HIGH PRESSURE STUDIES OF THE CONDUCTION BANDS 
OF GERMANIUM AND GALLIUM ARSENIDE

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ABSTRACT

In order to understand fully and predict accurately the behaviour of transferred electron devices in materials like GaAs an exact knowledge is required of both the structure of the conduction band and of the magnitude of the intervalley parameters. High pressure techniques provide a powerful tool for the study of these parameters and details of their application are described in this thesis.

Under pressure different band edges move in energy at different rates giving rise to electron transfer between states which leads to information about the relative strengths of the various scattering processes. By extrapolation back to atmospheric pressure the normal position of the various states in energy and k-space may be obtained. The band structure of germanium at high pressures becomes similar to that of silicon at atmospheric pressure, making \( \Delta_{1c} \) minima accessible to direct electrical investigation. Here the temperature dependence of the electron mobility has been measured in both the \( L_{1c} \) and \( \Delta_{1c} \) valleys of germanium. The \( L_{1c} \) mobility was found to vary with the characteristic \( T^{-1.5} \) temperature dependence typical of acoustic deformation potential scattering. On the other hand the \( \Delta_{1c} \) electron mobility was found to vary from \( \approx 800 \text{ cm}^2\text{v}^{-1}\text{s}^{-1} \) at room temperature to \( \approx 6400 \text{ cm}^2\text{v}^{-1}\text{s}^{-1} \) at 120K, corresponding to a temperature dependence of \( T^{-2.7} \), similar to that in silicon. The analysis of both the \( L_{1c} \) and \( \Delta_{1c} \) mobilities show that the \( L_{1c} \) valley mobility is dominated by the acoustic deformation potential scattering whereas the \( \Delta_{1c} \) valley mobility is dominated by the intervalley scattering. Using the effective mass ratios \( m^*_t = 0.288, m^*_c = 1.353 \) and an acoustic deformation potential
of 3.61eV gave \( \Delta_{1c} \) intervalley coupling constants as \( 3.7 \times 10^8 \text{eV cm}^{-1} \) and \( 2.9 \times 10^8 \text{eV cm}^{-1} \) for 430K-LO and 320K-LA phonons respectively. A negligible coupling constant was found for the low energy, 100K-LA phonons in agreement with the already published results for silicon and GaP.

To obtain good agreement with the high pressure results the electron effective mass in the \( \Delta_{1c} \) valleys of germanium was found to be about 50% higher than the measured effective mass in silicon. Since the interpretation of the pressure dependence of the transport properties of semiconductors strongly dependent on the effective mass of electrons, attempts were made to measure this parameter by magneto-phonon technique using ultra-pure material. Although it was not possible to observe the magneto-phonon oscillations in germanium as a function of pressure, nevertheless pressure effects on ultra-pure material made it possible to determine with some accuracy the pressure coefficients for both the \( L_{1c} \) and \( \Delta_{1c} \) valleys of germanium. The measured pressure coefficients are:

\[
\frac{dE_{L}}{dP} = 4.8 \pm 0.2 \times 10^{-6} \text{eV bar}^{-1},
\]

\[
\frac{dE_{\Delta}}{dP} = -2.4 \pm 0.4 \times 10^{-6} \text{eV bar}^{-1}.
\]

These values of pressure coefficients are independent of the density of states of the minima involved or their atmospheric pressure energy separation. However, taking the density of states effective mass ratios of \( m^*_L = 0.50 \), \( m^*_\Delta = 1.58 \) and \( m^*_V = 0.4 \) for the \( L_{1c}, \Delta_{1c} \) minima of the conduction band and the valence band respectively, best fits to the experimental resistivity were obtained giving the energy separation \( \Delta E_{L-\Delta} = 0.21 \pm 0.01 \text{ eV} \) at atmospheric pressure and \( (L_{1c} - \Delta_{1c}) \) band crossover at 29 \pm 2 k.bar.

The study of GaAs under uniaxial stress has confirmed the \( \Gamma-L-X \)
(iii)

The resistance of a number of samples with (100) stress was measured up to 10 k-bar using four probe method. No exponential change beyond 5 k-bar was found in contradiction to the observations of previous workers. The analysis of the (100) stress results appear to resolve the discrepancies between the stress and electroreflectance data and suggest that the large value of the shear deformation potential \( \Gamma_{\text{u}}^x = (21 \pm 9) \text{eV} \), obtained by other workers must be revised downwards and should have a value closer to 8.0 eV as observed for silicon. A possible explanation as to why those workers obtained such a large value of the deformation potential is also given.

The measured electron effective mass in the \( \Gamma_{1c} \) minimum under uniaxial stress agrees well with the resistance-stress results. It was found that the effective mass is proportional to the applied stress with the constants of proportionality as

\[
\frac{\Delta m^*}{m_0} (100) = (0.23 \pm 0.06) \% \text{ k bar}^{-1}
\]

\[
\frac{\Delta m^*}{m_0} (111) = (0.075 \pm 0.015) \% \text{ k bar}^{-1}
\]
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PUBLICATIONS

The following papers, based on this work, have been published in the scientific literature.


3. The influence of high stress on the $\Gamma_{1c}$ conduction band effective mass of GaAs. *Solid State communications, 34*, 335 (1980).


LIST OF SYMBOLS

\( E_g \)  
Fundamental Energy gap

\( E_0 \)  
Energy difference between the conduction and valence bands at the \( \Gamma \)-point

\( E_1 \)  
Energy difference between the conduction and valence bands at the \( L \)-point.

\( E_2 \)  
Energy difference between the conduction and valence bands at the \( X \)-point.

\( E_C \)  
Conduction band energy.

\( E_V \)  
Valence band energy.

\( E_{V1} \)  
Heavy hole band energy

\( E_{V2} \)  
Light hole band energy

\( E_{V3} \)  
Split off band energy

\( E_F \)  
Fermi Energy

\( h \)  
Planck's constant

\( \hbar \)  
\( \frac{\hbar}{2\pi} \)

\( k_B \)  
Boltzmann Constant

\( k \)  
Wave vector

\( \Delta \)  
Spin orbit splitting

\( m_o \)  
Free electron mass

\( m^* \)  
Effective mass

\( m_{DS} \)  
Density of states effective mass

\( N_C \)  
Density of states of the Conduction band.

\( N_V \)  
Density of states of the Valence band.

\( F \)  
Electric field

\( v \)  
Electron velocity

\( \mu_n \)  
Electron mobility

\( \mu_p \)  
Hole mobility

\( \mu_d \)  
Deformation potential scattering mobility
(vii)

\begin{align*}
E_1 & \quad \text{Acoustic deformation potential} \\
D & \quad \text{Density of the material} \\
s & \quad \text{Sound velocity} \\
\rho & \quad \text{Resistivity} \\
\sigma & \quad \text{Conductivity} \left( \sigma = \frac{1}{\rho} \right) \\
e & \quad \text{Electron charge} \\
E & \quad \text{Electron energy} \\
T & \quad \text{Temperature} \left( \text{K} \right) \\
p & \quad \text{Electron momentum} \\
\mu_{i,v} & \quad \text{Intervalley scattering mobility} \\
\mu_{i,I} & \quad \text{Ionized impurity scattering mobility} \\
E_p & \quad \text{Momentum matrix element} \\
\omega & \quad \text{Phonon frequency} \\
e^* & \quad \text{Effective charge} \\
M & \quad \text{Reduced mass of the atom} \\
\Omega & \quad \text{Volume of the unit cell} \\
\theta & \quad \text{Polar phonon temperature} \\
\omega_L & \quad \text{Longitudinal optical phonon frequency} \\
\omega_p & \quad \text{Plasma frequency} \\
e & \quad \text{Dielectric constant} \\
K & \quad \text{Band anisotropy factor} \\
\tau & \quad \text{Relaxation time} \\
J & \quad \text{Current density} \\
V_H & \quad \text{Hall voltage} \\
R_H & \quad \text{Hall constant} \\
P & \quad \text{Hydrostatic pressure} \\
\chi & \quad \text{Uniaxial stress} \\
B & \quad \text{Magnetic field}
\end{align*}
\(d\) Sample thickness
\(I\) Sample current
\(\gamma\) Scattering factor
\(F_T\) Gunn threshold field
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CHAPTER 1

INTRODUCTION

The pioneer work of P.W. Bridgman and W. Paul on the electrical properties of semiconductors under pressure laid the foundation of high pressure research in the thirties. However, their field of investigation was limited due to the scarcity of good quality material. After high purity single crystals became available the interest in the high pressure research grew enormously.

Pressure is a useful variable together with temperature and alloying experiments for the determination of band structure parameters. Under pressure different band edges move in energy at different characteristic rates from which they can be identified. The variation of band structure with alloy composition is sometimes qualitatively similar to the effect of pressure on one of the components. Hence it may be possible to study an alloy system by the application of pressure to one of the components. The observation of electron transfer under pressure in conjunction with high field measurements can also give information about the relative strengths of the various scattering processes between band states. These are required for an assessment of device possibilities.

In order to understand fully and predict accurately the behaviour of transferred electron devices in materials like GaAs two pieces of information are essential. Firstly, the structure of the conduction band is required including the knowledge of higher lying minima. Secondly, the magnitude of the electron-phonon intervalley scattering parameters are required. In theoretical calculations it is normally assumed that intervalley scattering between the L- minima is as measured in germanium, while intervalley X or A valley scattering is as measured in silicon. In order to test these assumptions we have undertaken both measurements in one material. Germanium was chosen since it allows the study of the intervalley L- scattering at atmospheric pressure and intervalley X- scattering at
high pressures.

Bridgeman\(^{(1)}\) was the first to study n-type germanium up to a pressure of \(\approx 100\) k-bar under quasi hydrostatic conditions. Later Drickamer and Minomura\(^{(2)}\) extended the pressure range, under nearly hydrostatic conditions, to \(\approx 400\) k-bar and observed a semiconductor to metal phase transition between 120 - 125 k-bar. The above experiments, in which the pressure was not easily controllable especially in the low pressure region, did not provide any information about the intervalley scattering strengths. On the other hand the studies of Nathan et al\(^{(3)}\) were only up to 30 k-bar, where the pressure was insufficient to isolate carriers in the \(\Delta\)-valleys.

After the development of the high pressure technique, using epoxy resin by Pitt and Lees\(^{(4)}\), at S.T.L., Harlow, England, it became possible to apply pressures to single crystals of germanium well in excess of the \((111) - (100)\) crossover and then to lower the temperature to 100K in a controlled manner. Fletcher et al\(^{(5)}\) were the first to apply this technique to a pressure of \(\approx 65\) k-bar to single crystals of Ge and studied the interband scattering. The work to be reported here is an extension of the above experiments to the measurements of temperature dependence of the electron mobility in the \(\Delta\)-valleys of Ge which provides the \(X\)-intervalley scattering parameters.

To establish the correct band structure of GaAs including the positions of the higher lying minima, the second important parameter required as mentioned earlier, GaAs was studied under uniaxial stress. There existed some controversy about the conduction band ordering in GaAs. Vinson et al\(^{(6)}\) and Adams et al\(^{(7)}\), by studying the effects of the hydrostatic and uniaxial stress on the threshold for the Gunn effect, suggested for the first time that the \(L\) minima are below the \(X\) minima with an energy separation of \(\Delta E_{\Gamma-L} = 0.38\) eV and \(\Delta E_{\Gamma-X} = 0.4\) eV. Aspnes\(^{(8)}\), from the
electroreflectance measurements, agreed with the above conduction band ordering but gave slightly different energy separations as $\Delta E_{T-L} = 0.29\text{eV}$ and $\Delta E_{T-X} = 0.48\text{eV}$. Measurements of Harris et al\textsuperscript{(9)} and Pickering et al\textsuperscript{(10)} of the effect of the (100) uniaxial stress on both the low-field resistivity and on the threshold fields for the Gunn effect agree with one another but gave an anomalously high value for the deformation potential $E_u^x$ of $21(\pm 9)\text{eV}$ compared to about $8\text{eV}$ for silicon and germanium. With all these discrepancies in mind it was decided to undertake the low field resistivity measurements by using a more suitable four probe method in an attempt to resolve the apparent discrepancy between different measurements.

After giving a general review of the band structure of the group IV and III-V compounds in Chapter 2, the effects of pressure on band structure and electrical conductivity are described in Chapters 3 and 4. Chapter 5 deals, in detail, with the experimental arrangements. In Chapters 6, 7 and 8 we give an account of the results of the pressure experiments on n-type germanium, ultra pure germanium and GaAs respectively. These results not only throw light on the pressure coefficients of different energy minima of the conduction bands of Ge but also provide information about the intervalley $L$ and intervalley $X$ scattering strengths. It also removes some of the apparent discrepancy between the high stress and the electroreflectance data for GaAs. Finally in Chapter 9 the implications of the results and further developments are discussed.

During the period of investigation we have made use of the "SERC High pressure facility at S.T.L. Harlow, for the hydrostatic pressure while for the uniaxial stress we have used the apparatus developed at Surrey University."
2.1. CRYSTAL STRUCTURE AND BINDING

The group IV semiconductors except β-tin and lead crystallize into diamond structure whereas the III-IV compounds (i.e. Phosphides, Arsenides and Antimonides of Ga, In, Al and B) crystallize into the zinc-blende structure. The only difference between the two types of structure is that in the diamond lattice all the atoms are identical whereas in the zinc-blende structure atoms of group III and V occupy alternate lattice sites. So in zinc-blende structure each atom of the chemical species is surrounded by four nearest neighbour atoms of the other chemical constituent forming a regular tetrahedron. The diamond and zinc-blende lattices can be described as two intertwined face-centred cubic lattices as shown in Figure 2.1.

The crystal atoms in a diamond structure are bound by pure homopolar cohesive forces which act as links between the neighbouring atoms. In III-V compounds group III atoms have three valence electrons whereas group V atoms have five valence electrons. The sum of the valence electrons of the two nearest neighbours is therefore always eight. A covalent bond may be formed if the pentavalent atom gives away one valence electron to the trivalent atom such that each atom will have four valence electrons on average as in the diamond lattice. But this covalent bond will not be completely identical with diamond lattice because of the unequal net charges on their atomic cores i.e. -e on the III atom and +e on the V atom. This type of bond, in which the centre of density of the electron distribution is half-way between III\(^{3+}\) and V\(^{5+}\) ions, is characterised by the formula III\(^{-1}\) V\(^{+1}\).

The other possibility is a heteropolar or ionic bond. In this case
FIG. 2.1 THE DIAMOND OR ZINC-HELDE LATTICE.
the group III atom loses all its valence electrons to group V atom, so that both atoms have closed electron shells and the bond is formed by the electrostatic attraction of ions. This case can be represented by the formula \( \text{III}^{+3} \text{V}^{-3} \).

A continuous transition is also possible between these two extremes with an important intermediate case where the centre of density of the electron distribution is moved to such an extent towards the pentavalent atom that the effective charge on the lattice atom is zero. This case, which is described by the formula \( \text{III}^0 \text{V}^0 \), represents neutral bonding. Theoretical calculations of Coulson et al\(^{(11)}\) for the effective charges of trivalent and pentavalent lattice atoms with zinc-blende structure show that the magnitude of the effective charge is always less than one, which means that the binding is only slightly ionic in nature.

Many attempts have been made to correlate the band structure and properties of the III-V compounds with those of group IV elements in terms of their crystal structure and binding. Madelung\(^{(12)}\) discusses this subject in some detail and argues that since the lattice constants of the elements within the isoelectronic row of the periodic table, e.g. Ge, GaAs, ZnSe etc. are found to be the same (within 1%) the heteropolar contribution to the III-V bond would not be large, hence there is predominantly covalent bonding.

2.2. BAND STRUCTURE

The band structure of the III-V compounds is basically similar to that of the group IV elements i.e. Ge and Si. Although there are some differences caused by the absence of inversion symmetry in the crystal lattice, such fine details are not important for pressure experiments. The accepted band structures, at atmospheric pressure, for GaAs, Ge and Si are shown in Figure 2.2.

From the Figure it is clear that the valence bands of all three semiconductors have a maximum at \( k = 0 \), the centre of the Brillouin zone,
INTERACTION AT ATMOSPHERIC PRESSURE.

FIG. 2.2. BAND STRUCTURE OF GAS, GERMANIUM AND SILICON WITH INCORPORATION OF SPIN-ORBITT.

(a) Ge

(b) Si

(c) Gas
normally referred to as the Γ-point. There is a two-fold degeneracy in
the valence band, there being a heavy-hole band and a light-hole band which
form the top of the band. There is a third band split off by spin orbit
interaction which forms the lowest maximum of the valence band. The
conduction band structure of all the semiconductors consists of minima
in \( k = 000 (\Gamma_{1c}-\text{point}), k = 111 (L_{1c}-\text{point}) \) and \( k = 100 (X_{1c}-\text{point}) \) directions.

The lowest energy minima in the conduction band of different semiconductors
lie in one of the above mentioned crystallographic directions.

In GaAs the lowest conduction band energy state lies at the centre of
the Brillouin zone, the \( \Gamma_{1c} \) point, and consists of a single minimum. There
is a controversy about the next higher minima. It was thought that the
X-valleys are below the L-valleys. But the recent experimental and
theoretical work of Vinson et al\(^{(6)}\) and Aspnes\(^{(8)}\) showed that L-valleys are
below the X-valleys. Again there is a controversy about the actual position
of the X-valleys in the Brillouin zone. Welber et al\(^{(13)}\) using Raman
spectroscopy found that the X-minima are about 10% away from the zone
boundary. Thus instead of three equivalent valleys at the zone boundary
they needed six valleys, at the \( \Delta_{1c} \) points, as in silicon, to explain
their experimental results in contrast to the high pressure results of Pitt
and Lees\(^{(4)}\) for GaAs where they concluded that the minima are situated at
the zone edge. Hence we have left out this point and drew the Γ-L-X band
ordering as shown in Figure 2.2.

As a result of the theoretical calculations by Herman\(^{(14)}\) and the
cyclotron resonance experiments of Lincoln\(^{(15)}\) and Berkeley\(^{(16)}\) groups it
became accepted that the lowest energy minima in the conduction band of
germanium lie at the \( L_{1c} \) points and consists of four equivalent valleys.
The next higher minimum is at the \( \Gamma_{1c} \)-point and still slightly higher in
energy are the set of six equivalent minima in the (100) directions in \( k \)
space at about 85% of the way from the centre of the Brillouin zone to its
boundary.
In case of silicon, on the other hand, various experiments established that the lowest energy minima are in the (100) directions approximately the same amount inwards from the zone boundary as the X-valleys in Ge, hence six in number. The next higher minima, having four equivalent valleys, are at the L\textsubscript{1c}-points but still higher is a single minimum at the Γ\textsubscript{1c}-point.

The surfaces of constant energy at the centre of the Brillouin zone are spherical, thus the effective mass of the electrons is isotropic. The constant energy surfaces around other symmetry points L\textsubscript{1c} and Δ\textsubscript{1c} are ellipsoidal. Since in germanium and silicon the lowest lying minima, at atmospheric pressure, are at the L\textsubscript{1c} and Δ\textsubscript{1c} points respectively, their constant energy surfaces are ellipsoidal. The electron effective mass in these cases is anisotropic and has two components called the transverse, \textit{m}_t, and longitudinal, \textit{m}_l, effective masses. The constant energy surfaces of the electrons in the Γ\textsubscript{1c}, L\textsubscript{1c} and Δ\textsubscript{1c} minima are shown in Figure 2.3.

2.3. k.p THEORY

Shockley\textsuperscript{18} and Dresselhaus\textsuperscript{16,19} were the first to use "k.p" perturbation technique to calculate the shape of the bands in the vicinity of the most important symmetry points for semiconductors with diamond and zinc-blende structures. Later Kane\textsuperscript{20} developed a more rigorous treatment to calculate the band structure of InSb. With this method he treated exactly the interaction of two closely spaced conduction and valence bands through the "k.p" and "k-independent" spin orbit interaction. He then treated the interactions with higher bands by second order perturbation. This technique was extended to calculate the band structure of the other III-V compounds by Braunstein and Kane\textsuperscript{21}.

According to Kane's analysis the effective mass of the carriers could
FIG. 2.3(a) CONSTANT ENERGY SURFACES FOR ELECTRONS IN THE $P_{1c}$ MINIMUM AS IN GaAs.
FIG. 2.3 (b) CONSTANT ENERGY SURFACES FOR ELECTRONS IN THE $L_{1c}$ MINIMA AS IN GERMANIUM.
FIG. 2(c) CONSTANT ENERGY SURFACES FOR ELECTRONS IN THE $A_6c$ MINIMA AS IN SILICON.
be written as

\[
\frac{1}{m^*_i} = \frac{1}{m_0} + \frac{2}{m_0} \left[ \sum_{n'} \frac{|i.p_{nn'}|^2}{E_n(k') - E_{n'}(k'_0)} \right]
\]

where \(i\) is a unit vector in the direction of the \(i\)th principal axis and \(\frac{2}{m_0} |i.p_{nn'}|^2\) represents the square of the momentum matrix element relating to the conduction and valence bands. The other term within the brackets is the sum of the reciprocals of the band energies involved in the interaction. The expressions for the effective mass of the electrons in a particular band i.e. \(\Gamma_{1c}\), \(L_{1c}\) and \(\Delta_{1c}\) or \(\chi_{1c}\) could be derived from equation 2.1 provided the respective band energies and momentum matrix element are known.

2.3.1. \(\Gamma_{1c}\) EFFECTIVE MASS

The effective mass of electrons in the \(\Gamma_{1c}\) conduction band can be written from equation 2.1 as

\[
\frac{m_0}{m^*(\Gamma_{1c})} = 1 + \frac{2}{m_0} \sum_{n'} \frac{|<\Gamma_{1c}|P|n'>|^2}{E(\Gamma_{1c}) - E(n')} \quad 2.2
\]

In polar semiconductors \(\Gamma_{1c}\) band interact with \(\Gamma_{15c}\) and \(\Gamma_{15v}\), as discussed by Cardona\(^{(22)}\). He treated \(E_P\), the momentum matrix element as constant with a value of 20.8eV for all the III-V compounds. But recently Lawaetz\(^{(23)}\) and Hermann et al\(^{(24)}\) claim that in order to calculate the effective mass parameters more accurately one has to take not only still higher lying bands but also determine the momentum matrix accurately. According to Hermann et al\(^{(24)}\) five band k.p theory the equation 2.2 can be written as

\[
\frac{m_0}{m^*(\Gamma_{1c})} = 1 + \frac{E_{P-\Gamma}}{3} \left( \frac{2}{E_0} + \frac{1}{E_0 + \Delta_0} \right) - \frac{E_{P-\Gamma}}{3} \left( \frac{2}{E(\Gamma_8) - E_0} + \frac{1}{E(\Gamma_7) - E_0} \right) + C \quad 2.3
\]
The energy levels are illustrated in Figure 2.2. $E_{p-\Gamma}$ relates to the coupling of the conduction band with the valence band while $E'_{p-\Gamma}$ relates to its coupling with the higher lying minima. $C$ is a correction for even higher lying bands and Hermann et al.\(^{(24)}\) concludes that $C$ can be taken as constant and equal to -2. They also conclude that $E_{p-\Gamma} = 29eV$ and $E'_{p-\Gamma} = 6eV$ for GaAs.

In germanium-like structure the interaction between $\Gamma_{1c}(\Gamma_{2-})$ with higher lying bands vanishes for parity reasons, as pointed out by Cardona.\(^{(22)}\) So ignoring the second and third terms in equation 2.3 gives the effective mass for $\Gamma_{2-}$ band in diamond structure as

$$\frac{m_0}{m^*(\Gamma_{2-})} = 1 + \frac{E_{p-\Gamma}}{3} \left[ \frac{2}{E_0} + \frac{1}{E_0 + \Delta_0} \right]$$

2.4

### 2.3.2 $L_{1c}$ EFFECTIVE MASS

The transverse effective mass at the $L_{1c}$ point is given entirely by the interaction with $L_{3c}$ and $L_{3y}$ bands because all the other bands are far away in energy. Thus $m^*(L_{1c})$ can be obtained from equation 2.1 as:

$$\frac{m_0}{m^*(L_{1c})} = 1 + \frac{E_{p-L}}{3} \left( \frac{2}{E_1} + \frac{1}{E_1 + \Delta_1} \right) - \frac{E_{p-L}}{E_1 - E_1}$$

2.5

Again for germanium type structures the equation 2.5 could be simplified by ignoring the higher band interaction terms as

$$\frac{m_0}{m^*(L_{1c})} = 1 + \frac{E_{p-L}}{3} \left( \frac{2}{E_1} + \frac{1}{E_1 + \Delta_1} \right)$$

2.6

where $E_1$ is the \( E(L_{1c}) - E(L_{3y}) \) energy gap and $\Delta_1$ is the spin orbit splitting of $L_{3y}$. The value of the constant $E_{p-L}$, in this case, quoted by Cardona.\(^{(22)}\) is $\approx 25eV$. 
The longitudinal mass at $L^c$ band is determined by its interaction with other $L_1$, $L_1'$ states which are very far in energy. Hence this mass must be close to the free electron mass.

