The Pressure Dependence of Transferred Electron 
Effects In 
Gallium Arsenide, Indium Phosphide and Indium Arsenide 

by

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A Thesis submitted to the Faculty of Mathematical and 
Physical Sciences at the University of Surrey for the 
Degree of Doctor of Philosophy

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March 1976
ABSTRACT

The high electric field properties of GaAs have been investigated using a uniaxial stress apparatus, developed at the University of Surrey, and the hydrostatic pressure equipment at STL. An initial increase of the Gunn effect threshold field with pressure was observed, in contrast to previous measurements which are explained qualitatively in terms of pressure effects on non-ohmic contacts. Comparison of the results with Monte-Carlo calculations suggests that it may be incorrect to ignore the $L_{1c}$ minima as in previous analyses. Indeed, best agreement is obtained with the $L_{1c}$ valleys at 0.38 eV and the $X_{1c}$ valleys at 0.40 eV above the $\Gamma_{1c}$ minimum. Uniaxial stress measurements of low-field resistivity and the threshold field also provide evidence that the $L_{1c}$ and $X_{1c}$ valleys are at approximately the same energy.

Deformation potentials of the conduction band have been determined:

- $\Gamma_{1c}$ valley, $(\Xi_d^0-a) = -7(\pm 2)$ eV; $X_{1c}$ valleys, $\Xi_d^X = 21(\pm 9)$ eV and $(\Xi_d^X-a) = -5(\pm 5)$ eV; $L_{1c}$ valleys, $\Xi_d^L = 22(\pm 3)$ eV and $(\Xi_d^L-a) = -10(\pm 3)$ eV.

High field measurements have also been made on InP and InAs. The InP threshold field results agree with preliminary calculations using a 2-level $\Gamma$-$L$ model. The InAs results extend earlier data into the region where the Gunn effect is the dominant mechanism over avalanche breakdown and the $\Gamma$-$L$ sub-band gap is determined as 0.94(±0.07) eV. The threshold field is found to increase approximately proportional to the effective mass in the range 33-42 kbar and these results are also compared with Monte-Carlo calculations.

Impurity levels have been observed both in the forbidden gap and degenerate with the conduction band. Information on their positions is discussed and their effects on high field behaviour considered.
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**List of Symbols**

- \( a \) - deformation potential of valence band
- \( A \) - area
- \( b \) - deformation potential of valence band
- \( B \) - magnetic field
- \( d \) - deformation potential of valence band
- \( d' \) - sample thickness
- \( D \) - density
- \( e \) - electronic charge = \( 1.60206 \times 10^{-19} \) C
- \( E \) - energy
- \( E_g \) - band gap
- \( E_C \) - conduction band energy
- \( E_D \) - impurity level energy
- \( E_F \) - Fermi energy
- \( E_v \) - valence band energy
- \( F \) - electric field
- \( F_T \) - threshold field
- \( g \) - degeneracy factor
- \( h \) - Planck's constant = \( 6.6252 \times 10^{-34} \) Js.
- \( \hbar \) - \( h/2\pi = 1.0544 \times 10^{-34} \) Js.
- \( i \) - current
- \( j \) - current density
- \( k_B \) - Boltzmann's constant = \( 1.38044 \times 10^{-23} \) J.K\(^{-1}\)
- \( k \) - wave vector
- \( K \) - mobility anisotropy factor
- \( L \) - length
- \( m^* \) - effective mass
- \( m_0 \) - free electron mass = \( 9.1083 \times 10^{-31} \) kg
- \( M \) - momentum matrix
- \( n \) - electron concentration
- \( N \) - density of states
- \( N_A \) - acceptor concentration
- \( N_D \) - donor concentration
- \( p \) - electron momentum
- \( P \) - pressure
- \( P_s \) - scattering probability
- \( r \) - Hall scattering factor
- \( R \) - resistance
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<td>$\tau$</td>
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CHAPTER 1
INTRODUCTION

The discovery by J B Gunn\(^{(1)}\) in 1963 that the current flowing through a sample of bulk GaAs became unstable at high electric fields marked the beginning of a period of intense research into new semiconductor devices and materials. This observation of microwave oscillations in n-type GaAs and InP\(^{(2)}\) showed the feasibility of simple solid state oscillators and continued the trend towards miniaturisation started by transistors. Gunn diodes are now widely used as sources and amplifiers in telecommunication systems and are finding increasing applications in signal processing and logic circuits.

