11} + c_{33} = \rho (\sqrt{\nu_{10}^2 - (\nu_{11}^2 + \nu_{13}^2 + \nu_{13}^2 + \nu_{13}^2)}/2) \] 4.15

The procedure used to determine the elastic constants will now be described. The density of TGS was taken to be 1680 Kg/m³ (Konstantinova et al. 1960) and all measured ultrasonic wave velocities have been corrected for transducer delay (see section 3.9).

The first velocity measurements were made on a single parallelepiped sample with polished faces perpendicular to the [001], [010] and [100] directions in the reference orthogonal frame. From the nine velocity measurements made on this cube the magnitude and sign of three elastic constants \( c_{44}, c_{66} \) and \( c_{22} \) can be obtained, along with the magnitude of \( c_{44} \). The next sample to be prepared had a pair of faces polished perpendicular to the [101] direction. Then measurement of the velocity of
the [010] polarized shear mode permitted the sign and magnitude of $c_{46}$ to be determined. After measurement of the velocities of the other two modes in the [101] direction there was sufficient velocity data, combined with elastic constants previously determined to enable a further six elastic constants $c_{11}$, $c_{33}$, $c_{66}$, $c_{13}$, $c_{36}$ and $c_{13}$ to be obtained.

Evaluation of the elastic constants from the velocity data began with the determination of $c_{22}$, $c_{44}$ and $c_{66}$. These elastic constants were obtained directly from the measured velocities $v_9$, $v_8$ and $v_2$ respectively (equations 4.6, 4.9 and 4.3). Once $c_{44}$ and $c_{66}$ had been obtained, $c_{46}$ was the next elastic constant to be determined. This could be obtained in two ways:

(i) using the equations for $v_4$ or $v_6$ from table 4.1 gave the magnitude of $c_{46}$;

(ii) using the equation for $v_{11}$ from table 4.1 (or equation 4.12) gave the magnitude and sign of $c_{46}$.

The next set of elastic constants to be obtained was $c_{11}$, $c_{66}$, $c_{33}$, $c_{36}$ and $c_{13}$. These elastic constants were obtained from the solution of five equations (4.4, 4.5, 4.10, 4.11 and 4.15). The first step taken to solve these equations was to manipulate them in such a way that an expression containing $c_{66}$ in terms of measured velocities was obtained. This was done in the following way:

(i) Substitution of 4.4 into 4.5 to eliminate $c_{11}$

$$c_{66}(\rho v_1^2 + \rho v_3^2 - c_{66}) - c_{11}^2 = \rho v_1^2 v_3^2 \quad 4.16$$

(ii) Substitution of 4.10 into 4.11 to eliminate $c_{33}$

$$c_{66}(\rho v_7^2 + \rho v_9^2 - c_{66}) - c_{33}^2 = \rho v_7^2 v_9^2 \quad 4.17$$
Equations 4.16 and 4.17 can be manipulated so that \( c_{1B} \) and \( c_{3B} \) can be expressed in terms of measured velocities and an elastic constant \( c_{oo} \):

\[
c_{1B} = \pm \left( c_{oo} \left( \rho v_1^2 + \rho v_3^2 - c_{oo} \right) - \rho v_1^2 v_3^2 \right)^{1/2} \tag{4.18}
\]

\[
c_{3B} = \pm \left( c_{oo} \left( \rho v_7^2 + \rho v_9^2 - c_{oo} \right) - \rho v_7^2 v_9^2 \right)^{1/2} \tag{4.19}
\]

It should be noted that if the equations for \( c_{1B} \) and \( c_{3B} \) are substituted into 4.15 there would be an expression containing measured velocities and an unknown elastic constant \( c_{oo} \), but four different combinations of \( c_{1B} \) and \( c_{3B} \) would have to be considered which would lead to four values being obtained for \( c_{oo} \). If equation 4.15 is squared on both sides (4.20), it is shown below that only two different combinations of \( c_{1B} \) and \( c_{3B} \) need to be considered giving two possible values for \( c_{oo} \). This is best illustrated by the following example:

\[
(t c_{1B} + t c_{3B})^2 = \left( \rho (v_1^2 + v_{12}^2 - (v_1^2 + v_9^2 + v_9^2)/2) \right)^2 \tag{4.20}
\]

The four different permutations on the left hand side are:

(i) \(-c_{1B}, -c_{3B}(c_{1B} - c_{3B})^2 = c_{1B}^2 + 2c_{1B}c_{3B} + c_{3B}^2 \tag{4.21}
\]

(ii) \(c_{1B}, c_{3B}(c_{1B} + c_{3B})^2 = c_{1B}^2 + 2c_{1B}c_{3B} + c_{3B}^2 \tag{4.22}
\]

(iii) \(-c_{1B}, c_{3B}(c_{1B} - c_{3B})^2 = c_{1B}^2 - 2c_{1B}c_{3B} + c_{3B}^2 \tag{4.23}
\]

(iv) \(c_{3B}, -c_{1B}(c_{3B} - c_{1B})^2 = c_{3B}^2 - 2c_{1B}c_{3B} + c_{1B}^2 \tag{4.24}
\]

It can be seen that 4.21 and 4.22 are equivalent; 4.23 and 4.24 are also equivalent identities. Therefore we only need to consider the grouping of \((c_{1B} + c_{3B})\) or \((c_{1B} - c_{3B})\) in the solution of equation 4.20. Substituting \( c_{1B} \) and \( c_{3B} \) into equation 4.20 the following expression containing \( c_{oo} \) in terms of measured velocities...
was obtained:

\[
\left( c_{bb} \rho v_1^2 + \rho v_3^2 - c_{bb} \right) - \rho v_1^2 \rho v_2^2 \right)^{1/2}
\]

\[
= \left( \text{case 1} \left( c_{bb} \rho v_1^2 + \rho v_3^2 - c_{bb} \right) - \rho v_1^2 \rho v_2^2 \right)^{1/2}
\]

\[
= \left( \rho \left( v_{10}^2 + v_{12}^2 \right) - \left( v_1^2 + v_3^2 + v_2^2 + v_7^2 \right)/2 \right)^2
\]

4.25

The convention set up to analyse 4.25 is as follows, one solution for \( c_{bb} \) was obtained by taking the "top" sign in the and the second solution was obtained by using the "bottom" sign. In future equations of this type will be abbreviated to \( \pm \) (or \( \mp \)) as appropriate. Equation 4.25 was solved numerically using Newton’s method, the solution being given by

\[
(c_{bb})_{n+1} = (c_{bb})_n - \frac{\left( A - \text{case 2} \right) B - c^2}{A}
\]

4.26

where

\[
A = \left( c_{bb} \rho v_1^2 + \rho v_3^2 - c_{bb} \right) - \rho v_1^2 \rho v_2^2 \right)^{1/2}
\]

\[
B = \left( c_{bb} \rho v_1^2 + \rho v_3^2 - c_{bb} \right) - \rho v_1^2 \rho v_2^2 \right)^{1/2}
\]

\[
C = \rho \left( v_{10}^2 + v_{12}^2 \right) - \left( v_1^2 + v_3^2 + v_2^2 + v_7^2 \right)/2
\]

Evaluation of 4.26 revealed one solution for \( c_{bb} \) for each case. By back substitution of \( c_{bb} \) into 5.18 and 5.19 the magnitudes of \( c_{18} \) and \( c_{39} \) were found. The signs of \( c_{18} \) and \( c_{39} \) were obtained with the aid of equation 4.15, the signs being selected such that good agreement is obtained with the value of the velocity sum. \( c_{11} \) and \( c_{33} \) were obtained by back substituting the values obtained of \( c_{18} \), \( c_{39} \) and \( c_{bb} \) into 4.4 and 4.10.
The following results were obtained for the two cases

<table>
<thead>
<tr>
<th>+ case</th>
<th>- ve case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{bb} = 1.08 \times 10^{10}$</td>
<td>$c_{bb} = 1.43 \times 10^{10}$</td>
</tr>
<tr>
<td>$c_{11} = 4.41 \times 10^{10}$</td>
<td>$c_{11} = 4.06 \times 10^{10}$</td>
</tr>
<tr>
<td>$c_{33} = 2.73 \times 10^{10}$</td>
<td>$c_{33} = 2.38 \times 10^{10}$</td>
</tr>
<tr>
<td>$c_{15} + c_{35} = -0.41 \times 10^{10}$</td>
<td>$c_{15} + c_{35} = -0.37 \times 10^{10}$</td>
</tr>
<tr>
<td>$c_{35} = -1.8 \times 10^{7}$</td>
<td>$c_{35} = 7.0 \times 10^{7}$</td>
</tr>
<tr>
<td>$c_{15} = -2.1 \times 10^{7}$</td>
<td>$c_{15} = -1.04 \times 10^{10}$</td>
</tr>
</tbody>
</table>

all units are $\text{Nm}^{-2}$

To eliminate one set of solutions, the physical principles involved in the propagation of ultrasonic waves in the sample need to be considered. Huntington et al (1969) showed that $c_{bb}$ must be smaller than $c_{11}$, if this condition was not met, it would lead to the identification of the $[100]$ propagating $[001]$ polarized shear mode with the $[100]$ propagating pseudo-longitudinal mode. In some cases this condition is enough to eliminate one set of solutions (and was used by Huntington et al (1969) in their work on anthracene), but unfortunately for TGS this did not turn out to be the case. To assist in the selection of a valid solution, the particle displacement vectors for the longitudinal mode in the $xz$ plane were considered (note there will be no $u_z$ component for the particle displacement vector as the $[010]$ polarized shear mode is pure).

For the $[100]$ direction the ratio of the particle displacement vectors is given by

$$\frac{u_3}{u_1} = \frac{-c_{15}(c_{bb} - \rho v^2)}{(c_{bb} - \rho v^2)(c_{bb} - \rho v^2)}$$

4.27
and for the [001] direction

\[
\frac{u_3}{u_1} = \frac{-c_{44} (c_{44} - PV^2)}{(c_{44} - PV^2)(c_{33} - PV^2)}
\]

where \( \nu \) is the velocity of the longitudinal mode.

Substituting values for the elastic constants and longitudinal mode velocities gives for the +ve case

- [100] longitudinal mode, \( u_1 = 0.999, u_3 = 0.014, \nu = 0.8^\circ \)
- [001] longitudinal mode, \( u_1 = -0.141, u_3 = 0.99, \nu = 8.1^\circ \)

and for the -ve case

- [100] longitudinal mode, \( u_1 = 0.999, u_3 = 0.016, \nu = 0.9^\circ \)
- [001] longitudinal mode, \( u_1 = 0.472, u_3 = 0.881, \nu = 28.2^\circ \)

where \( \theta \) is the angle between the propagation direction of the wavefronts and the particle displacement vector.

On inspection of the particle displacement vectors it can be seen that both solutions are plausible. For the [100] direction both solutions give a particle displacement vector which is close to the direction of propagation, but in the [001] direction there is a notable difference. The solution set which gave the least off-axis particle displacement vectors was considered to be the most likely. In this case the positive solution set with \( c_{66} = 1.08 \times 10^{10} \text{Nm} \) was selected. This can be justified on experimental grounds for TGS. If the longitudinal mode was off-axis by approximately \( 28^\circ \) difficulty would be experienced in injecting ultrasonic waves into the sample; however this was found not to be the case.

The next elastic constant to be determined was \( c_{13} \). By rearranging equation 4.14 an expression was obtained
expressing \( c_{13} \) as a function of measured velocities and known elastic constants:

\[
c_{13} = c_{15} + c_{33} + c_{55} + \quad 4.29
\]

\[
\pm \left( (c_{11} + 2c_{55} + 2c_{15})(c_{55} + c_{33} + 2c_{35}) - 4\rho^2 v_{10}v_{12}^2 \right)^{1/2}
\]

Two solutions for \( c_{13} \) were obtained. The selection of the correct solution was made by considering the particle displacement vectors of the longitudinal wave in the [101] direction. The ratio of the particle displacement vectors is given by

\[
\frac{u_3}{u_1} = \frac{(c_{15} + c_{33} + c_{55})(c_{33} + c_{44} + 2c_{45})/2 - \rho v^2)/2}{(c_{55} + c_{33} + 2c_{35})/2 - \rho v^2)} \quad 4.30
\]

It should be noted that as the [010] polarized shear mode is pure there will be no \( u_2 \) component of the particle displacement vector. A condition is imposed on this ratio of the particle displacement vectors \( (u_3/u_1) \) in that it must be positive. If this condition is not met, it results in the identification of a longitudinal mode with a shear mode. The two solutions obtained for \( c_{13} \) were

(i) \( c_{13} = 1.67 \times 10^{10} \text{ Nm}^{-2} \), \( u_3/u_1 = 0.685 \)

(ii) \( c_{13} = -3.05 \times 10^{10} \text{ Nm}^{-2} \), \( u_3/u_1 = -0.686 \)

The second solution was rejected as it is physically impossible.

A computer program was written to assist in the determination of the first ten elastic constants of a monoclinic crystal and is listed in appendix 2.A.

At this point I wish to pass on a warning to fellow workers evaluating elastic constants of a monoclinic crystal. If propagation of ultrasonic waves in the xz plane is considered, the following relationship is
obtained between the quasi-longitudinal and quasi-shear modes:

\[ \rho v_L^2 + \rho v_S^2 = c_{11} l_x^2 + c_{12} (1^2 + l_x^2) + c_{33} l_x^2 + 2c_{15} l_x l_y + 2c_{35} l_x l_y \]

This expression contains 5 unknown elastic constants. At a first glance it suggests that if the velocities of the quasi-shear and quasi-longitudinal mode were to be measured for five directions in the plane, five equations linking the elastic constants would be obtained and that these could be solved to give unique solutions for the elastic constants without having to consider particle displacement vectors. Unfortunately this is not so, evaluation of the determinant of the components reveals it to be zero. This means that the equations are singular and that no unique solution exists. This is not a wild goose worth chasing.

4.3 Determination of the elastic constants \( c_{12}, c_{26} \) and \( c_{23} \)

Determination of the remaining three elastic constants \( c_{12}, c_{26} \) and \( c_{23} \) required the measurement of the quasi-longitudinal and quasi-shear modes for the [011] and [110] directions in the orthogonal reference frame. These measurements were performed on two samples with appropriately cut and polished faces. On the substitution of the relevant terms into the Christoffel determinant (4.2) a rather lengthy cubic equation is produced from which it would be difficult to isolate expressions for each root in terms of elastic constants; even if this
could be achieved it may be of little value. The relationships between the roots and coefficients of the cubic equation are more useful in a procedure to evaluate the elastic constants, these are given below.

for the [110] direction

\[ 4p^2(V_{13}^2 + V_{14}^2 + V_{19}^2 + V_{14}V_{19}) = (c_{66} + c_{22})(c_{66} + c_{44}) + (c_{11} + c_{66})(c_{66} + c_{22} + c_{68} + c_{44}) - (c_{15} + c_{46})^2 - (c_{12} + c_{66})^2 - (c_{28} + c_{44})^2 \]  
\[ \text{equation 4.32} \]

\[ \rho^2V_{13}^2V_{14}V_{19} = 1/8 [(c_{11} + c_{66})(c_{66} + c_{22})(c_{68} + c_{44}) - 2(c_{15} + c_{46})(c_{15} + c_{46}) - (c_{11} + c_{66})(c_{28} + c_{44})\] 
\[ - (c_{68} + c_{44})(c_{12} + c_{66})^2 - (c_{15} + c_{46})^2(c_{66} + c_{22})] \]  
\[ \text{equation 4.33} \]

\[ \rho(V_{13}^2 + V_{14}^2 + V_{19}^2) = c_{66} + (c_{11} + c_{22} + c_{68} + c_{44}) \]  
\[ \text{equation 4.34} \]

and for the [011] direction

\[ 4p^2(V_{16}^2 + V_{16}^2 + V_{17}^2 + V_{17}^2) = (c_{22} + c_{44})(c_{44} + c_{33}) + (c_{22} + 2c_{44} + c_{33})(c_{66} + c_{68}) - (c_{46} + c_{33})^2 - (c_{46} + c_{28})^2 - (c_{44} + c_{23})^2 \]  
\[ \text{equation 4.35} \]

\[ \rho^2V_{16}^2V_{17}V_{18} = 1/8 [(c_{66} + c_{68})(c_{22} + c_{44})(c_{44} + c_{33}) - 2(c_{46} + c_{33})(c_{46} + c_{23})(c_{66} + c_{68}) - (c_{46} + c_{33})(c_{44} + c_{23})^2 \] 
\[ - (c_{46} + c_{28})^2(c_{44} + c_{33} - (c_{22} + c_{44})(c_{66} + c_{33})^2) \]  
\[ \text{equation 4.36} \]

\[ \rho(V_{16}^2 + V_{17}^2 + V_{18}^2) = c_{44} + (c_{66} + c_{68} + c_{22} + c_{33})/2 \]  
\[ \text{equation 4.37} \]

On examination of equations 4.32 to 4.37 it can be seen that \( c_{28} \) is common to the [011] and [110] directions. The evaluation procedure adopted to obtain the values of the elastic constants \( c_{12}, c_{28}, c_{23} \) was to manipulate the equations for the [110] direction (equations 4.32 to
4.34) to obtain an expression for $c_{26}$ in terms of known elastic constants and experimentally measured velocities. Once $c_{26}$ was obtained, values for $c_{23}$ and $c_{12}$ could be obtained by back substituting and further manipulation of the relevant equations. Rearranging equation 4.32

$$RT = X^2 + Y^2$$  \hspace{1cm} 4.38

where $RT = (c_{66} + c_{22})(c_{66} + c_{44}) + (c_{11} + c_{66})(c_{66} + c_{22} + c_{66} + c_{44}) - (c_{16} + c_{46})^2 - 4p^2(v_{13}^2v_{14} + v_{13}^2v_{18} + v_{14}v_{18})$

$$Y = (c_{12} + c_{66}) \quad X = (c_{26} + c_{46})$$

Rearranging equation 4.33

$$GA*X*Y - LM*X^2 - SD*Y^2 = RE$$  \hspace{1cm} 4.39

where $RE = 8p^2v_{13}^2v_{14}v_{18} - (c_{16} + c_{46})^2(c_{66} + c_{22}) - (c_{11} + c_{66})(c_{66} + c_{22})(c_{66} + c_{44})$

$$GA = 2(c_{16} + c_{46}) \quad LM = c_{11} + c_{66} \quad SD = c_{66} + c_{44}$$

Rearranging 4.38

$$Y = \pm (RT - X^2)^{1/2}$$  \hspace{1cm} 4.40

and substituting into 4.39, an expression containing $c_{26}$ in terms of known elastic constants and measured velocities was obtained.

$$GA*X*\pm(RT - X^2)^{1/2} - LM*X^2 - SD*(RT - X^2) = RE$$  \hspace{1cm} 4.41

Equation 4.41 was evaluated numerically for the two solution cases $-(RT - X^2)$ and $(RT - X^2)$ using Newton's method to obtain a value for $X$, from which $c_{26}$ can be extracted. The necessary formula is
\[ X_{n+1} = X_n - \frac{f(X_n)}{f'(X_n)} \quad 4.42 \]

where \( X_n = (c_{33} + c_{44}) \)

\[
f(X_n) = GA*X* \pm (RT - X^2) \frac{1}{1/2} - LM*X^2 - SD*(RT - X^2) - RE
\]

\[
f'(X_n) = GA* \pm (RT - X^2) \frac{1}{1/2} - GA*X^2 \pm (RT - X^2)^{-1/2} - 2*LM*X + 2*SD*X
\]

It was found on evaluation of 4.42 that no real solution could be obtained for \( c_{33} \) in either case. Finding real solutions to equations involving the last three elastic constants is a difficulty cited by numerous workers on monoclinic crystals. To find a solution for \( c_{33} \), the procedure suggested by Krupnyi et al (1973) was followed. This involved finding the value of \( X \) such that \( df/dx = 0 \) (ie a minimum point) and adopting this value as the solution. This minimum point was found numerically using Newton's method. Where a solution of \( X^n \) corresponds to the condition \( f' = 0 \)

\[ X_{n+1} = X_n - \frac{f'(X_n)}{f''(X_n)} \quad 4.43 \]

where

\[
f''(X_n) = -GA*X* \pm (RT - X^2)^{-1/2} - X^3 \pm (RT - X^2)^{-3/2}*GA
\]

\[
- GA*2*X* \pm (RT - X^2)^{-1/2} - 2*LM + 2*SD
\]

\[
f'(X_n) = GA* \pm (RT - X^2)^{1/2} - GA*X^2* \pm (RT - X^2)^{-1/2} - 2*LM*X + 2*SD*X
\]

The values of \( X \) obtained from 4.43 were confirmed to be minima by using \( f'' \) (the second derivative). Evaluation of 4.43 produced two solutions for \( c_{33} \). Values for the elastic constant \( c_{12} \) were obtained by substituting the value obtained for \( c_{33} \) into 4.44 (rewritten 4.38):
\[ c_{12} + c_{46} = \pm (RT - (c_{20} + c_{44})^2)^{1/2} \] 4.44

It is obvious that each value of \( c_{20} \) substituted into equation 4.44 will result in two values being generated for \( c_{12} \). The last remaining constant \( c_{23} \) is obtained by rewriting 4.35:

\[ c_{23} + c_{23} = \pm (RX - (c_{46} + c_{23})^2)^{1/2} \] 4.45

where \( RX = (c_{22} + 2c_{44} + c_{33})(c_{66} + c_{88} - (c_{46} + c_{33})^2 + (c_{22} + c_{44})(c_{44} + c_{33}) - 4P^2(\nu_{14}\nu_{17}^2 + \nu_{17}\nu_{18}^2 + \nu_{18}\nu_{19}^2) \)

For each value of \( c_{23} \) substituted into 4.45 two values for \( c_{23} \) will be generated.