2.3.3. $\Delta_{L^c\rightarrow L^c}$ EFFECTIVE MASS

The only energy gap at the $X$-point known experimentally is the $X_4-X_{1c}$. The transverse effective mass is governed only by the interaction of $X_4$ with $X_{1c}$. No correction due to the admixture of $X_4-X_3$ wave functions in polar semiconductors can be made since no information about the position of $X_3$ is available. Hence the transverse effective mass at $X_{1c}$ can be written from equation 2.1 as

$$
\frac{m_0}{m^*(X_{1c})} = 1 + \frac{E_{p-x}}{E_2^2}
$$

where $E_2$ is the $E(X_{1c}-X_4)$ energy separation.

The value of momentum matrix element, $E_{p-x}$ can be estimated from the measured value of the transverse mass in silicon, where the lowest conduction band minima are in the (100) direction. The value of $E_{p-x}$ thus found is 19eV.

2.4. ELECTRON TRANSPORT AT LOW FIELDS

In a semiconductor crystal the motion of electrons in the conduction band (and holes in the valence band) under the influence of the applied field $F$ is described as a sequence of accelerations by the field followed by the collisions with the lattice accompanied by energy and momentum transfer. As a result the charge carriers tend to move with an average drift velocity $v = \frac{F}{\mu}$ superimposed on their random thermal velocity. $\mu$, is called the mobility of the carriers. In order to determine the mobility of the carriers the various scattering mechanisms present in the system have to be considered. These scattering mechanisms and their
contributions to the electron mobility are described briefly here.
The formulae, for different scattering mechanisms, cited in the next
sections are based on the assumption of spherical constant energy
surfaces i.e., isotropic relaxation time. As these assumptions are not
strictly true for Group IV semiconductors an appropriate correction is
applied as will be discussed in Chapter 6.

2.4.1. DEFORMATION POTENTIAL SCATTERING (ACOUSTIC LATTICE SCATTERING)

This is the dominant scattering mechanism in the L_{1c} valleys of
germanium at room temperature. Shockley and Bardeen\(^{(25,26)}\) developed the
concept of a deformation potential in order to gain an insight of the
mechanism of lattice scattering. It could be briefly described as follows.

As a result of thermal agitation, the atoms in a crystal are
vibrating in a random fashion with respect to their neighbours giving
rise to two modes of phonon vibrations. These modes are called longitudinal
acoustic and transverse acoustic modes. A passage of longitudinal
vibrations through a crystal give rise to alternate regions of compression
and extension of the crystal lattice i.e., deforming the crystal lattice
slightly. When the crystal is compressed, the positions of the energy
bands are altered in such a way that the forbidden gap is increased
whereas it is reduced in the condition of an extension. This effect causes
a local variation in the energy associated with the conduction band edge.
A similar variation in the energy of the valence band produces a small
potential fluctuation which acts as a scattering centre for the incident
electron giving rise to the deformation potential scattering. Shockley and
Bardeen derived an expression for mobility due to the deformation potential
scattering as:

\[
\mu_d = \frac{2(2\pi)^{\frac{3}{2}} e \hbar D s^2}{3(m^*)^{\frac{5}{2}} (k_B T)^{\frac{3}{2}} E_1^2} \quad \text{cm}^2\text{V}^{-1}\text{s}^{-1}
\]
where \( D \) is the density of the material
\[ s \text{ the velocity of longitudinal phonons} \]
\[ E_1 \text{ acoustic deformation potential (eV)} \]
\[ m^* \text{ the effective mass of the electrons.} \]

In the derivation of the above expression the scattering by the optical as well as transverse acoustic phonons have been neglected.

The optical phonons do not contribute to the lattice scattering mobility in non-polar semiconductors, as pointed out by Seitz\(^{(27)}\), because their unit cells contain two atoms of the same species in contrast to the III-V compounds where two atoms of the unit cell are of different species giving rise to interaction between electrons and long wavelength optical phonons. Shockley and Bardeen also ignored the scattering of the electrons by the transverse acoustic modes because, according to them, these modes do not give rise to dilatation. But the elastoresistance experiments of Smith\(^{(28)}\) have shown that shear as well as dilatation can shift the conduction band minima, thus making the analysis much more complex. Herring and Vogt\(^{(29)}\) have done such calculations and concluded that the transverse acoustical modes are about half as effective as the longitudinal modes in scattering conduction electrons in germanium for reasonable values of the deformation potentials.

However we confine ourselves to the simple longitudinal mode scattering as represented by equation (2.8) and treat \( E_1 \), the deformation potential, as an adjustable parameter to include the contribution due to the transverse mode interaction.

### 2.4.2. INTERVALLEY SCATTERING

The other important scattering mechanism in both group IV and III-V compounds is that of intervalley scattering. In this scattering, unlike deformation potential scattering, the electron changes its momentum by a large amount. Hence this scattering process must involve either emission or
absorption of an energetic phonon.

Herring\(^{(30)}\) has considered intravalley optical and intervalley scattering in some detail. He gives an expression for the scattering probability as:

\[
\frac{1}{\tau} = W_o + W_a + W_e
\]

where

\[
W_o = \frac{k_B T}{\hbar \omega} \left( \frac{E}{\hbar \omega} \right)^{\frac{1}{2}}
\]

\[
W_a = \frac{w_2 \left( \frac{k_B T}{\hbar \omega} - 1 \right)^{\frac{1}{2}}}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1}
\]

\[
W_e = \frac{w_2 \left( \frac{E}{\hbar \omega} - 1 \right)^{\frac{1}{2}}}{1 - \exp \left( \frac{\hbar \omega}{k_B T} \right)}
\]

for \( E > \hbar \omega \)

or \( W_e = 0 \) for \( E < \hbar \omega \)

The first term, \( W_o \), represents the optical intravalley scattering, the second term, \( W_a \), the intervalley scattering with absorption of a phonon and the third term, \( W_e \), the intervalley with emission of a phonon.

By substituting the component probabilities in equation 2.9 it can be written:

\[
\tau = \frac{1}{w_1} \left[ \left( \frac{E}{\hbar \omega} \right)^{\frac{1}{2}} \left( \frac{k_B T}{\hbar \omega} \right) + \frac{w_2}{w_1} \left[ \left( \frac{E}{\hbar \omega} + 1 \right)^{\frac{1}{2}} + \frac{\left( \frac{E}{\hbar \omega} - 1 \right)^{\frac{1}{2}}}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \right] \right]^{-1}
\]

where \( E \) is the electron energy.

The ratio \( \frac{W_a}{W_1} \) is the measure of the relative strengths of the phonons involved in the intervalley scattering to that involved in the intravalley scattering.

2.4.3. POLAR OPTICAL SCATTERING

Polar optical scattering is the most important scattering mechanism
in the \( \Gamma_1c \) minima in III-V compounds. This is caused by the strong polarization connected with the relative motion of the two unequal partially ionized atoms within the unit cell of the lattice.

Analysis of polar optical scattering has been given by Howarth and Sondheimer\(^{31}\). Ehrenreich\(^{32}\) later modified their theory to allow for non-parabolic bands and gives the expression for mobility as:

\[
\mu_{p,0} = 26.15 \times 10^{50} \frac{M \Omega}{e^*} \left[ \frac{m^*}{m}\right]^{3/2} \left[ \frac{T}{300} \right]^{1/2} (\exp Z-1) G(Z) \text{ cm}^2\text{v}^{-1}\text{s}^{-1}
\]

where \( T \) is the lattice temperature

\( e^* \) is the Callen effective charge

\( M \) is the reduced ion mass in Kg.

\( \Omega \) is the volume of the primitive cell in m\(^3\).

\( \theta \) is the polar phonon temperature

\( Z = \theta/T \)

The function \( G(Z) \) has been given by Ehrenreich\(^{33}\) and is shown in Figure 2.4 as a continuous function of \( Z \) for discrete values of \( \omega_p/\omega_\nu \). Where \( \omega_p \) is the plasma frequency. More recently Fortini\(^{34}\) has discussed the subject and gave somewhat higher values of the function \( G(Z) \) as shown by the dotted line in Figure 2.4.

2.4.4. IONIZED IMPURITY SCATTERING

The ionized impurity scattering contribution to the electron mobility, in case of non-degenerate semiconductors according to Brooks\(^{35}\) is given by the relation:

\[
\mu_{i,I} = \frac{2^{7/2} (k_B T)^{3/2} (4\pi e_o)^2}{N_i \pi^{3/2} e^3 (m^*)^{1/2} \ln Y}
\]

where \( \ln Y = \ln (1+b) - \frac{b}{1+b} \)}
FIG. 2.4 $f(Z, \omega_p/\omega_2)$ vs $Z$, AFTER EHRENREICH (---) AND FORTINI (--.--.--.)
and \[ b = \frac{6 \varepsilon_0 m^* (k_B T)^2}{\pi n^* \hbar^2 e^2} \]

\[ n^* = n + (n + N_A) \left(1 - \frac{n + N_A}{N_D}\right) \]

\( N_i = 2N_A + n \) is the total density of ionized impurity centres in cm\(^{-3}\) and \( n \) is the free carrier concentration. \( N_A, N_D \) are the densities of acceptors and donors respectively.

2.4.5. OTHER SCATTERING MECHANISMS

The other types of scattering mechanisms such as neutral impurity scattering, scattering by dislocations and other lattice defects, are of minor importance in good quality crystals. However Erginsoy \((36)\) has studied neutral impurity scattering and Dexter et al \((37)\) have given a detailed account of the scattering by dislocations. The electron-hole scattering will affect the mobility but it is normally negligible because the samples are either n-type or p-type. Since the energy and momentum both are conserved, electron-electron scattering has no direct effect on mobility.

2.4.6. LOW FIELD MOBILITY

In a semiconductor, in the presence of an electric field, \( F \), the current density, \( J \), is given by

\[ J = \sigma F \]

The conductivity \( \sigma \) is determined by the number of carriers and their mobility. In an intrinsic material, where there are two types of carriers, electrons and holes, the conductivity is given by

\[ \sigma = n \, e \, \mu_n + p \, e \, \mu_p \]

where \( n \) and \( p \) are the electron and hole densities respectively and \( \mu_n, \mu_p \) being their mobilities. In n-type wide band gap materials, the hole current could be neglected, hence the conductivity relation reduces to \( \sigma = n \, e \, \mu_n \).
In the presence of $N$ scattering mechanisms, the mobility, $\mu$, is approximated by the relation

$$\mu = \sum_{1}^{N} \frac{1}{\mu_i}$$

where $\mu_i$ is the mobility associated with the $i$th scattering process alone as discussed in the previous section. The expression 2.13 assumes that the individual scattering mechanisms are independent of one another and is generally referred to as Matthiessen's rule.

Both $\mu$ and $n$ can be determined experimentally by the Hall effect and resistivity measurements to be described in Chapter 6.
3.1. Hydrostatic Pressure

The application of hydrostatic pressure does not affect the symmetry of the crystal (if there is no phase change) and so symmetry degeneracies are not removed. Changes in symmetry are produced only by the application of uniaxial stress producing significant changes in electronic properties.

Hydrostatic pressure simply causes a decrease in the crystal volume and hence a decrease in the lattice constant. Therefore the band edges which are not required by symmetry to be degenerate may be moved with respect to one another. Simply one would expect the wave function overlap to broaden with decreasing interatomic spacing, the bands therefore to widen, and the energy gap to decrease. However, experimentally this is not found to be so, and the observations show that the energy gaps may either decrease or increase, with respect to the valence band, depending on which minimum \((\Gamma, L, X)\) of the conduction band is the lowest. A comparison of the pressure coefficients of several semiconductors led Paul\(^{(38)}\) to formulate the empirical rule. This states that the pressure coefficients of the energy difference between two states of a given symmetry is approximately independent of the material in which it is measured.

Several workers have considered the effect of the change in lattice constant on band structure. Paul and Brooks\(^{(39)}\) associated the electrons in the \(\Gamma_{1c}\) and \(X_{1c}\) valleys with \(s\) and \(p\) type wave functions respectively and argued that the energy of the \(s\) state would increase whereas that of the \(p\) state would decrease. This argument seems to agree with the experimental observation. But in fact due to the separation of bonding
and anti-bonding states, with decreasing inter-atomic spacing, the energy between conduction and valence bands at a particular symmetry point \((\Gamma, L, X)\) always increases with pressure i.e. \(\frac{dE_0}{dp}, \frac{dE_1}{dp}, \frac{dE_2}{dp}\) are all positive as shown in Fig. 3.1. It so happens that although the energy gap \(E_2\) increases with pressure at the \(X\)-point the valence band also broadens i.e. energy of \(X_4\) increases which makes \(X_1\) look either stationary or even move downward with respect to the valence band. Table 3.1 illustrates the pressure coefficients of \(\Gamma_{1c}, L_{1c}\) and \(X_{1c}\) valleys in some of the zinc blende and diamond type semiconductors relative to the valence band maximum.

Optical measurements on different minima provide a good illustration of the empirical rule. Fig. 3.2 shows the absorption edge energies as a function of pressure obtained by different workers for silicon, germanium and gallium antimonide.

Silicon has its conduction band minima, at atmospheric pressure, in the \(<100>\) direction, whose pressure coefficient is small and negative. Thus the energy gap is observed to decrease slowly with pressure. Ge has \(L_{1c}\) minima lowest and its energy gap is seen to increase first with pressure then at about 30 k-bar, where \(L_{1c}\) and \(A_{1c}\) minima crossover, the energy gap starts decreasing with the increase of pressure. GaSb on the other hand, having \(\Gamma_{1c}\) minima the lowest, shows two band crossing effects. First the energy increases due to the \(\Gamma_{1c}\) minima movement but at about 8 k-bar, where it crosses the \(L_{1c}\) minima, change in the rate of increase of energy gap with pressure is observed. Near about 30 k-bar the \(L_{1c}-X_{1c}\) crossover takes place and a decrease in energy gap is observed. Melz calculated several pressure coefficients using a pseudopotential approach and justified the empirical rule as well. Camphausen et al have also calculated the pressure coefficients for a number of III-V compounds in good agreement with experiment by using the dielectric theory of the chemical bond developed by Phillips and Van Vechten which also takes
FIG. 3.1 VARIOUS BAND EDGES OF GaAs AND THEIR PRESSURE COEFFICIENTS (μeV/bar).
TABLE 3.1
Pressure coefficients of conduction band extrema in some Diamond and Zinc blende type semiconductors, relative to the valence band maximum (x 10^{-6}eV bar^{-1})

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{dE_T}{dp} )</th>
<th>( \frac{dE_L}{dp} )</th>
<th>( \frac{dE_X}{dp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Theory</td>
<td>Exp.</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>Ge</td>
<td>14.2</td>
<td>14.3</td>
<td>5.0</td>
</tr>
<tr>
<td>AlSb</td>
<td>10.0</td>
<td>13.5</td>
<td>-</td>
</tr>
<tr>
<td>GaP</td>
<td>10.0</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>GaAs</td>
<td>11.0</td>
<td>11.0</td>
<td>-</td>
</tr>
<tr>
<td>GaSb</td>
<td>14.7</td>
<td>14.7</td>
<td>5.0</td>
</tr>
<tr>
<td>InP</td>
<td>10.0</td>
<td>9.5</td>
<td>2.5*</td>
</tr>
<tr>
<td>InAs</td>
<td>10.0</td>
<td>12.2</td>
<td>5.0*</td>
</tr>
<tr>
<td>InSb</td>
<td>17.0</td>
<td>15.8</td>
<td>5.0*</td>
</tr>
</tbody>
</table>

* These are the values which have been used to fit available experimental data and are not directly measured results.
FIG. 3.2 ABSORPTION EDGE ENERGIES VS PRESSURE FOR SILICON, GERMANIUM AND GaSb.
into account the contributions to the energy states from d-type core electrons.

With the empirical rule reasonably established, it is possible to determine from pressure experiments which of the conduction band minima is the lowest simply by observing its pressure coefficient. Pressure allows us therefore to observe the interesting phenomenon of band cross-over and the subsequent electron transfer to other minima as they become lower in energy than the normally lowest minima at atmospheric pressure. After the electron transfer to the new minima, which have therefore become available for direct observation at high pressure, a basic comparison of scattering theories and band structure is possible.

A detailed analysis, based on the deformation potential theory introduced by Bardeen and Shockley\(^{46}\), of the relative movement of the band edge extrema under the influence of an applied stress, in elastic conditions, is carried out by Costato and Reggiani\(^{47}\). The change in energy of a state, \(\delta E\), is related to the change in volume, \(\delta V\), produced by pressure, by the equation

\[
\delta E = \varepsilon \frac{\delta V}{V}
\]

where \(\varepsilon\) is the deformation potential constant of the conduction and valence bands i.e. the change in energy of the state per unit strain \(\varepsilon\). Hence

\[
\delta E = \varepsilon : \varepsilon
\]

where both \(\varepsilon\) and \(\varepsilon\) are second-rank tensors. For a hydrostatic compressive pressure, \(P\), the relation may be written

\[
\delta E = -\varepsilon [3(S_{11} + 2 S_{12})]
\]

Where \(S_{ij}\) are the components of the compliance tensor. Following the formalism of Herring and Vogt\(^{29}\) for the deformation potential of the conduction band, and of Pikus and Bir\(^{48}\) for the deformation potential of the valence band it can be shown that for cubic crystals,

\[
\varepsilon = \varepsilon_d + \frac{1}{3} \varepsilon_u - a
\]
where $\varepsilon_d$ and $\varepsilon_u$ are the deformation potential constants of the conduction band and are defined as follows:

$\varepsilon_d$ represents the energy shift due to an elongation in the two directions normal to the symmetry axis (Z-axis) i.e. a dilation, $e_{xx} = \frac{u}{2}$, $e_{yy} = \frac{u}{2}$ produces a shift $\varepsilon_d u$.

$\varepsilon_u$ represents the energy shift due to an elongation along Z-axis combined with a contraction in the two normal directions, i.e. a uniaxial shear, $e_{xx} = e_{yy} = \frac{u}{2}$, $e_{zz} = u$ produces a shift $\varepsilon_u u$.

$a$ is the deformation potential constant for the valence band and is defined as the shift of the average position of the valence band maxima per unit dilation.

From equations (3.3) and (3.4) the average shift of the conduction band, $E_c$, and of the valence band, $E_v$, under hydrostatic compressive pressure, $P$, can be written as:

$$\frac{dE_c}{dP} = - (\varepsilon_d + \frac{1}{3} \varepsilon_u) \left( S_{11} + 2 S_{12} \right)$$

and

$$\frac{dE_v}{dP} = - a \left( S_{11} + 2 S_{12} \right)$$

3.2. UNIAXIAL STRESS

The general effect of a uniaxial stress on the band structure of a semiconductor is to shift the energy of all the valleys due to pure dilation of the crystal (which is one-third of that caused by a hydrostatic pressure of the same magnitude) and also to remove the degeneracies of any equivalent valleys which are not symmetrical to the direction of the applied stress. The energy of the valleys whose symmetry axes are parallel to the stress direction is lowered with respect to the energy of the equivalent valleys which are not parallel to the direction of the applied stress.
The shift of the conduction band edge under uniaxial stress is related to the six strain components, so the equation (3.2) may be written as

$$\delta E_c = \sum_{j=1}^{6} \varepsilon_j \bar{\varepsilon}_j$$  \hspace{1cm} (3.7)

Since the strains are small, 1%, the change in energy with strain may be described by a first order dependence, $\varepsilon_j$ assumed independent of the strain. Using the definitions of $\varepsilon_d$ and $\varepsilon_u$ given earlier and from symmetry considerations, the energy shift of the valleys in the (100) direction due to (100) stress is given by

$$\frac{\delta E}{\delta \chi^{(100)}} = - (\varepsilon_d + \frac{1}{3} \varepsilon_u) (S_{11} + 2 S_{12}) \hspace{1cm} \begin{bmatrix} 2 \varepsilon_u S_{11} - S_{12} \end{bmatrix} \begin{bmatrix} 010 \end{bmatrix}, \begin{bmatrix} 001 \end{bmatrix}$$  \hspace{1cm} (3.8)

Similarly, the shift of (111) valleys due to (111) stress is

$$\frac{\delta E}{\delta \chi^{(111)}} = - (\varepsilon_d + \frac{1}{3} \varepsilon_u) (S_{11} + 2 S_{12}) \hspace{1cm} \begin{bmatrix} -\frac{1}{3} \varepsilon_u S_{44} \end{bmatrix} \begin{bmatrix} 111 \end{bmatrix}$$  \hspace{1cm} (3.9)

Fig. 3.3 illustrates the movement of the various valleys of the conduction band of GaAs with respect to the average position of the valence band under (100) and (111) stress.

The degeneracy of the valence band at $k = 0$ is also lifted by uniaxial stress. This subject has been discussed, in some detail, by several authors. The valence band edge at $k = 0$ without any strain is four-fold degenerate separated by a two-fold degenerate band split off by the spin orbit interaction. The application of a uniaxial stress splits the heavy and light hole bands and it is known that the heavy hole band moves upwards whereas the light hole band moves downwards in energy relative to their average position. Also because of the hydrostatic
FIG. 3.3 MOVEMENT OF GaAs CONDUCTION BAND MINIMA RELATIVE TO THE MEAN POSITION OF THE VALENCE BAND.
pressure component of the strain, the average position of these bands as well as that of the spin-orbit split off band is shifted relative to the conduction band, as illustrated schematically in Fig. 3.4. The three valence bands are labelled as \( v_1, v_2, v_3 \) and their energies relative to the conduction band minimum as \( E_1, E_2, E_3 \) respectively.

Under (100) stress the energies of these bands at \( k = 0 \), assuming that the splitting, \( \delta E \), between heavy hole and light hole bands is smaller than the spin-orbit splitting, can be written as\(^{(50)}\):

\[
\begin{align*}
\Delta E_1^{(100)} &= -\frac{1}{3} \Delta_0 + \delta E_H - \frac{1}{2} \delta E_{100} - \frac{1}{3} (\delta E_{100})^2 / \Delta_0 + \ldots \\
\Delta E_2^{(100)} &= -\frac{1}{3} \Delta_0 + \delta E_H + \frac{1}{2} \delta E_{100} \\
\Delta E_3^{(100)} &= +\frac{2}{3} \Delta_0 + \delta E_H + \frac{1}{2} (\delta E_{100})^2 / \Delta_0 + \ldots
\end{align*}
\]

(3.10)

Where \( \delta E_H = a (s_{11} + 2s_{12}) \chi^{(100)} \) and \( x \) is the shift of the energy gap \( E_g \), due to the hydrostatic component of the strain, and

\[
\delta E_{100} = 2 b (s_{11} - s_{12}) \chi^{(100)}
\]

is the linear splitting of the upper valence bands and \( b \) is defined as the deformation potential constant of the valence band.

Similarly under (111) stress the energies of the three valence bands are:

\[
\begin{align*}
\Delta E_1^{(111)} &= -\frac{1}{3} \Delta_0 + \delta E_H - \frac{1}{2} \delta E_{111} - \frac{1}{3} (\delta E_{111})^2 / \Delta_0 + \ldots \\
\Delta E_2^{(111)} &= -\frac{1}{3} \Delta_0 + \delta E_H + \frac{1}{2} \delta E_{111} \\
\Delta E_3^{(111)} &= +\frac{2}{3} \Delta_0 + \delta E_H + \frac{1}{2} (\delta E_{111})^2 / \Delta_0 + \ldots
\end{align*}
\]

(3.11)
FIG. 3.4 BAND STRUCTURE OF GaAs FOR THE LOWEST CONDUCTION BAND AND HIGHEST VALENCE BAND AND ITS STRESS DEPENDENCE.
Where $\delta E_{\text{H}}$ is the same as defined before but $\delta E_{\text{111}}$ is the splitting of the upper valence bands under the (111) stress and is given by $\delta E_{\text{111}} = \left(\frac{d}{\sqrt{3}}\right) s_{44}$ where $d$ is again defined as the deformation potential constant of the valence band.
CHAPTER 4
EFFECTS OF PRESSURE ON ELECTRON TRANSPORT

4.1. HYDROSTATIC PRESSURE

The conductivity of a semiconductor will, in general, be affected by pressure if either the properties of the band minima normally occupied by the charge carriers change or the carriers transfer to another energy state. Since the effects of pressure on conductivity of an intrinsic semiconductor are more pronounced than those of the extrinsic semiconductor, we consider the two cases separately.