The mechanism responsible for the oscillations was subsequently confirmed to be the transfer of electrons from high mobility to low mobility states at higher energies in the conduction band. Ridley and Watkins\(^{(3)}\) and Hilsum\(^{(4)}\) had previously predicted that GaAs had the required band structure and Kroemer\(^{(5)}\) later pointed out that Gunn's observations could be explained by the transferred electron effect. The high pressure experiments of Hutson et al\(^{(6)}\), in which the threshold field for oscillations decreased with decreasing sub-band energy gap, were used as direct evidence for this explanation.

The Gunn effect was also observed in InP\(^{(1)}\), CdTe\(^{(7)}\) and ZnSe\(^{(8)}\), but, until recently, most practical developments had been with GaAs. As knowledge of band structures increased, other materials were considered which might have better or different properties. Oscillations were observed in InAs\(^{(9)}\) and InSb\(^{(10)}\) under the influence of pressure and the idea was put forward of designing a semiconductor to have certain desired properties. This could be achieved by alloying two binary compounds in suitable proportions to produce a mixed crystal with an optimum band structure for a particular application. Interest in new materials was further stimulated by the proposal of Hilsum and Rees\(^{(11)}\) in 1970 that high field conduction in InP and certain alloys should
involve three sets of band states, resulting in improved device properties.

Pressure is a very useful variable together with temperature and alloying experiments for determination of band structure parameters. Under pressure the different band edges move in energy at different rates and electron transfer between states may occur and become observable. By extrapolation back to atmospheric pressure the normal position of the various states in energy and k-space may be obtained. The variation of band structure with alloy composition is often similar to the effect of pressure on one of the components and hence it may be possible to study an alloy system by the application of pressure to an end member. The observation of electron transfer under pressure in conjunction with high fields can also give information on the relative strengths of the various scattering processes between band states which is required for an assessment of device possibilities.

The work to be reported in this thesis has involved the development of a uniaxial stress apparatus at the University of Surrey to be used in conjunction with the hydrostatic pressure equipment at Standard Telecommunication Laboratories Limited. After a review of band structure theory and the effects of pressure in Chapters 2 and 3, the apparatus is described in detail in Chapter 4. Chapters 5, 6 and 7 give an account of pressure experiments which throw new light on the band structure of GaAs. New data on InP and InAs are presented in Chapters 8 and 9 respectively. Finally, the implications of the results are discussed in Chapter 10.
CHAPTER 2
BAND STRUCTURE AND THE VELOCITY-FIELD CHARACTERISTIC

2.1. GUNN EFFECT IN GaAs

In 1963 J B Gunn(1) discovered that microwave current oscillations were produced when high electric fields were applied to n-type GaAs. The mechanism responsible for these oscillations was subsequently confirmed to be the transferred electron effect proposed earlier by Ridley and Watkins(3) and Hilsum(4). The Gunn effect has been the subject of many books and reviews (12-14) and its main features may be understood by consideration of the band structure of GaAs, which is shown schematically in Fig. 2.1.

The lowest conduction band minimum ($\Gamma_{1c}$), which is situated at the centre of the Brillouin Zone and is normally occupied by the conduction electrons, has an effective mass of 0.0665$m_e$(15). Other subsidiary minima, occurring at higher energies along $\langle100\rangle$ and $\langle111\rangle$ directions, have higher effective masses, e.g. 0.41$m_e$(16) for an $X_{1c}$ valley assuming it is at the zone edge. Under the influence of a high electric field, the electrons in the $\Gamma_{1c}$ valley, which have a high mobility, are accelerated and gain energy from the field. When the electrons acquire energies greater than the intervalley energy difference, they transfer rapidly with increasing field to the next highest satellite valleys (accepted to be the $X_{1c}$ valleys) because of their relatively large density of states. In these higher states the electrons have a lower mobility and this results in a velocity-field characteristic as shown in Fig. 2.2. Beyond a threshold field, $F_m$, the average velocity of the electrons decreases with increasing field, i.e. there exists a region of negative differential mobility (NDM).