At the present stage in the evaluation procedure two values for \( c_{23} \) and four values each for \( c_{23} \) and \( c_{12} \) have been obtained. The selection of the correct values for the elastic constants was made by using information obtained on the particle displacement vectors to eliminate physically impossible solutions. It can be shown that the following relationships exist between the ratios of the particle displacement vectors for the [110] direction:

\[
\frac{u_3}{u_2} = \frac{\frac{1}{2}(c_{12}+c_{66})\frac{1}{2}(c_{20}+c_{44}) - \frac{1}{2}(c_{19}+c_{46})\left(\frac{1}{2}(c_{66}+c_{22})-P\nu^2\right)}{\frac{1}{2}(c_{16}+c_{44})\frac{1}{2}(c_{20}+c_{44}) - \frac{1}{2}(c_{12}+c_{66})\left(\frac{1}{2}(c_{66}+c_{44})-P\nu^2\right)}
\]

Eq 4.46

\[
\frac{u_3}{u_1} = \frac{\frac{1}{2}(c_{12}+c_{66})\frac{1}{2}(c_{20}+c_{44}) - \frac{1}{2}(c_{19}+c_{46})\left(\frac{1}{2}(c_{66}+c_{22})-P\nu^2\right)}{\frac{1}{2}(c_{66}+c_{22})-P\nu^2\left(\frac{1}{2}(c_{66}+c_{44})-P\nu^2\right) - \left(\frac{1}{2}(c_{20}+c_{44})\right)^2}
\]

Eq 4.47
and for the [011] direction:

\[
\begin{align*}
    u_3 &= \frac{\frac{1}{2}(c_{44}+c_{23})\frac{1}{3}(c_{44}+c_{23}) - \frac{1}{2}(c_{44}+c_{33})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right)}{\frac{1}{2}(c_{46}+c_{35})\frac{1}{3}(c_{44}+c_{23}) - \frac{1}{2}(c_{46}+c_{25})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right)}
    \\
    u_2 &= \frac{\frac{1}{2}(c_{46}+c_{35})\frac{1}{3}(c_{44}+c_{23}) - \frac{1}{2}(c_{46}+c_{25})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right)}{\frac{1}{2}(c_{22}+c_{44})-P_V^2 - \left(\frac{1}{3}(c_{44}+c_{33})\right)^2}
\end{align*}
\]

Eq 4.48

\[
\begin{align*}
    u_3 &= \frac{\frac{1}{2}(c_{46}+c_{25})\frac{1}{3}(c_{44}+c_{23}) - \frac{1}{2}(c_{46}+c_{35})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right)}{\frac{1}{2}(c_{22}+c_{44})-P_V^2 - \left(\frac{1}{3}(c_{44}+c_{33})\right)^2}
    \\
    u_2 &= \frac{\frac{1}{2}(c_{46}+c_{35})\frac{1}{3}(c_{44}+c_{23}) - \frac{1}{2}(c_{46}+c_{25})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right)}{\frac{1}{2}(c_{46}+c_{25})\left(\frac{1}{3}(c_{22}+c_{44})-P_V^2\right) - \left(\frac{1}{3}(c_{44}+c_{33})\right)^2}
\end{align*}
\]

Eq 4.49

The particle displacement vectors of a longitudinal mode propagating in the [011] and [110] directions produced by the solution sets for the elastic constants \(c_{23}, c_{12}\) and \(c_{23}\) are given in Table 4.2 for an evaluation procedure started in the [110] direction.

On examination of the particle displacement vectors in Table 4.2 and eliminating physically impossible solutions, the following values were obtained for the last three elastic constants:

\[
\begin{align*}
    c_{23} &= -1.9 \times 10^{10} \text{ Nm}^{-2} \\
    c_{12} &= 1.89 \times 10^{10} \text{ Nm}^{-2} \\
    c_{33} &= 1.97 \times 10^{10} \text{ Nm}^{-2}
\end{align*}
\]

To check the accuracy of the values obtained for the elastic constants \(c_{23}, c_{12}\) and \(c_{23}\), the evaluation procedure was retraced for the [011] direction. This involved obtaining an expression for \(c_{23}\) using the relationships between products and roots (equations 4.35 to 4.37) for the [011] direction.

Equations 4.35 and 4.36 can be rewritten in the following form:
### Table 4.2 Particle displacement vectors

<table>
<thead>
<tr>
<th>Case</th>
<th>Particle Displacement Vectors</th>
<th>Propagation Vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Case</td>
<td>$c_{23} = 1.9 \times 10^{-2}$</td>
<td>$u_1 = 0.77$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 1.89 \times 10^{10}$</td>
<td>$u_2 = 0.636$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = 0.044$</td>
</tr>
<tr>
<td>Negative Case</td>
<td>$c_{23} = 9.0 \times 10^{5}$</td>
<td>$u_1 = 0.772$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 1.89 \times 10^{10}$</td>
<td>$u_2 = 0.635$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = 0.008$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case</th>
<th>Particle Displacement Vectors</th>
<th>Propagation Vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Case</td>
<td>$c_{23} = 1.97 \times 10^{10}$</td>
<td>$u_1 = 0.602$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 1.97 \times 10^{10}$</td>
<td>$u_2 = 0.592$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = 0.534$</td>
</tr>
<tr>
<td>Negative Case</td>
<td>$c_{23} = 4.05 \times 10^{10}$</td>
<td>$u_1 = -0.993$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 4.05 \times 10^{10}$</td>
<td>$u_2 = 0.063$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = 0.100$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case</th>
<th>Particle Displacement Vectors</th>
<th>Propagation Vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Case</td>
<td>$c_{23} = 9.0 \times 10^{5}$</td>
<td>$u_1 = 0.992$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 1.89 \times 10^{10}$</td>
<td>$u_2 = 0.063$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = -0.101$</td>
</tr>
<tr>
<td>Negative Case</td>
<td>$c_{23} = 9.0 \times 10^{5}$</td>
<td>$u_1 = -0.603$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = 1.89 \times 10^{10}$</td>
<td>$u_2 = 0.592$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u_3 = 0.535$</td>
</tr>
</tbody>
</table>
\[
X^2 + H^2 = KD \\
LA*X*H - OA*H^2 - JD*X^2 = NA
\]

where \( X = (c_{46} + c_{29}) \) \( H = (c_{44} + c_{33}) \)

\[
KD = (c_{22} + 2c_{44} + c_{33})(c_{46} + c_{29}) + (c_{22} + c_{44})(c_{44} + c_{33}) \\
- (c_{46} + c_{33})^2 - 4f^2(v_{16}v_{17} + v_{16}v_{18} + v_{17}v_{18}) \\
NA = 8f^2v_{16}v_{17}v_{18} - (c_{46} + c_{29})(c_{22} + c_{44})(c_{44} + c_{33}) \\
+ (c_{22} + c_{44})(c_{44} + c_{33})^2
\]

\[
LA = 2(c_{46} + c_{33}) \quad OA = c_{46} + c_{29} \quad JD = c_{44} + c_{33}
\]

Equations 4.50 and 4.51 contain two unknown elastic constants \( c_{29} \) and \( c_{23} \). By modifying 4.50 to obtain an expression for \((c_{44} + c_{29})\)

\[
H = \pm (KD-X^2)^{1/2} \quad 4.52
\]

and substituting the resulting equation (equation 4.52) into equation 4.51, the following expression was obtained:

\[
LA*\pm (KD-X^2)^{1/2}X - OA*(KD-X^2) - JD*X^2 = NA \quad 4.53
\]

This expression contains only one unknown elastic constant \( c_{29} \) expressed in terms of known elastic constants and velocities. A solution to 4.53 was sought numerically using Newtions method to obtain a value for \( X \)

where

\[
X_{n+1} = X_n - \frac{f(X_n)}{f'(X_n)} \quad 4.54
\]

where \( X_n = (c_{46} + c_{29}) \)

\[
f(X_n) = LA*\pm (KD-X^2)^{1/2}X - OA*KD + OA*X^2 - JD*X^2 - NA
\]

\[
f'(X_n) = LA*\pm (KD-X^2)^{1/2} - LA*\pm X^2*(KD-X^2)^{-1/2}
\]

\[
+ 2X*OA - 2JD*X
\]
No real solution could be found for X. As discussed earlier, if no real solution can be obtained for X, then the point at which X is a minimum can be adopted as the solution. This condition was obtained numerically using Newton's method where

$$X_{n+1} = X_n - \frac{f'(X_n)}{f''(X_n)} \quad 4.55$$

where

$$f'(X_n) = \text{LA} \times \sqrt{(\text{KD}-X^2)} - \text{LA} \times X^2 \times (\text{KD}-X^2)^{-1/2}$$

$$+ 2 \times X \times \text{QA} - 2 \times \text{JD} \times X$$

$$f''(X_n) = -\text{LA} \times X \times \sqrt{(\text{KD}-X^2)} - \text{LA} \times (\text{KD}-X^2)^{-3/2} \times X^3$$

$$- \text{LA} \times 2 \times X \times \sqrt{(\text{KD}-X^2)} - 2 \times \text{OA} - 2 \times \text{JD}$$

A solution for the elastic constant $c_{23}$ was obtained for each case. Values for $c_{23}$ were obtained by substituting the values obtained for $c_{26}$ into equation 4.52

$$c_{44} + c_{23} = H = \frac{1}{2} (\text{KD}-X^2)^{1/2} \quad 4.56$$

Note that each value of $c_{26}$ will generate two values for $c_{23}$. The values for the remaining elastic constant $c_{12}$ were obtained by using 4.40

$$c_{13} + c_{64} = Y \times (\text{RT}-X^2)^{1/2} \quad 4.57$$

Each value of $c_{26}$ generates two possible values for $c_{12}$. The selection of the set of elastic constants as the valid solution was made by considering the information contained in the particle displacement vectors. On inspection of this information (Table 4.3) the negative case for $c_{26}$ can be rejected as the solutions are physically impossible. The correct solutions for the elastic constants $c_{26}$, $c_{23}$, and $c_{12}$ obtained by starting the analysis in the [011] direction are
Table 4.3 Particle displacement vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{23} = -2.4 \times 10^9 \text{ Nm}^{-2}$</td>
<td>$c_{23} = 1.40 \times 10^9 \text{ Nm}^{-2}$</td>
</tr>
<tr>
<td>$c_{23}$ positive case</td>
<td>$c_{23}$ positive case</td>
</tr>
<tr>
<td>$c_{23} = 1.90 \times 10^{10} \text{ Nm}^{-2}$</td>
<td>$c_{23} = 1.97 \times 10^{10} \text{ Nm}^{-2}$</td>
</tr>
</tbody>
</table>

particle displacement vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_1 = 0.534; u_2 = 0.625; u_3 = 0.568$</td>
<td>$u_1 = -0.937; u_2 = 0.235; u_3 = 0.260$</td>
</tr>
</tbody>
</table>

propagation vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_\text{x} = 0.0; l_\text{y} = 0.707; l_\text{z} = 0.707$</td>
<td>$l_\text{x} = 0.0; l_\text{y} = 0.707; l_\text{z} = 0.707$</td>
</tr>
</tbody>
</table>

$c_{23}$ negative case

$c_{23} = -4.05 \times 10^{10} \text{ Nm}^{-2}$

particle displacement vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_1 = 0.936; u_2 = 0.235; u_3 = -0.261$</td>
<td>$u_1 = -0.535; u_2 = 0.625; u_3 = -0.569$</td>
</tr>
</tbody>
</table>

propagation vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_\text{x} = 0.0; l_\text{y} = 0.707; l_\text{z} = 0.707$</td>
<td>$l_\text{x} = 0.0; l_\text{y} = 0.707; l_\text{z} = 0.707$</td>
</tr>
</tbody>
</table>

$c_{12}$ positive case

$c_{12} = 1.89 \times 10^{10} \text{ Nm}^{-2}$

particle displacement vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_1 = 0.769; u_2 = 0.636; u_3 = -0.051$</td>
<td>$u_1 = 0.772; u_2 = 0.635; u_3 = -0.001$</td>
</tr>
</tbody>
</table>

propagation vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_\text{x} = 0.707; l_\text{y} = 0.707; l_\text{z} = 0.0$</td>
<td>$l_\text{x} = 0.707; l_\text{y} = 0.707; l_\text{z} = 0.0$</td>
</tr>
</tbody>
</table>

$c_{12}$ negative case

$c_{12} = -3.11 \times 10^{10} \text{ Nm}^{-2}$

particle displacement vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_1 = 0.772; u_2 = -0.636; u_3 = 0.001$</td>
<td>$u_1 = 0.769; u_2 = -0.637; u_3 = -0.051$</td>
</tr>
</tbody>
</table>

propagation vectors

<table>
<thead>
<tr>
<th>Positive Case</th>
<th>Negative Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_\text{x} = 0.707; l_\text{y} = 0.707; l_\text{z} = 0.0$</td>
<td>$l_\text{x} = 0.707; l_\text{y} = 0.707; l_\text{z} = 0.0$</td>
</tr>
</tbody>
</table>
\[c_{29} = -2.4 \times 9^7 \text{ Nm}^{-2}\]
\[c_{12} = 1.89 \times 10^{10} \text{ Nm}^{-2}\]
\[c_{23} = 1.90 \times 10^{10} \text{ Nm}^{-2}\]

These values compare favourably with the values obtained earlier from the procedure started in the [110] direction.

The most efficient way to determine values for the last three elastic constants is by first obtaining solutions for \(c_{29}\). If this was not carried out, a larger number of possible solutions for the remaining elastic constants \(c_{23}\) and \(c_{12}\) would have to be considered. Consider the following case, if the equations were evaluated such that \(c_{23}\) was to be obtained first, then two values for \(c_{23}\) would be expected and substitution of these values into equation 4.50 would result in four values for \(c_{29}\). \(c_{12}\) would then be obtained by substituting the known values of \(c_{29}\) into 4.38, each value of \(c_{29}\) generating two values for \(c_{12}\). This would lead to a set of solutions containing two values for \(c_{23}\), giving in turn four values for \(c_{29}\) followed by eight values for \(c_{12}\). A similar argument holds if a solution was sought for \(c_{12}\) first. If the procedure described in this section is followed, two values for \(c_{29}\) are obtained generating four values each for \(c_{12}\) and \(c_{23}\), a useful reduction in effort.

As the calculations progress the accuracy of the values obtained for the elastic constants deteriorates. In particular the values obtained for the last three elastic constants have a substantial error. The
deterioration in accuracy is caused by the lengthy expressions used involving experimental velocities which themselves contain errors.

A series of computer programs has been written to carry out the calculations described in this section and is listed in appendix 2.B and 2.C.

The evaluation procedure described here to obtain the elastic constants of a monoclinic crystal is not the only method which can be used. Prawer et al (1982) solved the necessary equations using a generalized Newton – Raphson algorithm. Alternatively Tylczynski (1981) describes a method to obtain values for $c_{11}$, $c_{33}$, $c_{66}$, $c_{13}$, $c_{16}$, $c_{36}$ only.

4.3 Consistency checks on measured velocities and obtained elastic constants.

Cross checks on the accuracy of the velocity measurements were made using the trace identities described by Huntington (1969). These trace relationships are expressions containing only velocities which are obtained by the manipulation of equations 4.3 to 4.14 and are given below. The corresponding values obtained for TBB at 20°C are also included.

$$\rho v_4^2 + \rho v_5^2 = \rho v_2^2 + \rho v_6^2$$  

1.65x10^{10} \text{ Nm}^{-2} \quad \text{1.65x10^{10} Nm}^{-2} 

$$\rho v_2^2 + \frac{1}{3}(\rho v_1^2 + \rho v_3^2 + \rho v_5^2 + \rho v_6^2) = \rho (v_{13}^2 + v_{14}^2 + v_{16}^2)$$  

5.54x10^{10} \text{ Nm}^{-2} \quad \text{5.53x10^{10} Nm}^{-2} 

$$\rho v_5^2 + \frac{1}{3}(\rho v_2^2 + \rho v_3^2 + \rho v_7^2 + \rho v_8^2) = \rho (v_{16}^2 + v_{17}^2 + v_{18}^2)$$  

4.92x10^{10} \text{ Nm}^{-2} \quad \text{4.87x10^{10} Nm}^{-2} 

$$\rho v_2^2 \rho v_6^2 - (\rho v_{11}^2 - \frac{1}{3}(\rho v_2^2 + \rho v_6^2))^2 = \rho v_4^2 \rho v_5^2$$  

0.63x10^{20} (\text{Nm}^{-2})^2 \quad \text{0.64x10^{20} (Nm}^{-2})^2
The extent to which these checks are verified attests to the internal consistency of the experimental data. A programme was written to carry out the above checks and is listed in Appendix 2.D.

A less useful test for accuracy can be carried out on the calculated elastic constants by checking that they obey the crystal stability conditions. The stability conditions are obtained by considering the strained energy ($E$) of a crystal (Nye (1957) p137)

\[ E = \frac{1}{2} c_{ij} S_i S_j \]

which must always be positive when the crystal is strained (or equal to zero in the unstrained state). If 4.58 is to be positive definite then the following conditions are true (see D.M. Bloom and F.E. Hohn 1978):

1. $c_{11} > 0$
2. Det $c_{ij} > 0$
3. Every principle minor determinant of $c_{ij}$ is positive

The necessary crystal stability conditions have been reported by Alers and Neighbours (1957) for crystals of higher symmetry and are given below for monoclinic crystals.

\[ c_{11} > 0 \quad c_{22} > 0 \quad c_{33} > 0 \quad c_{44} > 0 \quad c_{55} > 0 \quad c_{66} > 0 \]

\[ c_{11} c_{22} > c_{12}^2 \quad c_{11} c_{33} > c_{13}^2 \quad c_{11} c_{55} > c_{15}^2 \quad c_{22} c_{33} > c_{23}^2 \]

\[ c_{22} c_{55} > c_{25}^2 \quad c_{33} c_{55} > c_{35}^2 \quad c_{44} c_{66} > c_{46}^2 \]

\[ c_{11} c_{22} c_{33} + 2 c_{12} c_{13} c_{23} > c_{11} c_{23}^2 + c_{33} c_{12}^2 + c_{22} c_{13}^2 \]
\[ c_{11} c_{22} c_{55} + 2 c_{12} c_{25} c_{13} > c_{11} c_{25}^2 + c_{55} c_{12}^2 + c_{22} c_{15}^2 \]
\[ c_{22} c_{33} c_{55} + 2 c_{23} c_{35} c_{25} > c_{22} c_{35}^2 + c_{55} c_{23}^2 + c_{33} c_{25}^2 \]

Another potential use of the crystal stability
conditions is to assist in the selection of the correct set of solutions in the evaluation procedure for the elastic constants \(c_{12}, c_{23}, \text{ and } c_{25}\). The elastic constants derived in this work obeyed the crystal stability conditions.

4.4 A procedure for determination of the hydrostatic pressure derivatives of the elastic stiffness constants for a monoclinic crystal.

By measuring the hydrostatic pressure dependence of the ultrasonic wave velocities in the [001], [010], [100], [101], [110] and [011] directions the pressure derivatives of the elastic constants were obtained using the procedure described below.

The pulse echo overlap frequency was converted to a relative change \((\Delta W/W_0 - 1)\) in the natural velocity \(W\) (Thurston and Brugger 1964). The initial pressure derivatives of \(\rho v^2\) can be obtained using the following relationship due to Thurston (1965):

\[
(\rho v^2)_{p=0}' = \rho v_o^2(2S^iS_o + \lambda^T - 2N_m N_m S_{m_1 m_1}^T) \ 4.59
\]

where \(\lambda^T\) is the isothermal volume compressibility, \(N_m N_m S_{m_1 m_1}^T\) corresponds to the isothermal linear compressibility, \(f_o\) is the frequency required for pulse overlap at atmospheric pressure and \(f'\) is the associated pressure derivative determined as the gradient of the least square line of the frequency against pressure plot, normalized to \(f_o\). The equation in this form holds strictly only for pure mode directions, where the pressure dependence of the particle displacement vector
is zero. In a monoclinic crystal this is true for only a few modes. However, if the effect of pressure on the particle displacement vector is small, equation 4.59 can be taken as a reasonable approximation. Although in a determination of \((\rho v^2)_{\text{f}}\) through equation 4.59 the isothermal elastic constants should be used, the difference between isothermal and adiabatic elastic constants is not substantial compared with the experimental error and the adiabatic compliances will be employed. While determination of the elastic constants themselves leads to several possible solution sets (the correct one has been deduced by arguments based on the physics of ultrasonic wave propagation), a single solution is obtained for the pressure derivatives.

The argument used to obtain the pressure derivatives of the elastic constants follows a similar path to that described in section 4.1 for the determination of the elastic constants. The pressure derivatives are found by differentiation and manipulation of equations 4.3 to 4.15. The pressure derivative of \(c_{22}\), \(c_{44}\) and \(c_{66}\) can be obtained by differentiating 4.6, 4.9 and 4.3 respectively to obtain:

\[
\frac{\partial c_{22}}{\partial P} = \frac{\partial (\rho v^2)}{\partial P} \quad ; \quad \frac{\partial c_{44}}{\partial P} = \frac{\partial (\rho v^2)}{\partial P} \quad ; \quad \frac{\partial c_{66}}{\partial P} = \frac{\partial (\rho v^2)}{\partial P}
\]

The next pressure derivative, which can be easily found is that of \(c_{44}\), by differentiating 4.12

\[
\frac{\partial \rho v^2_{11}}{\partial P} = \frac{1}{2} \frac{\partial c_{44}}{\partial P} + \frac{\partial c_{66}}{\partial P} + \frac{\partial c_{46}}{\partial P} \quad 4.60
\]

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and substituting in known pressure derivatives, \(c_{46}\) can be obtained.

The pressure derivatives of \(c_{11}, c_{66}, c_{16}, c_{33}\) and \(c_{36}\) can be obtained by taking derivatives of equations 4.4, 4.5, 4.10, 4.11 and 4.15.

\[
\frac{\partial \rho v_1^2}{\partial P} + \frac{\partial \rho v_3^2}{\partial P} = \frac{\partial c_{11}}{\partial P} + \frac{\partial c_{66}}{\partial P} = A' \tag{4.61}
\]

\[
\frac{\partial \rho v_1^2}{\partial P} + \frac{\partial \rho v_3^2}{\partial P} = \frac{\partial c_{16}}{\partial P} + \frac{\partial c_{33}}{\partial P} \tag{4.62}
\]

\[
\frac{\partial \rho v_7^2}{\partial P} + \frac{\partial \rho v_7^2}{\partial P} = \frac{\partial c_{33}}{\partial P} + \frac{\partial c_{36}}{\partial P} = C' \tag{4.63}
\]

\[
\frac{\partial \rho v_7^2}{\partial P} + \frac{\partial \rho v_7^2}{\partial P} = \frac{\partial c_{36}}{\partial P} + \frac{\partial c_{36}}{\partial P} \tag{4.64}
\]

\[
\frac{\partial}{\partial P} \left( \rho (v_{10}^2 + v_{12}^2 - \frac{1}{2}(v_1^2 + v_3^2 + v_7^2 + v_8^2)) \right) = \frac{\partial c_{16}}{\partial P} \tag{4.65} \]

These equations do not contain a squared term; only one solution exists for each derivative. The pressure derivative of \(c_{66}\) can be obtained by manipulating equations 4.61 to 4.65 to yield the following equation for the derivative of \(c_{66}\) in terms of known elastic constants and measured \((\rho v^2)_{P=0};\)

\[
\frac{\partial c_{66}}{\partial P} = \frac{2E'c_{16}c_{36} + B'c_{36} + D'c_{16} - c_{16}c_{36}c_{66}A' - c_{16}c_{36}c_{66}C'}{(c_{36}c_{11} - c_{36}c_{66} + c_{16}c_{33} - c_{16}c_{36})} \tag{4.66}
\]
Then by back substitution into the relevant equations (4.61 to 4.65) the pressure derivatives of $c_{11}^*$, $c_{33}^*$, $c_{15}^*$ and $c_{36}^*$ were determined. The starting point for the determination of the pressure derivative $c_{13}^*$ was equation 4.14, which on differentiation by the product rule and rearranging gives:

\[
\frac{\partial c_{13}}{\partial P} = \frac{1}{2} (c_{15} + c_{36} + c_{13} + c_{66})^{-1} \left[ \left( c_{66} + c_{33} + 2c_{36} \right) \frac{\partial}{\partial P} (c_{11} + c_{66} + 2c_{16}) \right.
\]

\[
+ \left. \frac{\partial}{\partial P} \left( c_{11} + c_{66} + 2c_{16} \right) - \left( c_{66} + c_{33} + 2c_{36} \right) \right]
\]

\[
- 4 \left( \rho v_{10}^2 - v_{12}^2 + \rho v_{12}^2 v_{10} - \frac{\partial}{\partial P} \left( c_{11} + c_{33} + c_{66} \right) \right)
\]

The best method for obtaining the pressure derivatives of the remaining three elastic constants $c_{21}$, $c_{12}$ and $c_{13}$ is to substitute the measured velocities at different pressures into the equations (see section 4.2) for the [110] and [011] modes to obtain these elastic constants as a function of pressure. Then their derivatives can be obtained. Taking derivatives directly of these equations leads to serious cumulative errors in $c_{21}$, $c_{12}$ and $c_{13}$.