4.1.1. Intrinsic Conduction

In an intrinsic semiconductor the number of mobile carriers derived from impurities is small compared to the number of electron-hole pairs which are created by thermal excitation of the electrons across the energy gap. The density of these excited carriers, in intrinsic semiconductor, may be written as:

\[ n = p = (N_C N_V)^{\frac{3}{2}} \exp\left( -\frac{E_g}{2k_B T} \right) \]  

(4.1)

Where \( N_C \) and \( N_V \) are the effective density of states of conduction and valence bands respectively - which are in turn related to the effective masses of the carriers by

\[ N_i = 2 \left( \frac{2 \pi k_B T}{\hbar^2} \right)^{3/2} \left( m_i^* \right)^{3/2} \]  

(4.2)

Where \( i \) can be either \( C \) or \( V \) representing the conduction or the valence bands.

The conductivity of an intrinsic semiconductor, where \( n = p \) has the form:

\[ \sigma = n e (\nu_n + \nu_p) \]  

(4.3)
From equations (4.1) and (4.3) it follows that:

\[ \sigma = e \left[ (N_C N_V)^{1/2} (\mu_n + \mu_p) \exp \left( - \frac{E_g}{2k_B T} \right) \right] \]

\[ \ln \sigma = \frac{1}{2} \ln (N_C N_V) + \ln (\mu_n + \mu_p) - \frac{E_g}{2k_B T} + \ln e \]

\[ \frac{d}{dp} [\ln \sigma] = \frac{1}{2} \frac{d}{dp} [\ln (N_C N_V)] + \frac{d}{dp} [\ln (\mu_n + \mu_p)] - \frac{1}{2k_B T} \frac{dE_g}{dp} \] (4.4)

It can be shown that the first two terms, which represent the rate of change of density of states of the conduction and valence bands and the rate of change of mobility of carriers tend to cancel one another in the cases where the ionized impurity scattering is minimal. The exponential variation in \( n \) and \( p \) with \( E \), as shown in equation (4.1), can on the other hand be very large since change in \( E_g \) with pressure can be several \( k_B T \) hence a large variation in conductivity results.

Since the pressure effects in intrinsic material give an almost direct measure of the variation of the energy gap with pressure, they can be used to determine the pressure coefficients of different minima very accurately. Such measurements on ultra-pure germanium are reported in Chapter 7 for the pressure coefficients of the \( L_{1C} \) and \( A_{1C} \) minima.

4.1.2. Extrinsic Conduction

In extrinsic semiconductors most of the charge carriers which take part in conduction are provided by shallow donors or acceptors whose activation energy does not change appreciably with pressure. The intrinsic carriers can usually be neglected. Equation (4.1) does not apply in this case and the densities of \( n \) and \( p \) will be insensitive to pressure. The main effect of pressure on conductivity would, in this case, come through the term:-
\[ \frac{d}{dp} [\ln (\mu_n + \mu_p)] \] of equation (4.4)

which further reduces to
\[ \frac{d}{dp} [\ln \mu] \]  \hspace{1cm} (4.5)

Where \( \mu \) is the electron or hole mobility for \( n \) and \( p \)-type material respectively. Only the behaviour of \( n \)-type semiconductor under pressure will be dealt with here. This can be divided as follows.

(a) Changes within the valley:

In the low pressure region the conductivity of a \( n \)-type semiconductor shows a weak pressure dependence. This is because the electron effective mass changes within the valley, and influences \( \mu \) through equation (4.5) as they move away from the valence band under pressure. The change in effective mass can be calculated from the \( k.p \) theory, described in detail in Chapter 2. In general, an increase in energy gap with pressure, will cause an increase in the effective mass of the electrons approximately proportional to \( E_g \) if \( E_g > > \Delta \) the spin orbit splitting. This will cause a change in mobility since \( \mu \propto (m^*)^r \) where \( r \) depends on the scattering mechanism present. For polar optical scattering \( r = -\frac{3}{2} \) and for deformation potential scattering \( r = -\frac{5}{2} \). In both these cases a decrease in mobility hence a decrease in conductivity with pressure is observed. But for ionized impurity scattering, since \( r = +\frac{1}{2} \), mobility will increase with pressure.

(b) Electron Transfer Effect

The relative positions of the band minima under pressure changes significantly which give rise to the electron transfer effect. The electrons transfer to the higher approaching minima where their mobility may be very different and this redistribution of electrons among the bands gives rise to change in the average mobility of the electrons. The density of electrons in each minimum, \( i \), can be written as:-
\[ n_i = N_i \exp \left( \frac{E_i - E_F}{k_B T} \right) \]  

(4.6)

Where \( N_i \) is the effective density of states, as already defined by equation (4.2) and \( E_F \) is the Fermi energy.

For two bands it follows from equation (4.6) that

\[ \frac{n_2}{n_1} = \frac{N_2}{N_1} \exp \left( \frac{-\Delta E}{k_B T} \right) \]  

(4.7)

Where \( \Delta E \) is the energy separation between the two states.

If the conductivity in state 1 is given by \( \sigma_1 = n_1 e \mu_1 \) and that in state 2 by \( \sigma_2 = n_2 e \mu_2 \) then the total conductivity

\[ \sigma_T = \sigma_1 + \sigma_2 = e \left( n_1 \mu_1 + n_2 \mu_2 \right) \]

will change with pressure as the relative populations of the states change. Also the carrier concentration may be controlled by a deep impurity level for which \( \mu = 0 \) [this is commonly observed in III-V compounds but has not been seen in n-type germanium as will be discussed in Chapter 6]. If this level stays fixed relative to the valence band then when the conduction band minimum moves away with applied pressure, electrons will 'trap out' to this impurity level and the conductivity will decrease.

(c) Non-Equivalent Intervalley Scattering

At atmospheric pressure and at low electric fields the electrons are at the bottom of the normally occupied minima and do not scatter to the higher lying minima, hence the non-equivalent valley scattering is negligible. However, with the increase of pressure, as the bands approach one another, the non-equivalent intervalley scattering increases. It is maximum near the band cross-over where the two minima are at the same energy. After the cross-over when the satellite valleys move few \( k_B T \) below the lowest minima, at atmospheric pressure, all the electrons are transferred to this minima. The non-equivalent intervalley scattering
once again becomes negligible so the conductivity tends to saturate.

4.2. **UNIAXIAL STRESS**

Under uniaxial stress the changes in effective mass of electrons, as discussed under hydrostatic pressure, are about two orders of magnitude smaller. The observed large changes in conductivity, under uniaxial stress, have been explained by Smith\(^{28}\) and Herring\(^{30}\) in terms of the electron transfer effect and the intervalley scattering among the valleys whose degeneracy is lifted by stress. We have discussed the effect of uniaxial stress on the band structure in Section 3.2. Now we consider how those changes in band structure affect the electron transport.

The effect could easily be understood by considering the case of silicon. The constant energy surfaces are ellipsoids of revolution, which have their main axis along the cubic directions, as shown in Fig. 4.1. The longitudinal mass is about five times larger than the transverse mass, so that the mobility for each valley is considerably anisotropic. But since in an unstrained state the minima are degenerate and are occupied by the same number of electrons the cubic symmetry requirements made total mobility isotropic. Now suppose uniaxial stress is applied in the (100) direction as a result of which the degeneracy is lifted and symmetry destroyed. The energy of the (010) minima increases whereas that of (100) decreases with respect to the valence band. The electrons are transferred from the higher valleys into the lower lying valleys. This population transfer effect implies an unequal number of electrons in the valleys. In the case of ellipsoidal energy surfaces, as shown, the mobility in the (100) valleys is smaller in the x-direction than in y-direction. Consequently the overall conductivity becomes anisotropic with the smaller value in the (100) direction and continues decreasing with the increase of stress. On the other hand a compression
Fig. 4.1 SCHEMATIC DIAGRAM OF THE SURFACES OF CONSTANT ENERGY IN $K_x - K_y$ SPACE OF N-TYPE SILICON WITH (DOTTED LINES) AND WITHOUT (SOLID LINES) UNIAXIAL COMPRESSION IN 100 DIRECTION.

THE ENERGY SURFACES ALONG 001 ARE NOT CONSIDERED.

-X COMPRESSION STRESS, E APPLIED ELECTRIC FIELD.

THE MOBILITY ANISOTROPY IS INDICATED BY $\mu_t$ AND $\mu_k$. 
in the (111) direction will affect all the valleys in the same way so no electron transfer can occur and hence no change in mobility or conductivity.

Another important contribution to the piezoresistance, as a consequence of the relative shift of the valleys, is the intervalley scattering. The equivalent intervalley scattering in silicon is believed to be a combination of "g" scattering and "f" scattering as already shown in Fig. 2.3 ć. A quantitative evaluation of both the electron transfer and the intervalley scattering effects is given in references (52,53).
5.1. **INTRODUCTION**

Stress can be applied to a solid in two ways:–

(a) **Hydrostatic pressure**

(b) **Uniaxial compression or tension.**

The range of true hydrostatic pressure is limited to only 30 k-bar because the most commonly used pressure transmitting fluids freeze at or below this pressure at room temperature. But recently a mixture of methanol:ethanol in the ratio of 4:1 has successfully been used by many workers \(^{(54,13)}\) to achieve pressures of about 100 k-bar at room temperature. More recently \(^{(55)}\) a pressure of \(\approx 250\) k-bar has been achieved by using the above medium and the diamond anvil cell.

Normally pressures beyond 30 k-bar are obtained by using solid pressure transmitting media such as epoxy resin or NaCl etc. These systems produce non-hydrostatic stresses below about 15 k-bar, but the media then begins to flow and produce a good approximation to hydrostatic pressure allowing pressures greater than 100 k-bar to be achieved. The hydrostatic pressure apparatus used for this work was developed by the S.T.L. high pressure group for Hall effect and resistivity measurements and consists of a liquid-medium piston and cylinder device for pressures to 18 k-bar \(^{(56)}\) and a solid medium Bridgman opposed anvil device for pressures up to \(\approx 100\) k-bar.

5.2. **THE BRIDGMAN OPPOSED ANVIL APPARATUS**

A schematic diagram of the apparatus assembly is shown in Fig. 5.1. The anvils used are made of tungsten carbide and are 3.8 cm in diameter with a 6° taper leading to 1.6 cm diameter flats. The mild steel jackets of 10.2 cm diameter around the anvils not only provide support for the
FIG. 5.1 CROSS SECTION OF OPPOSED ANVIL HIGH PRESSURE APPARATUS.
anvils but also enhance the magnetic flux obtained by magnetic coils as shown in Fig. 5.1.

The magnetic field coils, which consist of 600 turns of 24 S.W.G. copper wire, supply the magnetic field necessary for Hall effect experiments. Load is applied by a 500 ton hydraulic press to the anvils through mild steel four column die set. Low temperature measurements down to 100°K can be made, in this set up, by pumping liquid nitrogen through the insulated copper coil surrounding the anvils. A strain gauge load-cell is used to measure the load.

Recently a similar apparatus, as described above, has been developed at Surrey University with a facility for simultaneous optical and electrical measurements as a function of pressure. A bundle of optical fibres has been fed through the bottom anvil through which light pulses could be transmitted to the sample and photoconductivity measurements could be made.

5.2.1. The High Pressure (Solid Medium) Cell

The sample to be pressurised was encapsulated in epoxy resin at the centre of an epoxy loaded MgO ring. The rings, with dimensions as shown in Fig. 5.2, were made in a mould by curing a suspension of industrial (coarse grain) MgO in epoxy resin at 120°C for 24 hours. If fine grain MgO (normally used for chemical purposes) was used then the rings were found easily expandable under pressure with the result that they did not withstand higher pressure. The reason for this is that the fine particles being round in shape will slide over one another making rings to expand easily under pressure. In the case of coarse MgO, on the other hand, the particles being of irregular shape would not slide over one another under pressure. Hence the rings could stand up to higher pressures. The rings, after curing for 24 hours, were taken out of the mould and were machined down
FIG. 5.2 SAMPLE ENCAPSULATED IN MgO LOADED BRIDGMAN RING.
to the required size. Grooves were then cut to half the height of the rings to take sample leads and thermocouple as shown in Fig. 5.2. The ring was then placed on a sheet of Mylar and epoxy resin was poured into the centre of the ring and allowed to flow into the grooves. The clover leaf sample was cut with an ultrasonic cutter. Tin dots were alloyed and leads soldered to the four lobes of the clover leaf. This sample was then placed at the centre of the above prepared ring such that the leads passed through the grooves. Care was taken to eliminate any air bubbles from the centre of the ring to eliminate the chances of pressure loss. Another sheet of Mylar was placed on the top of the cell and the cell was clamped between these sheets of Mylar and cured for two hours at 80°C and at 120°C for about twenty-two hours. After curing, the sheets were removed and both sides of the cell were roughened by abrasive paper. Fine wires were connected to the sample leads for external electrical circuit and these leads were then insulated by using 0.01mm thick Mylar sheets with holes cut to the size of the cell. These sheets not only provide insulation but also a support for the sample thin leads. A dispersion of jeweller's rouge in methanol was painted on each side of the cell. This after evaporation of methanol provides a uniform coating of the high friction rouge and which prevents the cell from slipping between the anvils. The cell is then placed centrally between the anvil flats.

Application of load to the cell causes the MgO ring to expand outwards and resin to flow. Eventually with the increase of load it "locks on" by friction to the anvil face exerting pressure on the sample at the centre of the cell through the pressure transmitting media. In the pressure region of deformation of the MgO ring i.e. below about 15 k-bar, the sample may be subjected to non-hydrostatic stresses but above 15 k-bar the pressure becomes hydrostatic in nature. Measurements are possible during the loading only since the system is inelastic and the pressure is not known
on unloading. The dimensions of the gasket as shown in Fig. 5.2 are chosen, such that the ratio of the outer diameter to thickness of the ring is 10, to ensure that the sample did not fracture before 70 k-bar. Gaskets with smaller ratio suffered large plastic deformation resulting in crystal fracture (57).

5.3. THE PISTON AND CYLINDER APPARATUS

A schematic diagram of the apparatus is shown in Fig. 5.3. The cylinder is made of hot-worked die steel and has an outer diameter of 15 cm and height of 8.75 cm. This is pressed into a steel ring, of outer diameter 37.5 cm, on a 1° taper angle. The outer ring is held down by steel straps to prevent it rising on unloading. Safety spacers are also placed between the ring and die to prevent crushing at a sudden leakage of the pressure transmitting fluids.

The thrust piston, shown in Fig. 5.4 is made of hardened tool steel and is 3.8 cm in diameter. Leads to contact terminals at the end of the piston are passed out of the pressure chamber via hardened silver steel terminals ground into ceramic sleeves and then through a hole in the piston. Although the paths of the electrical leads through the piston provide regions of stress concentrations thereby reducing the piston's compressive strength, it is expected that the extrusion of the silver steel terminals down the holes will be the most serious limitation of this design at high pressure (59). The piston face accommodates eight silver steel terminals, which are evenly distributed round the piston face. At its centre a manganin gauge and a small toroidal magnetic field system are installed and are connected to four of the terminals. The rest of the four terminals are for sample connections.

A similar pressure cell has been developed at Surrey University with a smaller diameter piston which allows 8 k-bar to be achieved with
FIG. 5.3 SCHEMATIC DIAGRAM OF LIQUID-MEDIUM HYDROSTATIC PRESSURE APPARATUS.
FIG. 5.4 DETAILED DIAGRAM OF THRUST PISTON.
the 60-ton hydraulic press available. The piston also has a central hole through which a bundle of optical fibres is fed. On the piston face a sapphire window is provided, thus not only electrical but optical measurements as a function of pressure are possible. The liquid pressure transmitting medium used was 1:1 mixture of amyl alcohol and castor oil. This medium is suitable for pressure up to 18 k-bar above which it freezes.

Sealing between piston and sapphire window is provided by a thin aluminium foil and the seal around the piston is accomplished by a combination of a neoprene "O-ring" and a phosphor bronze ring. Below 4 k-bar the high pressure forces the bronze ring to expand and provide sufficient sealing by about 8 k-bar. Leakage is observed to occur mostly in the 4-6 k-bar pressure range. This is the region where the operation of both rings is most inefficient. One remedy, we have tried, to solve this problem is to accelerate the operation of the phosphor bronze ring by increasing the pressure quickly up to 8 k-bar. After the seals are properly working pressure could be decreased or increased and measurements could be made. A backing pad, with a U-groove milled in it to accommodate the electrical leads, was used on top of the piston. After connecting the sample to the terminals the piston was immersed in the liquid medium by placing the piston carefully into the cylinder bore. Trapping of air was minimized by overfilling the cylinder and allowing the excess of the liquid to leak out. The top die was then lowered slowly on to the piston, making sure that the electrical leads are seated correctly in their grooves. This is checked by rotating the piston since the correct seating allows free rotation. Pressure is then applied to the die set by the 500 ton press and measurements are made at 1 k-bar intervals on increasing and decreasing pressure cycles. After each pressure increment 15-20 minutes were allowed to elapse before a reading was taken, in order to achieve thermal equilibrium. In the pressure cell developed at Surrey a thermo-
couple is provided in the cylinder to monitor the temperature of the pressure transmitting medium accurately. The magnetic field for Hall effect measurements was supplied by a coil wound around a toroid of high quality mild steel. The coil is made of 870 turns of 0.18mm enamelled copper wire, with a resistance of 23.4 ohms. A current of 55mA produced a magnetic field of $1 \pm 0.03$ kGauss across the 0.75 mm toroid gap. At this low current heating effects on the coil resistance are negligible. The field is uniform at the centre of the pole faces, which has an area of $2 \times 1.8 \text{ cm}^2$. The effect of pressure on the toroid magnetic field was investigated by measuring the Hall constant of n-type GaAs as a function of pressure, and it was concluded that the effect is small, possibly not more than 0.4%.

5.4. PRESSURE CALIBRATION

5.4.1. Pressure Calibration of the Solid Cell

The pressure calibration of the solid cell was carried out by observing the load required for bismuth and Tl to undergo phase transitions. The transitions are known to occur at 25.4 k-bar for Bi (I-II), 76 k-bar for Bi (III-V) and 37 k-bar for Tl. These fixed points on the load-pressure curve shows that the calibration is linear between ±25 and 76 k-bar. The pressure reproducibility was estimated to be ±2 k-bar. The calibration curve is shown in Fig. 5.5. The region below 20 k-bar was estimated by making piezoresistance measurements on GaAs crystals and comparing the results with measurements in the liquid medium apparatus.

Before the series of experiments, to be described later, the 25.4 k-bar point on the calibration curve was checked by using 99.99% pure bismuth. A piece to fit the centre of a Bridgman ring was cut and contacts to it were made by 0.025 mm diameter copper wire, flattened at the ends, and fixed in the grooves of the ring with MgO loaded epoxy resin. Bismuth was
held in position by two epoxy discs. A constant current was passed through the sample and its resistance was monitored, by observing the potential difference across the sample, as the load was applied. At about 18 tons Bi underwent a transition showing a sharp decrease in resistance.

A load of 18 tons on the gasket, dimensions shown in Fig. 5.2 would produce a pressure of \( \frac{18}{\pi \left(\frac{1.27}{4}\right)^2} \approx 14.2 \) k-bar. But the transition pressure of Bi, as mentioned earlier, is established at 25.4 k-bar, which gives a pressure multiplication factor for the solid cell of \( \approx 1.8 \).

5.4.2. Pressure Calibration of the Liquid Cell

The pressure was monitored by a 100-ohm manganin coil coupled to a standard bridge circuit, as shown in Fig. 5.6. The output of the bridge is connected to a digital multimeter for monitoring the pressure. Before applying the load, the bridge was balanced by adjusting the potentiometer \( R_0 \) to give zero output, the output is then calibrated by introducing the resistance \( R_2' \) into the bridge and then adjusting the potentiometer to give an output of 17.4 mV. \( R_2' \) simulates the resistance of the manganin gauge at 15 k-bar. The change in manganin gauge resistance with pressure is 0.2473 \( \Omega \)/k-bar. The pressure-load curve is linear and is shown in Fig. 5.7.

5.5. **UNIAXIAL STRESS APPARATUS**

5.5.1. **Introduction**

The main difference between hydrostatic pressure and uniaxial stress is that in the former the symmetry of the crystal is preserved while the latter destroys it. Under the hydrostatic pressure, there is a little possibility of sample fracture. However, with uniaxial stress
FIG. 5.5  CALIBRATION CURVE FOR BRIDGMAN APPARATUS.
FIG. 5.6 MANGANIN GAUGE CIRCUIT DIAGRAM.
FIG. 5.7 PRESSURE CALIBRATION CURVE FOR THE PISTON-CYLINDER APPARATUS.

- ■ LOADING.
- □ UNLOADING.
this is normally the main problem. The crystal may be brittle, or it may cleave easily, limiting the maximum stress which can be applied along symmetry directions. It should be realised that it is almost impossible to produce a pure uniaxial stress, particularly under compression, since the ends of the sample should be perfectly free to move. A good approximation can be achieved by reducing friction at the anvil-sample interface by means of some material with a low yield stress such as Sn or Au. Shear stresses must be reduced to a minimum by taking care to obtain good alignment and ensuring that the anvil surfaces are flat and parallel. For pressures up to 20 k-bar tungsten carbide or sapphire anvils should be used preferably with an aspect ratio of 1:1 to avoid anvil fracture.

Previous methods for the application of uniaxial stress have included systems of weights, lever and push rods, weights, beam balance and pulling frame, spring, lever and pulling frame, and weights on a platform acting on a stylus. The systems using levers etc. have the disadvantage that, due to torque, unwanted shear stress will be present and should be taken into consideration. The use of a stylus can also produce large shear stresses if there is a slight misalignment and weights means that the stress cannot be applied smoothly at a uniform rate.

The apparatus, used in the experiments described later, was first suggested by J. Lees and developed by Pickering and Adams and later modified by the author. It is of a simple design operated by air pressure acting on a piston. By evacuating the whole apparatus, large stresses can be obtained with air pressures less than one atmosphere (1 bar), acting on the piston. The apparatus provides a high degree of control of the rate of application of the stress and the magnitude of the stress can easily be monitored by means of a manometer. Also, since the apparatus is normally under vacuum, it can easily be used at low temperature.
5.5.2. Apparatus Description

The apparatus, which is a piston and cylinder device, is shown in Fig. 5.8. The upper chamber of the apparatus is divided into two sections, above and below the piston, by a 1.5 mm thick sheet of neoprene rubber. A downward force is applied to the piston by evacuating the whole apparatus and then allowing air to enter the section above the piston. The top plate of the piston, which is of 3 mm thick brass, is 10 cm in diameter, 4.5 cm less than the internal diameter of the upper chamber of the apparatus in order to reduce effects due to the clamped outer edge of the rubber diaphragm (edge effects). A brass annulus is used to support the remaining area of the rubber. Care was taken to ensure that the piston top is flush with the ring when a sample is in position so that the rubber diaphragm lies on the piston in an unstrained state.

The hollow tube, and the outer tube in which it slides are of 1.3 mm stainless steel about 1 metre long and their outer diameters of about 2.2 cm and 2.8 cm respectively. Three teflon sleeves about 2 cm long are used as guides along the length of the tube. These guides must not be tight-fitting otherwise frictional losses will occur. But since the tube is fairly long a small amount of play is allowable without causing appreciable angular misalignment at the anvil/sample interface. This misalignment was further reduced by using, initially (59), an anodised bush, in the centre of the sample holder, as a guide for the upper anvil. This arrangement worked satisfactorily for cubic samples with evaporated contacts on the opposite faces in case of bulk materials, as shown by n-type silicon results. Silicon was used as a test material to check the overall performance of the system. This set up has drawbacks, to be discussed later, in the case of epitaxial samples. To circumvent these drawbacks a four probe method was used and for this the sample holder was modified as shown in Fig. 5.9.
FIG. 5.8 UNIAXIAL STRESS APPARATUS.
FIG. 5.9 ANVIL - SAMPLE HOLDER ASSEMBLY.
In this case the central guide for the upper anvil, anodised bush, was removed and its effect was compensated by increasing the length of the sample holder from 20 mm to 60 mm. The electrical connections to the sample were made through the air tight miniature coaxial connectors as shown in the sample holder. A tungsten carbide anvil, a cylinder of diameter of length 2 mm, is embedded in stainless steel, which is insulated from the piston by paxolin as shown. The sample is situated between this and a similar anvil in an assembly which is completely of stainless steel. A brass disc and a printed circuit board is used in such a way that the top surface of the lower anvil is flush with it. The whole apparatus is air tight, seals at the top being rubber "O" rings while those at the bottom are of indium to withstand low temperatures as required. The low temperatures are achieved by immersing the sample holder in a dewar containing liquid nitrogen. The temperature is monitored by means of a chromel-Alumel thermocouple fixed with indium into a blind hole in the upper anvil assembly, as shown in Fig. 5.9. A piston raising mechanism is incorporated in the upper part of the apparatus, access to which may be obtained by removing the plate containing the feed through connector for the thermocouple.