In this region the current flowing through the GaAs becomes unstable due to the formation of high field domains. A detailed analysis of the situation is complex and cannot be dealt with here, but
FIGURE 2.1 Band structure of GaAs
FIGURE 2.2 Form of velocity-field characteristic of GaAs
a basic understanding can be obtained from a consideration of Fig. 2.3. In the region of NDM any local field inhomogeneity, due to a random fluctuation in carrier density, (Fig. 2.3(a) and (b)) will grow, rather than decay. This is because electrons in this region travel more slowly than those entering or leaving it (Fig. 2.3(c)). The leading edge of the region becomes depleted and an accumulation forms behind it as shown in Fig. 2.3(d), the resulting field profile being shown in Fig. 2.3(e). If the voltage across the sample is kept constant, the field, and hence the drift velocity of the electrons, outside the domain will decrease. The domain ceases to grow and becomes stable when its velocity becomes equal to the velocity of the electrons outside the domain. The peak field to which the domain grows, $E_d$, can be related to the field outside the domain, $E_0$, by the equal areas rule (17), illustrated in Fig. 2.2 (shaded areas are equal). Hence, when a domain is formed, the current flowing through the sample, given by $j = nev_d$ where $n$ is the carrier concentration, will decrease. The domain travels across the sample and decays at the anode, resulting in an increase in current. Simultaneously, another domain is nucleated near the cathode and in this way current oscillations with a transit-time frequency are obtained, e.g. if the sample thickness is 10 pm, the frequency of the oscillations will be $\approx 10$ GHz.

2.2. DEPENDENCE OF THE VELOCITY-FIELD CHARACTERISTIC ON BAND STRUCTURE

2.2.1. Scattering Mechanism in the Central Valley

At room temperature the dominant electron scattering mechanism in the $\Gamma_{1c}$ valley is with polar optical (PO) phonons (18). The energy acquired by the electrons from the applied field is distributed to the lattice by the absorption or emission of polar optical phonons and at low fields the difference in temperature between the electrons and the lattice is relatively small. However, at high fields, the electrons
FIGURE 2.3 Illustration of dipole domain growth

FIGURE 2.4 Electron temperature vs. electric field
gain more energy between collisions than they can lose to the PO phonons (energy of LO phonons at k=0 in GaAs is ~0.035eV) and so the electron temperature, $T_e$, increases rapidly with field. This situation is due to the fact that at high energies (a few times the phonon energy) the scattering rate for PO mode scattering decreases with increasing energy. Therefore, the time between collisions increases with field and this has been shown\(^{(19)}\) to lead to "breakdown" at a critical field, $F_c$, for electrons in a single, parabolic valley (Fig. 2.4). Stratton\(^{(20)}\) showed that $F_c$ was given by

$$F_c = \frac{\left(\varepsilon_\infty^{-1} - \varepsilon_0^{-1}\right) m^* k_B \theta}{2\hbar^2}$$

(2.1)

where $\varepsilon_\infty$, $\varepsilon_0$ are the high frequency and static dielectric constants respectively and $\theta$ is the polar phonon temperature. An important parameter of the material, therefore, is the electron effective mass in the central valley, since $F_c$ is proportional to $m^*$. This might be expected since, if the electrons had a higher effective mass and hence lower mobility, higher fields would be required to raise the electron temperature.

Under normal conditions, the electrons occupy states in the $\Gamma_{1c}$ valley near the minimum. Here the constant energy surface is spherical and the electron energy is related to the wave-vector, $k$, by the simple parabolic relation,

$$E = \frac{\hbar^2 k^2}{2m^*}$$

(2.2)

At high energies however, the $\Gamma_{1c}$ valley is normally non-parabolic, i.e. there is no longer a parabolic relationship between $E$ and $k$, and therefore the effective mass is no longer a constant. Kane's theory\(^{(21)}\) gives the dependence of the effective mass, $m^*(E)$, on energy, $E$, as approximately
\[ m^*(E) = m^* \left[ 1 + \frac{E}{E_g} \left( 1 - \frac{m^*}{m_0} \right)^2 \right] \quad (2.3) \]

where \( m^* \) is the effective mass at the bottom of the band and \( E_g \) is the direct energy gap between the conduction and valence bands. Therefore, as electrons are excited to more non-parabolic parts of the \( \Gamma_{1c} \) valley by the field, their effective mass increases and this leads to a slower variation of electron temperature with field than in the parabolic case (Fig. 2.4). It should be noted that this effect will be more important in small-gap materials such as InAs and InSb.

At low fields, therefore, conduction is ohmic and the velocity-field characteristic is approximately linear, the gradient being determined by the effective mass at the bottom of the valley, since the mobility, \( \mu = \frac{v}{F} \), is proportional to \( m^*^{-3/2} \) for PO scattering. At a critical field, however, the energy of the electrons begins to increase rapidly with field and the \( v-F \) characteristic departs from its ohmic behaviour.