This provides a general procedure for determination of the hydrostatic pressure derivatives of the elastic constants for a monoclinic crystal and has been employed here.
5.1 Introduction

In this chapter the results of the experiments performed on crystals of TGS to obtain the ultrasonic wave velocity as a function of hydrostatic pressure and temperature are given. The experiments were carried out over a temperature range commencing at 20 °C (i.e., below the phase transition temperature) to a temperature of 65 °C which is above the phase transition. Experiments could not be performed at higher temperatures because the transducer-sample bond started to break down above 65 °C. From the measurements it was possible to obtain:

1. Values for all of the elastic stiffness constants and their pressure derivatives at room temperature.
2. Values for all of the elastic compliances at room temperature.
3. The temperature dependence of most elastic stiffness constants (the exceptions being $c_{22}$, $c_{12}$, $c_{13}$) over the temperature range 20 to 65 °C.
4. The pressure derivatives of most elastic stiffness constants at various temperatures over the range 20 - 65 °C (again with the exceptions of $c_{22}$, $c_{12}$, $c_{13}$).

Below its phase transition temperature, TGS is piezoelectric and this results in various vibrational modes being stiffened (see Auld (1973) or Dieulesaint and Royer (1980) for a more details). It can be shown that only modes 2, 5, 8, 11 (see Table 5.1) are subject to piezoelectric stiffening. No corrections to the velocity...
data were made to take account of piezoelectric effects as the necessary data to enable these corrections to be performed have not been reported, as yet, in the literature. Above the transition temperature TGS is not piezoelectric so no corrections are necessary.

5.2 Measurement of the elastic properties of TGS at room temperature

Ultrasonic wave velocities were measured for 18 different modes of vibration (table 5.1) in TGS at room temperature (20°C) and atmospheric pressure by using the pulse echo overlap system as described in section 3.5. The ultrasonic wave velocities quoted for each mode are the average value of several measurements. Velocity corrections due to multiple internal reflections at the transducer-sample boundary have been applied (see section 3.9), the velocities quoted in table 5.1 are the corrected ones.

Using the velocity measurements from table 5.1 and following the evaluation procedure described in section 4.2, the 13 elastic stiffness constants were determined; these are quoted in table 5.2 along with data obtained by other workers on this material (the data of Luspin and Hauret (1977) has been transferred to the axial set used by Konstantinova et al (1960) and in this work). In view of the accumulation of errors involved in the extraction of elastic stiffness constants, especially in $c_{23}$, $c_{23}$ and $c_{12}$, the agreement between the sets of data is more than reasonable.
Table 5.1 Pressure derivatives of the normalized overlap frequency and mode velocities for TGS

| Mode number | Direction of wave propagation | Polarization vector | Measured wave velocity (m/s) | $f'/f_0 \times 10^{-3}$ bar$^{-1}$ | $\left( \frac{\partial \nu^2}{\partial P} \right)_{P=0}$ |
|-------------|-------------------------------|---------------------|-----------------------------|-----------------------------------|--------------------------------olución|
| 1           | [100]                         | [100]               | 5130                        | 9.50                              | 9.51                          |
| 2           | [100]                         | [010]               | 1900                        | 3.50                              | 0.58                          |
| 3           | [100]                         | [001]               | 2520                        | 4.28                              | 1.18                          |
| 4           | [010]                         | [100]               | 2460                        | 3.93                              | 1.01                          |
| 5           | [010]                         | [010]               | 4460                        | 19.0                              | 13.4                          |
| 6           | [010]                         | [001]               | 1940                        | 3.78                              | 0.61                          |
| 7           | [001]                         | [100]               | 2510                        | 6.49                              | 1.35                          |
| 8           | [001]                         | [010]               | 2490                        | 4.55                              | 0.92                          |
| 9           | [001]                         | [001]               | 4050                        | 10.6                              | 5.78                          |
| 10          | [101]                         | [101]               | 2270                        | 5.15                              | 0.92                          |
| 11          | [101]                         | [010]               | 2280                        | 4.51                              | 0.821                         |
| 12          | [101]                         | [101]               | 4530                        | 11.4                              | 8.01                          |
| 13          | [110]                         | [110]               | 4560                        | 12.8                              | 9.73                          |
| 14          | [110]                         | [001]               | 2460                        | 4.41                              | 1.13                          |
| 15          | [110]                         | [110]               | 2460                        | 7.99                              | 1.86                          |
| 16          | [011]                         | [011]               | 4550                        | 12.8                              | 9.26                          |
| 17          | [011]                         | [011]               | 1840                        | 7.41                              | 0.896                         |
| 18          | [011]                         | [100]               | 2210                        | 5.62                              | 0.999                         |

1 bar = $10^5$ N m$^{-2}$. 
Table 5.2 The elastic stiffness constants of TGS in the orthogonal axial set used by Konstantinova et al (1960) at room temperature. The units are $10^{10}$ Nm$^{-2}$

<table>
<thead>
<tr>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{23}$</th>
<th>$C_{16}$</th>
<th>$C_{25}$</th>
<th>$C_{36}$</th>
<th>$C_{46}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.41</td>
<td>3.34</td>
<td>2.73</td>
<td>1.04</td>
<td>1.08</td>
<td>0.61</td>
<td>1.89</td>
<td>1.67</td>
<td>1.97</td>
<td>-0.21</td>
<td>-0.19</td>
<td>-0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>4.55</td>
<td>3.21</td>
<td>2.63</td>
<td>0.95</td>
<td>1.11</td>
<td>0.62</td>
<td>1.72</td>
<td>1.98</td>
<td>2.08</td>
<td>-0.30</td>
<td>-0.036</td>
<td>-0.500</td>
<td>-0.026</td>
</tr>
<tr>
<td>4.71</td>
<td>3.35</td>
<td>2.75</td>
<td>1.02</td>
<td>1.03</td>
<td>0.61</td>
<td>1.50</td>
<td>2.10</td>
<td>1.85</td>
<td>-0.18</td>
<td>-0.20</td>
<td>0.05</td>
<td>-0.02</td>
</tr>
<tr>
<td>4.61</td>
<td>2.79</td>
<td>1.12</td>
<td></td>
<td></td>
<td></td>
<td>2.10</td>
<td></td>
<td>-0.22</td>
<td></td>
<td></td>
<td>0.15</td>
<td>Tylczynski</td>
</tr>
</tbody>
</table>
The elastic compliances were determined using the derived elastic stiffness constants by following the procedure described in Appendix A and the values obtained are quoted in table 5.3 along with those determined from other workers data. It should be appreciated that the values obtained for the elastic compliances by this indirect method will not be as accurate as those obtained by experiments which measured the elastic compliances directly. This inaccuracy is due to a combination of factors, the principle ones being that we are using elastic stiffness constants which contain experimental error and also the loss of numerical accuracy inherent in the inversion of the tensor which involves a large number of terms.

Measurements were taken of the hydrostatic pressure derivatives of the ultrasonic wave velocity for 18 modes of vibration (the average values obtained from three experimental runs are quoted in table 5.1) from which values of the pressure derivatives of the elastic stiffness constants were obtained; these are given in table 5.4. It can be seen (table 5.1) that for every acoustic mode measured for TGS the ultrasonic wave velocity increased with pressure. Hence the pressure derivatives of the elastic stiffness constants are positive; $\partial C_{10}/\partial P$ is an exception but in itself does not correspond to any normal mode - it is obtained only in combination with other derivatives $\partial C_{ij}/\partial P$. 

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Table 5.3 The elastic compliances of TGS in the orthogonal axial set used by Konstantinova et al (1960) at room temperature. The units are $10^{-11}$ m$^2$N

<table>
<thead>
<tr>
<th>$S_{11}$</th>
<th>$S_{22}$</th>
<th>$S_{33}$</th>
<th>$S_{44}$</th>
<th>$S_{55}$</th>
<th>$S_{66}$</th>
<th>$S_{12}$</th>
<th>$S_{13}$</th>
<th>$S_{23}$</th>
<th>$S_{15}$</th>
<th>$S_{25}$</th>
<th>$S_{35}$</th>
<th>$S_{46}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.19</td>
<td>5.62</td>
<td>6.79</td>
<td>9.65</td>
<td>9.39</td>
<td>16.45</td>
<td>-1.13</td>
<td>-1.12</td>
<td>-3.35</td>
<td>0.23</td>
<td>0.21</td>
<td>0.32</td>
<td>-0.79</td>
<td>This work</td>
</tr>
<tr>
<td>3.29</td>
<td>6.98</td>
<td>10.85</td>
<td>10.53</td>
<td>10.73</td>
<td>16.15</td>
<td>-0.29</td>
<td>-2.27</td>
<td>-5.77</td>
<td>-0.14</td>
<td>-2.45</td>
<td>4.08</td>
<td>0.44</td>
<td>Konstantinova et al</td>
</tr>
<tr>
<td>3.27</td>
<td>4.87</td>
<td>7.74</td>
<td>9.81</td>
<td>10.11</td>
<td>16.40</td>
<td>-0.06</td>
<td>-2.47</td>
<td>-3.25</td>
<td>0.68</td>
<td>1.09</td>
<td>-1.44</td>
<td>0.32</td>
<td>Luspin &amp; Hauret</td>
</tr>
</tbody>
</table>
Table 5.4 Hydrostatic pressure derivatives of the elastic stiffness constants of TGS.

\[
\begin{align*}
\frac{\partial C_{11}}{\partial P} |_{P=0} &= 9.5, \\
\frac{\partial C_{12}}{\partial P} |_{P=0} &= 8.9, \\
\frac{\partial C_{13}}{\partial P} |_{P=0} &= 6.0, \\
\frac{\partial C_{15}}{\partial P} |_{P=0} &= -0.40, \\
\frac{\partial C_{22}}{\partial P} |_{P=0} &= 13.4, \\
\frac{\partial C_{23}}{\partial P} |_{P=0} &= 6.9, \\
\frac{\partial C_{25}}{\partial P} |_{P=0} &= 0, \\
\frac{\partial C_{33}}{\partial P} |_{P=0} &= 5.9, \\
\frac{\partial C_{35}}{\partial P} |_{P=0} &= 0.43, \\
\frac{\partial C_{44}}{\partial P} |_{P=0} &= 0.92, \\
\frac{\partial C_{46}}{\partial P} |_{P=0} &= 0.07, \\
\frac{\partial C_{66}}{\partial P} |_{P=0} &= 1.2, \\
\frac{\partial C_{66}}{\partial P} |_{P=0} &= 0.58.
\end{align*}
\]
5.3 Measurement of the temperature dependence of the elastic stiffness constants.

The experimental procedure adopted to obtain the temperature dependence of the ultrasonic wave velocity involved placing the sample inside the pressure cell, which was then heated without pressure being applied to the system. The ultrasonic wave velocity was measured using the pulse echo overlap technique. Experimental readings were taken at appropriate temperature increments while the sample was being heated. The heating rate selected was generally $\theta^\circ\text{C}$ per hour at temperatures removed from the phase transition, with the heating rate being reduced in the vicinity of the phase transition to permit any effects at the phase transition to be followed in greater detail.

The temperature dependence of the ultrasonic wave velocities were measured for vibrational modes numbers 1 to 12 over the temperature range $20 \ ^\circ\text{C}$ to $65 \ ^\circ\text{C}$. The numeric label assigned to each mode relates to table 5.1 which provides a description of the wave propagation and polarization vectors. The temperature dependences of ultrasonic wave velocities for modes 1 to 12 are presented in the form of plots of relative change in natural velocity $\Delta W/W_0$ versus applied temperature (figures 5.1 to 5.12), where $\Delta W/W_0$ is defined as

$$\Delta W/W_0 = \left( W_{(T)} - W_0 \right) / W_0$$

To obtain the velocity of the ultrasonic waves at elevated temperatures from these data, corrections have
Fig 5.1 Temperature dependence of the ultrasonic wave velocity for the X propagated longitudinal mode.

Fig 5.2 Temperature dependence of the ultrasonic wave velocity for the X propagated Y polarized shear mode.
Fig 5.3 Temperature dependence of the ultrasonic wave velocity for the $X$ propagated $Z$ polarized shear mode.

Fig 5.4 Temperature dependence of the ultrasonic wave velocity for the $Y$ propagated $X$ polarized shear mode.
Fig 5.5 Temperature dependence of the ultrasonic wave velocity for the $Y$ propagated longitudinal mode.

Fig 5.6 Temperature dependence of the ultrasonic wave velocity for the $Y$ propagated $Z$ polarized shear mode.
Fig 5.7 Temperature dependence of the ultrasonic wave velocity for the $Z$ propagated $X$ polarized shear mode.

Fig 5.8 Temperature dependence of the ultrasonic wave velocity for the $Z$ propagated $Y$ polarized shear mode.
Fig 5.9 Temperature dependence of the ultrasonic wave velocity for the Z propagated longitudinal mode.

Fig 5.10 Temperature dependence of the ultrasonic wave velocity for the [1 0 1] propagated [-1 0 1] polarized shear mode.
Fig 5.11 Temperature dependence of the ultrasonic wave velocity for the [1 0 1] propagated Y polarised shear mode.

Fig 5.12 Temperature dependence of the ultrasonic wave velocity for the [1 0 1] propagated longitudinal mode.
to be applied to account for changes in sample path length and density (which can only be measured at room temperature) due to thermal expansion.

The thermal expansion properties of TGS have been investigated by several workers. Most of these workers concentrated their effort in a narrow region either close to the phase transition (Ehses et al. (1978), Gillespie et al. (1974), Deguchi and Nakamura (1977), Deguchi (1979)) or investigated in detail the thermal expansion properties along one particular crystallographic direction (Imai (1977), Ema et al. (1979)). A few workers (Ganesan (1962), Ezhkova et al. (1959) and Stankowski and Malinowski (1980)) investigated the thermal expansion properties over a wide temperature range for several crystallographic directions. To carry out the corrections necessary to account for thermal expansion the data from Stankowski and Malinowski (1980) were used on the grounds that being the more recent work it was likely to be one of the more accurate determinations of the thermal expansion properties. Unfortunately they used a different orthogonal reference axial system so it was necessary to transfer their data to the frame of Konstantinova et al. (1960) used throughout this work. Plots of $\Delta l/l_0$ against temperature are given in figures 5.13 to 5.16 for the directions investigated in this work, where $\Delta l=l-l_0$, $l$ is the sample length at temperature $T$, $l_0$ is the sample length at room temperature.

It was assumed in the calculation of the transducer
Fig 5.13 Temperature dependence of the relative change in length along the X axis.

Fig 5.14 Temperature dependence of the relative change in length along the Y axis.
Fig 5.15 Temperature dependence of the relative change in length along the Z axis.

Fig 5.16 Temperature dependence of the relative change in length along the [1 0 1] axis.
delay that all properties except sample length were temperature independent. This is not an unreasonable assumption as any temperature induced changes are a correction to a correction, are second order and so can be ignored.

By applying corrections to the sample path length to account for thermal expansion and corrections to account for transducer delay to the data in figures 5.1 to 5.12 the ultrasonic wave velocities at elevated temperatures have been calculated and are presented in figures 5.17 to 5.28 in the form of velocity versus temperature plots. The velocities are also quoted in table 5.5 for modes 1 to 12 for 5 °C intervals. It can be seen that the ultrasonic wave velocity decreased as the temperature was increased. This trend continued above the phase transition. There are four more interesting modes (figures 5.24 to 5.27) where an anomaly occurs at the phase transition with the velocity increasing beyond the phase transition. The percentage change in velocity with temperature is more readily appreciated by examining the AW/Wo plots than the velocity against temperature plots.

From the velocity data obtained the elastic constants (with the exception of c₁₂, c₁₃, c₂₅) were calculated over the temperature range 20 °C to 65 °C in steps of 0.5 °C using the procedure described in section 4.2. Values for the density of TGS used in these calculations at elevated temperatures were determined by using the thermal expansion data along the principle axis to calculate the new sample volume at elevated temperature.
Fig 5.17 Temperature dependence of the ultrasonic wave velocity for the X propagated longitudinal mode corrected for transducer delay and thermal expansion.

Fig 5.18 Temperature dependence of the ultrasonic wave velocity for the X propagated Y polarized shear mode corrected for transducer delay and thermal expansion.
Fig 5.19 Temperature dependence of the ultrasonic wave velocity for the X propagated Z polarized shear mode corrected for transducer delay and thermal expansion.

Fig 5.20 Temperature dependence of the ultrasonic wave velocity for the Y propagated X polarized shear mode corrected for transducer delay and thermal expansion.
Fig 5.21 Temperature dependence of the ultrasonic wave velocity for the Y propagated longitudinal mode corrected for transducer delay and thermal expansion.

Fig 5.22 Temperature dependence of the ultrasonic wave velocity for the Y propagated Z polarized shear mode corrected for transducer delay and thermal expansion.
Fig 5.23 Temperature dependence of the ultrasonic wave velocity for the Z propagated X polarized shear mode corrected for transducer delay and thermal expansion.

Fig 5.24 Temperature dependence of the ultrasonic wave velocity for the Z propagated Y polarized shear mode corrected for transducer delay and thermal expansion.
Fig 5.25 Temperature dependence of the ultrasonic wave velocity for the $Z$ propagated longitudinal mode corrected for transducer delay and thermal expansion.

Fig 5.26 Temperature dependence of the ultrasonic wave velocity for the $[1 0 1]$ propagated $[-1 0 1]$ polarized shear mode corrected for transducer delay and thermal expansion.
Fig 5.27 Temperature dependence of the ultrasonic wave velocity for the [1 0 1] propagated \( \gamma \) polarized shear mode corrected for transducer delay and thermal expansion.

Fig 5.28 Temperature dependence of the ultrasonic wave velocity for the [1 0 1] propagated longitudinal mode corrected for transducer delay and thermal expansion.
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Table 5.5 Temperature variation of the ultrasonic wave velocity (corrected for thermal expansion and transducer delay) for TGS from 20 °C to 65 °C quoted for 5 °C steps. The units are ms⁻¹.
and as the samples mass remains constant the new density can hence be calculated. A plot of density against temperature is given in figure 6.29. The variations of the elastic constants with temperature are presented in figures 5.30 to 5.39. Values for the elastic constants at 5 °C intervals are also quoted in table 5.6.

The temperature derivatives of the elastic stiffness constants (\( T_{c_{ij}} \)) defined as

\[
T_{c_{ij}} = \frac{1}{c_{ij}} \frac{\Delta c_{ij}}{\Delta T}
\]

have been calculated in steps of 5 °C and are given in table 5.7. Values for \( c_{13} \) are subject to a wide margin of experimental error.

5.4 Measurement of the temperature dependence of pressure derivatives of elastic stiffness constants.

The hydrostatic pressure dependence of the ultrasonic wave velocities are presented as a plot of the relative change in natural wave velocity versus applied hydrostatic pressure (units Kbar = 10^8 Pa). The parameter \( \frac{\Delta W}{W_0} \) is defined as

\[
\frac{\Delta W}{W_0} = \frac{(W_P - W_0)}{W_0}
\]

where \( W_P \) is the natural velocity at a pressure \( P \). This provides a representation which is more easily interpreted and compared with other results than for example a plot of the raw echo overlap frequency versus
Fig 5.29 Temperature dependence of the density of TGS.

Temperature \( \degree C \)

Density \( \Delta p / \rho_0 \times 10^{-4} \)
Fig 5.30 Temperature dependence of $C_{11}$

Fig 5.31 Temperature dependence of $C_{13}$
Fig 5.32 Temperature dependence of $C_{15}$

Fig 5.33 Temperature dependence of $C_{22}$
Fig 5.34 Temperature dependence of $C_{33}$

Fig 5.35 Temperature dependence of $C_{35}$
Fig 5.36 Temperature dependence of $C_{44}$

Fig 5.37 Temperature dependence of $C_{46}$
Fig 5.38 Temperature dependence of $C_{55}$

Fig 5.39 Temperature dependence of $C_{66}$
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Table 5.6 Temperature variation of elastic stiffness constants of TGS from 20 °C to 65 °C quoted for 5 °C steps. The units are $10^{10} \text{Nm}^{-2}$. 
pressure. These are presented in figures 5.40 to 5.47 for modes 1 to 12 at 20 °C (below the phase transition temperature) and at 65 °C (above the phase transition temperature) on the same page. For modes 13 to 18 experiments were only performed at room temperature, results being given in figures 5.48 and 5.49.

To enable the pressure derivatives of the elastic constants to be obtained, it is necessary to calculate \((\delta_0 v^2)'_{p=0}\) for each mode (eq 2.59) where the values for \(f'\) are taken as the gradient of the least square lines and \(f_0\) as the intercept (i.e., at zero pressure). In calculating \((\delta_0 v^2)'_{p=0}\) it is assumed that values for linear compressibility and bulk modulus are independent of temperature. This is a reasonable assumption as any temperature corrections to these parameters will result in only second order corrections of \((\delta_0 v^2)'_{p=0}\) so can be ignored. The quantity \((\delta_0 v^2)'_{p=0}\) for modes 1 to 12 over the temperature range 20 to 65 °C are presented graphically in figures 5.50 to 5.61.

By using values for \((\delta_0 v^2)'_{p=0} = 0\) at selected temperatures the pressure derivatives of the elastic constants were calculated using the procedure described in section 4.5 and are tabulated in table 5.8.
Fig 5.40 Results of hydrostatic pressure experiments on TGS for modes propagated in the X direction at room temperature.

Fig 5.41 Results of hydrostatic pressure experiments on TGS for modes propagated in the X direction at 60°C.
Fig 5.42 Results of hydrostatic pressure experiments on TGS for modes propagated in the Y direction at room temperature.

Fig 5.43 Results of hydrostatic pressure experiments on TGS for modes propagated in the Y direction at 60°C.
Fig 5.44 Results of hydrostatic pressure experiments on TGS for modes propagated in the Z direction at room temperature.

Fig 5.45 Results of hydrostatic pressure experiments on TGS for modes propagated in the Z direction at 60 °C.
Fig 5.46 Results of hydrostatic pressure experiments on TGS for modes propagated in the [101] direction at room temperature.

Fig 5.47 Results of hydrostatic pressure experiments on TGS for modes propagated in the [101] direction at 60°C.
Fig 5.48 Results of hydrostatic pressure experiments on TGS for modes propagated in the (110) direction at room temperature.