5.5.3. Operation of the Apparatus

A rotary pump is connected to the upper chamber of the apparatus by means of a system of valves, as shown in Fig. 5.10. Stress is applied to the crystal by evacuating the whole apparatus and then slowly allowing air to enter the section above the piston through a needle valve. This allows the stress to be increased very slowly, e.g. 1 k-bar in 10 minutes, and reduces the risk of premature crystal fracture. The lower part of the apparatus is maintained under vacuum by continuously evacuating it while stress is applied. Closing the needle valve allows a constant stress to be maintained or stress may be reduced slowly by re-evacuating the upper
FIG. 5.10 SCHEMATIC DIAGRAM OF VACUUM SYSTEM.
section through the needle valve.

The difference in air pressure above and below the piston is measured by a manometer and from the knowledge of the area of the top plate of the piston and that of the sample, the force acting on the crystal can be found. Assuming no frictional losses, the stress acting on the crystal is simply the force divided by the crystal area. Even at zero differential air pressure, the weight of the piston acts on the crystal and this must be taken into account. The weight of the piston is kept to a base minimum while still having the required strength and is equal to 1.04 Kg. The stress, \( \chi \), on the sample can be calculated from:

\[
\chi = \frac{HD A_1}{A_2} \times 10^{-6} \frac{1}{1.0197} + \frac{W}{A_2} \times 10^{-6} \frac{1}{1.0197} \text{ k-bar}
\]  

(5.1)

Where \( H \) is the difference in the levels of Hg columns in cm.

\( D \) is the density of Hg (13.6 gm cm\(^{-3}\)).

\( A_1, A_2 \) are the areas of the top plate of the piston and of the sample respectively.

\( W \) is the weight of the piston.

The factor \( 10^{-6}/1.0197 \) converts gm cm\(^{-2}\) to k-bar.

With a top plate 10 cm in diameter, the maximum stress obtainable on a 0.5 mm x 0.5 mm sample is \( \approx 30 \) k-bar. However, for samples of different areas, the top plate and supporting ring may be replaced by different sizes to achieve the required available stress.

5.5.4. Anvil and Sample Preparation

After every few runs, or whenever the anvils are scratched or pitted, the anvils are repolished to optical flats. Stainless steel polishing discs with holes in the centre are placed over the anvils such that the upper surface of the discs are flush with the anvils top surface. This combination is then polished, first on a 3 \( \mu \)m diamond polishing
wheel and finally on a 1 μm wheel. After several polishings the anvils may become domed and they are then skimmed flat by grinding with diamond paste (6 μm down to 1 μm successively) on a piece of optically flat glass.

The anvils are cleaned with isopropyl alcohol. Small pieces of ≈ 1 μm thick gold foil (99.99% pure gold) or fine mylar sheet (2.5 μm) are then pressed on each anvil surface in order to produce as pure uniaxial stress as possible. The effect of any small imperfection in the anvil surface e.g. ≤ 1 μm should also be reduced by the gold or mylar. Pure gold is used because the presence of impurities would increase its yield strength particularly at low temperatures.

The samples used in these experiments were n-type GaAs grown by liquid epitaxy on semi-insulating substrates. The slices were cleaned and ohmic contacts, Au-Sn, were evaporated in the configuration, as shown in Fig. 5.11(a), by using photolithographic masking techniques. The slice, after alloying at 525°C for three minutes in the stream of hydrogen, was diamond sawn into 1 mm x 0.5 mm parallelopipeds such that each sample contained four electrodes. The samples, after cleaning by boiling in methanol and trichloroethylene alternately, were glued in small grooves of 0.5 mm thick (5.0 mm x 5.0 mm) pieces of paxolin on which four gold tapes were stuck down using sellotape as shown in Fig. 5.11(c). Paper glue was used to hold the samples in the grooves because it does not get very hard when dry to affect the stress. Gold wires were attached between the electrodes and the gold tapes by a pulse tip bonder. The cross-sectional area of the sample was measured by using a travelling microscope. The sides of the sample to which stress is to be applied were etched with

\[3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}\]

for a few seconds to remove the cutting damage. The sample was then placed in the sample holder on a small printed circuit board and electrical connections were made as shown in Fig. 5.11(d). One of the terminals of the printed circuit board was soldered to the brass disc of the lower anvil which is in contact with the body of the apparatus.
FIG. 5.11 SAMPLE CONFIGURATION.
FIG. 5.11 SAMPLE HOLDER AND LEAD CONNECTIONS.
and serve as a common terminal. The current was passed between the two outer electrodes and voltage was measured across the inner two electrodes. The upper anvil was placed on the sample carefully not to damage the sample and then the assembly was fixed in position at the bottom of the apparatus.

5.6. **CALIBRATION**

Although stress could be calculated directly from equation (5.1) it was also possible to check the overall system by measuring the piezoresistance of n-type silicon. Cubic samples with sides of about 0.5 mm were diamond sawn from a slice having typical carrier concentration of $1.5 \times 10^{16} \text{cm}^{-3}$ and resistivity, $\rho = 0.7 \ \Omega \ \text{cm}$. Ohmic contacts were achieved by diffusing Cr-Au on both sides. The change in resistivity with stress at room temperature on increasing and decreasing stress is measured and shown in Fig. 5.12. The results were consistent from sample to sample and, as can be seen, are reproducible on the decreasing stress cycle as well showing negligible frictional losses or damage to the sample. The results at $77^\circ \text{K}$ were also obtained and compared with theory, as shown in Fig. 5.13 following Smith's\textsuperscript{(28)} analysis.

The silicon band structure and its stress dependence has already been described in Chapter 4. Under (100) uniaxial stress the energy of the two valleys, having axes along the stress direction, is lowered with respect to the other four "perpendicular" valleys as already shown in Fig. 4.1. Thus electrons transfer from the later to the former. Since the mobility is now determined by the longitudinal effective mass, $m_\parallel$, which is greater than the transverse effective mass, $m_\perp$, the resistivity measured in this direction is expected to increase with stress. Since the resistance variation with stress is only linear\textsuperscript{(65)} for small stresses ($\lesssim 1 \ \text{k-bar}$) one has to take intervalley scattering into account to analyse the results.
FIG. 5.12 NORMALISED RESISTIVITY Vs <100>-STRESS FOR N-TYPE SILICON AT ROOM TEMPERATURE.
FIG. 5.13 NORMALISED RESISTIVITY Vs <100> STRESS FOR N-TYPE SILICON at 77 K.
For equivalent intervalley scattering both 'f' and 'g' scatterings, as discussed earlier, were considered. High temperature phonons (θ ≈ 600K) are believed to participate in f-scattering while a low temperature (θ ≈ 134K) cause g-scattering\(^{(66)}\). When a high stress causes splitting of the valleys by a few \(k_B T\), f-scattering will be completely eliminated and therefore the relaxation time, \(\tau\), is dependent on stress. However, at low temperature (≈ 77K), even at zero stress, f-scattering is negligible\(^{(67)}\) hence the relaxation time, \(\tau\), is now stress independent. One should have to use relatively pure samples because at low temperatures impurity scattering would be dominant. The resistivity, normalized to zero stress, may be written\(^{(68)}\) as:

\[
\frac{\rho}{\rho_0} = \frac{(2K + 1)(1 + 2 \exp - \frac{\Delta E}{k_B T})}{3 (1 + 2K \exp - \frac{\Delta E}{k_B T})}
\]

Where \(\Delta E\) is the splitting of the valleys and is equal to \(\varepsilon_u (s_{11} - s_{12}) \chi\) from equation (3.8). Where \(\chi\) is the stress and \(K = \frac{\mu_t}{\mu_L}\) (mobility anisotropy factor). The mobility anisotropy factor, \(K\), could be found from:

\[
\frac{\rho}{\rho_0} = \frac{1}{3} (2K + 1)
\]

Here \(\rho/\rho_0\) is the saturation value of the resistivity when virtually all the electrons have been transferred to the lower valleys. Thus \(\rho/\rho_0\) was first obtained from the experimental resistivity curve and \(K\) was calculated from equation(5.3). Then the experimental resistivity curve at 77°K may be compared with a calculated curve obtained from equation (5.2).

It is also seen that the rest of the curve between \(\rho_0\) and \(\rho_s\) is fitted well by theory for a value of \(\varepsilon_u = 8.5eV\), which is in good agreement with previous measurements\(^{(68)}\).

5.7. LOW TEMPERATURE CRYOSTAT

For low temperature, atmospheric pressure, measurements the "variable
temperature" (6 - 300K) cryostat was used. A schematic diagram of the cryostat is shown in Fig. 5.14 which comprises of a modular dewar, Oxford Instruments Md4A/1/SV type, with tail placed between the poles of an electromagnet, and a variable temperature insert.

The dewar consists of an outer vacuum chamber, liquid nitrogen vessel and a liquid helium vessel arranged as shown in Fig. 5.14. Since in the series of experiments, to be described later, temperatures only down to 77°K were required, liquid nitrogen was used in both liquid nitrogen and helium vessels. The walls of these chambers are all made of electro-polished stainless steel. The outer chamber has to be evacuated to a pressure of $\approx 10^{-5}$ or below before any of the inner chambers are evacuated, or filled with cryogenic refrigerants. This is done to avoid the collapsing of the inner vessels or to avoid condensation outside the cryostat. The outer chamber is also fitted with an automatic pressure relief mechanism which activates automatically in case of refrigerant leakage into the vacuum space. The liquid nitrogen and liquid helium chambers are separated by a vacuum jacket. Since the liquid nitrogen vessel terminates at the bottom of the dewar a high purity copper radiation shield (nitrogen tail) is attached to the base flange of the liquid nitrogen vessel as shown in Fig. 5.14.

The variable temperature insert, is of top loading type, comprising a full length, central sample tube surrounded by a pumpable vacuum jacket. This jacket and the inner vacuum chamber were filled with an exchange gas i.e. helium gas. An electric heater and a thermocouple are provided at the base of the insert. Leads for the heater and thermocouple are fed through the inner vacuum chamber and out of the system at the top through a 10 pin seal plug as shown. Similarly a vacuum seal plug is used at the top of the insert through which sample leads were fed. Two spare lead through seal plugs are provided near the base of the dewar for electrical
FIG. 5.14 LOW-TEMPERATURE CRYOSTATE.
connections to the tail if required. The liquid helium chamber near the sample block provides a reference junction for the thermocouple whereas the other junction is soldered to the sample block.

Since the sample block is cooled by radiation and conduction through the exchange gas in the sample tube and inner vacuum chamber the sample temperature control is achieved by balancing the rate of cooling of the sample at any temperature against the heating rate of the heater. To achieve this purpose "Oxford Instruments" precision temperature controller was used. At low temperatures the exchange gas pressure of 1000 mm of Hg was used in the inner vacuum chamber. But it should be reduced in steps as the temperature is raised whereas the exchange gas pressure is kept constant throughout the whole temperature range in the sample jacket.
CHAPTER 6

HYDROSTATIC PRESSURE MEASUREMENTS ON N-TYPE GERMANIUM

6.1. INTRODUCTION

The low field properties of n-type germanium at atmospheric pressure are well understood. The electrons occupy four ellipsoidal minima at the $L_{1c}$ points (i.e.,) in the (111) direction in k-space. With increasing pressure, however, the energy of the $L_{1c}$ minima increases whereas that of the $\Delta_{1c}$ minima decreases with respect to the top of the valence band. At a certain pressure the $L_{1c}$ and $\Delta_{1c}$ minima cross-over making the $\Delta_{1c}$ minima the lowest. Thus in n-type material the electrons transfer to the $\Delta_{1c}$ minima and the band structure becomes similar to that of silicon at atmospheric pressure. The $\Delta_{1c}$ minima then become available for direct electrical investigation and allow comparisons to be made concerning the electron scattering properties and effective masses in the equivalent valleys of the $L_{1c}$ and $\Delta_{1c}$ minima.

Pressure experiments are extremely useful in providing information about band parameters such as the sub-band energy gaps, effective masses, and the intervalley deformation potentials. It is essential to know such parameters if high field phenomenon such as the transferred electron effect are to be properly understood and meaningful calculations made. The high electric field properties of germanium have been discussed, in detail, by Fawcett and Paige(69). They suggest that the electron transfer to the higher density of states $\Delta_{1c}$ minima at high fields can explain all the reported data, including the negative differential mobility below 150K observed experimentally by McGroddy and Nathan(70).

The earlier high pressure experiments were confined to simple resistivity measurements below 30 k-bar(3) or p-n junction measurements by Jayaraman and Kosicki(71). In neither case was the pressure high...
enough to eliminate scattering to the $L_{1c}$ minima. But recently Fletcher and Pitt$^5$ have managed to pressurise single crystals of $n$-type germanium to about 65 k-bar, well beyond the (111) and (100) minima cross-over. The details of the high pressure apparatus and the technique used have already been described in Chapter 5. We have, in the work to be described here, used the same technique of pressurising $n$-type germanium crystals and measuring the resistivity and Hall voltage.

6.2. MEASUREMENT PROCEDURE

The standard Van der Pauw$^{72}$ technique was used for both resistivity and Hall voltage measurements. The clover leaf sample and the circuit used for these measurements are shown in Figure 6.1. A constant current was passed through the sample by using a bank of batteries and a 10 K Ω resistance box in series. A standard 1 Ω resistor is also incorporated in the circuit and a digital multimeter across it, as shown, to monitor the sample current. The output voltage from the sample was measured by a Keithley digital multimeter. A 4-port/12 terminal switch was introduced in the circuit, which allowed measurements to be made across different lobes around the clover leaf and with the reverse current.

The Hall voltage was measured in the presence of a magnetic field supplied by an electromagnet which had previously been calibrated for various current values. The Hall constant, $R_H$, and the carrier density, $n$, were determined from the relation $\frac{V_H}{d} = \frac{R_H}{B I} = -\frac{V}{n e}$ (6.1) where $V_H$ is the Hall voltage

d is the sample thickness

B is the magnetic field

I is the sample current

e is the electronic charge
FIG. 6.1  
(a) RESISTIVITY AND HALL VOLTAGE MEASUREMENT CIRCUIT.  
(b) CLOVER LEAF SAMPLE.
The scattering factor, \( \gamma \), defined by the ratio of Hall mobility to the drift mobility, depends on the carriers mean free time "\( \tau \)" and hence on the scattering mechanism present. Debye et al\(^9\) have quoted an experimentally determined value of \( \gamma = 1.1 \) for high resistivity germanium and that it remained constant with temperature in the 150K-300K range. This value of \( \gamma \) is within the limits of the experimental error of the theoretical predicted value of 1.18 for acoustic deformation potential scattering. The average of four Hall voltage readings, with the reversal of sample current and magnetic field, B, was taken to cancel out the extraneous voltages due to any contact effects. For resistivity measurements the average of eight readings, with current reversal, was taken without the magnetic field and the resistivity was then calculated by the formula\(^7\).

\[
\rho = \frac{\pi d}{\ln 2} \left[ \frac{V_{AB,CD} + V_{BC,DA}}{2} \right] f \frac{V_{AB,CD}}{V_{BC,DA}}
\] (6.2)

where \( V_{AB,CD} \) is the voltage across CD due to the flow of current between A and B, Figure 6.1. \( V_{BC,DA} \) is defined similarly. The factor \( f \) is called the non-uniformity function and is defined as the ratio \( \frac{V_{AB,CD}}{V_{BC,DA}} \). The magnitude of \( f = 1 \) is accurate within 1.0% for ratios less than 1.5.

The Hall mobility, \( \mu_H \), was then calculated by the relation

\[
\mu_H = \frac{R_H}{\rho} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}
\] (6.3)

6.3. EXPERIMENTAL ARRANGEMENTS

Clover leaf samples were cut from both the (111) and (100) oriented slices of Sb-doped germanium. The electrical characteristics of the samples used at atmospheric pressure and at room temperature are summarized as follows:
Since there may be some uniaxial stresses parallel to the direction of the load in the epoxy system at low pressures, both (100) and (111) oriented crystals were used. Although the uniaxial stresses may play a part in (111) samples at low pressure, in (100) samples these stresses will not change the degeneracy of the normally occupied (111) minima. In practice at high pressures the conductivity in both types samples converge and passes through a minimum, as observed by Fletcher et al.\(^5\), showing that the pressure system is hydrostatic in nature. Diffused tin contacts were used to which fine copper wire leads were soldered. The samples were pressurised in the MgO pressure cells, as described in Chapter 5. Load was increased continuously at the rate of = 2 k-bar per minute, at room temperature, and the resistivity and Hall voltage were monitored after equal intervals of 5 k-bar. After the (111)-(100) minima cross-over i.e. when the Δ\(_{1c}\) minima became lowest, the load was kept constant and the temperature was lowered to 100K. The resistivity and Hall voltage were then monitored as a function of temperature. Electron mobility in the Δ\(_{1c}\) minima was calculated by using equations 6.1 - 6.3. The results were analysed in terms of all the possible scattering mechanisms.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>ρ Ω-cm</th>
<th>n cm(^{-3})</th>
<th>(\mu_H) cm(^2)V(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCT 474 (100)</td>
<td>33.5</td>
<td>4.72x10(^{13})</td>
<td>3950</td>
</tr>
<tr>
<td>SCT 258 (111)</td>
<td>3.7</td>
<td>4.74x10(^{14})</td>
<td>3920</td>
</tr>
<tr>
<td>ESC 399 (111)</td>
<td>2.0</td>
<td>6.81x10(^{14})</td>
<td>3980</td>
</tr>
</tbody>
</table>

6.4. EXPERIMENTAL RESULTS

The variation of the normalized resistivity, \(\frac{\rho}{\rho_0}\), Hall constant, \(\frac{R_H}{R_H^0}\) and the Hall mobility, \(\frac{\mu_H}{\mu_{H_0}}\), with pressure for a typical sample are shown in Figure 6.2a,b,c. The \(\rho\) resistivity, as shown in Figure 6.2a increases slowly at low pressure mainly due to the increase in effective mass of the electrons in the L\(_{1c}\) valleys as they move away from the
Fig. 6.2 (a) Normalised Resistivity vs Pressure for SCT$_4$T$_4$ sample at 300 K.
FIG. 6.2 (b) NORMALISED HALL CONSTANT vs PRESSURE FOR SCT 474 SAMPLE at 300 K.
FIG. 6.2 (c) NORMALISED HALL MOBILITY vs PRESSURE FOR SCT 474 SAMPLE at 300 K.
valence band with pressure. At about 20 k-bar, as the $L_{1c}$ and $\Delta_{1c}$ minima approach one another the non-equivalent inter valley scattering between the two minima increases, which reduces the electron mobility. Also the electron transfer from the $L_{1c}$ to $\Delta_{1c}$ minima reducing the mobility further. All three processes make the resistivity rise rapidly. The maximum in resistivity at about 33 k-bar occurs when most of the electrons have transferred to the low mobility $\Delta_{1c}$ minima, but the non-equivalent inter valley scattering between the $L_{1c}$ and $\Delta_{1c}$ minima is still influencing the relaxation time. At about 65 k-bar when the $L_{1c}$ minima have moved a few $k_B T$ above the $\Delta_{1c}$ minima, the resistivity levels off at $\frac{\rho}{\rho_0} = 4.0 \pm 0.3$ showing that the electron transfer is complete and non-equivalent inter valley scattering is negligible.

It is seen from Figure 6.2b that the Hall constant, $\frac{R_H}{R_{H0}}$, passes through the characteristic band transfer maximum near the band cross-over. This effect has already been seen in transfer from high to low mobility bands in several semiconducting materials by Pitt and Lees.$^{(74)}$ By 65 k-bar the Hall constant returns to its original value at atmospheric pressure which implies that the electron transfer is complete without any carrier loss to deep lying impurity levels which might exist at atmospheric pressure above the $L_{1c}$ minima but below the $\Delta_{1c}$ minima. Such states are commonly seen in III-V compounds like GaAs as observed by Vyas et al.$^{(58)}$ Perhaps the fact that these impurity levels are not observed in germanium to date reflects the advanced state of the technology in growing crystals (i.e. the existence of these levels in the III-V compounds may be associated with crystal defects).

The Hall mobility, $\frac{\mu_H}{\mu_{H0}}$, as shown in Figure 6.2c, falls gradually at low pressure due to the increase in effective mass of the electrons as the $L_{1c}$ minima moves away from the valence band. Before the band cross-over the drop in mobility is largely due to the inter valley scattering
between the \( L_{1c} \) and \( \Delta_{1c} \) minima and also transfer of electrons to the lower mobility band. We note that the mobility does not pass through a minimum at band cross-over. This is because maximum scattering between the minima will occur when the \( L_{1c} \) minima are lower in energy than the \( \Delta_{1c} \) minima owing to the smaller density of states of the \( L_{1c} \) minima. These results are in good agreement with already reported results of Fletcher and Pitt\(^5\).

At about 65 k-bar, when \( \Delta_{1c} \) minima being the lowest, load was kept constant and resistivity and Hall voltage were monitored as a function of temperature. The variation of the resistivity and Hall constant with temperature of a typical sample is shown in Figure 6.3. The electron mobility in the \( \Delta_{1c} \) minima was then calculated following the same procedure as described earlier and the results are shown in Figure 6.4. Above 200°K where the mobility is dominated by phonon scattering, there is good agreement between the samples, indicating the effectiveness and reliability of the epoxy pressure-transmitting system. The divergence below 200K could be attributed, as will become evidence from the later analysis, to the varying amount of impurity scattering present in different samples.

In order to analyse completely the mobility variation with temperature in terms of the possible scattering mechanisms present and also because of the important part played by impurity scattering below 200K in each sample it is necessary to know, apart from other parameters, the density of ionized impurity scattering centres and the phonons involved. To sort out the phonons involved in the intervalley scattering one has to resort to the group theory and selection rules. The impurity centres, on the other hand, were found by analysing the measured electron mobility variation with temperature in the \( L_{1c} \) valley, as will be described later. The \( L_{1c} \) mobility was measured, in the same samples, at atmospheric pressure by using the low-temperature cryostat described in
Fig. 6.3 Hall constant and resistivity/low temperature variation in the $\Delta_{1c}$ valley of germanium.
FIG. 6.4 VARIATION OF HALL MOBILITY WITH TEMPERATURE FOR N-TYPE GERMANIUM AT 60 K bar.
Chapter 5. The variation of resistivity and Hall constant with temperature in the $L_{1c}$ minima of a sample is shown in Figure 6.5. The electron mobility, calculated in the usual way, is shown in Figure 6.6 for all the samples. Above 200K the electron mobility in the $L_{1c}$ valley also increases linearly, as can be seen from Figure 6.6, but below 200K different samples show varying amounts of impurity scattering. By analysing these results the density of impurity centres present in the samples could be found which in turn could be used in the subsequent analysis of the $\Delta_{1c}$ mobility results.

6.5. PHONON GROUPING AND SELECTION RULES

The symmetry and polarisation of phonons i.e. transverse or longitudinal, optical or acoustic, involved in intervalley scattering processes are usually given by group theory. A simple graphical approach is most helpful in identifying the symmetry of the phonons involved in different intervalley scattering processes. This approach also demonstrates very simply which of the intervalley transitions are of Umklapp type. Figure 6.7a shows the first Brillouin zone for the face centred cubic crystal structure, with the main symmetry directions indicated. Symmetry points inside the zone are labelled conventionally by Greek letters while those at the zone boundary are named by English letters. Figure 6.7b shows the location of the $L$-minima at the zone boundary. It can be seen from the figure that $L \leftrightarrow L$ scattering requires the participation of (100) type phonons of momentum $\hbar \mathbf{K}_{100}$ ($X$-phonons). The $X \leftrightarrow X$ scattering is demonstrated in Figure 6.7c. Again this process requires the participation of $X$-phonons, however, unlike $L \leftrightarrow L$ scattering it is of the Umklapp type since it involves transitions between distinct Brillouin zones. The other intervalley scatterings like $\Gamma \leftrightarrow L$ and $L \leftrightarrow X$ occur through the $L$-phonons whereas $\Gamma \leftrightarrow X$ will require $X$-phonons. The combination of the above processes can best be presented by considering a (110) type plane in the repeated zone structure as shown in Figure 6.7d. The group
FIG. 6.5 HALL CONSTANT AND RESISTIVITY/LOW TEMPERATURE VARIATION IN THE $L_{1c}$ VALLEY OF GERMANIUM.
FIG. 6.6 VARIATION OF HALL MOBILITY WITH TEMPERATURE FOR n-type GERMANIUM AT ATMOSPHERIC PRESSURE.
FIG. 6.7 (a) THE BRILLOUIN ZONE OF A FACE CENTRED CUBIC CRYSTAL WITH MAIN SYMMETRY POINTS AND DIRECTIONS INDICATED.
FIG. 6.7 (b) L→L SCATTERING OCCURS ALONG <100> DIRECTIONS.
FIG. 6.7 (c) $X \leftrightarrow X$ SCATTERING OCCURRING VIA (100) PHONONS.
Fig. 6.7 (d) Demonstration of intervalley scattering processes on a (110) type plane in the repeated zone structure.
selection rules, as discussed first by Lax and Hopfield\(^{75,76}\),
Streitwolf\(^{77}\) in general and by Herbert et al\(^{78}\) for germanium and
silicon in particular, restricts the phonon polarization as listed
below.