2.2.2. Importance of Values of Energy Gaps

As the energy of the electrons increases they may acquire enough energy to transfer to the satellite valleys. The actual value of the sub-band gap, \( \Delta E \), will affect the threshold field, but if \( \Delta E \) is on the rapidly increasing part of the \( T_g/F \) curve \( F_T \) will be less sensitive to the exact value of \( \Delta E \) than if it is on the more slowly increasing part (see Fig. 2.4). Obviously, \( \Delta E \) must be larger than several \( k_B T \) or thermal population of the upper valleys will mask any field-dependent transfer.

For the observation of the Gunn effect under normal conditions \( \Delta E \) must be smaller than the direct energy gap, \( E_g \), between the conduction and valence bands otherwise impact ionisation of electron-hole pairs across the band gap will occur before intervalley transfer can take
place. This latter situation exists in InAs and InSb and avalanche breakdown is observed in these materials instead of the Gunn effect, although it may be possible to observe both by means of short pulse techniques. At the critical field the number of electrons in the conduction band begins to increase rapidly and, although the electron velocity may not be increasing, the current in the experimentally observed i-V characteristic will show a marked increase since the current density, \( j = nev \).

2.2.3. Intervalley Scattering

Electrons with energy equal to the intervalley energy difference may be scattered by interaction with a phonon into the satellite valleys, assumed to lie at the edge of the Brillouin Zone in the \(<100>\) directions in GaAs. The longitudinal optical (LO) phonon is the only phonon allowed by group selection rules \(^{(22)}\) for causing transitions from the \( \Gamma \) to the \( X \) point.

The scattering probability, \( P_s \), is written, by analogy with acoustic deformation potential scattering (see Section 2.2.4) in the form

\[
P_s = \frac{\pi}{D \omega_{\Gamma X} V} \varepsilon_{\Gamma X}^2
\]

where \( D \) is the density of the material, \( \omega_{\Gamma X} \) is the frequency of the zone edge phonon, \( V \) is the crystal volume and \( \varepsilon_{\Gamma X} \) is the coupling constant for \( \Gamma-X \) transitions or the deformation potential field.

Therefore, the coupling constant is a very important parameter since it determines the relaxation time, \( \tau \), of hot electrons and the fraction of electrons transferred to the satellite valleys at a given field, and hence the shape of the velocity-field characteristic.

The scattering rate, \( \lambda_{\Gamma X} \), for intervalley scattering is proportional to the square of the coupling constant and is given by
\[ \lambda_{\text{ph}} = k_p \frac{E_{\text{ph}}^2}{\omega_{\text{ph}}} \times \left\{ \frac{N_o}{(N_o+1)} \right\} \] for absorption of phonon

\[ \lambda_{\text{em}} = k_p \frac{E_{\text{em}}^2}{\omega_{\text{em}}} \times \left\{ \frac{N_o}{(N_o+1)} \right\} \] for emission of phonon

(2.5)

where \( k_p \) is a constant of proportionality and \( N_o \) is the phonon occupation number given by

\[ N_o = \left[ \exp \frac{E_{\text{ph}}}{k_B T} - 1 \right]^{-1} \] (2.6)

Fawcett et al (23) presented calculations for GaAs for coupling constants in the range \( 2 \times 10^8 \) to \( 2 \times 10^9 \) eVcm\(^{-1} \) and their results are shown in Figs. 2,5 and 2,6. With strong coupling (high coupling constant) electrons with the energy of the sub-band gap have a high probability of transferring to the satellite valleys but this is compensated by a high probability of scattering back to the central valley. Weak coupling, however, increases \( \tau \) and hence allows the electrons to acquire more energy between scatterings. Therefore the electrons become heated at lower fields and for a given field the fraction of electrons in the satellite valleys is higher since the overall cooling effect of the intervalley scattering is lessened (see Fig. 2,5).

For weak coupling most of the transfer to the satellite valleys takes place over a narrow range of field and from Fig. 2,6 it can be seen that this leads to a lower threshold field and peak velocity and a larger NDM than strong coupling. Also shown in Fig. 2,6 is the velocity-field characteristic as measured by Ruch and Kino (24) using a time-of-flight technique. The good agreement with the calculated curve for \( E_{\text{ph}} = 1 \times 10^9 \) eVcm\(^{-1} \) would seem to indicate that this value is to be preferred although the spread in the experimental data does not allow a definite conclusion to be drawn.