Fig 5.49 Results of hydrostatic pressure experiments on TGS for modes propagated in the (011) direction at room temperature.
Fig 5.50 Temperature dependence of $(\rho_w^2)_{P=0}$ for mode 1 in TGS.

Fig 5.51 Temperature dependence of $(\rho_w^2)_{P=0}$ for mode 2 in TGS.
Fig 5.52 Temperature dependence of $\langle \rho W^2 \rangle_{\theta=0}$ for mode 3 in TGS.

Fig 5.53 Temperature dependence of $\langle \rho W^2 \rangle_{\theta=0}$ for mode 4 in TGS.
Fig 5.54 Temperature dependence of $(\rho_0 W^2)_{T=0}$ for mode 5 in TGS.

Fig 5.55 Temperature dependence of $(\rho_0 W^2)_{T=0}$ for mode 6 in TGS.
Fig 5.56 Temperature dependence of \( \langle \rho_0 W^2 \rangle_{T=0} \)
for mode 7 in TGS.

Fig 5.57 Temperature dependence of \( \langle \rho_0 W^2 \rangle_{T=0} \)
for mode 8 in TGS.
Fig 5.58 Temperature dependence of $\langle \rho \mathcal{H}^2 \rangle_{T=0}$ for mode 9 in TGS.

Fig 5.59 Temperature dependence of $\langle \rho \mathcal{H}^2 \rangle_{T=0}$ for mode 10 in TGS.
Fig 5.60 Temperature dependence of $\langle \rho \mu^2 \rangle_{p=0}$ for mode 11 in TGS.

Fig 5.61 Temperature dependence of $\langle \rho \mu^2 \rangle_{p=0}$ for mode 12 in TGS.
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Table 5.7 Temperature derivative TC₁₃ of elastic stiffness constants of TGS at selected temperatures. The units are $10^{-4}$/°C.
Table 5.8 Pressure derivatives of the elastic stiffness constants of T88 at selected temperatures. The units are
CHAPTER SIX
DISCUSSION OF ULTRASONIC PROPERTIES AND ELASTIC
BEHAVIOUR OF TGS.

6.1 Introduction

Considerable interest has been expressed by many workers over TGS, as it provides a convenient model system for the study of a second order ferroelectric phase transition of the order-disorder type. TGS has a Curie temperature of 49 °C near which anomalies in a variety of physical properties are observed, including a jump in the acoustic wave velocity and a peak in the magnitude of the corresponding absorption coefficient. These anomalies are observed when the wave vector \( k \) of the ultrasonic wave is perpendicular to the direction of the spontaneous polarization vector component \( P_z \), i.e. for the quasi-longitudinal and quasi-shear modes propagated in the \( XZ \) plane (the anomaly is not present for the \( Y \) polarized shear mode). The anomalous behaviour is most pronounced for the quasi-longitudinal mode propagated in the \( Z \) axis.

All the work reported in the literature concerning the ultrasonic properties of TGS can be split into two principal groups. The first group of work was concerned with the measurement of the ultrasonic wave velocities for several crystallographic directions. The data obtained was then used to calculate the elastic stiffness constants. Later studies of this type measured the variation of the ultrasonic properties over a broad temperature range (usually 20 to 65 °C) from which the
temperature dependence of the elastic stiffness constants could be obtained along with their associated temperature derivatives. The second group of work was concerned with developing a theoretical model to account for the anomalies observed in the ultrasonic properties at the phase transition. To substantiate any particular author's chosen theory, the ultrasonic properties of a single mode of vibration over a narrow temperature band centred at the phase transition were accurately measured. The experimental results obtained were compared with the predictions made by the selected theory. Two mechanisms have been put forward in the literature to account for the observed anomalies; one is based on a "relaxation" mechanism and the other on a "fluctuation" mechanism, these are briefly discussed in section 6.2. For a fluctuation model the Z axis longitudinal mode was generally chosen and for a relaxation model the Y longitudinal mode was selected.

The present work has been concerned with case one and presents the most comprehensive experimental data to date on the ultrasonic properties of TGS. The temperature dependence of the ultrasonic velocities for 12 modes of vibration over the temperature range 20 to 70 °C have been reported, from which the temperature derivatives of 10 elastic stiffness constants have been obtained. For the first time the pressure derivatives of the elastic stiffness constants at selected temperatures, above and below the phase transition are reported. No corrections have been made to take account of the dynamic
piezoelectric stiffening, as this effect is small when it is compared to experimental error. If piezoelectric corrections were to be made using the stiffened elastic theory (see Dieulesaint and Royer (1980) and Auld (1973) for a general introduction), then only modes 2, 5, 8 and 11 would be affected.

6.2 Theoretical models of the phase transition.

The theoretical base of much of the work concerned with the investigation of a second order phase transition is due to Landau. Landau theory states that the physical properties observed at a phase transition can be explained by postulating the existence of an order parameter which goes to zero at the phase transition point. In the case of TGS this order parameter is identified with the spontaneous polarization $P_2$, which disappears at the phase transition. Landau theory predicts that the relaxation time associated with the ordering parameter should increase hyperbolically as the phase transition temperature is approached.

The basic principle of relaxation theory is that, when an ultrasonic wave is propagating through a piezoelectric medium, the oscillations of the elastic strain produced by the acoustic waves can result in oscillations of the value of the spontaneous polarization by virtue of the piezoelectric effect (induced polarization is proportional to the elastic strain). It is the increasing magnitude of the relaxation time of this induced
polarization as the phase transition is approached which is the cause of the anomalies observed. For a more detailed explanation of relaxation theory as applicable to ultrasonic wave propagation see Landau and Khalatnikov (1954), O'Brien and Litovitz (1964).

By studying the piezoelectric matrices it can be seen that the longitudinal strains along the three crystallographic axes are coupled to the spontaneous polarization $P_2$; that coupling will also be observed for modes of propagation which have a shear stress component in the XZ plane (Gilletta (1961)). Due to the magnitude of the components in the matrix of piezoelectric coefficients for TGS, longitudinal waves propagated along the Z axis produce the highest variation in spontaneous polarization per unit strain compared to all other modes. Hence this particular mode shows the most anomalous behaviour.

From the above argument it would be expected that an anomaly should also be observed for a longitudinal mode propagated down the crystallographic Y axis. This is not the case. Lawson (1941) and Minaeva et al (1969) have shown that if the strains are set up by an ultrasonic wave with a wavelength short compared to the size of the crystal, then waves propagating along the ferroelectric axis are in fact decoupled from the spontaneous polarization, and hence no relaxation loss is to be expected for this direction of propagation.

Calculations by Geguzina and Krivoglaz (1968) find that the polarization relaxation time shows a strong
orientational dependence which depends on the angle between the ultrasonic wave vector $k$ and the direction of the spontaneous polarization vector $P_2$. The net effect is that the anomalous reduction in the ultrasonic wave velocity will only be readily observed when the ultrasonic wave vector $k$ is almost perpendicular to the polar axis. This strong orientational dependence can be seen in the work of Strukov et al (1976), who measured the ultrasonic wave velocity for a longitudinal mode propagated down the $Z$ axis and for a mode propagated in a direction which was 4 degrees "off axis" in the $XY$ plane. An increase of the ultrasonic wave velocity by 30 m/s was observed, which cannot be attributed solely to the usual anisotropy of the elastic properties.

The relaxation theory does not predict any anomalous behaviour for modes of propagation involving $YZ$ and $XY$ shear strains as these cannot be coupled to the spontaneous polarization $P_2$. Michelson (1976) proposed a mechanism to account for anomalous behaviour involving these modes by suggesting that in the presence of an ultrasonic wave the microscopic state of the crystal is inhomogeneous and that the free energy expansion used in the Landau theory should also include terms to account for the spatial derivatives of polarization and stress. He predicted that the maximum absorption of the ultrasonic waves must occur at the phase transition, in contrast to the relaxation mechanism for which it occurs at a point removed from the Curie point. No data can be found in the literature to support this hypothesis, and
our data has insufficient resolution of temperature to enable this question to be resolved.

The second theory which has been developed (Minaeva et al (1967) and Levanyuk (1966)) to explain the physical effects observed at the phase transition is a "fluctuation" model. This theory was originally used by Todo and Tatsuzaki (1974), Minaeva et al (1969), Strukov et al (1976), Zaporozhets et al (1970) and Kawashima et al (1976) to explain the anomalous behaviour observed for the Y propagated longitudinal mode, which according to relaxation theory should not have occurred. The "fluctuation" mechanism is based on the principle that as the vibrating ultrasonic wave causes changes in the temperature at a point then as the magnitude of the spontaneous polarization is temperature dependent, an oscillation of the spontaneous polarization will occur. This effect is independent of the direction of propagation of the ultrasonic waves and will be present for all modes of propagation.

A contribution to the magnitude of the ultrasonic wave velocity observed will be expected from the fluctuation theory for modes which also suffer from the relaxation effect. It has been shown that the contribution from the fluctuation mechanism is small when compared to contributions from the relaxation mechanism. Strukov and Yakushkin (1978) have shown that the fluctuation contribution is small for temperatures outside the region $t-t_e > 0.2 \, ^\circ C$. 

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Explanations of the discrepancies in the predictions made by the relaxation and fluctuation theories when compared to experimental results are centred around the behaviour of the domains in TGS in the vicinity of the phase transition point. Strukov and Yakushkin (1978) have shown that the magnitude of the acoustic anomaly observed in TGS crystals is dependent upon the method of sample growth. For a crystal grown in the ferroelectric phase there will be domain structures localized on the intrinsic impurities. These will only disappear after a lengthy annealing period at a temperature greater than the Curie point (Distler and Constantinova 1968). Such domain structures do not exist in crystals grown in the paraelectric phase (Strukov and Yakushkin 1978). In principle the nature of the point defects, which are responsible for the formation of the "defect domains", should also be considered, but their interaction mechanism with the acoustic waves is unclear at present.

In connection with the investigation of the fluctuation mechanism, several workers have investigated the ultrasonic properties of TGS by propagating a longitudinal mode down the ferroelectric axis (relaxation effects are not expected to be present for this mode) and observing an anomalous change in the ultrasonic wave velocity at the phase transition point. The early work of Todo and Tatsuzaki (1974), Minaeva (1969), Strukov et al (1976) and Zaporozhets et al (1970) had attributed this anomaly to the fluctuation mechanism, but the later work of Strukov and Yakushkin (1978)
suggested that the interaction of the ultrasonic waves with the domain structures in TGS present in the phase transition region was responsible for the observed anomalies. Zaporozhets and Tikhonov (1981) results showed that the magnitude of the observed anomalies was strongly influenced by the thermal and electrical conditions of the crystal under experimentation, which will affect the domain structure. It has been reported by Strukov and Yakushkin (1978) that crystals grown in the paraelectric phase did not show any anomalous behaviour for the $Y$ propagated longitudinal mode. In our work we find no anomalous behaviour for this mode.

The exact influence of the domain structures on the magnitude of the observed ultrasonic wave velocity is not clear at the present time and the reader is best referred to the papers cited and in turn their references so that he can form his own opinion.

6.3 Discussion of the present results

On examination of the experimental results reported here it can be seen that marked anomalous behaviour of the ultrasonic wave velocity for modes 8, 9, 10, 11 at the region of the phase transition has been observed (see Table 5.1 for mode identification). For mode 1 only a slight anomaly has been seen in the ultrasonic wave velocity in that it remained constant over the temperature region straddling the phase transition. The anomalies observed for modes 1, 9 and 10 can be accounted for by relaxation theory, but in the case of modes 8 and
the anomalous behaviour cannot be accounted for by the relaxation model. The observed anomaly for these modes can be accounted for by either the fluctuation model or by the mechanism described by Micheleson (1976). In the case of mode 11 the ultrasonic wave velocity changes by 20 m/s, but for the quasi-shear mode, which is subject to relaxation effects, the observed change is 120 m/s. The net effect of the interaction mechanisms described is to depress the magnitude of the ultrasonic wave velocity as the phase transition is approached. As the magnitude of the elastic stiffness constants are directly related to the observed ultrasonic wave velocity via the Christoffel equations, anomalies are observed in the magnitude of the calculated elastic stiffness constants.

On examination of the Christoffel equations, and by considering the modes which are subject to anomalous behaviour, it can be seen that out of the ten elastic stiffness constants determined we would expect $c_{22}$ and $c_{44}$ to show no anomalous behaviour at the phase transition. The most notable change observed in the remaining elastic stiffness constants occurs for $c_{33}$ which increases its magnitude by approximately 8% as the phase transition region is traversed. The elastic stiffness constant $c_{44}$ also shows a similar effect but with an increase in magnitude by 100%. This is not as significant as it first appears as the magnitude of $c_{44}$ is considerably smaller than that of $c_{33}$. The elastic stiffness constant $c_{44}$ shows similar behaviour, but is of
reduced magnitude compared to that of \( c_{33} \). The only other significant anomaly is in the measurement of \( c_{13} \), the magnitude of which shows a marked decrease of approximately 3% as the phase transition region is traversed. The properties of the remaining elastic stiffness constants show no measurable anomalous behaviour at the phase transition region.

On examination of the experimental data obtained at temperatures well removed from the phase transition, it can be seen that the temperature derivatives show differing characteristics in the ferroelectric phase as compared to those in the paraelectric phase. For \( c_{11}, c_{33} \) and \( c_{44} \), the temperature derivatives' magnitude is decreased in the paraelectric phase compared to those in the ferroelectric phase, while for \( c_{13}, c_{19}, c_{55} \) and \( c_{44} \), the temperature derivative changes sign and becomes positive. The magnitudes of the temperature derivatives for \( c_{44} \) and \( c_{22} \) are identical within experimental limits on either side of the phase transition. The temperature derivatives of the elastic stiffness constants have been reported for the paraelectric phase by Haussuhl and Albers (1977) who used their own unique axial system.

The temperature dependences of the elastic stiffness constants have also been investigated by two other groups of workers. Luspin and Hauret (1977) used a Brillouin scattering method to determine the elastic stiffness constants \( c_{11}, c_{22} \) and \( c_{33} \) while Tylczynski (1981) used an ultrasonic method and reported the temperature dependence
of $c_{11}, c_{33}, c_{13}, c_{35}, c_{15}$ and $c_{39}$. On comparing these workers' experimental data with the present work it can be seen that we have good agreement for the behaviour of $c_{33}$, although the results of Tylczynski (1981) indicate that the anomaly observed for this elastic stiffness constant occurs over a very narrow temperature range, whereas Luspin and Hauret (1977) along with this work show that the change occurs over a broad temperature band of approximately $5^\circ C$.

For $c_{11}$, Luspin and Hauret (1977) and Tylczynski (1981) found similar features, namely an anomaly at the phase transition, with the temperature derivative of the elastic stiffness constants in the paraelectric phase reduced in magnitude. The present work shows a similar result, but we disagree over the behaviour at the phase transition: there is no anomaly in the magnitude of this elastic stiffness constant.

For the elastic stiffness constants $c_{13}, c_{35}, c_{15}$ and $c_{39}$ we find substantial disagreement with the work of Tylczynski (1981). Considering $c_{39}$ first, Tylczynski (1981) shows that its magnitude decreases with temperature as the phase transition is approached, then increases as the phase transition region is traversed and then remains static in the paraelectric phase. The present work shows no such increase in magnitude at the phase transition, and in the paraelectric phase the magnitude decreases. Similarly for $c_{13}$ there is little agreement. We both agree that the magnitude of the elastic stiffness constant decreases with temperature,
but over the phase transition region we show that the magnitude decrease as the temperature increases, while Tylczynski (1981) shows the opposite. In the paraelectric phase the temperature derivative is negative while our work shows a positive derivative. However it should be noted that the experimental error involved in determining this particular elastic constant is large. For $c_{15}$ and $c_{36}$ we find an entire disagreement, but since these elastic stiffness constants are small in magnitude anyway, the experimental error is substantial.

It can be seen that generally the values for the pressure derivatives of the elastic stiffness constants increase with temperature, all derivatives show an anomaly at the phase transition varying from a slight effect in $\Delta c_{22}/\Delta P$ to the more larger change in $\Delta c_{44}/\Delta P$.

6.4 Elastic properties of TGS

Using the elastic stiffness constant set obtained in this work, the three wave velocities have been calculated for propagation directions at 1° intervals around the YZ, ZX and XY planes by computation of the eigenvalues of the Christoffel equations. The resultant cross-sections of the three elastic wave velocity surfaces, presented in figures 6.1 to 6.3 follow the crystal Laue symmetry. Additional calculations show that the velocity surface features exhibit no discernible change over the temperature range investigated in this work.

In general, in a crystal three distinct, mutually orthogonal elastic plane waves propagate along a given
Fig 6.1 Velocity surface of TGS for the YZ plane.
Fig 6.2 Velocity surface of TGS for the XZ plane.
Fig 6.3 Velocity surface of T88 for the XY plane.
direction, these modes being neither pure longitudinal or
pure transverse. However, along certain special
directions, the pure mode directions (or acoustic axis),
a pure longitudinal and two pure transverse waves do
propagate. Knowledge of these directions can be useful
because it is usually easier to excite such modes with X-
or Y- cut transducers and also there is no deviation of
the energy flux from the propagation direction —
minimizing the possibility of sidewall reflections. The
conditions for a pure mode direction are (Brugger (1965))

\[ E_{ijk} c_{ijrs} N_k N_j N_n N_s = 0 \]

for a monoclinic crystal in the XZ plane this can be
shown to take the form

\[ N_1 N_3 \left[ N_1^2 A_1 - N_2^2 c_{ij} \right] + N_1^2 (3 N_3^2 - N_1^2) C_{15} + N_2^2 (3 N_3^2 - N_3^2) C_{35} = 0 \]

or writing the direction cosine ratio \( N_1 / N_2 \) as \( u \)

\[-u^4 c_{15} + A_1 u^3 + 3 u^2 (c_{15} - c_{35}) - u_1 c_1 + c_{35} = 0 \]

Here, \( A_1 = c_{11} - 2c_{55} c_{13} \) and \( c_1 = c_{33} - 2c_{55} c_{13} \). Substituting
the elastic constant values obtained from this work
(Table 5.2) into this equation, shows that there is a
pure mode axis for TGS in the XZ plane at 9.4° from the
+Z axis towards the +X axis; this position is shown in
Fig 6.2. A second pure mode axis occurs at 106.5°.

By using the known elastic stiffness constants, the
particle displacement vectors for each of the three modes
of vibration for a given direction can be calculated. By
taking the vector dot product of the particle
displacement vector and the corresponding wave propagation vector, the angle of deviation between these two vectors can be obtained. This operation has been carried out for modes propagated in the XY, XZ, YZ planes in TGS and the results are plotted in Figs 6.4 to 6.6 (note we have only plotted the moduls of the angle of deviation). These plots are useful as they can indicate the best experimental modes to be used if it is not possible to use pure mode directions. Ideally one would look for the smallest deviation angle so that most of the input energy is coupled into this operating mode and not into other spurious modes. It can be seen that the choice of the [101] direction was not amongst the better selection in this work as it is a high off-axis case.

For TGS there are significant changes in the wave velocity as the crystal goes from the ferroelectric to the parelectric phase. Hence it is useful to know how the polarisation vector deviations from propagation direction alter with temperature. The appropriate calculation have been carried out with the results plotted in figures 6.7 to 6.9. In fact the deviations are not very large and should have little influence on the design of ultrasonic experiments carried out in the phase transition.

Knowledge of the elastic stiffness tensor components enables determination of a material's response to any applied stress within the Hooke's law regime. Youngs modulus $E$, the measure of the ratio of an applied longitudinal stress to the resulting longitudinal strain,
Fig 6.4 Deviation of the particle displacement vector from the wave propagation vector for TGS at 20°C for the YZ plane.

Fig 6.5 Deviation of the particle displacement vector from the wave propagation vector for TGS at 20°C for the XZ plane.
Fig 6.6 Deviation of the particle displacement vector from the wave propagation vector for TGS at 20 C for the XY plane.

Fig 6.7 Variation of the angle between the propagation direction vector and the particle displacement vector with temperature for an ultrasonic wave propagated in the [101] direction.
FIG 6.8 Variation of the angle between the propagation direction vector and the particle displacement vector with temperature for an ultrasonic wave propagated in the [100] direction.

FIG 6.9 Variation of the angle between the propagation direction vector and the particle displacement vector with temperature for an ultrasonic wave propagated in the [001] direction.
for a monoclinic crystal (Nye (1957)) is

\[ E = \left\{ J_1^2 S_{11} + 2 J_1^2 J_2^2 S_{12} + 2 J_1^2 J_3^2 S_{13} + 2 J_2^2 J_3^2 S_{15} + J_2^2 S_{22} + 2 J_2^2 J_3^2 S_{23} + 2 J_1 J_2^2 J_3 S_{25} + J_3^4 S_{33} + 2 J_1 J_3^2 S_{35} + J_1^2 J_3^2 S_{55} + J_1^2 J_2^2 S_{66} \right\}^{-1} \]

for a stress in the direction labelled by the direction cosine \( l_1, l_2, l_3 \). Young's modulus can be represented by a surface which gives a useful visual guide to the elastic behaviour of a crystal. Three plane (yz, xz and xy) cross-sections of this surface for TGS are presented in Fig 6.10 to 6.12. For a given stress applied along a crystallographic axis, the strain is greatest along the z-axis and least along the x-axis.

The volume compressibility \(-\Delta/P\) (where \( \Delta \) is the dilation) is \( S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31}) \) equal to \( 4.4 \times 10^{-11} \text{ m}^2\text{N} \) for TGS. Hence the bulk modulus, defined as the reciprocal of the compressibility is \( 2.27 \times 10^{11} \text{ Nm}^{-2} \) at 20 °C. Another elastic property commonly required is the linear compressibility, which is the relative decrease in length of a line when a crystal is subjected to hydrostatic pressure and is given by \( S_{11} l_1, l_1, l_1 \). Here \( l_1 \) is a unit vector in the direction of the stretch of the line. For a monoclinic crystal the linear compressibility is (Nye (1957))

\[ \beta = (S_{11} + S_{12} + S_{13}) J_1^2 + (S_{12} + S_{22} + S_{23}) J_2^2 + (S_{13} + S_{23} + S_{33}) J_3^2 + (S_{15} + S_{25} + S_{35}) J_3 J_1 \]

The marked anisotropic behaviour of the linear compressibility of TGS can be seen in the YZ, XZ and XY plane plots of the property in Figs 6.13 to 6.15.
Fig. 6.10 YZ plane cross-sections of the Young's modulus surface of TBS. Units are $10^{10}$ N m$^{-2}$. 
Fig 6.11 XZ plane cross-sections of the Young's modulus surface of T88. Units are $10^{10}$ N m$^{-2}$. 