<table>
<thead>
<tr>
<th>Material</th>
<th>Transition</th>
<th>Phonons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>(\Gamma_1 - L_1) Non-equivalent I.V. scattering</td>
<td>(L_1)</td>
</tr>
<tr>
<td></td>
<td>(L_1 - \Delta_1) Non-equivalent I.V. scattering</td>
<td>(L_0 + L_1)</td>
</tr>
<tr>
<td></td>
<td>(L_1 - L_1) Equivalent I.V. scattering</td>
<td>(L_0 + L_1)</td>
</tr>
<tr>
<td>Silicon</td>
<td>(\Delta_1 - \Delta_1) Equivalent I.V. scattering</td>
<td>(L_1)</td>
</tr>
</tbody>
</table>

The non-equivalent intervalley scattering in germanium has
already been studied by Fletcher et al\(^{(5)}\) therefore in this work we
concentrate only on the equivalent intervalley scattering. In principle
the scattering rates due to different phonons should be calculated
individually. However, when two phonons are close in energy such that
it becomes difficult to separate their contributions in the transport
calculations then they could be combined in one group of phonons e.g. high
energy or low energy phonon groups. The group is assigned with an energy
equal to the average of the individual phonon energies.

6.6. ASSIGNMENT OF BAND PARAMETERS

6.6.1. \(L_{1c}\)-valleys

The band parameters of germanium at atmospheric pressure - \(L_{1c}\)
valleys, are well known. The transverse and longitudinal effective
masses of electrons at the four equivalent \(L_{1c}\) points are known from
cyclotron resonance experiments\(^{(16)}\): \(m_t = 0.082\ m_0\) and \(m_L = 1.58\ m_0\)
at 4K. These values are in good agreement with later results from
magneto phonon experiments\(^{(79)}\): \(m_t = 0.086\ m_0\) and \(m_L = 1.52\ m_0\) measured
from 60 to 270K with no apparent temperature dependence. Either set of
results yields $m^*_{\text{D.S}} = 0.22 \, m_0$ which we assumed to be independent of temperature. The values of high and low frequency dielectric constants and density used are $15.98, 15.98, 5.32 \, (\text{gm cm}^{-3})$ respectively. The deformation potential $E_1$, for the intravalley acoustic scattering is given by Debye and Conwell as $9.4\, \text{eV}$. This agrees well with the value of $9.0\, \text{eV}$ as determined by Rode from a theoretical fit to the experimental mobility curve. Fawcett and Paige, however, give a value of $E_1 = 12\, \text{eV}$ which is rather high and its use gives a lattice limited mobility $43\%$ less than the measured mobility at room temperature. But $E_1 = 9\, \text{eV}$ on the other hand give a good agreement between theory and experimental mobility.

At low fields the electrons in the (111) valleys are subject to the following scattering processes:

(i) Intravalley acoustic modes.

(ii) Intravalley non-polar optical modes.

(iii) Equivalent intervalley scattering between (111) valleys.

(iv) Ionized impurity scattering.

All intervalley scattering occurs by singly ionized impurities, by transverse and longitudinal modes of long wavelength, and by non polar optical modes. Intervalley scattering is induced by LA and LO phonons of similar energies. Hence we combine non-polar scattering with intervalley scattering and assume that these scatterings occur through a single phonon of energy equivalent to $382 \, \text{K}$ as also used by Rode. This phonon energy, expressed in terms of equivalent temperature, has been taken from the dispersion curves given by Brockhouse and Iyenger, as shown in Figure 6.9.

6.6.2. $\Delta_1$ valleys

In (100) valleys the electrons are subject to the same processes as listed in section 6.6.1. with two exceptions. Firstly, non-polar optical scattering becomes negligible (Harrison), and secondly, since the (100) minima do not lie at the zone boundary, the equivalent intervalley scattering will have two components - $f$ and $g$ scattering, as already
discussed in Chapter 4. Hence the scattering processes in the (100) valleys are:

(i) Intravalley acoustic scattering.

(ii) Equivalent intervalley scattering between valleys lying on the same cube axis - g scattering.

(iii) Equivalent intervalley scattering between valleys lying on different cube axis - f scattering.

(iv) Ionized impurity scattering.

Long\(^{[67]}\) has discussed, in detail, the role of f and g type scattering in silicon. Assuming that the \(\Delta_{1c}\) valleys in germanium are located at the same place in k-space as in silicon we have adopted Long's approach to find the wave vector and energies of the phonons involved in intervalley scattering. It can be shown by simple geometrical argument that both f and g type scatterings are Umklapp processes and that all the wave vectors involved lie in [110] type planes. The momentum conservation conditions can be illustrated by vector diagram in a [110] plane cross-section of the reciprocal lattice as shown in Figure 6.8. It can be seen from Figure 6.8 that the phonon involved in g-scattering has its vector \(\sigma_g\) in a (100) direction and that the vector \(\sigma_f\) for f-scattering is only 11° off the (100) direction. Furthermore \(\sigma_g\) has a magnitude of 0.30 of the maximum in the (100) direction, while \(\sigma_f\) is exactly equal to the maximum \(\sigma\) in its direction.

After establishing the wave vectors of the intervalley phonons, we can find their energies from the lattice vibrational spectrum of germanium, shown in Figure 6.9, as determined by Brockhouse et al\(^{(81)}\). The vertical marks on the branches at 0.3 of the way from the zone centre to the boundary indicate the energies of phonons involved in g-scattering. Even though the f-scattering phonons are not quite in the (100) direction, we feel that they are close enough so that Figure 6.9 should provide a
Fig. 6.8 (110) type plane in the repeated zone structure, showing the momentum conservation conditions for the intervalley scattering processes. $k_{100}$ and $k_{111}$ are principal vectors of the reciprocal lattice.
good approximation to their energies, since the phonon spectrum should not change very rapidly with direction in the crystal. Under this assumption, the energies of the f-scattering phonons are given by the points at which the branches intercept the zone boundary. Thus from Figure 6.9 it is obvious that the energies of the phonons involved in g-scattering fall in two ranges i.e. high energy 430K-LO phonons and low energy 100K-LA phonons. But for f-scattering since LA and LO phonons have the same energy so 320K phonon was considered. These phonon energies are also similar to the ones used by Fawcett and Paige(69) in their high field transport calculations for germanium.

The electron effective masses in the (100) minima in germanium are not known. But Fawcett and Paige(69), as a result of high field calculations, predicted effective mass values of \( m_t = 0.288 \, m_0 \) and \( m_\perp = 1.353 \, m_0 \).

Fawcett and Paige(69) by taking silicon effective masses - \( m_t = 0.192 \, m_0 \), \( m_\perp = 0.902 \, m_0 \) (Rauch et al(84)) and germanium band parameters got a good agreement with the experimental results of Fletcher et al(5) for the low-field mobility-pressure results. However, when they used the resulting parameters to calculate the high-field transport properties, a significant positive differential mobility resulted at 77K in (100) direction, contrary to the negative differential mobility observed by McGroddy et al(70). This controversy was resolved by increasing the effective masses to those given above and by decreasing the coupling constant \( E_1 \) to 3.6eV. These are the values we have used in our calculations. The band parameters for both \( L_{1c} \) and \( \Delta_{1c} \) valleys are summarised in Table 6.1.
FIG. 6.9 LATTICE VIBRATION DISPERSION CURVES OF GERMANIUM.
( AFTER B.N. Brockhouse and P.K. Iyenger\textsuperscript{81} )
TABLE 6.1.

6.7. ANALYSIS OF RESULTS

In our analysis of the electron mobility in both the $L_{1c}$ and $A_{1c}$ minima of germanium we have not taken into account the conduction band anisotropy. This is because the correction due to band anisotropy is almost equal and opposite to the scattering factor, as shown below:

In a multi-valley system where the valleys are ellipsoidal, if the band anisotropy is given by, $\frac{m_L}{m_t} = K$ then the ratio of Hall to drift mobility could be written as (85):

$$\frac{\nu_H}{\nu} = \frac{\tau^2}{(\tau)^2} \times \frac{3K(K+2)}{(2K+1)^2}$$

(6.4)

In the equation (6.4) the first term, $\frac{\tau^2}{(\tau)^2}$ depends on the dominant scattering mechanism and can be estimated from the relation (86)

$$\frac{\tau^2}{(\tau)^2} = \frac{\Gamma(5/2 + 2s) \Gamma(5/2)}{[\Gamma(5/2 + s)]^2}$$

(6.5)

where $s$ is found from the relaxation time - energy relationship $\tau = E^s$

The second term in equation 6.4 depends on the band anisotropy.

Parameter | $L_{1c}$-valley | $A_{1c}$-valley |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective mass ratio $m_L/m_t$</td>
<td>1.588</td>
<td>1.353</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>5.33</td>
<td>5.33</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon_u = \varepsilon_\infty$</td>
<td>15.98</td>
<td>15.98</td>
</tr>
<tr>
<td>Longitudinal Sound Velocity (cm s$^{-1}$)</td>
<td>$5.4 \times 10^5$</td>
<td>$5.4 \times 10^5$</td>
</tr>
<tr>
<td>Acoustic Deformation Potential $E_1$(eV)</td>
<td>9.0</td>
<td>3.61</td>
</tr>
<tr>
<td>Intervalley Phonon Temperatures (K)</td>
<td>LO 430 (g-scattering)</td>
<td>LA 100 (g-scattering)</td>
</tr>
</tbody>
</table>
In the $L_{1c}$ minima since the acoustic deformation potential scattering is dominant, $s = -\frac{1}{2}$ and the band anisotropy factor, $K = \frac{1.588}{0.082} = 19.37$. Using these values in equations 6.4 and 6.5 gives

$$\frac{\mu_H}{\mu} = 1.18 \times 0.7857 = 0.93$$

which could be taken as unity within experimental error in $m_t$.

Similarly in the $\Delta_{1c}$ valley since intervalley scattering is dominant $s = +\frac{1}{2}$ and the band anisotropy factor $K = \frac{1.353}{0.288} = 4.698$

Hence $\frac{\mu_H}{\mu} = 1.105 \times 0.874 = 0.966$

which again could be taken as unity.

Therefore the assumption of isotropic conduction and $\gamma = 1$ is a reasonable approximation for germanium. Under this assumption the equations 2.6 and 2.10, with the $L_{1c}$ valley parameters as listed in Table 6.1, reduces to:

$$\frac{\mu_d}{L_{1c} \text{ valley}} = \frac{2.21 \times 10^9}{E_1^2 (\text{eV}) \times T^{3/2}} \text{ cm}^2 \text{v}^{-1} \text{s}^{-1}$$  \hspace{1cm} (6.6)

$$\frac{\mu_{\text{I.I}}}{L_{1c} \text{ valley}} = \frac{1.846 \times 10^{18} \times T^{3/2}}{N_1 [\ln(1+b) - \frac{b}{1+b}]}$$  \hspace{1cm} (6.7)

where $b = \frac{4.54 \times 10^{14} \times T^2}{n}$

and $N_1$, $n'$ are already defined as

$$n' = n + (n + N_A) \left(1 - \frac{n + N_A}{N_D}\right)$$

$$N_1 = 2 \frac{N_A}{N_D} + n$$

For the estimation of intervalley scattering, we assume that the average of the lifetime associated with this scattering is approximated by replacing the energy term in Herring and Vogt's formula - equation 2.8 equal to $\frac{3}{2} k_B T$. On this assumption equation 2.8 reduces, as deduced by Masahara Toyama et al (87) to:-
\begin{equation}
\mu_{I.V.} \approx \mu_d \left\{ \sum_i \frac{\omega_i}{\omega_A} \left( \frac{T}{T} \right)^{3/2} \left[ \frac{\left( \frac{T}{T} + \frac{2}{3} \right)}{\exp\left( \frac{T}{T} \right) - 1} + \frac{\left( \frac{T}{T} - \frac{2}{3} \right)}{1 - \exp\left( -\frac{T}{T} \right)} \right] \right\}^{-1}
\end{equation}

(6.8)

where \( \omega_A, \omega_i \) measure the strength of coupling of electrons to acoustic and to the ith intervalley phonons respectively. \( T_{ci} \) is the characteristic temperature of the ith phonon.

The second term in the square bracket vanishes for \( \frac{T}{T_{ci}} \leq \frac{2}{3} \).

The equation 6.8 can also be used for the \( \Delta_{1c} \) minima provided the appropriate phonon energies are used. The equations for acoustic deformation potential and the ionized impurity scattering for the \( \Delta_{1c} \) valley, using the \( \Delta_{1c} \) valley parameters, can be written as:

\[ \mu_d \bigg|_{\Delta_{1c} \text{ valley}} = \frac{3.075 \times 10^8}{E_1^2 \text{(eV)} \times T^{3/2}} \text{cm}^2 \text{v}^{-1} \text{s}^{-1} \]

(6.9)

\[ \mu_{I.I.} \bigg|_{\Delta_{1c} \text{ valley}} = \frac{1.238 \times 10^{18} \times T^{3/2}}{N_1 \left[ \ln(1+b) - \frac{b}{1+b} \right]} \text{cm}^2 \text{v}^{-1} \text{s}^{-1} \]

(6.10)

where \( b = \frac{9.993 \times 10^{14}}{n^2} \times T^2 \)

6.7.1. Curve Fitting

6.7.1.1. \( L_{1c} \) valley mobility

Since the measured electron mobility in both the \( L_{1c} \) and \( \Delta_{1c} \) valleys, as shown in Figures 6.4 and 6.6, shows the dominant part played by the ionized impurity scattering below 200K so in order to analyse the results completely it is essential to find the density of impurity centres. To do this we have used the results of Debye et al\(^{(73)}\) for sample 55 in which the mobility hardly departs from a straight line behaviour down to 100K, as shown in Figure 6.10, meaning that the impurity scattering in this sample is negligible. Thus including deformation potential scattering mobility from equation 6.6 with \( E_1 = 9\text{eV} \) and intervalley scattering mobility from equation 6.8, treating \( \alpha = \frac{\omega_i}{\omega_A} \) as adjustable parameter, a fit to the results of sample 55 was obtained, as shown in Figure 6.10. From the
FIG. 6.10 HALL MOBILITY VS TEMPERATURE FOR SAMPLE 55 WITHOUT THE IONISED IMPURITY SCATTERING.
resulting value of $\alpha$, the intervalley deformation potential was calculated from the Conwell's relation:

$$\alpha = \frac{2 D^2_1}{E^2_\perp} \omega^2_l$$

where $D_1$ is the intervalley deformation potential, $E_\perp$ and $\omega_l$ is listed in Table 6.2.

Using this value of $\alpha$ in equation 6.8 the intervalley scattering mobility could be calculated. Thus by combining the deformation potential scattering mobility with intervalley scattering mobility theoretical fits to our samples were obtained by introducing controlled amount of impurity scattering. The results are shown in Figure 6.11 a,b,c. The density of impurity scattering centres required for these fits are as listed in Table 6.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(N_{D^-N_A}(\text{cm}^{-3}))</th>
<th>(N_{D^+N_A}(\text{cm}^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye &amp; Conwell Sample 55</td>
<td>1.0 x 10^{13}</td>
<td>1.09 x 10^{13}</td>
</tr>
<tr>
<td>SCT 474</td>
<td>4.72 x 10^{13}</td>
<td>6.73 x 10^{15}</td>
</tr>
<tr>
<td>SCT 258</td>
<td>4.74 x 10^{14}</td>
<td>1.11 x 10^{16}</td>
</tr>
<tr>
<td>ESC 399</td>
<td>6.81 x 10^{14}</td>
<td>1.36 x 10^{16}</td>
</tr>
</tbody>
</table>

**TABLE 6.3**

Having established the density of impurity centres involved in the \(L_{1c}\) valley mobility, same electron density and ionized impurity density could be assumed to apply to the \(\Delta_{1c}\) minima,

6.7.1.2. \(\Delta_{1c}\)-valley mobility

For the \(\Delta_{1c}\) minima the deformation potential scattering mobility is calculated using equation 6.9 and the ionized impurity scattering mobility from equation 6.10 with the above deduced density of impurity scattering centres. The intervalley scattering, both $f$ and $g$ types can be calculated.
FIG. 6.11 (a) \( L_{\text{1c}} \) VALLEY MOBILITY WITH DIFFERENT SCATTERING MECHANISMS.
FIG. 6.11 (b) $L_{1e}$ VALLEY MOBILITY WITH DIFFERENT SCATTERING MECHANISMS.
FIG. 6.11 (c) \( L_{1c} \) VALLEY MOBILITY WITH DIFFERENT SCATTERING MECHANISMS.
from equation 6.8 with appropriate phonon energies. Thus including the deformation potential scattering, the ionized impurity scattering and the intervalley scattering best fits to the measured $\Delta_{1c}$ mobility were obtained, by treating $\alpha$'s as adjustable parameters, as shown in Figure 6.12 a,b,c. The resulting intervalley deformation potentials for the $\Delta_{1c}$ minima, calculated as described earlier, are as listed in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$L_{1c}$-valley</th>
<th>$\Delta_{1c}$-valley</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phonons</td>
<td>382K</td>
<td>430K 320K 100K</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.30</td>
<td>1.92 2.21 negligible</td>
</tr>
<tr>
<td>$D_1$ (eVcm$^{-1}$)</td>
<td>$3.2 \times 10^8$</td>
<td>$3.69 \times 10^8$ 2.94$\times 10^8$ negligible</td>
</tr>
</tbody>
</table>

**TABLE 6.2**

6.8. DISCUSSION AND CONCLUSION

From the measured electron mobility in both the $L_{1c}$ and $\Delta_{1c}$ valleys of germanium, as shown in Figures 6.4 and 6.6, a few points are worth noting:

(i) The magnitude of mobility, at room temperature, in the $L_{1c}$ valley of $\approx 4000$ cm$^2$V$^{-1}$s$^{-1}$ drops to $\approx 800$ cm$^2$V$^{-1}$s$^{-1}$ in the $\Delta_{1c}$ valley.

(ii) The gradient of the curve in the $L_{1c}$ valley near room temperature corresponds to $T^{-1.5}$ temperature dependence, typical for the deformation potential scattering, which is the dominant scattering mechanism in the $L_{1c}$ valley. But the gradient of the curve in the $\Delta_{1c}$ valley, near room temperature, corresponds to $T^{-2.7}$ temperature dependence similar to the silicon at atmospheric pressure. This behaviour is typical of the strong intervalley scattering. In fact that is exactly what we see when we plot the component mobilities, as shown in Figures, 6.11, 6.12, that the deformation potential scattering is
FIG. 6.12 (a) $\Delta_{1c}^\lambda$ VALLEY MOBILITY FOR SAMPLE SCT 474.

- Calculated Mobilities.
- Experimental Results.
- Calculated mobility excluding ionised impurity scattering.

HALL MOBILITY
$\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$

$\mu_{\text{TOTAL}}$
FIG. 6.12 (b) $\Delta_{1c}$ VALLEY MOBILITY FOR SAMPLE SCT 258.

- Calculated mobilities for different scattering mechanisms.
- Experimental mobility.

HALL MOBILITY
$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$

$\mu_{11}$
$\mu_{d}$
$\mu_{1,1}$
$\mu_{1,v}$
$\mu_{\text{TOTAL}}$

TEMPERATURE (K)
FIG. 6.12 (c) $\Delta_1 e$ VALLEY MOBILITY FOR SAMPLE ESC 399.

- CALCULATED MOBILITIES FOR DIFFERENT SCATTERING MECHANISMS.
- EXPERIMENTAL MOBILITY.
dominant in the $L_{1c}$ valley and the intervalley scattering in the $A_{1c}$ valley.

(iii) It is evident from Figure 6.11 that the intervalley scattering, at room temperature, is small and the impurity scattering is negligible. However, as the temperature is lowered the relative importance of the ionized impurity scattering, $\mu_{I,I}$, and the intervalley scattering, $\mu_{I,V}$, changes such that below 200K the ionized impurity scattering takes over the intervalley scattering mobility but still the deformation potential scattering remain dominant. Clearly from sample to sample the contributions due to deformation potential and intervalley scattering remain fixed, only the impurity scattering varies but a good fit to the experimental results can be obtained in each case.

(iv) As shown in Figure 6.12 intervalley scattering dominates the $A_{1c}$ valley mobility throughout the whole temperature range (300K - 100K). The acoustic deformation potential scattering is small and once again the impurity scattering is negligible at room temperature but has a slight effect at low temperatures. Although the contributions of the intervalley and acoustic deformation potential scattering are the same from sample to sample and the ionized impurity scattering is fixed from the $L_{1c}$ valley mobility analysis i.e. there are no adjustable parameters yet a good agreement with the measured mobility was obtained for each sample throughout the whole temperature range, showing nicely the divergence which occurs below 200K.

The analysis of the $L_{1c}$ valley mobility data revealed that for an acoustic deformation potential of 9.0eV we require intervalley deformation potential of $3.2 \times 10^8$ eV cm$^{-1}$ for the 382K phonon. This intervalley deformation potential agrees very well with $3.0 \times 10^8$ eV cm$^{-1}$ as calculated by Rode(82)
for germanium. In an attempt to consider the effect of the acoustic deformation potential $E_1$ we have used $E_1 = 12$ eV, also quoted in literature. Poor agreement was obtained with the absolute mobility values and its temperature variation.

The analysis of the electron mobility in the $\Delta_{1c}$ valley revealed that for an acoustic deformation potential of $3.61$ eV we require intervalley deformation potentials of $3.7 \times 10^8$ eV cm$^{-1}$ and $2.9 \times 10^8$ eV cm$^{-1}$ for the 430K and 320K phonons respectively. These parameters are particularly important for the calculations of high field transport properties. The high field calculations of Fawcett and Paige$^{(69)}$ gave values of the above parameters as $9.5 \times 10^8$ eV cm$^{-1}$ and $3.3 \times 10^8$ eV cm$^{-1}$ for the 430K and 320K phonons respectively. The deformation potentials for the low energy phonons agree very well but the high energy phonon deformation potential is somewhat high. To see the effect of $E_1$, the acoustic deformation potential, we have used different values and tried to retain the agreement with the experimental data. We find that acceptable agreement with experimental data is confined to small range of values of $E_1$ i.e. $3.0 \leq E_1 \leq 5.0$. For values outside these limits agreement with mobility-temperature variation becomes poor. The corresponding range of intervalley deformation potentials becomes $1.97 \times 10^8 \leq D_1 \leq 3.9 \times 10^8$ eV cm$^{-1}$ for 430K phonons and $2.8 \times 10^8 \leq D_2 \leq 3.07 \times 10^8$ eV cm$^{-1}$ for 320K phonons. This range of values for $D_1$ is in good agreement with the silicon value determined by Long$^{(67)}$. Recently, following a reassessment of the selection rules for scattering in silicon by Streitwolf$^{(77)}$ new estimates of this parameter in the range $3 \to 5 \times 10^8$ eV cm$^{-1}$ have been made by Jorgensen et al$^{(89)}$ and Herbert et al$^{(78)}$. Rode$^{(82)}$ has obtained a value
of $3.0 \times 10^8$ eV cm$^{-1}$ for silicon and Masaharu Toyama et al$^{(87)}$ a value of $7.0 \times 10^8$ eV cm$^{-1}$ for GaP.

In summary, we have measured the temperature dependence of the electron mobility in the $L_{1c}$ and $\Delta_{1c}$ minima of germanium. We developed a model to analyse the $L_{1c}$ mobility results and deduced the density of impurity centres involved in the scattering in the samples used. Since no carrier loss was observed as a function of pressure or temperature, the effect of ionized impurity scattering in the $\Delta_{1c}$ minima was deduced. With the effective mass ratios given by Fawcett and Paige$^{(69)}$, $\Delta_{1c}$ intervalley coupling constants were calculated and were found to be $3.7 \times 10^8$ eV cm$^{-1}$ and $2.9 \times 10^8$ eV cm$^{-1}$ for 430K and 320K phonons respectively. A negligible coupling constant was found for the low energy, 100K LA phonon, in agreement with the results of Rode$^{(82)}$ for silicon and GaP.

As a result of our analysis of the $\Delta_{1c}$ mobility in germanium the following conclusions are possible:-

(a) As is evident from its $T^{-2.7}$ temperature dependence, the electron mobility in the $\Delta_{1c}$ minimum of germanium is dominated by the intervalley scattering throughout the temperature range from room temperature to 100K, as is the case in Si and GaP. The intervalley scattering in the $L_{1c}$ minima of germanium is weak and this may be taken to imply that this might be the case in other materials as well.

(b) It is possible to predict the mobility variation with temperature for a pure germanium sample in the $\Delta_{1c}$ minima. This was calculated by ignoring the ionized impurity scattering i.e. by including the acoustic deformation scattering and intervalley scattering only. The resultant mobility variation is shown by dotted curve in Figure 6.12a.

(c) The effective masses in the $\Delta_{1c}$ valleys are somewhat higher than the measured masses in silicon. Fletcher et al$^{(5)}$ found that a 50% increase would give reasonable fits to their high pressure results
and also to the high field calculations of Fawcett and Paige (69). This hypothesis is also supported by our analysis of the ultra-pure material described in the next Chapter.