More recently, it has been pointed out by Herbert et al (25) that when the electrons occupy states a considerable distance from \( k = 0 \),
FIGURE 2.5 Fraction of electrons in \langle 100 \rangle\) valleys for various coupling constants (after ref 23)

FIGURE 2.6 Velocity-field curves for various coupling constants (after ref 23); dotted curve (ref 24)
as at transfer to the satellite valleys, the selection rules are relaxed and contributions to the scattering process can be made by phonons other than the LO phonon. The effective coupling constant can comprise a number of weighted contributions depending on the selection rules and phonon availability. The value of the coupling constant would, therefore, be expected to be dependent on the value of the sub-band energy gap, $\Delta E$, since if this is reduced the selection rules will become more stringent, the contributions from phonons other than the LO phonon will be reduced and the effective coupling constant will decrease. W. Fawcett (private communication), as a first approximation, has obtained a linear dependence of coupling constant on $\Delta E$.

Fawcett and Herbert\(^{(26)}\) have calculated intervalley coupling constants using screened and unscreened pseudopotentials. The theory is discussed in detail by Herbert\(^{(27)}\). Very briefly, the ionic cores are represented by pseudopotentials which are normally considered to be screened by the valence electrons. However, Herbert\(^{(27)}\) has suggested that, at high electric field strengths, the electron-phonon interaction may be unscreened due to the relatively long response time of the valence electrons. Best agreement with experimental data was obtained with an unscreened value of $1.1 \times 10^9$ eVcm\(^{-1}\).

2.2.4. Other Scattering Processes

Other scattering processes, apart from the polar optical and intervalley scattering already considered, may be important in determining the relaxation times and hence the mobilities of electrons in the central and satellite valleys.

(a) Acoustic Intravalley Scattering

This process, for scattering between initial and final states $(k,k')$ in the same valley, is far weaker than polar scattering at low energies, but may become comparable at higher energies. Its scattering
probability is of the form,

\[ p_s = \frac{a_s}{D_{xx}} |k-k'|^2 \]  \hspace{1cm} (2.7)

where \( s \) is the sound velocity in the material and \( \varepsilon \) is the deformation potential or change in lattice potential energy per unit strain (see Section 3.4).

(b) **Equivalent Intervalley Scattering**

This scattering between satellite valleys with the same energy is dominant over polar and acoustic intravalley scattering within the satellite valleys. Its scattering probability is of the form,

\[ p_s = \frac{\varepsilon_{xx}}{D_{xx}} \varepsilon_{xx}^2 \]  \hspace{1cm} (2.8)

where the coupling constant, \( \varepsilon_{xx}^2 \), is normally taken as \( 1 \times 10^9 \) eVcm\(^{-1}\) by analogy with Si (28).

(c) **Impurity and Electron-electron Scattering**

At high carrier concentrations and/or low temperatures these processes may contribute to \( \tau \) but they will not be considered here.

2.3. **Gunn Effect in Other Materials**

InP, CdTe and ZnSe are other binary compounds in which the Gunn effect has been observed. The two latter materials are apparently unattractive because of their rather high threshold fields and low peak velocities, but InP is becoming increasingly important in the development of transferred electron devices.

The band structure of InP is shown in Fig. 2.7. In this material the L valleys lie about 0.3 eV below the X valleys (29-30) and Hilsum and Rees (11)(31) suggested that, by analogy with the known \( \Gamma-L \) coupling constant in Ge of \( 2 \times 10^7 \) eVcm\(^{-1}\) (32), the coupling to the L valleys would be weaker than to the X valleys and that all three valleys would be involved in the transfer process. This, they predicted, would lead to a large NDM and peak-to-valley ratio and
\[ m^* = 5m_0 \]

\[ \Delta E \approx 0.5 \text{ eV} \]

\[ \Delta E \approx 0.8 \text{ eV} \]

\[ E_g = 1.34 \text{ eV} \]