*Note:* The diagram depicts the variation of Young's modulus with respect to the angle $	heta$ for a specific phi value. The units are given as $10^{10}$ N m$^{-2}$. The plots illustrate the variation across different orientations, showing how the modulus changes with angle.
Fig 6.12 XY plane cross-sections of the Young's modulus surface of TBS. Units are $10^5$ N m$^{-2}$. 
Fig 6.13 YZ plane cross-sections of the linear compressibility surface of TGS. Units are $10^{-16} \text{m}^2 \text{N}^{-1}$. 
Fig 6.14 XZ plane cross-sections of the linear compressibility surface of TGS. Units are \(10^{-15} \text{ m}^2 \text{ N}^{-1}\). 

\[ \text{Linear Compressibility} \]

\[ \theta / \text{Deg} \quad (\phi = 0) \]
Fig 6.15 XY plane cross-sections of the linear compressibility surface of TGS. Units are $10^{-9}$ m$^2$ N$^{-1}$. 
There is a simplifying feature of the elastic behaviour of TGS which is a helpful guide and may well be of practical value. This can be seen by considering the elastic stiffening constant matrix which collates the elastic constants. Now the elastic constants \( C_{19}, C_{29}, C_{39} \) and \( C_{49} \) are an order of magnitude smaller than the others (Table 5.2). If they were zero, the matrix would be that for an orthorhombic crystal. The wave velocity (Fig 6.1 to 6.3), Young's modulus (Fig 6.10 to 6.12) and compressibility surfaces (Fig 6.13 to 6.15) cross-sections, especially those of YZ and XY planes, show clearly this pseudo-orthorhombic elastic behaviour of TGS. In the XZ plane the surfaces are rotated away from the crystallographic X- and Z-axis to the acoustic axes; there is some distortion because the two acoustic axes in the xz plane are not perpendicular to each other.

The unit cell volume of TGS is 0.640 nm\(^3\); there are two formula units, each comprising 37 atoms, per primitive unit cell (Wood and Holden (1957). Hence there are \( 3N (=222) \) degrees of freedom and therefore 3N phonon modes at the Brillouin zone centre. This complex vibrational spectrum makes for difficulties in quantitative analysis of lattice vibration properties. Thus it is useful to have an estimate of the elastic Debye temperature, \( \Theta_d \), corresponding to the acoustic modes alone, which can be obtained from the measured elastic constants by integrating

\[
\Theta_d^e = \left( \frac{9N}{4\pi^2 \hbar^3 V} \right)^{1/3} \frac{\hbar}{k} \left[ \int \left( \frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3} \right) \frac{d^3 \mathbf{q}}{2\pi^3} \right]^{1/3}
\]
over velocity space. Here the $v_i$ (i= 1,2,3) are the three velocities obtained as the eigenvalues of the Christoffel equations for a given direction. This integration has been carried out over the whole of velocity space for all three modes (the curves in Fig 6.1 to 6.3 show only the YZ, XZ and XY plane cross-sections of these velocity surfaces). The integral over solid angle has been approximated by a sum taken at 10288 points each subtending an equal solid angle $\Delta \Omega$ of $1.218 \times 10^{-3}$ steradians. The Debye temperature $\Theta_d$ of TGS calculated from the room temperature elastic constants (table 5.2) is 170 K. Using the room temperature, rather than low temperature elastic constant data, can be expected to produce quite a large error (of the order of 10 k) in $\Theta_d$. Lawless (1976) found that the low-temperature specific heats of several ferroelectrics, including TGS, are complex and involve, in addition to the Debye $T^3$ term, a $T^{3/2}$ component, which he ascribed to a contribution from domain walls. He obtained a value of 107 K for $\Theta_d$ for TGS. Thus there is a substantial difference between the Debye temperature obtained from the specific heat and elastic constants, perhaps not surprisingly in view of the complexities of the lattice dynamical behaviour and the domain wall effects which must be present in TGS.
APPENDIX 1

Determination of the elastic compliances.

The elastic compliances are determined from the elastic stiffness constants by using the following relationship (Nye 1957)

\[ S_{qr} = \Delta c_{qr} / \Delta c \]

where \( \Delta c \) is the determinant of the elastic stiffness matrix and \( \Delta c_{qr} \) is the relevant minor determinant associated with \( S_{qr} \). The expansion of the determinants has been carried out, so as to express each of the elastic compliances as a function of numerous elastic stiffness constants. The obtained relationships are given overleaf.

To check that no errors had occurred during the expansion of the determinants the values derived for the elastic compliances using the relationships overleaf were compared with those obtained using an alternative numerical method (which involved finding the inverse of the elastic stiffness matrix). There were found to be no differences in the magnitudes of the calculated elastic compliances.
\[ \Delta C = (c_{66}c_{44} - c_{46}^2) \times \{ \\
\quad c_{11}c_{22}(c_{33}c_{88} - c_{38}^2) - c_{11}c_{23}(c_{23}c_{85} - c_{33}c_{25}) \\
\quad + \ c_{11}c_{29}(c_{23}c_{85} - c_{33}c_{29}) - c_{12}(c_{33}c_{88} - c_{38}^2) \\
\quad + \ c_{12}c_{23}(c_{13}c_{88} - c_{35}c_{15}) - c_{12}c_{29}(c_{13}c_{35} - c_{15}c_{33}) \\
\quad + \ c_{13}c_{12}(c_{23}c_{88} - c_{35}c_{29}) - c_{22}c_{13}(c_{13}c_{85} - c_{35}c_{15}) \\
\quad + \ c_{13}c_{25}(c_{13}c_{29} - c_{33}c_{10}) - c_{15}c_{12}(c_{23}c_{35} - c_{33}c_{25}) \\
\quad + \ c_{15}c_{22}(c_{13}c_{39} - c_{33}c_{19}) - c_{15}c_{23}(c_{13}c_{29} - c_{23}c_{15}) \} \\
\{ \\
\quad S_{11} = (c_{44}c_{66} - c_{46}^2)[c_{22}(c_{33}c_{88} - c_{38}^2) - c_{29}(c_{23}c_{35} - c_{33}c_{35})] / \Delta C \\
\quad S_{12} = (c_{46}^2 - c_{66}c_{44})[c_{12}(c_{33}c_{88} - c_{38}^2) - c_{23}(c_{13}c_{85} - c_{35}c_{15}) + c_{29}(c_{13}c_{35} - c_{15}c_{33})] / \Delta C \\
\quad S_{13} = (c_{44}c_{66} - c_{46}^2)[c_{12}(c_{23}c_{88} - c_{25}c_{35}) - c_{22}(c_{13}c_{85} - c_{35}c_{15}) + c_{29}(c_{13}c_{25} - c_{23}c_{15})] / \Delta C \\
\quad S_{15} = (c_{46}^2 - c_{66}c_{44})[c_{12}(c_{23}c_{35} - c_{33}c_{29}) - c_{22}(c_{13}c_{39} - c_{15}c_{33}) + c_{25}(c_{13}c_{25} - c_{15}c_{23})] / \Delta C \\
\quad S_{22} = (c_{44}c_{66} - c_{46}^2)[c_{11}(c_{33}c_{88} - c_{38}^2) - c_{13}(c_{13}c_{85} - c_{15}c_{35}) + c_{19}(c_{13}c_{35} - c_{15}c_{33})] / \Delta C \\
\quad S_{23} = (c_{46}^2 - c_{66}c_{44})[c_{11}(c_{23}c_{85} - c_{25}c_{35}) - c_{12}(c_{13}c_{85} - c_{35}c_{15}) + c_{18}(c_{13}c_{25} - c_{23}c_{15})] / \Delta C \} \]
\[ S_{29} = (c_{66}c_{44} - c_{46}^2)[c_{11}(c_{23}c_{39} - c_{29}c_{33}) - c_{12}(c_{13}c_{35} - c_{33}c_{19}) + c_{13}(c_{13}c_{25} - c_{19}c_{23})] / \Delta C \]

\[ S_{33} = (c_{44}c_{66} - c_{46}^2)[c_{11}(c_{22}c_{39} - c_{29}^2) - c_{12}(c_{12}c_{35} - c_{19}c_{25}) + c_{18}(c_{12}c_{25} - c_{19}c_{22})] / \Delta C \]

\[ S_{39} = (c_{46}^2 - c_{44}c_{66})[c_{11}(c_{22}c_{35} - c_{23}c_{29}) - c_{12}(c_{12}c_{35} - c_{23}c_{19}) + c_{13}(c_{12}c_{25} - c_{22}c_{19})] / \Delta C \]

\[ S_{44} = c_{66}c_{11}[c_{22}(c_{33}c_{39} - c_{39}^2) - c_{23}(c_{23}c_{39} - c_{29}c_{35}) + c_{25}(c_{23}c_{39} - c_{39}c_{29})] - c_{12}c_{66}[c_{12}(c_{33}c_{39} - c_{39}^2) - c_{23}(c_{33}c_{39} - c_{29}c_{35}) + c_{25}(c_{33}c_{39} - c_{39}c_{29})] + c_{23}(c_{13}c_{39} - c_{39}c_{19}) + c_{25}(c_{13}c_{39} - c_{39}c_{19})] + c_{66}c_{13}[c_{12}(c_{23}c_{39} - c_{39}c_{29}) - c_{22}(c_{13}c_{39} - c_{39}c_{19})] + c_{29}(c_{13}c_{29} - c_{23}c_{19}) - c_{18}c_{66}[c_{12}(c_{23}c_{39} - c_{29}c_{35}) - c_{22}(c_{13}c_{39} - c_{29}c_{19})] - c_{22}(c_{13}c_{39} - c_{19}c_{33}) + c_{23}(c_{13}c_{29} - c_{23}c_{19})] / \Delta C \]

\[ S_{46} = -c_{46}c_{11}[c_{22}(c_{33}c_{39} - c_{39}^2) - c_{23}(c_{23}c_{39} - c_{39}c_{29}) + c_{25}(c_{23}c_{39} - c_{39}c_{29})] + c_{46}c_{12}[c_{12}(c_{33}c_{39} - c_{39}^2) - c_{23}(c_{33}c_{39} - c_{39}c_{29}) + c_{25}(c_{33}c_{39} - c_{39}c_{29})] - c_{23}(c_{13}c_{39} - c_{39}c_{19}) + c_{25}(c_{13}c_{39} - c_{39}c_{19})] - c_{46}c_{13}[c_{12}(c_{23}c_{39} - c_{39}c_{29}) - c_{22}(c_{13}c_{39} - c_{39}c_{19})] + c_{29}(c_{13}c_{29} - c_{23}c_{19}) + c_{46}c_{18}[c_{12}(c_{23}c_{39} - c_{39}c_{29}) - c_{22}(c_{13}c_{39} - c_{39}c_{19})] + c_{22}(c_{13}c_{39} - c_{39}c_{19}) + c_{23}(c_{13}c_{29} - c_{23}c_{19})] / \Delta C \]

\[ S_{66} = (c_{66}c_{44} - c_{46}^2)[c_{11}(c_{22}c_{33} - c_{23}^2) - c_{12}(c_{12}c_{33} - c_{23}c_{13}) + c_{13}(c_{12}c_{23} - c_{22}c_{13})] / \Delta C \]
\[ S_{66} = c_{44}c_{11}[c_{22}(c_{33}c_{55} - c_{35}) - c_{23}(c_{23}c_{55} - c_{35}c_{25}) + \\
  c_{25}(c_{25}c_{35} - c_{33}c_{25})] - c_{12}c_{44}[c_{12}(c_{33}c_{55} - c_{35}^2) - \\
  c_{23}(c_{13}c_{55} - c_{15}c_{35}) + c_{25}(c_{13}c_{35} - c_{15}c_{33})] + \\
  c_{13}c_{44}[c_{12}(c_{23}c_{55} - c_{25}c_{35}) - c_{22}(c_{13}c_{55} - c_{35}c_{15}) + \\
  c_{25}(c_{13}c_{29} - c_{23}c_{15})] - c_{16}c_{44}[c_{12}(c_{23}c_{39} - c_{33}c_{25}) - \\
  c_{22}(c_{13}c_{39} - c_{33}c_{15}) + c_{23}(c_{13}c_{29} - c_{15}c_{23})] / \Delta C \]
The following computer program calculates the values of the 10 most readily obtained elastic stiffness constants for a monoclinic crystal using the sample density and the experimentally measured ultrasonic wave velocities for modes $V_1$ to $V_{12}$ (for mode identification see Table 4.1).

10 REM ******************************************************
20 REM *** Determination of 10 elastic constants ***
30 REM *** for a monoclinic crystal. ***
40 REM *** c Solid State Physics ***
50 REM *** University of Bath June 1983 ***
60 REM ******************************************************
70 FT=0: DIM C(10)
80 MODE 7
90 PRINT '****** Routine to find ten""" Elastic constants""" of a monoclinic crystal"""
10 REM c Solid State June 1983"
110 TIME=0: REPEAT UNTIL TIME>500
120 REM print out velocities as user check
130 READ DNsREM density
140 DN=INT(DN*10)/10
150 READ VI, V2, V3, V4, V5, V6, V7, V8, V9
160 READ VA, VB, VC
170 VA=INT(VA*10)/10: VB=INT(VB*10)/10
180 VC=INT(VC*10)/10
190 CLS: PRINT'****** how many significant """" figures in the velocity"""" range 1 to 5 """";
210 DA=V1: GOSUB 2120: V1=DA
220 DA=V2: GOSUB 2120: V2=DA
230 DA=V3: GOSUB 2120: V3=DA
240 DA=V4: GOSUB 2120: V4=DA
250 DA=V5: GOSUB 2120: V5=DA
260 DA=V6: GOSUB 2120: V6=DA
270 DA=V7: GOSUB 2120: V7=DA
280 DA=V8: GOSUB 2120: V8=DA
290 DA=V9: GOSUB 2120: V9=DA
300 DA=VA: GOSUB 2120: VA=DA
310 DA=VB: GOSUB 2120: VB=DA
320 DA=VC: GOSUB 2120: VC=DA
330 CLS
340 PRINT'****** density = "; DN;" kg/m^3"
350 PRINT'****** v1 = "; V1;" m/s"
360 PRINT'****** v2 = "; V2;" m/s"
370 PRINT'****** v3 = "; V3;" m/s"
380 PRINT'****** v4 = "; V4;" m/s"
390 PRINT "v5 = ";v5;" m/s"
400 PRINT "v6 = ";v6;" m/s":PRINT" Press any
key to continue":A=GET:CLS
410 PRINT "v7 = ";v7;" m/s"
420 PRINT "v8 = ";v8;" m/s"
430 PRINT "v9 = ";v9;" m/s"
440 PRINT "v10 = ";v10;" m/s"
450 PRINT "v11 = ";v11;" m/s"
460 PRINT "v12 = ";v12;" m/s"
470 PRINT Press any key to continue":A=GET:CLS
480 REM evaluation of elastic constants c66,c22,c44,c46
490 PRINT How many significant figures" determined to (1 to 5)"
500 REPEAT:A=GET:UNTIL A>48 AND A<56:BA=A-49
510 REM determine c66
520 C6=DN*V2^2:CI=C6
530 GOSUB 2030
540 C6=CI:REM saving rounded elastic constants
550 REM calculate c22
560 C2=DN*V5^2:CI=C2
570 GOSUB 2030
580 C2=CI
590 REM calculate c44
600 C4=DN*V8^2:CI=C4
610 GOSUB 2030
620 C4=CI
630 REM calculate c46
640 CC=0.5*(2*DN*V8^2-(C4+C6)):CI=CC
650 GOSUB 2030
660 CC=CI
670 REM the easy four now determined
680 CLS:PRINT "c22 = ";c22;" Nm"
690 PRINT "c66 = ";c66;" Nm"
700 PRINT "c44 = ";c44;" Nm"
710 PRINT "c46 = ";c46;" Nm"
720 PRINT Press any key to continue":OGET("FX21, 0"):A=GET
730 CLS:PRINT "i need to think this over for a bit"
740 REM using equations to get c55 first
750 REM in sheet a=pa, b=pd, d=pe ,f=pm, z=x=x
760 PA=DN*(V1^2+V3^2):D7=1
770 PD=DN*DN*V1^2*V3^2
780 PE=DN*(V7^2+V9^2)
790 PM=DN*DN*V7^2*V9^2
800 DX=(V^2+VC^2-0.5*(V1^2+V3^2+V9^2+V7^2))*DN
810 ZX=DX^2
820 REM set up system to search for root using newtons
method
830 FDR I=1 TO 100
840 CS=I*1.0E09
850 QW=CG*(PA-CG)-PD:QP=CG*(PE-CG)-PM
860 IF WQ<0 OR QP<0 THEN 1010
870 IF FT=0 THEN U=SQR(WQ)+SQR(QP):GOTO 890
880 U=SQR(WQ)-SQR(QP):REPEAT deals with negative case
890 FT=U^2-ZX
900 BF=(PA-2*CG)/SQR(WQ)
910 BK=(PE-2*CG)/SQR(QP)
920 BP=U*(BF+BK)
930 CL=CG
940 CG=CL-TP/BP;REM new cg
950 IF ABS(CG-CL)>.002 THEN 1000
960 CI=CG:GOSUB 2030:CG=CI;REM constant rounded
970 IF C(D7-1)<CG THEN C(D7)=CG;D7=D7+1
980 REM elements same so continue
1000 GOTO 850; REM repeat iteration
1010 NEXT I
1020 REM need to check various solutions
1030 IF C(1)=0.0 THEN 1060
1040 IF C(2)<0.0 THEN 1070
1050 C5=C(1):TB=1;GOTO 1120;REM we have a single solution
so continue
1060 PRINT" no real solution for c55 ..."
1070 USING exact solution";STOP
1080 *FX21,0
1090 PRINT" ;Press any key to continue";A=GET
1100 FOR I=1 TO 10;IF C(I+1)=0 THEN TB=I;I=10
1110 NEXT I
1120 REM now calculate c11, c15, c33, c35 from the
relevant equations
1130 FOR K=1 TO TB
1140 C5=C(K)
1150 REM get ell
1160 C1=PA-C5:CI=C1;GOSUB 2030:C1=CI
1170 REM get c33
1180 C3=PE-C5:CI=C3;GOSUB 2030:C3=CI
1190 REM initial we can only obtain magnitude of c35 and
1200 REM solve for c35
1210 CS=C5*C3-PM
1220 IF CS<0 THEN PRINT" no real solution for
1230 C35";GOTO 1250
1240 CF=SQR(CS)
1250 CI=CF;GOSUB 2030:CF=CI
1260 REM get c15
1270 CS=C1*C5-PM
1280 IF CS<0.0 THEN PRINT" no real solution for c15";GOTO
1290 1300
1300 CX=SQR(CS)
1310 CI=CX;GOSUB 2030:CX=CI
1320 REM must deal with case of above to not known, +
sign problem
1330 REM user must make decision on sign of c15 and c35
1340 CLS;PRINT" *** user decision ***"
1350 PRINT" c15 +c35 = "";CI=DX;GOSUB
2030:DX=CI;PRINTDX
1340 PRINT" c15 = ";CI
1350 PRINT" c35 = ";CI
1360 PRINT" c15+c35 both -ve ..........1"
1370 PRINT" c15+c35 both +ve ..........2"
1380 PRINT" c15 -ve c35 +ve ..........3"
1390 PRINT" c15 +ve c35 -ve ..........4"
1400 PRINT" Select option";*FX21,0
1410 A=GET

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1420 IF A=49 THEN CX=-CX:CF=-CF:GOTO 1470
1430 IF A=50 THEN 1470
1440 IF A=51 THEN CX=-CX:GOTO 1470
1450 IF A=52 THEN CF=-CF:GOTO 1470
1460 PRINT "range 1 to 4 please":GOTO 1410
1470 PRINT "REM decision made"
1480 IF FT=0 THEN CLS:PRINT "SOLVED FOR +VE CASE"
1490 CLS:PRINT "SOLVED FOR -VE CASE SOLUTION":K
1500 PRINT "c5=";C5;" nm"
1510 PRINT "c11=";C11;" nm"
1520 PRINT "c33=";C33;" nm"
1530 PRINT "c35=";CF;" nm"
1540 PRINT "c15=";CX;" nm"
1550 PRINT "Press a key to continue":A=GET:CLS
1560 REM calculate polarisation vectors for x axis
1570 PRINT "polarisation vectors":VT=V1*V1
1580 RU=CC*(C6-DN*VT)/((C6-DN*VT)*(C5-DN*VT))
1590 PRINT "for x prop long u3/u1=";RU
1600 U1=1:U3=RU:NC=SQR(1+RU*RU):U1=U1/NC:U3=U3/NC:REM
1610 PRINT "normilsed vectors u1=";INT(1000*U1)/1000;
1620 PRINT "u3=";INT(1000*U3)/1000:VT=V9*V9:REM now do
1630 FOR z axis
1640 U1=1:U3=RU:NC=SQR(1+U1*U1):U1=U1/NC:U3=U3/NC
1650 PRINT "normilsed vectors u1=";INT(1000*U1)/1000;
1660 PRINT "u3=";INT(1000*U3)/1000:REM polarisation vectors are done"
1670 PRINT "press any key to continue":*FX21,0
1680 A=GET:CLS
1690 REM calculate c13
1700 ZT=(C1+C5+C3+2*CX)*(C5+C3+2*CF)-4*DN^2*VAA^2*VC^2
1710 PRINT "solving for c13"
1720 PRINT "positive square root"
1730 IF ZT<0 THEN PRINT "no real solution for c13":END
1740 CU=SQR(ZT)-(CX+CF+C5):CI=CU:GOSUB 2030:CU=CI
1750 GOSUB 1960
1760 PRINT "c13=";CU;" n/m"
1770 PRINT "long mode prop [101]
1780 U3/U1=";INT(RU*1000)/1000
1790 U1=1:U3=RU:NC=SQR(1+RU*RU):U1=U1/NC:U3=U3/NC
1800 PRINT "normilsed vectors u1=";INT(1000*U1)/1000;
1810 PRINT "u3=";INT(1000*U3)/1000
1820 PRINT "negative square root"
1830 CU=-SQR(ZT)-(CX+CF+C5):CI=CU:GOSUB 2030:CU=CI
1840 GOSUB 1960
1850 PRINT "c13=";CU;" n/m"
1860 PRINT "long mode prop [101]
1870 U3/U1=";INT(RU*1000)/1000
1880 FOR tb number of solutions
1890 IF FT=1 THEN END
1900 IF FT=0 THEN CLS:PRINT "SOLVED FOR +VE CASE"
1910 CLS:PRINT "SOLVED FOR -VE CASE SOLUTION":K
1920 REM looping for tb number of solutions
1930 IF FT=1 THEN END
1940 \text{FT}=1; \text{D7}=1; \text{FOR } J=1 \text{ TO } 10; C(J)=0; \text{NEXT}; \text{CLS}; \text{PRINT}"

need to think this over"

1950 \text{FOR } I=1 \text{ TO } 10; C(I)=0; \text{NEXT } I; \text{GOTO } 830

1960 YA=0.5*(C6+C4+2*CC)

1980 YC=0.5*(C5+C3+2*CF)

1990 VT=DN*VC*VC

2000 RU=-YA*(YB-VT)/((YB-VT)*(YC-VT))

2010 RETURN

2020 END

2030 REM rounding routine for elastic constants

2040 BB=BA+1

2050 IC=\text{INT}\left((CI*10^{BB})/1.0E10\right)

2060 CD=\text{INT}\left((CI*10^{BA})/1.0E10\right)

2070 BI=IC-10*CD

2080 IF BI<5 THEN 2100

2090 CD=CD+1

2100 CI=CD*1.0E10/\left(10^{BA}\right)

2110 RETURN

2120 REM rounding routine for velocities

2130 BE=BD+1

2140 IC=\text{INT}\left((DA*10^{BE})/1.0E03\right)

2150 CD=\text{INT}\left((DA*10^{BD})/1.0E03\right)

2160 BI=IC-10*CD

2170 IF BI<5 THEN 2190

2180 CD=CD+1

2190 DA=CD*1.0E3/\left(10^{BD}\right)

2200 RETURN

2210 REM data input

2220 REM density

2230 DATA 1680

2240 DATA 5127.6, 1899.6, 2518.4

2250 DATA 2456.6, 4460.4, 1939.6

2260 DATA 2510.6, 2488.3, 4045.8

2270 DATA 2273.0, 2283.6, 4527.0
APPENDIX 2.B

The following computer program calculates the elastic stiffness constants $c_{12}$, $c_{25}$ and $c_{23}$ using the procedure described in section 4.3.