Recent band structure calculations have suggested that the effective masses in the (100) minima of germanium are slightly larger (Cohen and Bergstresser (90), Herman et al (91)) comparable (Cardona and Pollak (92), Dresselhaus and Dresselhaus (93)) than the silicon. However, there is no experimental evidence. It would be useful to actually measure the effective masses in the \( \Delta_{1c} \) or \( X_{1c} \)-minima by magneto-phonon measurements. To this end attempts have been made using germanium and GaAs in collaboration with high magnetic field studies group at Clarendon Laboratory, Oxford. Magneto-phonon oscillations were clearly observed in GaAs at room temperature to 22 k-bar. Above 22 k-bar in all the samples used the resistivity started to increase by orders of magnitude making magneto-phonon oscillations too noisy to measure although temperature was lowered to 77K. This is interpreted as due to trap out of carriers to the impurity level below the \( X_{1c} \) minima as has already been reported by Pitt and Lees (74). The detailed account of the rate of change of \( \Gamma_{1c} \) effective mass with pressure and its comparison with the k.p theory could be found elsewhere (94).

In germanium, although ultra-pure material was used which essentially remained intrinsic even above \( L_{1c} - \Delta_{1c} \) cross-over, it was not possible to measure the magneto-phonon oscillations. The oscillations were extremely weak and were invariably masked by fluctuations in resistivity caused by the applied pressure. Although the preliminary attempts to measure the effective mass of electrons in the \( X_{1c} \) or \( \Delta_{1c} \) minima were not entirely fruitful, success with GaAs can still be anticipated. Up till now pure GaAs samples with carrier density in the range \( 10^{13} - 10^{14} \text{cm}^{-3} \) have been tried to avoid the impurity scattering which obviously kills the magneto-phonon oscillations. But in the light of the problem of carrier trap-out...
one should strike a compromise and use moderately doped samples so that at high pressure even if the carriers trap out to the above mentioned level there will be some conducting carriers left over in the $X_{1c}$ minima to give magneto phonon oscillations. Preparations are being made to use material with carrier density in the $10^{15}$-$10^{16}$ cm$^{-3}$ range.
7.1. INTRODUCTION

The major effect of hydrostatic pressure on an intrinsic semiconductor, as discussed in Chapter 4, is to decrease its conductivity by changing the electron and hole densities as the band gap increases. Hence measurements of the pressure dependence of the conductivity give a direct measure of the variation of the energy gap so the pressure coefficients for different minima could be deduced.

Although the pressure coefficients, for different minima, in different semiconductors, have been calculated theoretically by many workers as mentioned in Chapter 3. Miller and Taylor\(^{(95)}\) were the first to measure experimentally the pressure dependence of the energy gap in germanium up to a pressure of 12 k-bar at temperature of 400K to achieve intrinsic conduction. Later, Paul and Brooks\(^{(96)}\) and Michel et al\(^{(97)}\) repeated the above experiments, using purer single crystals, in the temperature range of 298K-398K and up to 2.7 k-bar pressure. As a result of the above measurements it became generally accepted that the pressure coefficient of the energy gap (\(L_{1c}\) minima) in germanium is

\[
\frac{\Delta E}{\Delta P} = 5 \times 10^{-6} \text{ eV bar}^{-1}
\]

Silicon, on the other hand, was studied by Paul and Pearson\(^{(98)}\) under pressure. They found that the energy gap in silicon (\(\Delta_{1c}\) minima) decreases with pressure, opposite to that of germanium, with the rate:

\[
\frac{\Delta E}{\Delta P} = -1.5 \times 10^{-6} \text{ eV bar}^{-1}
\]

In a general review article on germanium and silicon, Paul\(^{(99)}\) pointed out that the minima with (100) symmetry (\(\Delta_{1c}\) or \(X_{1c}\)) are expected to have a pressure coefficient anywhere between 0 and \(-2 \times 10^{-6} \text{ eV bar}^{-1}\).
Pitt more recently suggests that in order to interpret some experimental results on III-V compounds a value closer to $-3.0 \times 10^{-6}$ eV bar$^{-1}$ would be more appropriate for the minima with (100) symmetry. Moreover Aspnes gives $\Gamma$-X separation in GaAs as 0.48 eV at atmospheric pressure. Pitt and Lees from the higher pressure studies concluded that the $\Gamma_{1c}$ and $X_{1c}$ minima in GaAs cross over at 32 k-bar. This implies the $\Gamma_{1c} - X_{1c}$ pressure coefficient to be

$$\frac{dE_{\Gamma-X}}{dP} = 15 \times 10^{-6} \text{ eV bar}^{-1}$$

Now if Welber's measured pressure coefficient for the energy gap $\frac{dE_{\Gamma_{1c}}}{dP} = 11.5 \times 10^{-6}$ eV bar$^{-1}$, with respect to the valence band, is assumed to be correct then the pressure coefficient for the $X_{1c}$-minima becomes

$$\frac{dE_{X}}{dP} = (11.5 - 15) = -3.5 \times 10^{-6} \text{ eV bar}^{-1}.$$  

In view of these uncertainties and because of the central role played by germanium in theories of Van Vechten, Phillips and Camphausen et al. it was decided to study the pressure coefficients of both $L_{1c}$ and $A_{1c}$ minima in ultra-pure material.

7.2. EXPERIMENTAL SET UP

Measurements of the variation of resistivity with pressure have been made using both solid and liquid pressure transmitting media. Clover leaf samples cut from both (111) and (100) oriented slices were used. Both orientations were used to check the role of non-hydrostatic stresses in the epoxy system in the low pressure region as explained in the last Chapter. Ohmic contacts to the ultra-pure samples were achieved by implanting As$^+$ ions ($1 \times 10^{15}$ cm$^{-3}$) to the small areas of the clover leaf lobes. The samples were then laser annealed using a multi-mode Q switched ruby laser [E = 0.7 J cm$^{-2}$ and pulse of 25 ns]. Gold-tin was then evaporated and the samples were thermally annealed. Gold wires were attached using
a pulse tip bonder. The rest of the sample preparation and the experimental techniques used have been described in the last chapter.

7.3. EXPERIMENTAL RESULTS

The measured resistivity with pressure for both (100) and (111) oriented samples is shown in Figures 7.1 and 7.2 respectively. Although the density of electrons remain always equal to the density of holes, at low pressure the sign of the Hall voltage corresponded to electron conduction since the electron mobility in the L_{1c} minima of germanium is greater than the hole mobility i.e. \( \mu_e > \mu_h \). At high pressure the Hall voltage changes sign simply because \( \mu_p > \mu_A \). To check the role of uniaxial stresses, in the solid medium, at low pressure, one of the (100) samples was also pressurised using the piston and cylinder apparatus. The results are shown in Figure 7.1 by solid triangles. In the piston and cylinder apparatus the pressure can be monitored very accurately from the response of a standard manganin gauge. As is evident from Figure 7.1 the results of both liquid and solid media agree very well up to the maximum available pressure of 15 k-bar. This is as expected since the uniaxial stresses, as explained before, are believed to be in the (100) direction and does not split the normally occupied (111) valleys.

The results for the (111) oriented samples, as shown in Fig.7.2, show a slight scatter at low pressure. This is probably due to the influence of uniaxial stresses, but as the pressure is increased the system becomes more hydrostatic in nature and the scatter in the results disappear near 15 k-bar. Since the material used is slightly inhomogeneous different samples show different degrees of extrinsic conduction to be discussed later.

7.4. ANALYSIS OF RESULTS

The Hall voltage is small and its pressure dependence difficult to
FIG. 7. NORMALISED RESISTIVITY VS PRESSURE OF ULTRA PURE GERMANIUM (100) SAMPLES.

- Experimental results using liquid medium.
- Experimental results using solid medium.
FIG. 7.2 NORMALISED RESISTIVITY VS PRESSURE OF ULTRA PURE GERMANIUM (111) SAMPLES USING SOLID MEDIUM.
measure accurately, also its interpretation is complicated. The conductivity, on the other hand, arises from a relatively simple algebraic sum of the contributions from carriers in each band. Since the Fermi level, \( E_F \), is far from the band edges, we may write carrier densities in the following way:

\[
n = N_c \exp \left( \frac{E_c - E_F}{k_BT} \right) \tag{7.1}
\]

and

\[
p = N_v \exp \left( \frac{E_v - E_F}{k_BT} \right) \tag{7.2}
\]

where \( N_c \) and \( N_v \) are the effective density of states of the conduction and valence bands respectively.

At room temperature some of the electrons will be excited from the normally occupied \( L_{1c} \) minima to the higher minima. Due to the small density of states of the \( L_{1c} \) minima as compared to the \( \Delta_{1c} \) minima, the carriers will scatter to the \( \Delta_{1c} \) minima. Moreover, the \( L_{1c} \) minimum, having a pressure coefficient of \( +14.0 \times 10^{-6} \) eV bar\(^{-1}\), will move rapidly away from the valence band as soon as pressure is applied - hence eliminating the chance of carriers being scattered to it. Therefore equation 7.1 is to be modified in terms of the \( L_{1c} \) and \( \Delta_{1c} \) band carrier densities as:

\[
n_L = N_{CL} \exp \left( \frac{E_{CL} - E_F}{k_BT} \right) \tag{7.3}
\]

\[
n_\Delta = N_{CA} \exp \left( \frac{E_{CA} - E_F}{k_BT} \right) \tag{7.4}
\]

where \( N_{CL} \), \( N_{CA} \) and \( N_v \) can be written from equation 4.2 as

\[
N_{CL} = 2 \left[ \frac{2 \pi k_B T (m^*_{DS})_{L}}{\hbar^2} \right]^{3/2} \tag{7.5}
\]

\[
N_{CA} = 2 \left[ \frac{2 \pi k_B T (m^*_{DS})_{\Delta}}{\hbar^2} \right]^{3/2} \tag{7.6}
\]

\[
N_v = 2 \left[ \frac{2 \pi k_B T (m^*_{DS})_V}{\hbar^2} \right]^{3/2} \tag{7.7}
\]

where \( m^*_{DS} \) is the density of states effective mass given by

\[
m^*_{DS} = (m_t^2 m_p) \left( \frac{1}{3} \right) \left( \frac{2}{3} \right)
\]

\( v \) being the number of minima involved.
Thus if the effective masses of the carriers are known then the density of states effective mass and hence the density of states of a particular minima could be calculated.

In an intrinsic semiconductor total number of electrons is always equal to the total number of holes, i.e.

\[ n = p \]  
(7.8)

In the case of germanium equation 7.8 could be written as

\[ n_L + n_\Delta = p \]  
(7.9)

or

\[ n_1^2 = n \times p = (n_L + n_\Delta) \times p \]  
(7.10)

The expressions for the Fermi energy, \( E_F \) and the intrinsic carrier density can be written from the above equations as: (see Appendix B, C)

\[ E_F = \frac{\hbar^2}{2m_e^*} \ln \left[ \frac{N_\Delta}{N_V} \exp \left( -\frac{E_\Delta}{k_BT} \right) + \frac{N_L}{N_V} \exp \left( -\frac{E_L}{k_BT} \right) \right] \]  
(7.11)

and

\[ n_1 = n = p = \left[ N_L N_\Delta \exp \left( -\Delta \frac{E_L}{k_BT} \right) + N_\Delta N_V \exp \left( -\Delta \frac{E_\Delta}{k_BT} \right) \right] \]  
(7.12)

Thus assuming the density of states effective mass ratios the Fermi energy could be calculated from equation 7.11 and hence the carrier densities from equations 7.2, 7.3 and 7.4. The electrical conductivity then becomes

\[ \sigma = e \left[ n_L \mu_L + n_\Delta \mu_\Delta + p \mu_p \right] \]  
(7.13)

The electron mobilities, \( \mu_L \) and \( \mu_\Delta \) were obtained from the results described in the last Chapter and the mobility of holes, \( \mu_p \), was taken to be 1900 \( \text{cm}^2\text{v}^{-1}\text{s}^{-1} \) and assumed to be pressure independent. Thus the conductivity can be calculated at different pressures from equation 7.13 provided \( n_L \), \( n_\Delta \) and \( p \) can be calculated from the pressure coefficients of the \( L_{1_c} \) and \( \Delta_{1_c} \) minima with respect to the top of the valence band.

7.5. Discussion

The rate of change of conductivity with pressure could be written from equation 4.4 as:

Thus if the effective masses of the carriers are known then the density of states effective mass and hence the density of states of a particular minima could be calculated.

In an intrinsic semiconductor total number of electrons is always equal to the total number of holes, i.e.

\[ n = p \]  
(7.8)

In the case of germanium equation 7.8 could be written as

\[ n_L + n_\Delta = p \]  
(7.9)

or

\[ n_1^2 = n \times p = (n_L + n_\Delta) \times p \]  
(7.10)

The expressions for the Fermi energy, \( E_F \) and the intrinsic carrier density can be written from the above equations as: (see Appendix B, C)

\[ E_F = \frac{\hbar^2}{2m_e^*} \ln \left[ \frac{N_\Delta}{N_V} \exp \left( -\Delta \frac{E_\Delta}{k_BT} \right) + \frac{N_L}{N_V} \exp \left( -\Delta \frac{E_L}{k_BT} \right) \right] \]  
(7.11)

and

\[ n_1 = n = p = \left[ N_L N_\Delta \exp \left( -\Delta \frac{E_L}{k_BT} \right) + N_\Delta N_V \exp \left( -\Delta \frac{E_\Delta}{k_BT} \right) \right] \]  
(7.12)

Thus assuming the density of states effective mass ratios the Fermi energy could be calculated from equation 7.11 and hence the carrier densities from equations 7.2, 7.3 and 7.4. The electrical conductivity then becomes

\[ \sigma = e \left[ n_L \mu_L + n_\Delta \mu_\Delta + p \mu_p \right] \]  
(7.13)

The electron mobilities, \( \mu_L \) and \( \mu_\Delta \) were obtained from the results described in the last Chapter and the mobility of holes, \( \mu_p \), was taken to be 1900 \( \text{cm}^2\text{v}^{-1}\text{s}^{-1} \) and assumed to be pressure independent. Thus the conductivity can be calculated at different pressures from equation 7.13 provided \( n_L \), \( n_\Delta \) and \( p \) can be calculated from the pressure coefficients of the \( L_{1_c} \) and \( \Delta_{1_c} \) minima with respect to the top of the valence band.

7.5. Discussion

The rate of change of conductivity with pressure could be written from equation 4.4 as:
\[
\frac{d}{dp} \left( \ln \rho \right) = \frac{1}{2} \frac{d}{dp} \left[ \ln(N_c N_v) \right] + \frac{d}{dp} \left[ \ln(\mu_n + \mu_p) \right] - \frac{1}{2k_B T} \frac{dE_g}{dp} \tag{7.14}
\]

where \( \mu_n \) is some suitable average of \( \mu_L \) and \( \mu_A \).

In germanium it can be shown that the last term in equation 7.14 is dominant. The first two terms are two orders of magnitude smaller and are of opposite sign to one another so tend to cancel. So the above complicated equation reduces to:

\[
\frac{d}{dp} \left( \ln \rho \right) = -\frac{1}{2k_B T} \frac{dE_g}{dp} \tag{7.15}
\]

Although germanium has \( L - \Gamma - A \) conduction band ordering at atmospheric pressure since \( \Gamma_{1c} \) minimum does not contribute to the high pressure results, as explained earlier, we consider \( L - A \) band ordering.

At low pressure where \( E_A >> E_L \) the second term in equation 7.12 becomes negligible and the effective band gap, \( E_g^* \), is dominated by \( E_L \) so the equation 7.15 becomes:

\[
\frac{d}{dp} \left( \ln \rho \right) = -\frac{1}{2k_B T} \frac{dE_L}{dp} \tag{7.16}
\]

At high pressure where \( E_L >> E_A \) the first term in equation 7.12 becomes negligible and the effective energy gap, \( E_g \) is, in this case dominated by \( E_A \) so equation 7.15 reduces to:

\[
\frac{d}{dp} \left( \ln \rho \right) = \frac{1}{2k_B T} \frac{dE_A}{dp} \tag{7.17}
\]

Thus in the very high and very low pressure regions where the variation of \( \ln \rho \) is linear, as shown in Figure 7.1, \( \frac{dE_L}{dp} \) and \( \frac{dE_A}{dp} \) can be obtained directly from the gradient of the experimental curve without knowledge of any other parameter.

This analysis holds only for a perfectly pure sample and it was first necessary to establish that no significant extrinsic conduction occurred. To this end the temperature dependence of the Hall mobility was monitored down to 100K at atmospheric pressure. The mobility variation of one of the samples is shown in Figure 7.3. A transition from n-type to p-type
FIG. 7.3 HALL MOBILITY VARIATION WITH TEMPERATURE.
conductivity occurred at 150K. It is interesting to note from Figure 7.3 that the transition is very sharp and the mobility after the transition has achieved a value similar to the one before the transition. This is so because in germanium at 150K the mobility of electrons and holes happens to have similar magnitudes as shown by the results of Morin and Maita(102) in Figure 7.4. From the transition temperature, where Hall constant or mobility goes to zero, the number of electrons, n, and that of holes, p, may be calculated, (see Appendix D). The extrinsic conduction was then calculated and is listed in Table 7.1 for all the samples used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orientation</th>
<th>$\Delta \sigma$ (mhos cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>$5.96 \times 10^{-4}$</td>
</tr>
<tr>
<td>B</td>
<td>111</td>
<td>$4.933 \times 10^{-3}$</td>
</tr>
<tr>
<td>C</td>
<td>111</td>
<td>$7.687 \times 10^{-3}$</td>
</tr>
<tr>
<td>D</td>
<td>111</td>
<td>$8.723 \times 10^{-3}$</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>$9.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**TABLE 7.1.**

In the case of the most pure sample, A, taking small extrinsic conduction of $5.96 \times 10^{-4}$ mhos cm$^{-1}$, as given in Table 7.1, into account and assuming the density of states effective mass ratios in the valence band and the L$_{1c}$ and A$_{1c}$ minima of the conduction band as $m^*_{v} = 0.40$, $m^*_{L} = 0.56$ and $m^*_{A} = 1.58$ respectively (i.e. $\frac{N_{A}}{N_{L}} = 4.86$ which gave a good agreement between theory and the experimental data of the last Chapter) best overall fit, as shown in Figure 7.5 was obtained with the following parameters:

\[
\frac{dE_{L}}{dP} = 4.8 \pm 0.2 \times 10^{-6} \text{ eV bar}^{-1}
\]

\[
\frac{dE_{A}}{dP} = -2.4 \pm 0.4 \times 10^{-6} \text{ eV bar}^{-1}
\]
FIG. 7.4  VARIATION OF ELECTRON AND HOLE MOBILITIES IN GERMANIUM WITH TEMPERATURE (AFTER MORIN & MAITA\textsuperscript{102})
FIG. 7.5 NORMALISED RESISTIVITY VS PRESSURE OF ULTRA PURE GERMANIUM AT 300 K.

(----- ) Using old pressure coefficients)
\[ \Delta E_{L-\Delta} = 0.21 \pm 0.01 \text{ eV at atmospheric pressure resulting in} \]

band crossing at 29 \pm 2 \text{ k-bar.}

In our analysis no account was taken of the increased resistivity due to the enhanced electron scattering between the \( L_{1c} \) and \( \Delta_{1c} \) minima near the band cross-over and this may account for the few rather high experimental points, in Figure 7.5, near the top. To demonstrate the sensitivity of these calculations to the adjustable parameters, the values given previously by Pitt\(^5\) of:

\[
\frac{dE_L}{dp} = 5.0 \times 10^{-6} \text{ eV bar}^{-1}
\]

\[
\frac{dE_{\Delta}}{dp} = -1.0 \times 10^{-6} \text{ eV bar}^{-1}
\]

and \( \Delta E_{L-\Delta} = 0.19 \text{ eV at atmospheric pressure were assumed. The} \]
calculated curve is also shown in Figure 7.5 by the dotted curve. Although at low pressure the agreement is reasonable clearly the discrepancy at high pressure is large.

Few samples showed intrinsic conductivity, but once the pressure coefficients are deduced from the purest sample, A, theoretical fits to the less pure samples were obtained simply by taking into account the respective amount of extrinsic conduction, as shown in Table 7.1. The resultant curves are plotted in Figures 7.5 and 7.6 and as can be seen good agreement between theory and experiment was obtained.

7.5.1. Density of States Ratio

Although the deduction of the pressure coefficients is independent of the density of states of the bands, as explained earlier, yet it is interesting to see what values other workers have used in their models. There is no direct measure of this parameter available in literature to date. The values published so far are:-
Expt. Results using Solid Medium.

Pure Intrinsic with revised Pressure Coefficients.

THEORETICAL FITS TO THE SAMPLES OBTAINED BY ADDING APPROPRIATE AMOUNT OF EXTRINSIC CONDUCTION (TABLE 7.1)

FIG. 7.6 NORMALISED RESISTIVITY VS PRESSURE OF HIGH PURITY GERMANIUM (111) SAMPLES AT 300 K.
In order to interpret the high pressure results, the ratio $\frac{N_\Delta}{N_L}$ needed to be between 4.2 - 5.5, as pointed out by Pitt et al.\(^{(5)}\). Fawcett and Paige\(^{(69)}\), as a result of high field calculations, predicted effective mass values for the $\Delta_{1c}$ minima in germanium which corresponds to $\frac{N_\Delta}{N_L} = 4.86$. This is within the range mentioned above and this is the one we have used in our analysis. However to examine the influence of this parameter we have also tried $\frac{N_\Delta}{N_L} = 2.7$, as given by Cardona and Poliak\(^{(92)}\) and recalculated the resistivity as shown in Figure 7.7.

In order to maintain overall fit any decrease in the density of states ratio, $\frac{N_\Delta}{N_L}$, must be accompanied by a decrease in energy separation, $\Delta E_{L-\Delta}$. A good fit using $\frac{N_\Delta}{N_L} = 2.7$ was obtained, as shown in Figure 7.7 with $\Delta E_{L-\Delta} = 0.17$ eV. However, this is a rather low band separation at atmospheric pressure when compared to the value of 0.20 eV measured by Slykhouse and Drickamer\(^{(103)}\).

7.6. CONCLUSION

From the series of pressure experiments on the ultra-pure germanium described here, we have been able to determine with some accuracy the pressure coefficients for both the $L_{1c}$ and $\Delta_{1c}$ minima, the latter for the first time. The resulting pressure coefficients being:

$$\frac{dE_L}{dP} = 4.8 \pm 0.2 \times 10^{-6} \text{ eV bar}^{-1}$$

$$\frac{dE_\Delta}{dP} = -2.4 \pm 0.4 \times 10^{-6} \text{ eV bar}^{-1}$$

These values are independent of the energy separation, $\Delta E_{L-\Delta}$ at atmospheric
FIG. 7.7 NORMALISED RESISTIVITY VS PRESSURE OF ULTRA PURE GERMANIUM WITH DIFFERENT DENSITY OF STATES RATIO.
pressure or the density of states of the minima. However, taking the
density of states effective masses $m^*_L = 0.56$, $m^*_\Delta = 1.58$ and $m^*_V = 0.4$ which
yielded good agreement with the results of the last Chapter resulted in
best fit over the whole curve with $\Delta E_{L-\Delta} = 0.21 \pm 0.01$ eV and band $(L_{1c} - \Delta_{1c})$
cross over at $29 \pm 2$ k-bar. The resultant energy separation $\Delta E_{L-\Delta}$ is in
good agreement with the value of $0.20$ eV measured by Slykhouse and
Drickamer\(^{103}\). The most significant point about these results to note is
the large negative pressure coefficient $\frac{dE_{\Delta}}{dp} = -2.4 \times 10^{-6}$ eV bar\(^{-1}\).
The most useful theory for the prediction of the band minima pressure
coefficients is based on the work of Van Vechten\(^{43,44,45}\). Using this
Camphausen et al\(^{41}\) were able to obtain relatively good agreement with
the measured pressure coefficients of the $\Gamma_{1c}$ and $L_{1c}$ band minima with
respect to the valence band but the agreement was worse at the $\Delta_{1c}$ or
$\chi_{1c}$ points where the predicted value was very small or even of the wrong
sign. Camphausen et al\(^{41}\) modified above theory by including the ionicity
and obtained reasonable agreement i.e. $\frac{dE_{\Delta}}{dp}$ in the range $0$ to $-1 \times 10^{-6}$ eV bar\(^{-1}\).
The value of $-2.4 \times 10^{-6}$ eV bar\(^{-1}\) which we obtain indicate that perhaps these
theories needs to be revised in the light of the most recent optical measure­
ments of the related band structure.
8.1. INTRODUCTION

Diamond and zinc-blende crystal structures have been studied, under uniaxial stress, by several authors\(^{(48,50,104)}\). The influence of uniaxial stress on the resistivity and threshold field of GaAs was first measured experimentally by Shyam, Allen and Pearson\(^{(105)}\) in 1966 for stresses up to 25 k-bar. These measurements were repeated in 1970 by Harris, Moll and Pearson\(^{(9)}\) in the stress ranges 0-11 k-bar for (100) samples and 0-19 k-bar for (111) samples. Significantly different results were obtained with little comments from the authors. No calibration measurements were given in either paper. In view of the work to be described later it seems unlikely that the high stress claimed by Shyam et al\(^{(105)}\) was actually achieved. Moreover at the stress levels quoted the hardened steel anvils used will be deformed, complicating the stress. Also, the stylus type apparatus used means that any slight misalignment will cause a large departure from uniaxial stress. They concluded, on the basis of the above measurements, that the \(\Gamma-X-L\) band structure ordering is correct for GaAs.