**FIGURE 2.7** Schematic band structure of InP.

**FIGURE 2.8** Calculated velocity-field characteristics for InP.
hence higher efficiencies. This '3-level' model has been the subject of considerable controversy since the original calculations were performed. Several measurements\(^{(33-35)}\) have since indicated that InP was acting as a 2-level oscillator with strong coupling to the L valleys. There is also uncertainty in the threshold field of InP, measurements ranging from 6 to 12 \(\text{kVcm}^{-1}\), but Fawcett and Herbert\(^{(26)}\), using a 2-level \(\Gamma\)-L model, calculate \(F_T\) to be 10 \(\text{kVcm}^{-1}\). The velocity-field characteristics as calculated by the 3-level\(^{(31)}\) (weak \(\Gamma\)-L coupling, strong \(L\)-X, strong \(\Gamma\)-X) and 2-level\(^{(26)}\) models (strong \(\Gamma\)-L coupling) are compared in Fig. 2.8, which illustrates the importance of the values of the coupling constants. In the 3-level case, the peak velocity drops sharply at threshold since transfer takes place rapidly to the L valleys. The increase in velocity beyond the valley velocity is due to transfer of electrons from L to X valleys (strong coupling) and thence back to the \(T\) valley (strong coupling).

The Gunn effect can also be observed in materials formed by alloying two binary compounds in suitable proportions to produce the required band structure. For example, Fig. 2.9 shows that, by alloying InSb and GaSb, a \(\text{Ga}_x\text{In}_{1-x}\text{Sb}\) alloy can be formed with a direct energy gap large enough to prevent avalanching before transfer and a sub-band gap large enough to prevent thermal population of the upper valleys. Similarly, by alloying a small amount of InAs with GaAs, the alloy \(\text{In}_x\text{Ga}_{1-x}\text{As}\) is formed which has a smaller direct energy gap (and hence effective mass) and a larger sub-band gap than GaAs. This material would therefore be expected to have a higher peak velocity than GaAs which should lead to higher peak-to-valley ratios and efficiencies. The Gunn effect has also been observed in InAs and InSb by use of the application of pressure to modify the band structure. This will be discussed in more detail later.
FIGURE 2.9 Affect of alloying InSb and GaSb
2.4. MONTE-CARLO METHOD FOR CALCULATION OF VELOCITY-FIELD CHARACTERISTIC

In order to interpret the band structure of a semiconductor it is important to be able to compare a measured v-F curve with one calculated on the basis of a theoretical model. Most methods for the calculation of the v-F characteristic attempt to consider all the electrons at a fixed time. The Monte-Carlo method, first used by Kurosawa\(^\text{[36]}\) and later adapted for GaAs by Fawcett et al\(^\text{[23]}\), calculates the behaviour of one electron as it undergoes many scattering events. The distribution function can be shown to be proportional to the time the electron spends in each \(k\)-state.

The three stages in the motion of an electron, i.e. time of drift in an electric field, undergoing a particular type of scattering event and arrival in a final state, are random quantities and are obtained from computer-generated random numbers whose probability distributions depend on the transition rates of the various processes and the value of the electric field. The probability, \(P_g(k_0,t)\), that an electron, initially at \(k=k_0\), will drift for a time, \(t\), and then be scattered between \(t\) and \(t'\) is

\[
P_g(k_0,t) = \lambda[k(t)] \exp \left\{- \int_0^t \lambda[k(t')] dt' \right\}
\]

(2.9)

where \(\lambda[k(t)]\) is the sum of the scattering rates of all possible processes.

To avoid the use of a large amount of computer time or storage, it is convenient if the integral in equation (2.9) can be evaluated analytically. This is not possible for the important polar scattering mechanism and to overcome this difficulty the "self-scattering" technique is used. A fictitious process is introduced which does not change \(k\), its scattering rate, \(S(k,k')\), being given by

\[
S(k,k') = [\gamma - \lambda(k)] \delta(k-k')
\]

(2.10)

where \(\gamma\) is a constant and \(\delta\) is the Kronecker delta function.
Equation (2.9) now becomes

\[ p_{g}(k_{o}, t) = \gamma e^{-\gamma t} \quad (2.11) \]

Thus, the electron behaves, effectively, as if a constant relaxation time, \( \frac{1}{\gamma} \), existed, adding greatly to the ease of the calculation. The disadvantage of this technique is that part of the time the electron is undergoing scattering which does not alter the distribution function. After a large number of real scattering events the distribution function becomes constant and the drift velocity is calculated as the accumulated velocities during the flight. Velocity-field characteristics are then built up from a series of values of drift velocity for various field strengths (see Section 5.5).
CHAPTER 3
EFFECT OF PRESSURE ON BAND STRUCTURE