50PRINT" SOLVING FOR C25 USING (O11)
DIRECTION"
60FOR I=1 TO 5000:NEXT I
100DIM C(10),D(100),B(100)
110PRINT" HOW MANY SIGNIFICANT FIGURES"
120PRINT" ARE THE CONSTANTS TO BE"'
130INPUT" DETERMINED TO (RANGE 1-5) ";BA
140IF BA<1 OR BA>5 THEN 110
150BA=BA-1
160REM INPUT ELASTIC CONSTANTS AND VELOCITIES NEEDED FROM DISC
170E*="":BC=BC+1
180INPUT" DATA FILE NAME "A*
190IF A*=" " THEN 180
200INPUT" DRIVE NUMBER OF DATA FILE "N
210*0,N,"R",A*,E*
220*R,A*:DN=VAL(A*)
230*R,A*:C1=VAL(A*)
240*R,A*:CU=VAL(A*)
250*R,A*:CX=VAL(A*)
260*R,A*:C2=VAL(A*)
270*R,A*:C3=VAL(A*)
280*R,A*:CF=VAL(A*)
290*R,A*:C4=VAL(A*)
300*R,A*:CC=VAL(A*)
310*R,A*:C5=VAL(A*)
320*R,A*:C6=VAL(A*)
330*R,A*:VD=VAL(A*)
340*R,A*:VE=VAL(A*)
350*R,A*:VF=VAL(A*)
360*R,A*:VG=VAL(A*)
370*R,A*:VH=VAL(A*)
380*R,A*:VI=VAL(A*)
390*C
391INPUT" OUTPUT TO PRINTER "A*:IF A*=" "
400PRINT":PRINT1,"":PRINT1,"
DENSITY=":DN;"KG/M^3"
410PRINT1,"":PRINT1,"" C11=":C1;" NM"
420PRINT1,"":PRINT1,"" C13=":CU;" NM"
430PRINT1,"":PRINT1,"" C15=":CX;" NM"
440PRINT1,"":PRINT1,"" C22=":C2;" NM"
450PRINT1,"":PRINT1,"" C33=":C3;" NM"
460 PRINT "$1", "•: PRINT$1, " C35="; CF; " NM"
470 PRINT$1," •: PRINT$1, " C34="; C4; " NM"
480 PRINT$1," •: PRINT$1, " C46="; CC; " NM"
490 PRINT$1, "$1: PRINT$1, " C55="; C5; " NM"
500 PRINT$1, "$1: PRINT$1, " C66="; C6; " NM"
510 PRINT" PRESS ANY KEY TO CONTINUE"
520 POKE 158, 0: REM EMPTY KEY BOARD
530 GET A$: IF A$="" THEN 530
540 PRINT$1," •: PRINT$1, "$1: PRINT$1, " V13="; VD; " M/S"
550 PRINT$1, "$1: PRINT$1, " V14="; VE; " M/S"
560 PRINT$1, "$1: PRINT$1, " VI5="; VF; " M/S"
570 PRINT$1, "$1: PRINT$1, " VI6="; VG; " M/S"
580 PRINT$1, "$1: PRINT$1, " V17="; VH; " M/S"
590 PRINT$1, "$1: PRINT$1, " V18="; VI; " M/S"
600 PRINT" PRESS ANY KEY TO CONTINUE"
610 POKE 158, 0
620 GET A$: IF A$="" THEN 620
630 PRINT" QUIET I'M TRYING TO THINK"
700 KD = (C2 + 2*C4 + C3) * (C6 + C5) + (C2 + C4) * (C4 + C3) - (CC + CF)^2
710 KD = KD - 4*DN^2*(VG^2*VH^2 + VG^2*VI^2 + VH^2*VI^2)
720 NA = 8*DN^3*VG^2*VH^2*VI^2 - (C6 + C5) * (C2 + C4) * (C4 + C3) - (C2 + C4) * (CC + CF)^2
730 LA = 2*(CC + CF); OA = C6 + C5; JD = C4 + C3
740 REM SECTION TO FIND REGION WHERE WE HAVE + SOLUTION
750 OA9 = SQR(KD); REM ADJUST
760 OA9 = -A9: REM A9, A8 FIXES LIMIT FOR ITERATIONS
770 REM DO FOR POSITIVE SECTION
780 PRINT" QUIET I'M TRYING TO THINK"
790 FOR I = 1 TO 10: C(I) = 0: NEXT I: REM CLEARS HOLDING ARRAY
800 X = A9: IF KD - X^2 < 0 THEN A9 = A9 - 1.0E07: GOTO 800: REM REDUCES A9 TO BOUNDARY
810 A8 = -A9: X = A8: Z = KD - X^2: GOSUB 2200: REM KICKS OUT IF ERROR
820 REM WE HAVE NOW HOMED IN FROM THE TOP AND BOTTOM TO GET ROOT NEAR BOUNDARY
830 FOR I = A8 TO A9 STEP 1.0E10
840 PRINT" • CASE I = "; I
850 X = I: GOSUB 2180: NEXT I: REM DEALING WITH POSITIVE CASE
860 X = A9: Z = KD - X^2: GOSUB 2200: REM DOES HIGH CASE LAST TO PREVENT DOUBLING
870 REM HUNT FOR POSITIVE SOLUTION TO C25
880 PRINT"
890 IF C(1) = 0 THEN GT = 1: GOTO 940: REM NO SOLUTION
900 IF C(2) = 0 THEN CT = 1: GOTO 960: REM ONE SOLUTION
910 FOR I = 2 TO 10
920 IF C(I) = 0 THEN CT = I - 1: I = 10
930 NEXT I: GOTO 960
940 PRINT" FOR THE POSITIVE CASE": GOSUB 2390
950 GOTO 980: REM JUMP TO -VE CASE C25 OF EXACT SOLUTION
960 PRINT$1," •: PRINT$1, "$1: PRINT$1, " SOLVING FOR C25 POSITIVE CASE": B$="C25 POSITIVE CASE"
970 GOSUB 2450: REM FINDS CONSTANTS FOR CT SOLUTIONS
980 REM NOW DO FOR -VE CASE OF C25
990 REM NOTE LIMITS ARE SAME, SO CAN USE A9 AND A8 OF LAST TIME

111
1000 PRINT "QUIET PLEASE!"
1010 FOR I = 1 TO 10: C(I) = 0: NEXT I: D7 = 1: REM CLEARS HOLDING ARRAY
1020 REM DO FOR LOW CASE
1030 X = A8: IZ = KD - X^2: GOSUB 2310
1040 REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE ROOT, NOW CHECK MID
1050 FOR I = A8 TO A9 STEP 1.0E10
1060 PRINT "CASE I = " ; I
1070 X = I: GOSUB 2290: NEXT I: REM DEALING WITH NEGATIVE CASE
1080 PRINT ""
1100 IF C(1) = 0 THEN GOTO 1150: REM NO SOLUTION FOUND
1110 IF C(2) = 0 THEN CT = 1: GOTO 1170: REM ONE SOLUTION
1120 FOR I = 1 TO 10
1130 IF C(I) = 0 THEN CT = I - 1: I = 10
1140 NEXT I: GOTO 1170
1150 PRINT "FOR THE NEGATIVE CASE": GOSUB 2390
1160 GOTO 1190: REM NOW JUMP BEST FIT CASE
1170 PRINT "SOLVING FOR C25 NEGATIVE CASE": B$ = "C25 NEGATIVE CASE"
1180 GOSUB 2450: REM CARRIES OUT EVALUATION OF CONSTANTS FOR C25 SOLUTIONS
1190 REM BEST FIT CASE +VE
1200 IF GT = 0 THEN 1680: REM WE HAVE AN EXACT SOLUTION SO BYPASS
1210 REM IF HERE TRYING BEST FIT
1220 PRINT "QUIET I'M TRYING TO THINK"
1230 FOR I = 1 TO 10: C(I) = 0: NEXT I: D7 = 1: REM CLEARS HOLDING ARRAY
1240 X = A8: IZ = KD - X^2: GOSUB 3230
1250 REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE ROOT, NOW CHECK MIDDLE
1260 FOR I = A8 TO A9 STEP 1.0E10
1270 PRINT "BEST FIT +VE CASE I = " ; I
1280 X = I: GOSUB 3210: NEXT I
1290 X = A9: IZ = KD - X^2: GOSUB 3230
1300 PRINT ""
1310 IF C(1) = 0 THEN 1360: REM NO SOLUTION FOUND
1320 IF C(2) = 0 THEN CT = 1: GOTO 1400: REM ONE SOLUTION
1330 FOR I = 1 TO 10
1340 IF C(I) = 0 THEN CT = I - 1: I = 10
1350 NEXT I: GOTO 1400
1360 PRINT "FOR THE POSITIVE BEST"
1370 PRINT "FIT CASE THEIR IS NO"
1380 PRINT "MINIMUM POINT"
1390 GOTO 1690: REM TRY -VE BEST FIT CASE
1400 GOSUB 3700: REM SORTS OUT MAX POINTS
1401 PRINT "PRESS ANY KEY TO CONTINUE": POKE 158, 0
1402 GET A$: IF A$ = "" THEN 1402
1403 PRINT "" 
1405 PRINT "SOLVING FOR BEST FIT C25 +VE CASE": B$ = "C25 BEST FIT +VE CASE"
1410 GOSUB 2450: REM CARRIES OUT EVALUATION OF CONSTANTS FOR CT SOLUTIONS
1420 FOR I = A8 TO A9 STEP 1.0E9: REM STORES FOR PLOT OF SOLUTION

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1430 X=I:IZ=KD-X^2
1440 IF IZ<0 THEN 1470
1450 F=LA*SQR(IZ)*X-OA*IZ-JD*X^2-NA
1460 K=K+1:D(K)=(X-CC)/1.0E10:B(K)=F:REM PLOT DIRECTELY
C25
1470 NEXT I
1480 K=K+1
1490 D(K)=X=C)/1.0E10:B(K)=F
1500 DS=ABS(B(I))
1510 FOR I=2 TO K
1520 IF DS<ABS(B(I)) THEN DS=B(I)
1530 NEXT I
1540 REM DS HOLDS LARGEST TIME
1550 FOR I=1 TO K
1560 B(I)=B(I)/DS
1570 NEXT I REM SCALED DATA
1580 A$="1"
1590$0,2,"W","+VE",""
1600$W,STR$(K)
1610 FOR I=1 TO K
1620$W,STR$(D(I))
1630$W,STR$(B(I))
1640$W,A$
1650$W,A$
1660 NEXT I
1670 C
1680 REM BEST FIT NEGATIVE CASE
1690 IF GX=0 THEN
1700 REM IF HERE TRYING BEST FIT
1710 PRINT"QUIET I'M TRYING TO THINK"
1720 PRINT"REM TRYING BEST FIT"
1730 FOR I=1 TO 10:C(I)=0:NEXT I:D7=1:REM CLEAR HOLDING
1740 X=AB:IZ=KD-X^2:GOSUB 3340
1750 REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE
1760 REM NOW CHECK MID
1770 FOR I=AB TO A9 STEP 1.0E10
1780 PRINT"BEST FIT CASE -VE I=";I
1790 X=I:GOSUB 3320:NEXT I:PRINT""
1800 X=A9:IZ=KD-X^2:GOSUB 3340
1810 IF C(1)=0 THEN 1850:REM NO SOLUTION FOUND
1820 IF C(2)=0 THEN CT=1:GOTO 1890:REM ONE SOLUTION
1830 FOR I=1 TO 10
1840 IF C(I)=0 THEN CT=I-1:I=10
1850 NEXT I:GOTO 1890
1860 PRINT"FOR THE NEGATIVE BEST"
1870 PRINT"FIT CASE THEIR IS NO"
1880 PRINT"MINIMUM POINT"
1890 GOSUB 5000:REM ROUTINE TO SORT OUT CORRECT VALUES
1900 PRINT"PRESS ANY KEY TO CONTINUE":POKE158,0
1910 GET A$:IF A$="" THEN 1892
1920 PRINT""  
1930 PRINT"SOLVING FOR BEST FIT C25 -VE CASE":B$="C25
1940 GOSUB 2450:K=0:REM CARRY OUT EVALUATION FOR CT
1950 SOLUTIONS
1910 FOR I=A8 TO A9 STEP 1.0E09:REM DUMP TO PLOTTER
1920X=I:IZ=KD—X^2
1930 IF IZ<0 THEN 1960
1940 F=-LA*X*SQR(IZ)—OA*IZ-JD*X^2-NA
1950 K=K+1:D(K)=(X—CC)/1.0E10: REM PLOT OUT AACTUAL
1960 NEXT I
1970 K=K+1
1980 D(K)=(A8—CC)/1.0E10: B(K)=F: REM PLOT OUT ACTUAL
1990 DS=ABS(B(1))
2000 FOR I=2 TO K
2010 IF DS<ABS(B(I)) THEN DS=B(I)
2020 NEXT I
2030 REM DS HOLDS LARGEST TERM
2040 FOR I=1 TO K
2050 B(I)= B(I)/DS
2060 NEXT I: REM TERM CORRECTED TO 1
2070 A$="1"
2080 SIF "W", "—VE", ""
2090 W,STR$(K)
2100 FOR I=1 TO K
2110 W,STR$(D(I))
2120 W,STR$(B(I))
2130 W,A$
2140 W,A$
2150 NEXT I
2160 C
2170
2180 IZ=KD—X^2
2190 IF IZ<0 THEN 2280
2200 TP=LA*SQR(IZ)*X—OA*IZ—JD*X^2—NA
2210 BP=LA*SQR(IZ)—LA*X—X/SQR(IZ)+OA*X-JD*2*X
2220 XL=X: REM NOW GET NEXT GUESS
2230 X=XL—TP/BP: REM NEW GUESS
2240 IF ABS(XL—X)>1.0E06 THEN 2180:REM REPEAT ITERATION
2250 C=1:GOSUB 3440:X=Ci:REM CONSTANT FOUND AND ROUNDED
2260 IF C(D7—1)<>X THEN C(D7)=X; D7=D7+1
2270 REM ELEMENT SAME SO CONTINUE
2280 RETURN
2290 IZ=KD—X^2
2295 REM ROUTINE CALCULATES X, WHERE X=C25+C46
2300 IF IZ<0 THEN 2380
2310 TP=—LA*X*SQR(IZ)—OA*IZ—JD*X^2—NA
2320 BP=—LA*SQR(IZ)+(LA*X^2)/SQR(IZ)—2*JD*X+2*OA*X
2330 XL=X: REM NOW GET NEW GUESS
2340 X=XL—TP/BP: REM NEW GUESS
2350 IF ABS(XL—X)>1.0E06 THEN 2290:REM REPEAT ITERATION
2360 C=1:GOSUB 3440:X=Ci:REM CONSTANT FOUND AND ROUNDED
2370 IF C(D7—1)<>X THEN C(D7)=X; D7=D7+1
2380 RETURN
2390 PRINT" USING (011) DIRECTION NO"
2400 PRINT" SOLUTION CAN BE FOUND FOR C25:
2410 PRINT" PRESS ANY KEY TO CONTINUE"
2420 POKE 158,0
2430 GET A$: IF A$="" THEN 2430
2440 PRINT" " : RETURN
2450 FOR I=1 TO CT:REM REPEATS CALCULATIONS CT TIMES
REM NOW CALCULATE C23
2520 DZ = KD - (CA + CC)^2
2530 IF 0 > DZ THEN 2860: REM NO SOLUTION FOR C23
2540 REM
2550 DZ = SQR(DZ)
2560 M1 = DZ - C4: REM +VE CASE FOR C23
2570 M2 = -DZ - C4: REM -VE CASE FOR C23
2580 C23 = M1: REM +VE CASE FOR C23
2590 REM NOW NEED POLARISATION VECTORS
2600 CB = M1: GOSUB 3080: REM GETS POLARISATION VECTORS
2610 REM C23 -VE CASE
2620 C23 = M2
2630 CB = M2: GOSUB 3080
2640 REM C23 AND C25 FOUND NOW GET C12
2650 EX = (C6 + C2) * (C5 + C4) + (C1 + C6) * (C6 + C2 + C5 + C4) - (CX + CC)^2 - (CA + CC)^2
2660 EX = EX - 4 * DN^2 * (VD^2 * VE^2 + VD^2 * VF^2 + VE^2 * VF^2)
2670 IF 0 > EX THEN 2890
2680 EX = SQR(EX)
2690 M1 = EX - C6: REM +VE CASE
2700 M2 = -EX - C6: REM -VE CASE
2710 C12 = M1: REM +VE CASE
2720 REM NEED POLARISATION VECTORS
2730 GOSUB 2920
2740 REM C12 -VE CASE
2750 C12 = M2
2760 REM NOW GET POLARISATION VECTORS
2770 GOSUB 2920: REM LOOKING AT (110)
2780 POKE 158, 0: PRINT" PRESS ANY KEY TO CONTINUE"
2790 GET A$: IF A$ = "" THEN 2810
2800 PRINT" "
2810 NEXT I
2820 PRINT" PLEASE WAIT"
2830 RETURN
2840 REM SUBROUTINE TO GET POLARISATION VECTORS (110)
2850 U1 = 0.25 * (CE + C6) * (CA + CC) - 0.5 * (CX + CC) * (0.5 * (C6 + C2) - DN * VD^2)
2860 U2 = 0.25 * (CX + CC) * (CA + CC) - 0.5 * (CE + C6) * (0.5 * (C5 + C4) - DN * VD^2)
2870 REM U1 MUST BE POSITIVE
2880 U1 = 1.0
2890 U3 = 0Z / DC
2900 U2 = DB * U3 / OZ
3000 REM NORMILSE
3010 UT=U1^2+U2^2+U3^2: UT=SQR(UT)
3020 U1=U1/UT; U2=U2/UT; U3=U3/UT
3025 PRINT£1," U3/U2=";INT(0Z*1000/0B)/1000;
3030 PRINT£1," U3/U1=";INT(0Z*1000/0B)/1000;
3035 PRINT£1," NORMILISED VECTORS ARE";
3040 PRINT£1," U1=";INT(U1*1000)/1000;
3045 PRINT£1," U2=";INT(U2*1000)/1000;
3050 PRINT£1," U3=";INT(U3*1000)/1000;
3055 PRINT£1," PROP VECT X=0.707 Y=0.707 Z=0.0";
3070 RETURN
3080 REM SUBROUTINE TO GET POLARISATION VECTORS (O11)
3090 DD=0.25*(CC+CA)*(C4+CB)-0.5*(CC+CF)*(0.5*(C2+C4)-DN*V^2)
3100 ED=0.25*(CC+CF)*(C4+CB)-0.5*(CC+CA)*(0.5*(C4+C3)-DN*V^2)
3110 FD=(0.5*(C2+C4)-DN*V^2)*(0.5*(C4+C3)-DN*V^2)-0.5*(C4+C3)^2
3120 REM U2 ALWAYS POSITIVE
3130 U2=1.0: U3=OD/0E: U1=OD*U3/OD
3140 UT=U1^2+U2^2+U3^2: UT=SQR(UT) REM NORMILISED
3150 U1=U1/UT: U2=U2/UT: U3=U3/UT
3155 PRINT£1," U3/U2=";INT(0Z*1000/0E)/1000;
3160 PRINT£1," U3/U1=";INT(0D*1000/0F)/1000;
3170 PRINT£1," NORMILISED VECTORS ARE";
3180 PRINT£1," U1=";INT(U1*1000)/1000;
3190 PRINT£1," U2=";INT(U2*1000)/1000;
3195 PRINT£1," U3=";INT(U3*1000)/1000;
3200 PRINT£1," PROP VECT X=0.0 Y=0.707 Z=0.707";
3200 RETURN
3210 IF Z<KD-X^2 THEN 3210
3220 IF Z<0 THEN 3310
3230 TP=LA*SQR(<IZ)-<LA*X^2)/SQR(IZ)-2*JD*X+2*OA*X
3240 BP=-LA*X/SQR(IZ)+LA*(IZ^-1-5)*X^3+LA*2*X/SQR(IZ)-2*JD+2*OA
3250 XL=X REM NOW GET NEW GUESS
3260 X=XL-BP/TP REM NEW GUESS
3270 IF ABS(XL-X)>1.0E06 THEN 3210 REM REPEAT ITERATION
3280 CI=X: GOSUB 3440: X=CI REM CONSTANT FOUND AND ROUNDED
3290 IF C(D7-1)<X THEN C(D7)=X:D7=D7+1
3300 REM ELEMENTS THE SAME SO CONTINUE
3310 RETURN
3320 IF Z<KD-X^2 REM BEST FIT -VE CASE
3330 IF Z<0 THEN 3420
3340 TP=-LA*SQR(IZ)+(LA*X^2)/SQR(IZ)-2*JD*X+2*OA*X
3350 BP=-LA*X/SQR(IZ)+LA*(IZ^-1.5)*X^3+LA*2*X/SQR(IZ)-2*JD+2*OA
3360 X=REM NOW GET NEXT GUESS
3370 X=XL-BP/TP REM NEW GUESS
3380 IF ABS(XL-X)>1.0E06 THEN 3320 REM REPEAT ITERATION
3390 CI=X: GOSUB 3440: X=CI REM CONSTANT FOUND AND ROUNDED
3400 IF C(D7-1)<X THEN C(D7)=X:D7=D7+1
3410 REM ELEMENTS THE SAME SO CONTINUE
REM ROUNDING ROUTINE FOR ELASTIC CONSTANTS
3450BB=BA+1
3460IC=INT((CI*10^BB)/1.0E10)
3470CD=INT((CI*10^BA)/1.0E10)
3480BI=IC-10*CD
3490IF B1<5 THEN 3510
3500CD=CD+1
3510CI=CD*1.0E10/(10^BA)
3520RETURN
3700PRINT" FOR THE POSITIVE BEST FIT CASE"
3710PRINT" MINIMUM OR MAXIMUM POINT'S ARE"
3720FOR I=1 TO CT
3730PRINT" POINT "";I"; AT C25="; (C(I)-CC)/1.0E10:REM
3740NEXT I
3750REM NOW ELIMINATE FALSE TERMS
3760AU=AU+1:X=C(AU):IZ=KD-X^2
3770DF=-LA*X/SQR(IZ)-LA*(IZ^-1.5)*X^3-LA*2*X/SQR(IZ)-2*J
3780DU=LA*X*SQR(IZ)-JD*X^2-0A*IZ-NA
3790IF DU<0 THEN 3830:REM -VE CASE
3800IF DF>0 THEN 3890:REM OK TRUE MIN POINT
3810REM IF HERE WE HAVE A MAXIMUM SO DISCOUNT
3820G0T0 3850:REM SHIFTER
3830IF DF<0 THEN 3890:REM MIN POINT SO OK
3840FOR I=AU+1 TO CT
3850C(I-1)= C (I):NEXT I:REM THROWS OUT WRONG POINT
3860CT=CT-1:AU=AU-1
3870IF AU=CT THEN RETURN
3880G0T0 3760
3890RETURN
5000PRINT" FOR THE NEGATIVE BEST FIT CASE"
5010PRINT" MINIMUM OR MAXIMUM POINT'S ARE"
5020FOR I=1 TO CT
5030PRINT" POINT "";I"; AT C25="; (C(I)-CC)/1.0E10:REM
5040NEXT I
5050REM NOW ELIMINATE FALSE TERMS
5060AU=AU+1:X=C(AU):IZ=KD-X^2
5070DF=LA*X/SQR(IZ)+LA*(IZ^-1.5)*X^3+LA*2*X/SQR(IZ)-2*JD
5080DU=-LA*X*SQR(IZ)-JD*X^2-0A*(IZ)-NA
5090IF DU<0 THEN 5130:REM -VE CASE
5100IF DF>0 THEN 5160:REM OK TRUE MIN POINT
5110REM IF HERE WE HAVE A MAXIMUM SO DISCOUNT .7391120GOTO
5120REM SHIFTER
5130IF DF<0 THEN 5160:REM MIN POINT SO OK
5140FOR I=AU+1 TO CT
5150C(I-1)= C (I):NEXT I:REM THROWS OUT WRONG POINT
5160CT=CT-1:AU=AU-1
5170IF AU=CT THEN RETURN
5180G0T0 5060
5190RETURN
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APPENDIX 2.C