However, the recent analysis of Vinson et al\(^{(6)}\) and Adams et al\(^{(7)}\) of the influence of hydrostatic pressure and uniaxial stress on the threshold for the Gunn effect in GaAs supported \(\Gamma-L-X\) band ordering. Best overall agreement was obtained with \(\Delta E_{\Gamma-L} = 0.38\text{eV}\) and \(\Delta E_{\Gamma-X} = 0.40\text{eV}\) for the \(\Gamma_{1c}-L_{1c}\) and \(\Gamma_{1c}-X_{1c}\) sub-band gaps respectively. Aspnes\(^{(8)}\) agrees with the above band structure ordering but concluded, from the electroreflectance measurements that \(\Delta E_{\Gamma-L} = 0.29\text{eV}\) and \(\Delta E_{\Gamma-X} = 0.48\text{eV}\).

Measurements reported by Harris, Moll and Pearson\(^{(9)}\) and by Pickering and Adams\(^{(10)}\) of the influence of (100) stress on both the low field...
resistivity and on the threshold field for the Gunn effect, $F_T$, were
in agreement with one another but gave an anomalously high value for
the deformation potential $\varepsilon_X^{u}$ of 21 ± 9eV compared to about 8eV for
silicon and germanium. The sample configurations of both Harris et al.\textsuperscript{9}
and Pickering et al.\textsuperscript{10} were chosen for the observation of Gunn
oscillations but were also used for the low-field resistivity measurements.
Since it was mainly to fit to the (100) stress results that the small
$\Gamma$-X separation was chosen in disagreement with the electroreflectance
data. Because these results yielded such a large value of $\varepsilon_X^{u}$, it was
decided to repeat the low-field resistivity measurements using a more
suitable four terminal sample arrangement. Just for confirmation the
influence of (111) stress is also observed although the results of
Pickering and Adams\textsuperscript{10} agree very well with already reported results\textsuperscript{9}
for GaAs, germanium, and silicon.

8.2. SAMPLE DETAILS

The characteristics of the samples, which were grown on (100)
oriented semi-insulating substrates by vapour phase epitaxy at S.T.L.
except the slice L267, which was grown on (110) oriented substrate at
Max. Planck Institute Germany, are given in Table 8.1. Ohmic contacts
to the slice were made by evaporating Au-Sn and nickel, in the form of
parallel electrodes, and then alloying at 525°C for three minutes.
The slice was then cut into parallelepiped containing four electrodes,
as shown in Figure 5.11, with a diamond saw. Gold wires were attached to
the electrodes using a pulse-tip bonder as explained in Section 5.5.
Sample Carrier Density Mobility Layer Thickness
\( \text{cm}^{-3} \) \( \mu \text{cm}^2 \text{V}^{-1} \text{S}^{-1} \) \( \times 10^{-6} \text{cm} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( 7.8 \times 10^{14} )</th>
<th>7800</th>
<th>62.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>R 225D</td>
<td>( 3.0 \times 10^{14} )</td>
<td>8200</td>
<td>26.0</td>
</tr>
<tr>
<td>R 300A</td>
<td>( 1.1 \times 10^{15} )</td>
<td>7900</td>
<td>15.0</td>
</tr>
<tr>
<td>R 242E</td>
<td>( 4.9 \times 10^{14} )</td>
<td>7850</td>
<td>13.5</td>
</tr>
<tr>
<td>S 179A</td>
<td>( 9.0 \times 10^{14} )</td>
<td>7350</td>
<td>12.5</td>
</tr>
<tr>
<td>S 171D</td>
<td>( 1.0 \times 10^{15} )</td>
<td>6900</td>
<td>11.0</td>
</tr>
<tr>
<td>S 181A</td>
<td>( 4.5 \times 10^{15} )</td>
<td>5700</td>
<td>11.0</td>
</tr>
<tr>
<td>S 183A</td>
<td>( 2.8 \times 10^{15} )</td>
<td>6220</td>
<td>10.0</td>
</tr>
<tr>
<td>L 267</td>
<td>( \approx 10^{14} )</td>
<td>8000</td>
<td>15.0</td>
</tr>
</tbody>
</table>

TABLE 8.1.

8.3. EXPERIMENTAL ARRANGEMENT

The major disadvantage of using Gunn diodes with an epitaxial layer on an n+ substrates as used by Harris et al\(^{(9)}\) and Pickering and Adams\(^{(10)}\) is that the active layer is close to the anvil where the strain is most likely to be non-uniform. Measurements on bulk silicon by Pickering and Adams\(^{(10)}\) have shown that the stress is uniform through the volume of the sample - however, bulk n-type GaAs samples suffer from trap-out to deep levels under uniaxial stress. It was therefore decided, in the experiments to be described here, to use epitaxial layers on semi-insulating substrates with the stress direction parallel to the layer-substrate interface. By using a four terminal system, the effects due to the contacts were reduced and the active area was restricted to the central region away from the anvils. The sample arrangement of Figure 5.11 was used. Two sizes of voltage electrodes were used since they, as will be discussed later, distort the current flow through the epitaxial layer. The uniaxial stress
apparatus and the measuring technique as described in Section 5.5 were used in these measurements.

8.4. CRYSTAL ORIENTATION

The orientation of the slices was checked by electron microscopy using "ELECTRON CHANNELING PATTERN" analysis. Both (100) and (111) oriented samples were used. Since (110) plane contains both (100) and (111) type directions, as shown in Figure 8.1, a (110) oriented substrate, L 267, was selected and n+ layer was grown on it in collaboration with the Max. Planck Institute, West Germany. Both (100) and (111) oriented samples were cut from this slice by using the above technique.

8.5. EXPERIMENTAL RESULTS

8.5.1. (111) Stress

As already mentioned, the bulk GaAs samples suffer from deep impurity trap = 0.15eV below the $\Gamma_{1c}$ minimum giving resistivity rise as soon as stress is applied. The analysis of this effect has already been reported by Pickering et al.(10). Neither the epitaxial (on n+ substrates) samples they used, nor the n+ on semi-insulating substrates samples we have used, show any evidence of such an impurity level.

The variation of normalised resistivity for the (111) samples with stress is shown in Figure 8.2. It can be seen that up to 5 k-bar no appreciable change was observed, the reason for which is discussed later. Beyond 5 k-bar, when one of the $L_{1c}$ valley approaches $\Gamma_{1c}$ minimum, the resistivity begins to increase. These results can be explained by the thermal redistribution of electrons between the $\Gamma_{1c}$ and $L_{1c}$ valleys. Unfortunately the quality of the parallelopiped samples we have used was not good and we could only achieve stresses up to 7 k-bar when the crystals fractured. But since the results to this point agree with Pickering and Adams(10) and Harris et al.(9) and because Pickering and
FIG. 8.1 110 PLANE WITH 100 AND 111 TYPE DIRECTIONS SHOWN.
FIG. 8.2 NORMALISED RESISTIVITY VS <111> STRESS FOR EPITAXIAL GaAs SAMPLE.

- ASSUMING $\frac{d AE}{dx} = -14.5 \times 10^{-6}$ eV bar$^{-1}$
- and $\frac{N_L}{N_T} = 15$
- EXPERIMENTAL
  - PICKERING et al.
  - THIS WORK.
Adams\textsuperscript{(10)}, analysis gave shear deformation potentials $\Xi_u^L = 22 \pm 3$ eV and $(\Xi_d^L - \alpha) = -10 \pm 3$ eV which agrees very well with those for $L_{1c}$ valleys in germanium\textsuperscript{(47)} of 18.95 eV and -10.07 eV respectively and also with the results of GaSb\textsuperscript{(106)} of $\Xi_u = 16.0 \pm 3.5$ eV, we decided to concentrate on the effects of (100) stress on GaAs.

8.5.2. (100) Stress

The variation of the low-field resistivity with (100) stress is shown in Figure 8.3. Also shown in this figure, for comparison, are the results of Harris et al\textsuperscript{(9)} and Pickering and Adams\textsuperscript{(10)}. It can be seen that the resistance increases showly and linearly up to 10 k-bar above which the samples broke. No evidence was found of the steep increase of resistivity beyond 5 k-bar which has been observed by Harris et al and Pickering and Adams and which has been attributed to the electron transfer to the approaching $X_{1c}$ minima.

In the measurements shown in Figure 8.3 both directions of current were used for each reading and no asymmetry was observed. Also in some of the samples measurements were made both on increasing as well as decreasing stress cycles and no hysteresis effects were observed as shown in Figure 8.3. No detectable difference was observed with samples of different layer thickness suggesting that the strain at the surface was the same as that over the whole cross-section. Also it suggests that the in-built strain due to lattice mismatch between the epitaxial layer and the substrate was not severe since it is expected that this would be more pronounced in the thinner layers.

8.6. ANALYSIS OF RESULTS

8.6.1. (111) Stress Results

No observable change in resistivity below 5 k-bar was detected within experimental error, as shown in Figure 8.2. In fact in this stress
FIG 8.3 NORMALISED RESISTANCE VS STRESS.

FULL SYMBOLS- CONFIGURATION OF FIG. 5.11(a)
OPEN SYMBOLS- CONFIGURATION OF FIG. 5.11(b)

(- - - -) Simple kp theory
(- - - -) Harris, Moll & Pearson
(- - - -) Pickering & Adams
(- - - -) Zeman Study

▲ LOADING CYCLE
▼ UNLOADING CYCLE

NORMALISED RESISTANCE

(100) UNIAXIAL STRESS ( Kbar)
range two processes are occurring simultaneously. They are:

(a) A decrease in resistance of 0.5% due to dimensional changes in the sample (Appendix E).

(b) An increase in resistance due to an increase in the \( \Gamma_{1c} \) effective mass. Using the measured change in effective mass with (111) stress, to be described in Section 8.7, of 0.075\% k.bar\(^{-1}\) gives an increase in resistance of 0.5% to 5 k.bar. However, this is expected to be partially reduced due to the splitting of the heavy and light hole valence bands which reduces the effective band-gap increase.

The effects of (a) and (b) appear to cancel to 5 k bar and the increase in resistivity beyond this stress is attributed to the transfer of electrons to the descending \( \Gamma_{1c} \) valley. A detailed analysis, as mentioned earlier, has been given by Pickering et al\(^{(10)}\).

8.6.2. (100) Stress Results

The resistance increase with (100) stress as shown in Figure 8.3 is always linear up to 10 k.bar above which samples broke. In this case the resistance decrease due to the dimensional changes of the sample to 5 k.bar is 0.95% (Appendix E). Whereas the measured effective mass change of 0.23% k.bar\(^{-1}\), to be described in Section 8.7, gives an increase of 1.7% in resistivity. Hence a net small increase in resistance to 5 k.bar was observed. Beyond 5 k.bar since the resistance continues to increase linearly, without any sign of exponential change, these results need to be analysed more rigorously as follows:

The uniaxial stress removes the degeneracy of the valence band. As explained in Section 3.2 that the energy of the light hole band increases whereas that of the heavy hole band decreases relative to their mean position. Assuming that the splitting, \( \delta E \), between light and heavy hole bands is small compared to the spin orbit splitting then the quadratic
terms in equation 3.10 could be ignored. The rate of separation of these bands from the bottom of the conduction band can be written as:

\[
\frac{dE_1}{dx_{100}} = a (s_{11} + 2 s_{12}) - b (s_{11} - s_{12}) \quad (8.1)
\]

\[
\frac{dE_2}{dx_{100}} = a (s_{11} + 2 s_{12}) + b (s_{11} - s_{12}) \quad (8.2)
\]

\[
\frac{dE_3}{dx_{100}} = a (s_{11} + 2 s_{12}) \quad (8.3)
\]

The \( \Gamma_{1c} \) effective mass expression (equation 2.4)

\[
\frac{m^*}{m_0} = \left[ 1 + \frac{E_{p-\Gamma}}{3} \frac{2E_0}{E_0 + \Delta_0} \right]^{-1} \quad \text{in this case can be written as}
\]

\[
\frac{m^*}{m_0} = \left[ 1 + \frac{E_{p-\Gamma}}{3} \left( \frac{1}{E_1} + \frac{1}{E_2} + \frac{1}{E_3} \right) \right]^{-1} \quad (8.4)
\]

Note that the first term inside the curly bracket of equation 2.4 has been split into two terms, \( E_1 \) and \( E_2 \) because in the previous case two bands (heavy and light hole bands) were degenerate at \( k = 0 \) but under uniaxial stress they split.

Assuming GaAs band parameters at zero stress of \( \frac{m^*}{m_0} = 0.068 \)

\( E_1 = E_2 = 1.42\text{eV} \)

\( E_3 = 1.7606\text{eV} \)

\( E_{p-\Gamma} = 20.8\text{eV} \) (assumed constant with pressure)

and the elastic compliance constants\(^{(107)}\) as

\( s_{11} = 1.173 \times 10^{-6} \text{ bar}^{-1} \)

\( s_{12} = -0.366 \times 10^{-6} \text{ bar}^{-1} \)

\( a(s_{11} + 2 s_{12}) = -3.36 \times 10^{-6} \text{ eV bar}^{-1} \) from hydrostatic pressure experiments\(^{(74)}\).
Using these parameters in equations 8.1 - 8.3 the variation of resistance with stress was calculated, as shown in Figure 8.3 when mobility $\mu \propto m^{-3/2}$ was assumed - appropriate for polar optical phonon scattering.

8.7. STRESS DEPENDENCE OF THE EFFECTIVE MASS

Since the interpretation of stress dependence of the transport properties of semiconductors strongly depend on the effective mass of the electrons, it was decided to measure, experimentally, the $\Gamma_{1c}$ effective mass as a function of stress. The change in the effective mass of electrons produced by the application of uniaxial stress can be detected by measuring the variation in the Zeeman splitting of the 2p donor level with stress at a fixed magnetic field. This is accomplished by observing the $1s-2p_-$ and $1s-2p_+$ transition energies.

These experiments were carried out at the Clarendon Laboratory, Oxford in collaboration with Cooke, R.A. et al. Using a far infra-red Fourier spectrometer and a stress apparatus incorporated with 6.5 Tesla superconducting magnet. The technique and the apparatus is described, in detail, elsewhere.

The sample characteristics and dimensions used are summarized as in Table 8.2. The compressional stress was applied parallel to the long dimensions of the sample which was parallel to the magnetic field.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_D-N_A (77K)$ cm$^{-3}$</th>
<th>$\mu$ 77K cm$^2$V$^{-1}$s$^{-1}$</th>
<th>Epitaxial Layer Thickness x $10^{-3}$ m.m.</th>
<th>Dimensions (mm)$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 464 (100)</td>
<td>$3 \times 10^{14}$</td>
<td>$8.1 \times 10^5$</td>
<td>32</td>
<td>$0.3 \times 1.5 \times 4.0$</td>
</tr>
<tr>
<td>L 267 (111)</td>
<td>$\approx 10^{14}$</td>
<td>$\approx 10^5$</td>
<td>15</td>
<td>$0.5 \times 0.5 \times 1.0$</td>
</tr>
</tbody>
</table>

TABLE 8.2.
The variation of the effective mass with uniaxial stress was measured for stress applied parallel to both (100) and (111) directions. The percentage change in $m^*$ is plotted for each direction in Figures 8.4 and 8.5 respectively. The error bars arise chiefly from the experimental uncertainty involved in measuring the peak positions. From this data the stress dependence of $m^*$ calculated for both the stress directions is shown in Table 8.3. The errors quoted represent the maximum uncertainties which are calculated from the gradients of the lines with maximum and minimum slopes which pass through all the error bars, rather than the r.m.s. value.

<table>
<thead>
<tr>
<th>Stress Direction</th>
<th>Parameter</th>
<th>Theory (Aspnes and Cardona)</th>
<th>Infra-Red Reflection (Abstreiter and Cardona)</th>
<th>Raman (Abstreiter and Cardona)</th>
<th>Far Infra-Red (This work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>$\Delta m^* k^{-1}$</td>
<td>0.45</td>
<td>0.18±0.08</td>
<td>0.4±0.08</td>
<td>0.23±0.06</td>
</tr>
<tr>
<td></td>
<td>$\chi_{\max}$ k-bar</td>
<td>-</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>(111)</td>
<td>$\Delta m^* k^{-1}$</td>
<td>0.24</td>
<td>0.00±0.1</td>
<td>-0.16±0.08</td>
<td>0.075±0.015</td>
</tr>
<tr>
<td></td>
<td>$\chi_{\max}$ k-bar</td>
<td>-</td>
<td>4.5</td>
<td>4.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

**TABLE 8.3**

In comparing these errors with the theoretical values of Aspnes and Cardona$^104$ and the results of unpublished Raman and infra-red reflection data (Abstreiter and Cardona, private communication) it should be noted that the mass changes reported here are for the cyclotron mass$^104$ perpendicular to the stress direction. The theory of Aspnes and Cardona$^104$ predicts a linear dependence, with magnitudes given in Table 8.3. Also shown are the best straight line gradients of the unpublished data, the errors being estimated by the same means as for the results described here.

8.8. DISCUSSION

Although the low field resistivity measurements as a function of (111)
FIG. 8.4  THE VARIATION OF THE EFFECTIVE MASS OF n-GaAs for UNIAXIAL STRESS APPLIED PARALLEL TO 111 DIRECTION. THE POINTS MARKED ○ WERE OBTAINED WITH INCREASING STRESS, THE POINT □ BEING OBTAINED ON REDUCING THE APPLIED STRESS TO ZERO.
FIG. 8.5  THE VARIATION OF THE EFFECTIVE MASS OF n-GaAs FOR UNIAXIAL STRESS APPLIED PARALLEL TO 100 DIRECTION. THE POINTS MARKED • WERE OBTAINED WITH INCREASING STRESS, THE POINT □ BEING OBTAINED ON REDUCING THE APPLIED STRESS TO ZERO.
stress, reported here, are limited to only 7 k-bar the general trend agrees with the results of Pickering and Adams\(^{(10)}\). The validity of the analysis of (111) stress results of Pickering and Adams\(^{(10)}\) is self evident because the values of the energy separation, \(\Delta E(\Gamma_{1c} - L_{1c}) = 0.29 (\pm 0.05)\text{eV}\) and the deformation potentials for the (111) valleys of \(\varepsilon^L_u = 22(\pm 7)\text{eV}\) and \((\varepsilon^L_d - a) = -11 (\pm 3)\text{eV}\) agrees well with the already reported measurements\(^{(9)}\) of the energy gap and with the deformation potentials for the (111) valleys in Ge, GaSb\(^{(106)}\).

The (100) stress results, on the other hand, poses difficulties due to the controversy between different methods of measurements as mentioned in the beginning of the Chapter. It is due to this reason that we concentrated on the (100) stress results and analysed them in detail. Clearly the (100) stress results shown in Figure 8.3 are in marked contrast to the previous works of Harris et al\(^{(9)}\) and Pickering and Adams\(^{(10)}\) which are also shown for comparison. No evidence was found of the exponential increase in resistance beyond 5 k-bar, which has been attributed to electron transfer to the descending \(X^c_{1c}\) minimum. Any change in intrinsic resistivity must therefore be explained either by the change in mobility of electrons in the \(\Gamma_{1c}\) minimum or the carrier loss to an impurity trap. The possibility of the existence of an impurity trap in such a high purity material was very remote, however, it was also looked at by monitoring the Hall effect as a function of temperature in some of the samples used. No change in the carrier density was observed down to 80K. The small increase in resistance, shown in Figure 8.3, therefore is attributed to the decrease in mobility due to the increase in the effective mass of the electrons.

The measured change in resistance with sample configuration of Figure 5.11.b is larger than the expected "k.p" calculations. It is believed that this is due to the stress dependent contact resistances. This is, of course, unimportant in four terminal measurements except where
the large voltage electrodes, which act like metallic islands providing low resistance paths, distort the current flow. That the effect is due to contact resistance changes is supported by the fact that similar results are obtained when the resistance is simply monitored between two electrodes using a Keithley digital multimeter. The effect of the contact resistance, described above, can be minimised by reducing the size of the voltage electrodes, as in Figure 5.11.a and the effect on the results with this sample configuration is obvious as shown in Figure 8.3. Zeeman study experiments were performed using specimens of various sizes and aspect ratios and, within experimental error, these produced essentially the same results. In some samples measurements on the decreasing stress cycle were also tried and the results shown in Figures 8.4 and 8.5 do not display any hysteresis. The results of Figures 8.4 and 8.5 yielded effective mass change with (100) stress of $0.23 \pm 0.06\% \text{k-bar}^{-1}$. Taking the extreme values into account the resistivity was calculated and the results after correcting for the sample dimensional changes are also shown in Figure 8.3 by the shaded area. Clearly the results of resistivity change with stress fall within the experimental error of the Zeeman study results.

It is of considerable interest to consider why Harris et al\textsuperscript{(9)} and Pickering and Adams\textsuperscript{(10)} observed such a large increase in resistance beyond 5 k-bar. The most likely explanation is that the stress in the active layer was non-uniform. This would certainly be true if there were any appreciable ripples on the surface of the samples or the anvil faces which could not be filled by the gold or Mylar layer. The sample surfaces were scanned under the electron microscope and the photographs of both the upper and lower surface of a typical GaAs sample used by Pickering and Adams\textsuperscript{(10)} are shown in Figure 8.6. Also shown, for comparison, is one of the silicon sample surfaces which were used for apparatus calibration. It is clear that the GaAs sample has very uneven surfaces as compared to
FIG. 8.6 SURFACES OF A GaAs SAMPLE TO WHICH STRESS WAS APPLIED.
UPPER SURFACE OF A SILICON SAMPLE USED FOR CALIBRATION OF THE UNIAXIAL STRESS APPARATUS.

LOWER SURFACE OF A SILICON SAMPLE USED FOR CALIBRATION OF THE UNIAXIAL STRESS APPARATUS.

FIG. 8.6 SURFACES OF SILICON SAMPLE TO WHICH STRESS WAS APPLIED.
the silicon sample surfaces. The samples used in this work were cleaned hydrochemically and then both sides, to which stress was to be applied, were etched with $3\text{H}_2\text{SO}_4 + 1\text{H}_2\text{O}_2 + 1\text{H}_2\text{O}$ to remove the cutting damage and surface ripples. The possibility of having ripples on the anvil faces was also investigated. The anvils were polished following the technique described in Chapter 5. Then the surfaces were checked for flatness by the microprobe analysis and the results are shown in Figure 8.7. It is clear that the surfaces are reasonably flat, especially in the middle of the anvil, where the $0.5 \times 0.5 \text{mm}^2$ size samples were positioned.

Going back to the results of Harris et al.\(^{(9)}\) and Pickering and Adams\(^{(10)}\) and assuming that the exponential resistivity increase, they observed, is indeed due to the approach of the $X_{1c}$ and $\Gamma_{1c}$ minima. Then the $\Gamma_{1c} - X_{1c}$ separation of $0.48\text{eV}$ and the value of $\varepsilon_{u}^{X}$ for GaAs of $8.0\text{eV}$ as in silicon implies that a pressure of about $35 \text{k-bar}$ was reached over some areas of the crystal surface. This is extremely unlikely for pure uniaxial stress but perhaps the high stress could be withstood by small areas supported by the surrounded crystal and the friction at the anvil interface. The stress situation is then closer to hydrostatic which causes $\Gamma_{1c} - X_{1c}$ cross-over at $32 \text{k-bar}$$^{(74)}$. This is certainly true in the case of pancake sample configuration used by Harris et al.\(^{(9)}\). A variation in the relative magnitude of the hydrostatic and (100) uniaxial stress components would also explain the rather large scatter in the experiments' results from sample to sample and the differences between the works of Harris et al.\(^{(9)}\) and Pickering and Adams\(^{(10)}\).

8.9. CONCLUSION

From the uniaxial stress experiments, described here, several band structure parameters for GaAs have either been confirmed or
THE SURFACE OF THE UPPER ANVIL CHECKED FOR FLATNESS.

FIG. 8.7 SURFACES OF THE UPPER AND LOWER ANVILS AFTER BEING POLISHED.