3.1. GENERAL BAND STRUCTURE CONSIDERATIONS

The important semiconductors, Ge and Si, crystallise in the diamond structure, i.e. the four nearest neighbours of each atom in the lattice are arranged in a tetrahedral configuration. This structure is equivalent to two interpenetrating face-centred cubic lattices. Other semiconductors such as the III-V compounds, GaAs, InAs, InP, InSb, GaSb and GaP and the II-VI compound, CdTe for example, have the zincblende structure which differs from the diamond structure only in that the two sub-lattices are of atoms of different species. As might be expected from this similarity in crystal structure, the above-mentioned semiconductors possess similar band structures. The conduction bands consist of various minima at the Brillouin zone centre and along the axes of symmetry. The main differences in the materials are the location of these minima in energy and $k$-space. The valence bands are all very similar, consisting of three bands with maxima at or near the zone centre. The two upper ones are degenerate at the maximum but have different effective masses - heavy hole and light hole bands. The third band is separated from the other two by the spin-orbit interaction\(^{(37)}\).

3.2. PHYSICAL EFFECTS OF PRESSURE

The application of hydrostatic pressure does not affect the symmetry of the crystal (if there is no phase change) and so no symmetry degeneracies are removed. The pressure causes simply a decrease in the crystal volume and hence a decrease in lattice constant. Therefore any band edges which are not required by symmetry to be degenerate may be moved with respect to one another.
Very simply, it might be expected that decreasing the lattice constant would broaden the atomic energy levels and hence lead to decreasing forbidden energy gaps. Experimentally, the energy gaps may either decrease or increase, depending on which minimum (Γ, L or X) 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 coefficient of the energy difference between two states of given symmetry is approximately independent of the material in which it is measured. Table 3.1 illustrates that, relative to the valence band maximum, the pressure coefficient of the Γ minimum is 10 to 15 \(x 10^{-6}\) eVbar\(^{-1}\), that of the L valleys is \(\approx 5 \times 10^{-6}\) eVbar\(^{-1}\) and of the X valleys \(\approx 1.5 \times 10^{-6}\) eVbar\(^{-1}\).

<table>
<thead>
<tr>
<th>Material</th>
<th>Pressure Coefficient of Γ</th>
<th>X</th>
<th>L</th>
<th>(x10^{-6}) eVbar(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>14</td>
<td>-1.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>-1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>11</td>
<td>-0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InP</td>
<td>9.5</td>
<td>-2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>InAs</td>
<td>10</td>
<td>-2</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>InSb</td>
<td>15</td>
<td>-1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>11</td>
<td>-1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>GaSb</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The existence of the Empirical Rule can be rationalised from the considerations of Section 3.1, in that it would be expected that the displacement of energy levels would be similar in different materials of the same crystal structure when the lattice constant is varied. In fact, the agreement is not so striking when the volume coefficients are compared due to the differences in compressibility and the reason for this is not clear.
Several authors have considered the effect of a change in lattice constant on the band structure. Paul and Brooks\textsuperscript{(39)} associated the F, L and X levels with the s, p and d-like atomic orbitals and suggested that pressure would have more effect on the large volume, spherically symmetric s-levels than on the more complex p and d-levels. Hence F minima might be expected to exhibit a larger pressure variation than L or X minima. Melz\textsuperscript{(40)} calculated several pressure coefficients using a pseudopotential approach and obtained some justification for the Empirical Rule. More recently, pressure coefficients in fairly good agreement with experiment have been calculated by Camphausen et al\textsuperscript{(41)} using the dielectric theory of the chemical bond developed by van Vechten\textsuperscript{(42)}.

3.3. EFFECT OF PRESSURE ON CONDUCTIVITY

The conductivity of a material will, in general, be affected by pressure if either the properties of the band minimum normally occupied by the charge carriers change or the carriers transfer to another energy state.

As an example of the former, the effective mass will change with pressure. The effective mass, $m^*$, is dependent on the direct energy gap, $E_g$, from Kane's, $k.p$ theory\textsuperscript{(21)},

$$m^* = \frac{m_0}{[1 + \frac{E_p}{3E_g} + \frac{1}{E_g + \Delta}]}^{-1} \tag{3.1}$$

where $E_p = \frac{2m^*_0 \hbar^2}{\pi^2} = 20\text{eV}$\textsuperscript{(43)} for most III-V compounds, $m$ is the momentum-matrix element between the conduction and valence states and $\Delta$ is the spin-orbit splitting in the valence band. Therefore, if $E_g$ increases with pressure, $m^*$ will also increase, approximately proportional to $E_g$ if $E_g \gg \Delta$. This will cause a decrease in mobility, $\mu$ (e.g. $\mu = m^{3/2}$ for PO mode scattering) and hence a
decrease in conductivity, $\sigma$, since $\sigma = n \mu$ ($n$=carrier concentration).