The following computer program calculates the elastic stiffness constants $c_{12}$, $c_{25}$ and $c_{23}$ using the procedure described in section 4.3. This being the second method described in section 4.3.

```plaintext
50PRINT"FIND C25 USING [110] DIRECTION"
60FOR I=1TO500:NEXT I
100DIM C(10), D(100), B(100)
110PRINT"HOW MANY SIGNIFICANT FIGURES"
120PRINT"ARE THE CONSTANTS TO BE"
130INPUT"DETERMINED TO (RANGE 1-5)"; BA
140IF BA<1 OR BA>5 THEN 110
150BA=BA-1
160REM INPUT ELASTIC CONSTANTS AND VELOCITIES NEEDED FROM DISC
170E*=""; BC=BC+1
180INPUT"DATA FILE NAME"; A*
190IF A*="" THEN 180
200INPUT"DRIVE NUMBER OF DATA FILE"; N
210$D,N,"R",A$,E$
220$R,A$:DN=VAL(A$)
230$R,A$:C1=VAL(A$)
240$R,A$:CU=VAL(A$)
250$R,A$:CX=VAL(A$)
260$R,A$:C2=VAL(A$)
270$R,A$:C3=VAL(A$)
280$R,A$:CF=VAL(A$)
290$R,A$:C4=VAL(A$)
300$R,A$:CC=VAL(A$)
310$R,A$:C5=VAL(A$)
320$R,A$:C6=VAL(A$)
330$R,A$:VD=VAL(A$)
340$R,A$:VE=VAL(A$)
350$R,A$:VF=VAL(A$)
360$R,A$:VG=VAL(A$)
370$R,A$:VH=VAL(A$)
380$R,A$:VI=VAL(A$)
390$C
391INPUT"OUTPUT TO PRINTER"; A$: IF A*="" THEN
392IF LEFT*(A*,1)="Y" THEN N=4: GOTO 394
393N=3
394OPEN 1, N
395PRINT""
400PRINT"":PRINT$1,"":PRINT$1,""
410PRINT$1,"":PRINT$1,"" C11="",C1;" NM"
420PRINT$1,"":PRINT$1,"" C13="",CU;" NM"
```

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430 PRINT $1, ":PRINT $1," C15=" CX 
440 PRINT $1, ":PRINT $1," C22=" C2; " NM 
450 PRINT $1, ":PRINT $1," C33=" C3 
460 PRINT $1, ":PRINT $1," C35=" CF 
470 PRINT $1, ":PRINT $1," C44=" C4 
480 PRINT $1, ":PRINT $1," C46=" CC 
490 PRINT $1, ":PRINT $1," C55=" C5 
500 PRINT $1, ":PRINT $1," C66=" C6; " NM 
510 PRINT" PRESS ANY KEY TO CONTINUE" 
520 POKE 158,0 REM EMPTY KEY BOARD 
530 GET A$: IF A$="" THEN 530 
540 PRINT" ":PRINT $1," V13="; VD; " M/S 
550 PRINT $1, ":PRINT $1," V14=" VE; " M/S 
560 PRINT $1, ":PRINT $1," V15=" VF; " M/S 
570 PRINT $1, ":PRINT $1," V16=" VG; " M/S 
580 PRINT $1, ":PRINT $1," V17=" VH; " M/S 
590 PRINT $1, ":PRINT $1," V18=" VI; " M/S 
600 PRINT" PRESS ANY KEY TO CONTINUE" 
610 POKE 158,0 
620 GET A$: IF A$="" THEN620 
630 PRINT 
640 RT=(C6+C2)*(C5+C4)+(C1+C6)*(C6+C2+C5+C4)-(CX+CC)^2 
650 RT=RT-4*DN^2*(VD^2*VE^2+VE^2*VF^2+VF^2*VE^2) 
660 RE=8*DN^3*VD^2*VE^2*VF^2-(C6+C5)*(C2+C4)*(C4+C3)+(C2+C4)^2 
670 GA=2*(CX+CC) 
680 LM=C1+C6 
690 SD=C5+C4 
700 KD=(C2+2*C4+C3)*(C6+C5)+(C2+C4)*(C4+C3)-(CC+CF)^2 
710 KD=KD-4*DN^2*(VG^2*VH^2+VH^2*VI^2+VI^2*VG^2) 
720 NA=8*DN^3*VG^2*VH^2*VI^2-(C6+C5)*(C2+C4)*(C4+C3)+(C2+C4)^2*(CC+CF)^2 
730 LA=2*(CC+CF) 
740 REM SECTION TO FIND REGION WHERE WE HAVE + SOLUTION 
750 A9=SQR(RT): REM ADJUST 
760 A8=—A9: REM A9,A8 FIXES LIMIT FOR ITERATIONS 
770 REM DO FOR POSITIVE SECTION 
780 PRINT” QUIET I'M TRYING TO THINK" 
790 FOR I=1 TO 10: C(I)=0: NEXT I: REM CLEARS HOLDING ARRAY 
800 X=A9: IF RT-X^2<0 THEN A9=A9-1.0E07: GOTO 800: REM REDUCES A9 TO BOUNDRY 
810 AB=-A9: REM A9,A8 FIXES LIMIT FOR ITERATIONS 
820 PRINT" QUIET I'M TRYING TO THINK" 
830 FOR I=1 TO 10: C(I)=0: NEXT I: D7=1: REM CLEARS HOLDING ARRAY 
840 A9=X: IF RT-X^2<0 THEN A9=A9-1.0E07: GOTO 800: REM REDUCES A9 TO BOUNDRY 
850 REM WE HAVE NOW HOMED IN FROM THE TOP AND BOTTOM TO 
860 REM FIND ROOT NEAR BOUNDRY 
870 REM WE HAVE NOW HOMED IN FROM THE TOP AND BOTTOM TO 
880 REM FIND ROOT NEAR BOUNDRY 
890 IF C(1)=0 THEN GT=1: GOTO 940: REM NO SOLUTION 
900 IF C(2)=0 THEN CT=1: GOTO 960: REM ONE SOLUTION 

119
FOR I=2 TO 10
   IF C(I)=0 THEN CT=I-1:I=10
NEXT I:GOTO 960
PRINT" FOR THE POSITIVE CASE":GOSUB 2390
GOTO 980:REM JUMP TO -VE CASE C25 OF EXACT SOLUTION
FOR C25
   PRINT" SOLVING FOR C25 POSITIVE CASE":B$="C25 POSITIVE CASE"
   GOSUB 2450:REM FINDS CONSTANTS FOR CT SOLUTIONS
   REM NOW DO FOR -VE CASE OF C25
   REM NOTE LIMITS ARE SAME, SO CAN USE A9 AND A8 OF LAST TIME
   PRINT"QUIET PLEASE!"
   FOR I=1 TO 10:C(I)=0:NEXT I:D7=1:REM CLEARS HOLDING ARRAY
   REM DO FOR LOW CASE
   X=A8:IZ=RT-X^2:GOSUB 2310
   REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE ROOT, NOW CHECK MID
   FOR I=A8 TO A9 STEP 1.0E10
   PRINT" - CASE I=":I
   X=I:GOSUB 2290:NEXT I:REM DEALING WITH NEGATIVE CASE
   X=A9:IZ=RT-X^2:GOSUB 2310
   PRINT" "
   IF C(1)=0 THEN GX=1:GOTO 1150:REM NO SOLUTION FOUND
   IF C(2)=0 THEN CT=1:GOTO 1170:REM ONE SOLUTION
   FOR I=1 TO 10
   IF C(I)=0 THEN CT=I-1:I=10
   NEXT I:GOTO 1170
   PRINT" FOR THE NEGATIVE CASE":B$="C25 NEGATIVE CASE"
   GOSUB 2450:REM CARRYS OUT EVALUATION OF CONSTANTS FOR C25 SOLUTIONS
   REM BEST FIT CASE +VE
   IF GT=0 THEN 1680:REM WE HAVE AN EXACT SOLUTION SO BY PASS
   PRINT"QUIET I'M TRYING TO THINK"
   FOR I=1 TO 10:C(I)=0:NEXT I:D7=1:REM CLEARS HOLDING ARRAY
   X=A8:IZ=RT-X^2:GOSUB 3230
   REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE ROOT, NOW CHECK MIDDLE
   FOR I=A8 TO A9 STEP 1.0E10
   PRINT" BEST FIT +VE CASE I=":I
   X=I:GOSUB 3210:NEXT I
   X=A9:IZ=RT-X^2:GOSUB 3230
   PRINT" 
   IF C(1)=0 THEN 1360:REM NO SOLUTION FOUND
   IF C(2)=0 THEN CT=1:GOTO 1400:REM ONE SOLUTION
   FOR I=1 TO 10
   IF C(I)=0 THEN CT=I-1:I=10
   NEXT I:GOTO 1400
   PRINT" FOR THE POSITIVE BEST" 
   PRINT" THERE IS NO MINIMUM POINT" 
   GOTO 1690:REM TRY -VE BEST FIT CASE.

120
1400GOSUB 3700:REM SORTS OUT MAX POINTS
1401PRINT"PRESS ANY KEY TO CONTINUE":POKE 158,0
1402A$:IF A$="" THEN 1402
1403PRINT"
1405PRINT"SOLVING FOR BEST FIT C25 +VE CASE":B$="C25
BEST FIT +VE CASE"
1410GOSUB 2450:REM CARRYS OUT EVALATION OF CONSTANTS FOR
CT SOLUTIONS
1420FOR I=A8 TO A9 STEP .0E10:REM STORES FOR PLOT OF
SOLUTION
1430X=I:IZ=RT-X^2
1440IF IZ<0 THEN 1470
1450F=GA*SQR(IZ)*X-SD*IZ-LM*X^2-RE
1460K=K+1:D(K)=(X-CC)/1.0E10:B(K)=F:REM PLOT DIRECTELY
C25
1470NEXT I
1480K=K+1
1490D(K)=(A8-CC)/1.0E10:X=A8:B(K)=GA*SQR(IZ)*X-SD*IZ-LM*
X^2-RE
1500DS=ABS(B(1))
1510FOR I=2 TO K
1520IF DS<ABS(B(I)) THEN DS=B(I)
1530NEXT I
1540REM DS HOLDS LARGEST TIME
1550FOR I=1 TO K
1560B(I)=B(I)/DS
1570NEXT I:REM SCALED DATA
1580$0,2,"W","+VE",""
1590$W,STR$(K)
1600$W,STR$(D(I))
1610$W,STR$(B(I))
1620$W,A$
1630$W,A$
1640$W,A$
1650$W,A$
1660NEXT I
1670$C
1680REM BEST FIT NEGATIVE CASE
1690IF GX=0 THEN
1700REM IF HERE TRYING BEST FIT
1710PRINT"QUIET I'M TRYING TO THINK"
1720PRINT"
1730FOR I=1 TO 10:C(I)=0:NEXT I:D7=1:REM CLEAR HOLDING
ARRAY
1740X=A8:IZ=RT-X^2:GOSUB 3340
1750REM HAVE NOW HOMED IN FROM TOP AND BOTTOM TO CAPTURE
ROOT NOW CHECK MID
1760FOR I=A8 TO A9 STEP .0E10
1770PRINT"BEST FIT CASE -VE I=";I
1780X=I:GOSUB 3320:NEXT I:PRINT"
1790X=A9:IZ=RT-X^2:GOSUB 3340
1800IF C(1)=0 THEN 1850:REM NO SOLUTION FOUND
1810IF C(2)=0 THEN CT=1:GOTO 1890:REM ONE SOLUTION
1820FOR I=1 TO 10
1830IF C(I)=0 THEN CT=I-1:I=10
1840NEXT I:GOTO 1890
1850PRINT"FOR THE NEGATIVE BEST"
1860PRINT"FIT CASE THEIR IS NO"
1870PRINT" MINIMUM POINT"
18801890GOSUB 5000:REM ROUTINE TO SORT OUT CORRECT VALUES
1891PRINT" PRESS ANY KEY TO CONTINUE":POKE158,0
1892GET A$:IF A$="" THEN 1892
1893PRINT" "
1894PRINT" SOLVING FOR BEST FIT C25 -VE CASE":B$="C25
1895BEST FIT -VE CASE"
1900GOSUB 2450:K=0:REM CARRY OUT EVALATION FOR CT
SOLUTIONS
1910FOR I=A8 TO A9 STEP 1.0E09:REM DUMP TO PLOTTER
1920X=I:IZ=RT-X^2
1930IF IZ<0 THEN 1960
1940F=-GA*X*SQR(IZ)-SD*IZ-LM*X^2-RE
1950K=K+1:D(K)=(X-CC)/1.0E10:B(K)=F:REM PLOT OUT AACTUAL
C25
1960NEXT I
1970K=K+1
1980D(K)=(A8-CC)/1.0E10:X=A8:B(K)=-GA*X*SQR(IZ)-SD*IZ-LM
*X^2-RE
1990DS=ABS(B(1))
2000FOR I=2 TO K
2010IF DS<ABS(B(I)) THEN DS=B(I)
2020NEXT I
2030REM DS HOLDS LARGEST TERM
2040FOR I=1 TO K
2050B(I)=B(I)/DS
2060NEXT I:REM TERM CORRECTED TO 1
2070A$=" 1"
2080$W,2,"W","-VE","
2090$W,STR$(K)
2100FOR I=1 TO K
2110$W,STR$(D(I))
2120$W,STR$(B(I))
2130$W,A$
2140$W,A$
2150NEXT I
2160*C
2170122
2180IZ=RT-X^2
2190IF IZ<0 THEN 2280
2200TP=GA*SQR(IZ)*X-SD*IZ-LM*X^2-RE
2210BP=GA*SQR(IZ)-GA*X^2/SQR(IZ)-2*LM*X+2*SD*X
2220XL=X:REM NOW GET NEXT GUSS
2230X=XL-TP/BP:REM NEW GUSS
2240IF ABS(XL-X)>1.0E06 THEN 2180:REM REPEAT ITERATION
2250C=16GOSUB 3440:X=C:REM CONSTANT FOUND AND ROUNDED
2260IF C(D7-1)<X THEN C(D7)=X:D7=D7+1
2270REM ELEMENT SAME SO CONTINUE
2280RETURN
2290IZ=RT-X^2
2300IF IZ<0 THEN 2380
2310TP=-GA*X*SQR(IZ)-SD*IZ-LM*X^2-RE
2320BP=-GA*SQR(IZ)+(GA*X^2)/SQR(IZ)-2*LM*X+2*SD*X
2330X=X:REM NOW GET NEW GUSS
2340X=XL-TP/BP:REM NEW GUESS
2350IF ABS(XL-X)>1.0E06 THEN 2290:REM REPEAT ITERATION
2360 CI=X: GOSUB 3440: X=CI: REM CONSTANT FOUND AND ROUNDED
2370 IF C(D7-1)<<X THEN C(D7)=X: D7=D7+1
2380 RETURN
2390 PRINT " USING (110) DIRECTION NO"
2400 PRINT " SOLUTION CAN BE FOUND FOR C25":
2410 PRINT " PRESS ANY KEY TO CONTINUE"
2420 POKE 158, 0
2430 GET A*: IF A$="" THEN 2430
2440 PRINT "": RETURN
2450 FOR I=1 TO CT: REM REPEATS CALCULATIONS CT TIMES
2460 CA=C(I)-CC
2470 PRINT £1,"": PRINT £1," SOLUTION": I; "FOR THE": B$ 
2480 PRINT £1,"": PRINT £1," C25=": $CA; " NM"
2490 PRINT £1,"": PRINT £1," C12 +VE CASE"
2500 PRINT £1,"": PRINT £1," C12=": &DZ; " NM"
2510 REM NOW CALCULATE C12
2520 DZ=RT-(CA+CC)^2
2530 IF 0>DZ THEN 2860: REM NO SOLUTION FOR C12
2540 DZ=SQR(DZ)
2550 M1=DZ-C6: REM +VE CASE FOR C12
2560 M2=-DZ-C6: REM -VE CASE FOR C12
2570 CI=M1: GOSUB 3440: M1=CI: CI=M2: GOSUB 3440: M2=CI
2580 PRINT £1,"": PRINT £1," C12 +VE CASE"
2590 PRINT £1,"": PRINT £1," C12=": $M1; " NM"
2600 REM NOW NEED POLARISATION VECTORS
2610 CE=M1: GOSUB 2920: REM GETS POLARISATION VECTORS
2620 PRINT £1,"": PRINT £1," C12 -VE CASE"
2630 CE=M2: GOSUB 2920
2640 REM C12 AND C25 FOUND NOW GET C23
2650 EX=(C2+2*C4+C3)*(C6+C5)+(C2+C4)*(C4+C3)-(CC+CF)^2-(C+C+CA)^2
2660 EX=EX-4*DN^2*(VGA2*VH^2+VH^2*VI^2+VG^2*VI^2)
2670 IF 0>EX THEN 2890
2680 M1=EX-C4: REM +VE CASE
2690 M2=-EX-C4: REM -VE CASE
2700 CI=M1: GOSUB 3440: M1=CI: CI=M2: GOSUB 3440: M2=CI
2710 PRINT £1,"": PRINT £1," C23 +VE CASE"
2720 PRINT £1,"": PRINT £1," C23=": $M1; " NM": CB=M1
2730 REM NEED POLARISATION VECTORS
2740 GOSUB 3080
2750 PRINT £1,"": PRINT £1," C23 -VE CASE"
2760 PRINT £1,"": PRINT £1," C23=": $M2; " NM": CB=M2
2770 REM NOW GET POLARISATION VECTORS
2780 REM C12 AND C25 FOUND NOW GET C23
2790 POKE 158, 0: PRINT " PRESS ANY KEY TO CONTINUE"
2800 GET A*: IF A$="" THEN 2810
2810 PRINT "": RETURN
2820 NEXT I
2830 PRINT " PLEASE WAIT"
2840 RETURN
2850 PRINT £1,"": PRINT £1," NO REAL SOLUTION CAN BE"
2860 PRINT £1,"": PRINT £1," NO REAL SOLUTION CAN BE"
2870 PRINT £1,"": PRINT £1," BE FOUND FOR C12"
2880 GOTO 2650: REM LOOK FOR C23 NOW
2890 PRINT £1,"": PRINT £1," NO REAL SOLUTION CAN"
2900 PRINT £1,"": PRINT £1," BE FOUND FOR C23"
2910 GOTO 2830
2920 REM SUBROUTINE TO GET POLARISATION VECTORS (110)
29300 Z = 0.25*(CE+C6)*(CA+CC) - 0.5*(CX+CC)*(0.5*(C6+C2) - DN*VD^2):REM U3
29400 B = 0.25*(CX+CC)*(CA+CC) - 0.5*(CE+C6)*(0.5*(C5+C4) - DN*VD^2):REM U2
29500 C = (0.5*(C6+C2) - DN*VDA^2)*(0.5*(C5+C4) - DN*VD^2) - 0.5*(CA+CC)^2

REM U1 MUST BE POSITIVE
29700 U1 = 1.0
29800 U3 = 0Z/0C
29900 U2 = 0B*U3/0Z
30000 REM NORMALISE
30100 UT = U1^2 + U2^2 + U3^2: UT = SQR(UT)
30200 U1 = U1/UT: U2 = U2/UT: U3 = U3/UT
30250 PRINT E1, " U3/U2 = " INT(0Z*1000/0B)/1000; " U3/U1 = " INT(0Z*1000/0C)/1000;
30300 PRINT E1, " NORMILISED VECTORS ARE"
30400 PRINT E1, " U1 = " INT(U1*1000)/1000;
30500 PRINT E1, " U2 = " INT(U2*1000)/1000;
30600 PRINT E1, " U3 = " INT(U3*1000)/1000
30650 PRINT E1, " PROP VECT X = 0.707 Y = 0.707 Z = 0.0"
30700 RETURN

30800 REM SUBROUTINE TO GET POLARISATION VECTORS (011)
30900 D = 0.25*(CC+CA)*(C4+CB) - 0.5*(CC+CF)*(0.5*(C2+C4) - DN*VD^2)
31000 E = 0.25*(CC+CF)*(C4+CB) - 0.5*(CC+CA)*(0.5*(C4+C3) - DN*VD^2)
31100 F = (0.5*(C2+C4) - DN*VGA^2)*(0.5*(C4+C3) - DN*VG^2) - 0.5*(C4+CB)^2
31200 REM U2 ALWAYS POSITIVE
31300 U2 = 1.0: U3 = OD/0E: U1 = OF*U3/OD
31400 UT = U1^2 + U2^2 + U3^2: UT = SQR(UT): REM NORMALISED
31500 U1 = U1/UT: U2 = U2/UT: U3 = U3/UT
31550 PRINT E1, " U3/U2 = " INT(OD*1000/0B)/1000;
31600 PRINT E1, "U3/U1 = " INT(OD*1000/0C)/1000;
31700 PRINT E1, " NORMILISED VECTORS ARE"
31800 PRINT E1, "U1 = " INT(U1*1000)/1000;
31900 PRINT E1, "U2 = " INT(U2*1000)/1000;
31950 PRINT E1, "U3 = " INT(U3*1000)/1000
32000 PRINT E1, " PROP VECT X = 0.0 Y = 0.707 Z = 0.707"
32050 RETURN