THE SURFACE OF THE LOWER ANVIL CHECKED FOR FLATNESS.
revised. Although it is very difficult to assign exact energy values to the \( L_{1c} \) and \( X_{1c} \) valleys at atmospheric pressure by the above study nevertheless it has confirmed \( \Gamma-L-X \) band ordering for GaAs. This study also confirms not only the shear deformation potentials for the \((111)\) valleys of \( \Xi^L_{uu} = 22 \pm 7 \text{eV} \) and \( (\Xi^L_{ud} - a) = -11 (\pm 3) \text{eV} \) as obtained by Pickering and Adams\(^{10}\) but also appear to resolve the anomalously large value required for the deformation potential, \( \Xi^X_{uu'} \), for the \((100)\) valleys. The close proximity of the \( L_{1c} \) and \( X_{1c} \) minima chosen by Vinson et al\(^{6}\) to produce best overall fit to the high-field data was mainly influenced by the drop in the threshold field, \( F_T \) for the Gunn effect due to small apparent \((100)\) stress. However, if as discussed earlier, the load was highly non-uniform a much higher \( L_{1c} - X_{1c} \) separation would be accommodated since the threshold would be governed by the high stress regions. The value of the deformation potential, for the \((100)\) valleys in GaAs, of \( \Xi^X_{uu} = (21 \pm 9) \text{eV} \) obtained by Pickering and Adams\(^{10}\) must also be revised downwards to about \( 8 \text{eV} \) as observed in silicon.

The Zeeman experimental data also confirms the stress results and it can be concluded that the change in the effective mass in the \( \Gamma_{1c} \) conduction band of GaAs is proportional to the applied stress. The constants of proportionality measured are:

\[
\frac{\Delta m^*}{m_o} (100) = (0.23 \pm 0.06) \% \text{ k-bar}^{-1}
\]

\[
\frac{\Delta m^*}{m_o} (111) = (0.075 \pm 0.015) \% \text{ k-bar}^{-1}
\]
High pressure measurements have been made on the electrical properties of germanium and gallium arsenide. The electron mobility in the $L_{1c}$ valleys of germanium was found to vary from $\approx 4000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ at room temperature to $\approx 13,000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ at 100 K corresponding to a $T^{-1.5}$ temperature dependence. It was also found that the $L_{1c}$ mobility is dominated by the acoustic deformation potential scattering throughout the above temperature range. The $A_{1c}$ mobility, on the other hand, was found to vary from $\approx 800 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ at room temperature to $\approx 6400 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ at 120K corresponding to a $T^{-2.7}$ temperature dependence. The $A_{1c}$ mobility was found to be dominated by the intervalley scattering in the above temperature range.

A theoretical model has been developed to analyse the above experimental results. The validity of the above model was checked by analysing the $L_{1c}$ mobility results which yielded good agreement with already published results of Rode\textsuperscript{(82)} for germanium. The model was then, after slight modifications, used to analyse the $A_{1c}$ mobility. The analysis of the $A_{1c}$ mobility with the Fawcett and Paigl's\textsuperscript{(69)} predicted values of the effective mass ratios of $m_t = 0.28$, $m_z = 1.353$ and acoustic deformation potential, $E_1 = 3.61 \text{eV}$, gave intervalley coupling constants as $3.7 \times 10^8 \text{eV cm}^{-1}$ and $2.9 \times 10^8 \text{eV cm}^{-1}$ for the 430K-LO and 320 K-LA phonons respectively.

Since the above analysis is sensitive to the effective mass values it was tried to measure this parameter in the $A_{1c}$ or $X_{1c}$ minima using germanium and gallium arsenide. Clear magneto-phonon oscillations were observed to 22 k.bar in GaAs above which the oscillations become too noisy for reliable measurements and the resistivity started to increase by orders of magnitude. This is interpreted as due to carrier trap out
to impurity level below the $X_{1c}$ minima as already reported by Pitt and Lees\(^{(4)}\). Due to this carrier trap out it was not possible to obtain the ($\Gamma_{1c} - X_{1c}$) cross over which is believed to occur at 32 k.bar and measure the magneto phonon oscillations in the $X_{1c}$ valleys of GaAs. In the case of germanium, although ultra-pure material was used which remained intrinsic even above $L_{1c} - \Delta_{1c}$ cross over, it was not possible to measure the magneto phonon effect with pressure. The oscillations were found to be extremely weak and they were masked by fluctuations in resistivity caused by the applied pressures. Nevertheless, the pressure effects on the ultra pure germanium made it possible to measure the pressure coefficients for the $\Delta_{1c}$ minima independent of the band parameters. From the analysis of the n-type and ultra pure germanium it is concluded that in order to obtain good agreement between theory and experimental results $\Delta_{1c}$ minima effective mass should be 50% higher than the measured effective mass in silicon. The measured pressure coefficients for the $L_{1c}$ and $\Delta_{1c}$ minima in germanium are:

$$\frac{dE_{L_{1c}}}{dP} = 4.8 \pm 0.2 \times 10^{-6} \text{ eV bar}^{-1}$$
$$\frac{dE_{\Delta_{1c}}}{dP} = -2.4 \pm 0.4 \times 10^{-6} \text{ eV bar}^{-1}.$$

The most significant point to note about these results is the large negative pressure coefficient for the $\Delta_{1c}$ minima. Camphausen et al\(^{(41)}\), on the basis of Van Vechten's quantum dielectric theory\(^{(43-45)}\), were able to obtain excellent agreement with the measured pressure coefficients for the $\Gamma_{1c}$ and $L_{1c}$ minima with respect to the valence band. But the agreement was worse at the $\Delta_{1c}$ or $X_{1c}$ point where the predicted value was very small or even of the wrong sign.

Even by including the ionicity, as they suggested, would give pressure coefficients for the $\Delta_{1c}$ or $X_{1c}$ minima in the range\(^{(41)}\)
o to $-1 \times 10^{-6}$ eV bar$^{-1}$. The value of $-2.4 \times 10^{-6}$ eV bar$^{-1}$
which we obtained in an non ionic material is therefore significant
and indicates that Van Vechten's theory needs to be revised in the
light of most recent optical measurements of related band structures.

The observed variation of the $\Gamma_{1c}$ effective mass to 22 k.bar gave
a good agreement with the simple three band "k.p" theory but the
agreement became worse when the recent refinements$^{(23,24)}$ to the
theory, in which it is claimed that the higher lying minima must be
taken into account, were considered. The uncertainties in these
measurements are probably the absolute value of the pressure and the
energy gap. The former has been achieved by calibrating the pressure
cell as a function of the load and comparing changes in a variety of
semiconductor parameters with those observed using liquid pressure
transmitting media. The latter was derived from the measured pressure
coefficient of Welber et al$^{(101)}$. It would be far better if it were
possible to measure directly the energy gap as well as effective mass
using pressure as the dummy variable. To this end an optical fibre has
been introduced into the system such that the photoconductive edge
and the magneto phonon effect could be measured simultaneously. The
preliminary results seem to confirm the above agreement with simple
"k.p" theory but needs further investigation.

The uniaxial stress apparatus was modified and the sample configuration
improved for a more suitable four-probe measurement. The uniaxial
stress results confirmed the $\Gamma$-L-X band ordering for GaAs at atmospheric
pressure. The analysis of the (100) stress results have resolved the
discrepancies between the stress and electroreflectance data and
suggest that the large value of the shear deformation potential
$\Gamma_{1c}^X = (21 \pm 9)$ eV must be revised downwards and should have a value
in line with those observed for similar materials.
APPENDIX A

DISTRIBUTION OF ELECTRONS IN UNIAXially DEFORMED n-TYPE SILICON

The conductivity of a crystal of n-type Si in a <100> direction, in the absence of stress, is given by

\[ \sigma_0 = n_{z}^{0} \mu_{z}^{0} + 2n_{t}^{0} \mu_{t}^{0} \]  \hspace{1cm} (A.1)

where \( n_{z} \), \( \mu_{z} \) and \( n_{t} \), \( \mu_{t} \) are the electron densities and mobilities in the ellipsoids parallel to and perpendicular to the (100) axis, respectively. The ratio of resistivity in the presence of a uniaxial (100) stress to that in the absence of stress is given by

\[ \frac{\rho_{S}}{\rho_{0}} = \frac{\frac{n_{z}^{0} \mu_{z}^{0} + 2n_{t}^{0} \mu_{t}^{0}}{n_{z}^{s} \mu_{z}^{s} + 2n_{t}^{s} \mu_{t}^{s}}}{\frac{n_{z}^{0} \mu_{z}^{0} + 2n_{t}^{0} \mu_{t}^{0}}{n_{z}^{0} \mu_{z}^{0} + 2n_{t}^{0} \mu_{t}^{0}}} \]  \hspace{1cm} (A.2)

At 77K, since f-scattering is negligible(67), \( \mu_{z}^{0} = \mu_{z}^{s} \) and \( \mu_{t}^{0} = \mu_{t}^{s} \), assuming no significant distortion of the ellipsoids. Hence,

\[ \frac{\rho_{S}}{\rho_{0}} = \frac{n_{z}^{0} + 2n_{t}^{0} \mu_{t}^{0}}{n_{z}^{s} + 2n_{t}^{s} \mu_{t}^{s}} \]  \hspace{1cm} (A.3)

where \( K = \frac{\mu_{t}^{0}}{\mu_{t}^{s}} = \frac{\mu_{t}^{s}}{\mu_{t}^{s}} \) is the mobility anisotropy factor.

Since \( n_{t}^{0} = n_{z}^{0} \), equation (A.3) may be written

\[ \frac{\rho_{S}}{\rho_{o}} = \frac{n_{z}^{0}(2K+1)}{n_{z}^{s} + 2n_{t}^{s}K} = \frac{(n_{z}^{0}/n_{z}^{s})(2K+1)}{1 + 2K(n_{t}^{s}/n_{z}^{s})} \]  \hspace{1cm} (A.4)

Now, the total number of electrons is given by

\[ N = n_{z}^{s} + 2n_{t}^{s} = 3n_{z}^{0} \]  \hspace{1cm} (A.5)

Therefore,
From Boltzmann statistics, the redistribution of electrons due to a splitting of the <100> valleys, $\Delta E$, is given by

$$\frac{n_t^s}{n_L^s} = \exp \left( -\frac{\Delta E}{k_B T} \right)$$

(A.7)

Therefore, from equations (A.6) and (A.7)

$$\frac{n_L^o}{n_L^s} = \frac{1}{3} (1+2\exp \left( -\frac{\Delta E}{k_B T} \right))$$

(A.8)

and equation (A.4) becomes

$$\rho_s = \frac{(2K+1)(1+2\exp \left( -\frac{\Delta E}{k_B T} \right))}{3(1+2K\exp \left( -\frac{\Delta E}{k_B T} \right))} \rho_o$$

(A.9)

From equation (3.8),

$$\Delta E = \bar{\Sigma}_u (s_{11} - s_{12}) \chi$$

Therefore, if $K$ is known, a variation of $\rho_s$ with stress, $\chi$, may be fitted to equation (A.9) and a value of $\bar{\Sigma}_u$ obtained. When the applied stress is high enough ($>>k_B T$), all the electrons will be transferred to the two ellipsoids parallel to the stress direction and the resistivity will saturate. In this situation, $n_L^s = N$ and $n_t^s = 0$.

Therefore from equation (A.2)

$$\frac{\rho_{sat}}{\rho_o} = \frac{(\mu_L^o + 2\mu_t^o)^N}{N\mu_L^s}$$

(A.10)

$$= \frac{1+2K}{3}$$

(A.11)

Thus, the value of $K$ can be found from the saturation value of resistivity and inserted into equation (A.9).
The anisotropy factor, $K$, will vary from sample to sample since it is given by

$$K = \frac{\mu_t}{\mu_{t'}} = \frac{\tau_t}{\tau_{t'}} \frac{m_{t'}}{m_t} \quad (A.12)$$

where $\tau_t$, $\tau_{t'}$ and $m_t$, $m_{t'}$ are the relaxation times and effective mass components respectively. $\tau_t/\tau_{t'}$ will depend on the relative strengths of the various scattering mechanisms.
APPENDIX B
CALCULATIONS OF THE FERMI ENERGY

In an intrinsic semiconductor since the Fermi level is well away from the band edges the Boltzmann statistics may be applied according to which the density of carriers in the conduction and valence bands at TK can be written as:

\[ n = N_C \exp \left( \frac{E_C - E_F}{k_B T} \right) \]  \hspace{1cm} (B.1)

and

\[ p = N_V \exp \left( \frac{E_F - E_V}{k_B T} \right) \]  \hspace{1cm} (B.2)

In case of germanium, at room temperature there will be some electrons in the \( \Delta_{1c} \) minima therefore equation (B.1) can be written as:

\[ n_L = N_{CL} \exp \left( \frac{E_L - E_F}{k_B T} \right) \]  \hspace{1cm} (B.3)

\[ n_{\Delta} = N_{C\Delta} \exp \left( \frac{E_{\Delta} - E_F}{k_B T} \right) \]  \hspace{1cm} (B.4)

Also for an intrinsic semiconductor

\[ n = n_L + n_{\Delta} = p \]  \hspace{1cm} (B.5)

Now substituting the values of \( n_L \), \( n_{\Delta} \) and \( p \) from equations (B.2), (B.3) and (B.4) we get

\[ N_{CL} \exp \left( \frac{E_L - E_F}{k_B T} \right) + N_{C\Delta} \exp \left( \frac{E_{\Delta} - E_F}{k_B T} \right) = N_V \exp \left( \frac{E_F - E_V}{k_B T} \right) \]  \hspace{1cm} (B.6)

Dividing both sides of (B.6) by \( N_V \).

\[ \frac{N_{CL}}{N_V} \exp \left( \frac{E_L - E_F}{k_B T} \right) \frac{N_{C\Delta}}{N_V} \exp \left( \frac{E_{\Delta} - E_F}{k_B T} \right) = \exp \left( \frac{E_F - E_V}{k_B T} \right) \]

or

\[ \frac{N_{CL}}{N_V} \left[ \exp \left( \frac{-E_L}{k_B T} \right) \times \exp \left( \frac{E_F}{k_B T} \right) \right] + \frac{N_{C\Delta}}{N_V} \left[ \exp \left( \frac{-E_{\Delta}}{k_B T} \right) \times \exp \left( \frac{E_F}{k_B T} \right) \right] = \exp \left( \frac{-E_F}{k_B T} \right) \times \exp \left( \frac{E_V}{k_B T} \right) \]
Dividing both sides by \( \exp \left( \frac{E_F}{k_B T} \right) \) we have

\[
\frac{N_{CL}}{N_V} \exp \left( -\frac{E_L}{k_B T} \right) + \frac{N_{CA}}{N_V} \exp \left( -\frac{E_{\Delta}}{k_B T} \right) = \exp \left( -\frac{2E_F}{k_B T} \right) \exp \left( \frac{E_V}{k_B T} \right)
\]

Taking valence band as reference i.e. \( E_V = 0 \)

\[
\frac{N_{CL}}{N_V} \exp \left( -\frac{E_L}{k_B T} \right) + \frac{N_{CA}}{N_V} \exp \left( -\frac{E_{\Delta}}{k_B T} \right) = \exp \left( -\frac{2E_F}{k_B T} \right)
\]

or

\[
-\frac{2E_F}{k_B T} = \ln \left[ \frac{N_{CL}}{N_V} \exp \left( -\frac{E_L}{k_B T} \right) + \frac{N_{CA}}{N_V} \exp \left( -\frac{E_{\Delta}}{k_B T} \right) \right]
\]

or

\[
E_F = -\frac{k_B T}{2} \ln \left[ \frac{N_{CL}}{N_V} \exp \left( -\frac{E_L}{k_B T} \right) + \frac{N_{CA}}{N_V} \exp \left( -\frac{E_{\Delta}}{k_B T} \right) \right]
\]  \( \text{(B.7)} \)
APPENDIX C

EXPRESSION FOR THE INTRINSIC CARRIER DENSITY

The carrier densities in different bands in germanium can be written as:

\[ n_{L} = N_{CL} \exp \left( -\frac{E_{L} - E_{F}}{k_{B}T} \right) \]  \hspace{1cm} (C.1)

\[ n_{\Delta} = N_{CA} \exp \left( -\frac{E_{\Delta} - E_{F}}{k_{B}T} \right) \]  \hspace{1cm} (C.2)

\[ p = N_{V} \exp \left( -\frac{E_{F} - E_{V}}{k_{B}T} \right) \]  \hspace{1cm} (C.3)

For an intrinsic material it is possible to write:

\[ n_{i}^{2} = n \times p \]

\[ n_{i}^{2} = (n_{L} + n_{\Delta}) \times p \]  \hspace{1cm} (C.4)

From the equations (C.1), (C.2), (C.3) and (C.4) we can write:

\[ n_{i}^{2} = [N_{CL} \exp \left( -\frac{E_{L} - E_{F}}{k_{B}T} \right) + N_{CA} \exp \left( -\frac{E_{\Delta} - E_{F}}{k_{B}T} \right)] N_{V} \exp \left( -\frac{E_{F} - E_{V}}{k_{B}T} \right) \]

\[ n_{i}^{2} = N_{CL} N_{V} \exp \left( -\frac{E_{L} - E_{V}}{k_{B}T} \right) + N_{CA} N_{V} \exp \left( -\frac{E_{\Delta} - E_{V}}{k_{B}T} \right) \]

Taking \( E_{V} = 0 \)

\[ n_{i} = n = p = [N_{CL} N_{V} \exp \left( -\frac{E_{L}}{k_{B}T} \right) + N_{CA} N_{V} \exp \left( -\frac{E_{\Delta}}{k_{B}T} \right)]^{\frac{1}{2}} \]
APPENDIX D
CALCULATION OF EXTRINSIC CARRIERS

For a mixed conductor obeying classical statistics the electrical conductivity and the Hall coefficient can be expressed as:

\[ \sigma = n e \mu_n + p e \mu_p \]  \hspace{1cm} (D.1)
\[ R_H = -\frac{3\pi}{8e} \frac{nc^2 - p}{(nc + p)^2} \]  \hspace{1cm} (D.2)

Where \( c = \frac{\mu_n}{\mu_p} \), the ratio of electron and hole mobilities.

And \( n, p \) are their densities respectively.

At transition temperature the Hall coefficient, \( R_H = 0 \), therefore equation (D.2) becomes

\[ nc^2 - p = 0 \]  \hspace{1cm} (D.3)

By solving equations (D.1) and (D.3) simultaneously one can find the densities of electrons, \( n \), and holes, \( p \), provided their mobilities are known. The mobility of electrons, \( \mu_n \), and the mobility of holes, \( \mu_p \), at the transition temperature could be found from the experimental results of Morin and Maita\(^{102}\) represented in Figure 7.4. So by monitoring the resistivity and Hall coefficient as a function of temperature, the transition temperature was found and then by solving equations (D.1) and (D.3) the carrier densities i.e. \( n \) and \( p \) could be found. The difference between densities of electrons and holes would give the extrinsic carriers.
APPENDIX E

EFFECTS OF THE SAMPLE DIMENSIONAL CHANGES
ON RESISTIVITY

The resistance of a sample is given by
\[ R = \frac{\rho L}{A} \]  
(E.1)
where \( \rho \), \( L \) and \( A \) are the resistivity, length and area of the sample respectively.

or \( AR = \rho L \)

Differentiating we get
\[ A \frac{dR}{dx} + R \frac{dA}{dx} = \rho \frac{dL}{dx} + \frac{L}{\rho} \frac{d\rho}{dx} \]

Dividing throughout by \( \rho L \)
\[ \frac{1}{R} \frac{dR}{dx} + \frac{1}{A} \frac{dA}{dx} = \frac{1}{L} \frac{dL}{dx} + \frac{1}{\rho} \frac{d\rho}{dx} \]

or
\[ \frac{1}{\rho} \frac{d\rho}{dx} = \frac{1}{R} \frac{dR}{dx} + \frac{1}{A} \frac{dA}{dx} - \frac{1}{L} \frac{dL}{dx} \]

Hence the change in resistivity due to sample dimensions changes could become
\[ \frac{1}{\rho} \frac{d\rho}{dx} = \frac{1}{A} \frac{dA}{dx} - \frac{1}{L} \frac{dL}{dx} \]  
(E.2)

Thus the change in resistivity could be calculated provided we know how the length and the area of the sample changes with stress which could be calculated from the Young's modulus.

The Young's modulus can be defined as
\[ \frac{1}{E} = \frac{\text{STRAIN}}{\text{STRESS}} \]

This expression in terms of elastic compliance constants in the direction of unit vector, for a cubic crystal, can be written as \((112)\):
\[ \frac{1}{E} = s_{11} - 2 \left( s_{11} - s_{12} - \frac{1}{2} s_{44} \right) \left( \frac{L_1^2}{2} \frac{L_2^2}{2} + \frac{L_2^2}{3} \frac{L_3^2}{3} + \frac{L_3^2}{3} \frac{L_1^2}{1} \right) \]  
(E.3)

Since in cubic crystals Young's modulus is not isotropic. The
variation with direction depends on the factor \((l_1^2 + l_2^2 + l_3^2 + l_4^2 l_5^2 l_6^2 l_7^2)\). This factor is zero for the (100) directions and has its maximum value of \(\frac{1}{3}\) in the (111) directions.

Now volume is given by

\[ V = A \times Z \]

or

\[ \frac{dV}{dx} = A \times \frac{dZ}{dx} + Z \times \frac{dA}{dx} \]

Dividing both sides by \(A \times Z\)

\[ \frac{1}{V} \frac{dV}{dx} = \frac{1}{Z} \frac{dZ}{dx} + \frac{1}{A} \frac{dA}{dx} \]

or

\[ \frac{1}{A} \frac{dA}{dx} = \frac{1}{V} \frac{dV}{dx} - \frac{1}{Z} \frac{dZ}{dx} \]

\[ \Delta A = (\frac{\Delta V}{V} - \frac{\Delta Z}{Z}) \times \text{STRESS} \]

Now change in volume is independent of the stress direction and could be written as

\[ \frac{\Delta V}{V} = (s_{11} + 2s_{12}) \times \text{STRESS} \quad \text{(E.5)} \]

So the stress induced changes in the length, volume and the area of the sample could be calculated by using equations (E.3), (E.4) (E.5) and the compliance constants.

The compliance constants for GaAs are

- \(s_{11} = 1.173 \times 10^{-6} \text{ bar}^{-1}\)
- \(s_{12} = -0.366 \times 10^{-6} \text{ bar}^{-1}\)
- \(s_{44} = 1.684 \times 10^{-6} \text{ bar}^{-1}\)

(a) (100) Stress

For (100) stress equation (E.3) reduces to

\[ \frac{1}{E} = s_{11} \]

or

\[ \frac{\Delta Z}{Z} = s_{11} \times \text{stress} \]

\[ = 1.173 \times 10^{-6} \times 5 \times 10^3 \]

\[ \frac{\Delta Z}{Z} = 5.865 \times 10^{-3} \text{ (for 5 k.bar)} \]
From equation (E.5) the change in volume for 5 k.bar becomes
\[ \frac{\Delta V}{V} = 2.205 \times 10^{-3} \]  
(E.7)

Now from (E.4), (E.6) and (E.7) we have
\[ \frac{\Delta A}{A} = (2.205 \times 10^{-3} - 5.865 \times 10^{-3}) \]
\[ \frac{\Delta A}{A} = -3.66 \times 10^{-3} \]  
(E.8)

Substituting equation (E.8), (E.6) in equation (E.2) we get the change in resistivity up to 5 k.bar as
\[ \frac{\Delta \rho}{\rho} = (-3.66 \times 10^{-3} - 5.865 \times 10^{-3}) \]
\[ \frac{\Delta \rho}{\rho} = 9.525 \times 10^{-3} \]
\[ \therefore \frac{\Delta \rho}{\rho} = 0.95\% \text{ for } 5 \text{ k.bar} \]

(b) (111) Stress
For (111) stress equation (E.3) becomes
\[ \frac{1}{E} = s_{11} - \frac{2}{3} (s_{11} - s_{12} - \frac{1}{2} s_{44}) \]
or \[ \frac{\Delta L}{L} = (7.083 \times 10^{-7}) \times \text{STRESS} \]

So the change in length for 5 k.bar becomes
\[ \frac{\Delta L}{L} = 7.083 \times 10^{-7} \times 5 \times 10^3 = 3.542 \times 10^{-3} \]  
(E.9)

From equations (E.4), (E.7) and (E.9) we have
\[ \frac{\Delta A}{A} = (2.205 \times 10^{-3} - 3.542 \times 10^{-3}) \]
\[ \frac{\Delta A}{A} = -1.337 \times 10^{-3} \]  
(E.10)

Substituting equations (E.9), (E.10) in equation (E.2) we get the change in resistivity for 5 k.bar as
\[ \frac{\Delta \rho}{\rho} = -1.337 \times 10^{-3} - 3.542 \times 10^{-3} \]
\[ \frac{\Delta \rho}{\rho} = -4.879 \times 10^{-3} \]
\[ \frac{\Delta \rho}{\rho} = 0.5\% \text{ for } 5 \text{ k.bar} \]
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