32100 IZ = RT-X^2
32200 IF IZ < 0 THEN 3310
32300 TP = GA*SQR(IZ) - (GA*X^2)/SQR(IZ) - 2*LM*X + 2*SD*X
32400 BP = GA*X/SQR(IZ) - GA*(IZ-1.5)*X^3 - GA*2*X/SQR(IZ) - 2*L+2*SD
32500 XL = X:REM NOW GET NEW GUESS
32600 X = XL-TP/ BP:REM NEW GUESS
32700 IF ABS(XL-X) > 1.0E06 THEN 3210:REM REPEAT ITERATION
32800 CI = X: REM CONSTANT FOUND AND ROUNDED
32900 IF C(D7-1) < X THEN C(D7) = X: D7 = D7 + 1
33000 REM ELEMENTS THE SAME SO CONTINUE
33100 RETURN
33200 IZ = RT-X^2:REM BEST FIT -VE CASE

124
3330 IF IZ<0 THEN 3420
3340 TP=-GA*SQR(IZ) + GA*(IZ^-1.5)*X^3+GA*2*X/SQR(IZ)-2*LM+2*SD
3350 BP=GA*X/SQR(IZ)+GA*(IZ^-1.5)*X^3+GA*2*X/SQR(IZ)-2*LM
3360 XL=X:REM NOW GET NEXT GUESS
3370 X=XL-TP/BP:REM NEW GUESS
3380 IF ABS(XL-X)>1.0E06 THEN 3320:REM REPEAT ITERATION
3390 CI=X:GOSUB 3440:X=CI:REM CONSTANT FOUND AND ROUNDED
3400 IF C(D7—1)<X THEN C(D7)=X:D7=D7+1
3410 REM ELEMENTS THE SAME SO CONTINUE
3420 RETURN
3430
3440 REM ROUNDING ROUTINE FOR ELASTIC CONSTANTS
3450 BB=BA+1
3460 CI=INT((CI*10^BB)/1.0E10)
3470 CD=INT((CI*10^BA)/1.0E10)
3480 CI=CD+1
3490 CI=CD*1.0E10/(10^BA)
3500 RETURN
3700 PRINT" FOR THE POSITIVE BEST FIT CASE"
3710 PRINT" MINIMUM OR MAXIMUM POINT'S ARE"
3720 FOR I=1 TO CT
3730 PRINT" POINT ";I; " AT C25="; (C(I)-CC)/1.0E10:REM C(I) CONTAINS C46+C25
3740 NEXT I
3750 REM NOW ELIMINATE FALSE TERMS
3760 AU=AU+1:X=C(AU):IZ=RT-X^2
3770 DF=-GA*X/SQR(IZ)+GA*(IZ^-1.5)*X^3+GA*2*X/SQR(IZ)-2*LM
3780 DU=-GA*X*SQR(RT-X^2)-LM*X^2-SD*(RT-X^2)-RE
3790 IF DU<0 THEN 3800:REM OK TRUE MIN POINT
3800 REM IF HERE WE HAVE A MAXIMUM SO DISCOUNT
3810 GOTO 3740:REM SHIFTER
3820 IF DF<0 THEN 3800:REM OK TRUE MIN POINT SO OK
3830 REM SHIFTER
3840 FOR I=AU+1 TO CT
3850 C(I-1)=C(I):NEXT I:REM THROWS OUT WRONG POINT
3860 CT=CT—1:AU=AU-1
3870 IF AU=CT THEN RETURN
3880 GOTO 3760
3890 RETURN
5000 PRINT" FOR THE NEGATIVE BEST FIT CASE"
5010 PRINT" MINIMUM OR MAXIMUM POINT'S ARE"
5015 AU=0
5020 FOR I=1 TO CT
5030 PRINT" POINT ";I; " AT C25="; (C(I)-CC)/1.0E10:REM C(I) CONTAINS C46+C25
5040 NEXT I
5050 REM NOW ELIMINATE FALSE TERMS
5060 AU=AU+1:X=C(AU):IZ=RT-X^2
5070 DF=GA*X/SQR(IZ)+GA*(IZ^-1.5)*X^3+GA*2*X/SQR(IZ)-2*LM+2*SD
5080 DU=-GA*X*SQR(RT-X^2)-LM*X^2-SD*(RT-X^2)-RE
5090 IF DU<0 THEN 5130:REM -VE CASE
IF DF > 0 THEN 5190: REM OK TRUE MIN POINT
REM IF HERE WE HAVE A MAXIMUM SO DISCOUNT
GOTO 5150: REM SHIFTER
IF DF < 0 THEN 5190: REM MIN POINT SO OK
REM SHIFTER
FOR I = AU + 1 TO CT
C(I-1) = C(I): NEXT I: REM THROWS OUT WRONG POINT
REM
CT = CT - 1: AU = AU - 1
IF AU = CT THEN RETURN
GOTO 5060
RETURN
APPENDIX 2.D

The following computer program was used to perform the consistency checks on measured velocities and obtained elastic stiffness constants as described in section 4.4.

100POKE 144,49
110PRINT" TRACE RELATIONS"
120PRINT" OR PUT ANOTHER WAY"
130PRINT" IS YOUR DATA ANY GOOD"
140PRINT" C SOLID STATE JAN 1982"
150FOR I =1 TO 5000:NEXT
160REM PRINT OUT VELOCITY AS USER CHECK
170REM VELOCITY HELD IN V1-VH USING HEX FORMAT
180READ DN:REM DENSITY
190DN=INT(DN*10)/10
200READ VI, V2, V3, V4, V5, V6, V7, V8, V9
210VI=INT(V1*10)/10: V2=INT(V2*10)/10
220V3=INT(V3*10)/10: V4=INT(V4*10)/10
230V5=INT(V5*10)/10: V6=INT(V6*10)/10
240V7=INT(V7*10)/10: V8=INT(V8*10)/10
250V9=INT(V9*10)/10
260READ VA, VB, VC, VD, VE, VF, VG, VH, VI
270VA=INT(VA*10)/10: VB=INT(VB*10)/10
280VC=INT(VC*10)/10: VD=INT(VD*10)/10
290VE=INT(VE*10)/10: VF=INT(VF*10)/10
300VG=INT(VG*10)/10: VH=INT(VH*10)/10
310VI=INT(VI*10)/10
320PRINT" DENSITY="; DN; " KG/M^3"
330PRINT" V1="; VI; " M/S"
340PRINT" V2="; V2; " M/S"
350PRINT" V3="; V3; " M/S"
360PRINT" V4="; V4; " M/S"
370PRINT" V5="; V5; " M/S"
380PRINT" V6="; V6; " M/S"
390PRINT" V7="; V7; " M/S"
400PRINT" V8="; V8; " M/S"
410PRINT" V9="; V9; " M/S"
420PRINT" PRESS ANY KEY TO CONTINUE"
430POKE 158,0
440GET A$: IF A$="" THEN 440
450PRINT" "
460PRINT" V9="; V9; " M/S"
470PRINT" V10="; VA; " M/S"
480PRINT" V11="; VB; " M/S"
490PRINT" V12="; VC; " M/S"
500PRINT" V13="; VD; " M/S"
510PRINT" V14="; VE; " M/S"
520PRINT" V15="; VF; " M/S"
530PRINT" V16="; VG; " M/S"
540PRINT" V17="; VH; " M/S"
550PRINT" V18="; VI; " M/S"
560PRINT" PRESS ANY KEY TO CONTINUE"
570POKE 158,0
580GETA$: IF A$="" THEN 580
590PRINT" HOW MANY SIGNIFICANT "
600PRINT" FIGURES IN THE VELOCITY"
610INPUT" RANGE 1-5 " ; BD: BD=BD-1
620IF BD>4 OR BD<0 THEN PRINT" OUT OF RANGE"; GOTO 610
630DA=V1: GOSUB 1030: V1=DA: DA=V2: GOSUB 1030: V2=DA
640DA=V3: GOSUB 1030: V3=DA
650DA=V4: GOSUB 1030: V4=DA
660DA=V5: GOSUB 1030: V5=DA
670DA=V7: GOSUB 1030: V7=DA
680DA=V8: GOSUB 1030: V8=DA
690DA=V9: GOSUB 1030: V9=DA
700DA=VA: GOSUB 1030: VA=DA
710DA=VB: GOSUB 1030: VB=DA
720DA=VC: GOSUB 1030: VC=DA
730DA=VE: GOSUB 1030: VE=DA
740DA=VF: GOSUB 1030: VF=DA
750DA=VG: GOSUB 1030: VG=DA
760DA=VH: GOSUB 1030: VH=DA
770DA=VI: GOSUB 1030: VI=DA
780DA=V6: GOSUB 1030: V6=DA
790DA=VD: GOSUB 1030: VD=DA
800REM WE NOW USE THE FOUR CHECK RELATIONSHIPS TO TEST
GOODNESS OF DATA
810PRINT" CHECK 1"
820PRINT" V6+V4=V2+V8"
830MA=V6^2+V4^2: MA=INT(MA*1000/1.0E07)/1000
840MB=V2^2+V8^2: MB=INT(MB*1000/1.0E07)/1000
850PRINT" ;MA; " VS " ;MB
860PRINT" CHECK 2"
870PRINT" V2+0.5*(V5+V8+V1+V3)=V13+V14+V15"
880MC=VD^2+VE^2+VF^2: MC=INT(MC*1000/1.0E07)/1000
890MD=V2^2+0.5*(V5^2+V8^2+V1^2+V3^2): MD=INT(MD*1000/1.0E07)/1000
900PRINT" ;MC; " VS " ;MD
910PRINT" CHECK 3"
920PRINT" V16+V17+V18=V8+0.5*(V2+V5+V9+V7)"
930ME=V8^2+V1^2+V1+V2: ME=INT(ME*1000/1.0E07)/1000
940MF=V8^2+0.5*(V2^2+V5^2+V9^2+V7^2): MF=INT(MF*1000/1.0E07)/1000
950PRINT" ;ME; " VS " ;MF
960PRINT" CHECK 4"
970PRINT" V6*V4=V2*V8-(V11-0.5*(V2+V8))^2"
980MG=V6^2*V4^2: MG=INT(MG*1000/1.0E14)/1000
990MH=V2^2*V8^2-(V2^2+0.5*(V2^2+V8^2))^2
1000MH=INT(MH*1000/1.0E14)/1000
1010PRINT" ;MH; " VS " ;MH
1020POKE144,46:
1030REM ROUNGING ROUTINE FOR VELOCITYS
1040BE=BD+1
1050IC=INT((DA*10^BE)/1.0E03)
1060CD=INT((DA*10^BD)/1.0E03)
1070BI=IC-10*CD
1080IF BI<5 THEN 1100
1090CD=CD+1
1100 DA = CD * 1.0E03 / (10^BD)
1110 RETURN
1120 REM DATA INPUT
1130 REM DENSITY
1140 DATA 1680
1150 REM V1, V2, V3
1160 DATA 5127.6, 1899.6, 2518.4
1170 REM V4, V5, V6
1180 DATA 2456.6, 4460.4, 1939.6
1190 REM V7, V8, V9
1200 DATA 2510.6, 2488.3, 4045.8
1210 REM V10, V11, V12
1220 DATA 2273.0, 2283.6, 4527.0
1230 REM V13, V14, V15
1240 DATA 4555.6, 2457.6, 2443.9
1250 REM V16, V17, V18
1260 DATA 4551.6, 1843.9, 2205.3
APPENDIX 2.E

The following computer program calculates the pressure derivatives of the elastic stiffness constants for a monoclinic crystal. To perform the required calculations, the program requires the following data: elastic stiffness constants, elastic compliances, sample density, experimentally measured ultrasonic wave velocities and the f'/f₀ values.

10 REM CALCULATION OF PRESSURE DERIVATIVES FOR FIRST TEN ELASTIC CONSTANTS
20 REM NEED ELASTIC CONSTANTS, COMPLIANCES + INITIAL VELOCITIES AND F'/F₀
30 MODE 7
40 READ C1, CU, CX, C2, C3, CF, C4, CC, C5, C6
50 CLS
60 @%=&01050B
70 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Elastic Constants N/m²" 
80 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Elastic Constants N/m²" 
90 PRINT" C11 = ";C1;" N/m²" 
100 PRINT" C13 = ";CU;" N/m²" 
110 PRINT" C15 = ";CX;" N/m²" 
120 PRINT" C22 = ";C2;" N/m²" 
130 PRINT" C33 = ";C3;" N/m²" 
140 PRINT" C35 = ";CF;" N/m²" 
150 PRINT" C44 = ";C4;" N/m²" 
160 PRINT" C46 = ";CC;" N/m²" 
170 PRINT" C55 = ";C5;" N/m²" 
180 PRINT" C66 = ";C6;" N/m²"
190 PROCpause
200 REM NOW INPUT COMPLIANCES
210 READ S1, SE, SU, SX, S2, SB, SA, S3, SF, SC, S5, S6
220 CLS
230 PRINTCHR$(141)+CHR$(157)+CHR$(132)+" Elastic Compliances m²/N"
240 PRINTCHR$(141)+CHR$(157)+CHR$(132)+" Elastic Compliances m²/N"
250 PRINT" S11 = ";S1;" m²/N" 
260 PRINT" S12 = ";SE;" m²/N" 
270 PRINT" S13 = ";SU;" m²/N" 
280 PRINT" S15 = ";SX;" m²/N" 
290 PRINT" S22 = ";S2;" m²/N" 
300 PRINT" S23 = ";SB;" m²/N" 
310 PRINT" S25 = ";SA;" m²/N"
320 PROCpause
330 CLS
Elastic Compliances m^2/N

Elastic Compliances m^2/N

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Wave velocity m/s

Values for f'/fo

Values for f'/fo

Values for f'/fo
Values for f'/'fo"

830 PRINT "Z prop X pol shear F7 = ";F7;" KBar -1"
840 PRINT "Z prop Y pol shear F8 = ";F8;" KBar -1"
850 PRINT "Z prop longit F9 = ";F9;" KBar -1"
860 PRINT "101 prop -101 shear F10 = ";F10;" KBar -1"
870 PRINT "101 prop Y pol shear F11 = ";F11;" KBar -1"
880 PRINT "101 prop longit F12 = ";F12;" KBar -1"
890 PROC pause
900 REM NOW CALCULATE pV' - the corrected velocity
derivatives
910 BM=S1+S2+S3+2*(SE+SB+SU):REM BULK MODULUS
920 BA=S1+SE+SU;BB=SE+S2+SB;BC=SU+SB+S3;BD=SX+SA+SF
930 LC=BA:REM LC IS STORE FOR LINEAR COMPRESSIBILITY
940 REM DERIVATIVES OF DN*V^2 IS PUT BACK INTO F
950 REM NOTE /1.0E8 CONVERTS FROM KBAR TO NEWTONS/METER
960 REM DO FOR X DIRECTION
970 F1=DN*V1*V1*(2*F1/1.0E08+BM-LC*2)
980 F2=DN*V2*V2*(2*F2/1.0E08+BM-LC*2)
990 F3=DN*V3*V3*(2*F3/1.0E08+BM-LC*2)
1000 REM NOW FOR Y DIRECTION
1010 LC=BB
1020 F4=DN*V4*V4*(2*F4/1.0E08+BM-LC*2)
1030 F5=DN*V5*V5*(2*F5/1.0E08+BM-LC*2)
1040 F6=DN*V6*V6*(2*F6/1.0E08+BM-LC*2)
1050 REM NOW DO FOR Z DIRECTION
1060 LC=BC:REM LINEAR COMPRESSIBILITY
1070 F7=DN*V7*V7*(2*F7/1.0E08+BM-LC*2)
1080 F8=DN*V8*V8*(2*F8/1.0E08+BM-LC*2)
1090 F9=DN*V9*V9*(2*F9/1.0E08+BM-LC*2)
1100 REM NOW DO FOR (101) DIRECTION
1110 LC=BA*0.5+BC*0.5+BD*0.5
1120 F10=DN*VA*VA*(2*F10/1.0E08+BM-LC*2)
1130 F11=DN*VB*VB*(2*F11/1.0E08+BM-LC*2)
1140 F12=DN*VC*VC*(2*F12/1.0E08+BM-LC*2)
1150 REM NOW GRADIENTS ARE CORRECTED FOR PRESSURE
CHANGES
1160 CLS
1170 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Velocity
derivatives (p*v^2)"
1180 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Velocity
derivatives (p*v^2)"
1190 @%=&020306
1200 PRINT " X prop longit F1 = ";F1
1210 PRINT " X prop Y pol shear F2 = ";F2
1220 PRINT " X prop Z pol shear F3 = ";F3
1230 PRINT " Y prop X pol shear F4 = ";F4
1240 PRINT " Y prop longit F5 = ";F5
1250 PRINT " Y prop Z pol shear F6 = ";F6
1260 PROC pause
1270 CLS
1280 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Velocity
derivatives (p*v^2)"
1290 PRINTCHR$(141)+CHR$(157)+CHR$(132);" Velocity
derivatives (p*v^2)"
1300 PRINT " Z prop X pol shear F7 = ";F7
1310 PRINT " Z prop Y pol shear F8 = ";F8
1320 PRINT " Z prop long F9 = ";F9

132
1330 PRINT "101 prop -101 shear F10 = " ;F10
1340 PRINT "101 prop Y pol shear F11 = " ;F11
1350 PRINT "101 prop long F12 = " ;F12
1360 PROC pause
1370 CLS
1380 PRINT CHR$(141) + CHR$(157) + CHR$(132); "Pressure derivatives"
1390 PRINT CHR$(141) + CHR$(157) + CHR$(132); "Pressure derivatives"
1400 REM Z DESIGNATION IS A PRESSURE DERIVITIVE
1410 Z6=F2:Z2=F5:Z4=F8:REM C66,C22,C44 CALCULATED
1420 ZC=(2*F11-Z4-Z6)/2:REM C46 DERIVITIVE
1430 VDU28,0,24,39,2:REM SET WINDOW
1440 PRINT " d(C22)/dp
1450 PRINT " d (C44) / d p
1460 PRINT " d (C66)/dp
1470 PRINT " d(C46)/dp
1480 PROC pause
1490 CLS
1500 REM CALCULATE REMAINING DERIVITIVES BY EXACT MEANS
1510 REM P PREFIXES EQUATIONS IN NOTES
1520 PA=F1+F3
1530 PB=DN*V1*V1*F3+DN*V3*V3*F1
1540 PC=F7+F9
1550 PD=DN*V7*V7*F9+DN*V9*V9*F7
1560 PE=F10+F12-0.5*(F1+F3+F9+F7)
1570 REM NOW GET DERIVITIVE OF C55
1580 Z5=(PE*2*CX*CF+PB*CF+PD*CX-CF*C5*PA-CX*C5*PC)/(CF*C1-CF*C3+CX*C3-CX*C5)
1590 Z1=PA-Z5:REM DERIVITIVE OF C11
1600 Z3=PC-Z5:REM DERIVITIVE OF C33
1610 ZF=(C3*Z5+C5*Z3-PD)/(2*CF):REM DERIVITIVE OF C35
1620 Z1=(C1*Z5+2*CF)*(Z1+Z5+ZX)
1630 REM NOW GET DERIVITIVE OF C13
1640 M1=(C5+C3+2*CF)*Z1
1650 M2=(C1+C5+2*CF)*Z5
1660 M3=-4*(DN*VA*VA*F12+DN*VC*VC*F10)
1670 M4=2*(CX*CF+CU+C5)
1680 ZU=(M1+M2+M3)/M4
1690 ZU=ZU-(ZX+ZF+Z5)
1700 REM NOW PRINT LAST SIX DERIVITIVES
1710 CLS
1720 PRINT " d(C11)/dp = " ;Z1
1730 PRINT " d(C33)/dp = " ;Z3
1740 PRINT " d(C55)/dp = " ;Z5
1750 PRINT " d(C15)/dp = " ;ZX
1760 PRINT " d(C35)/dp = " ;ZF
1770 PRINT " d(C13)/dp = " ;ZU
1780 PROC pause
1790 REM DATA AREA HERE
1800 REM ELASTIC CONSTANTS units NM-2
1810 DATA 4.4081E10 :REM C11
1820 DATA 1.6994E10 :REM C13
1830 DATA -1.733E10 :REM C15
1840 DATA 3.3424E10 :REM C22
1850 DATA 2.7343E10 :REM C33
1860 DATA -.1615E10 :REM C35

133
1870 DATA 1.0402E10 : REM C44
1880 DATA 0.0529E10 : REM C46
1890 DATA 1.0745E10 : REM C55
1900 DATA .6062E10 : REM C66
1910 REM NOW COMPLIENCES units 1/nm-2
1920 DATA 3.2160E-11 : REM S11
1930 DATA -1.1296E-11 : REM S12
1940 DATA -1.1804E-11 : REM S13
1950 DATA 1.2229E-12 : REM S15
1960 DATA 5.5932E-11 : REM S22
1970 DATA -3.2903E-11 : REM S23
1980 DATA 4.0755E-12 : REM S25
1990 DATA 6.7648E-11 : REM S33
2000 DATA 1.8853E-12 : REM S35
2010 DATA 9.6140E-11 : REM S44
2020 DATA -8.3896E-13 : REM S46
2030 DATA 9.4337E-11 : REM S55
2040 DATA 1.6497E-10 : REM S66
2050 REM NOW READ IN DENSITY AND VELOCITIES
2060 DATA 1680 : REM DENSITY
2070 DATA 5127.6 : REM V1
2080 DATA 1899.6 : REM V2
2090 DATA 2518.4 : REM V3
2100 DATA 2456.6 : REM V4
2110 DATA 4460.4 : REM V5
2120 DATA 1939.6 : REM V6
2130 DATA 2510.6 : REM V7
2140 DATA 2488.3 : REM V8
2150 DATA 4045.8 : REM V9
2160 DATA 2273.0 : REM V10
2170 DATA 2283.6 : REM V11
2180 DATA 4527.0 : REM V12
2190 REM NOW READ IN f'/fo units KBar-1
2200 DATA 9.5008E-03 : REM F1
2210 DATA 3.5035E-03 : REM F2
2220 DATA 4.2808E-03 : REM F3
2230 DATA 3.9285E-03 : REM F4
2240 DATA 1.8990E-02 : REM F5
2250 DATA 3.7818E-03 : REM F6
2260 DATA 6.4870E-03 : REM F7
2270 DATA 4.5545E-03 : REM F8
2280 DATA 1.0610E-02 : REM F9
2290 DATA 5.1498E-03 : REM F10
2300 DATA 4.5116E-03 : REM F11
2310 DATA 1.1428E-02 : REM F12
2320 @%=10:STOP
2330 DEF PROCpause:*FX21,0
2340 PRINT CHR$(136);" Press a key to continue"
2350 A=GET:ENDPROC
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