The relative positions of two band minima may change under pressure and affect the distribution of electrons among the bands and any impurity states. The number of electrons in each minimum, $i$, is given by Fermi-Dirac statistics,

$$n_i = N_i F_{1/2} \left(\frac{E_{F_i} - E_i}{k_B T} \right)$$  \hspace{1cm} (3.2)

where $F_{1/2}$ is a Fermi-Dirac integral (see Appendix A), $N_i$ is the density of states given by

$$N_i = 2 \left(\frac{2\pi m_i^* k_B T}{\hbar^2} \right)^{3/2}$$ \hspace{1cm} (3.3)

and $m_i^*$ the density of states effective mass. If $E_F$, the Fermi energy, is well below $E_i$, then equations (3.2) for two states can be approximated by

$$\frac{n_2}{n_1} = \frac{N_2}{N_1} \exp \left(\frac{-\Delta E}{k_B T} \right)$$ \hspace{1cm} (3.4)

where $N_1$ and $N_2$ are the densities of states in states 1 and 2 and $\Delta E$ is the separation between them. If the conductivity in state 1 is given by $\sigma_1 = n_1 \mu$ and in state 2 by $\sigma_2 = n_2 \mu$, the total conductivity, $\sigma = n_1 \mu_1 + n_2 \mu_2$, 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 $\mu=0$. If the level stays fixed relative to the
valence band and the conduction band minimum moves away with applied pressure, electrons will "trap out" to the impurity level and the conductivity will decrease.

Since the pressure coefficients of the various states are markedly different, the variation of their properties with pressure can often lead to the identification of the state under observation.

34. QUANTITATIVE DESCRIPTION OF EFFECTS OF PRESSURE

The change in energy of a state, $\delta E$, is related to the change in volume, $V'$, produced by pressure, by the equation

$$\delta E = \frac{Z}{V'} \delta V'$$

where $Z$ is the deformation potential, i.e. the change in energy of the state per unit strain, $\varepsilon$.

Hence,

$$\delta E = Z \varepsilon$$

where, in general, both $Z$ and $\varepsilon$ are second-rank tensors.

For a hydrostatic compressive pressure, $P$, the relation may be written

$$\frac{\delta E}{\delta P} = -Z \frac{3}{3} (s_{11} + 2s_{12})$$

where the $s_{ij}$ are components of the compliance tensor relating the produced strain to the applied stress.

When the state under consideration lies along a symmetry direction the number of components of the deformation potential tensor is reduced and, using the formalism of Herring and Vogt\(^{(44)}\) for cubic crystals, equation (3.7) can be written, for the energy shift of the conduction band edge, $\delta E_c$, as

$$\frac{\delta E_c}{\delta P} = -3 \left( s_{d} + \frac{1}{3} s_{u} \right) (s_{11} + 2s_{12})$$

(3.8)
Here, $E_d$ and $E_u$ are deformation potentials of the conduction band defined as follows: $E_d$ represents the energy shift due to an elongation in the two directions normal to the symmetry axis ($z$-axis), i.e. a dilatation, $\varepsilon_{xx} = \frac{u}{2}$, $\varepsilon_{yy} = \frac{u}{2}$ produces a shift $E_d u$; $E_u$ represents the energy shift due to an elongation along the $z$-axis combined with a contraction in the two normal directions, i.e. a uniaxial shear, $\varepsilon_{xx} = -\varepsilon_{yy} = -\frac{u}{2}$, $\varepsilon_{zz} = u$ produces a shift $E_u u$.

Similarly, using the formalism of Pikus and Bir\(^{(45)}\), the energy shift of the valence band edge, $\delta E_v$, may be written as

$$\frac{\delta E_v}{\delta p} = -3a(s_{11} + 2s_{12})$$

(3.9)

where $a$, the deformation potential of the valence band, is defined as the shift of the centre of gravity of the valence band edge per unit dilatation.

In Table 3.2 the elastic compliances and deformation potentials\(^{(46)}\) of Si and Ge are tabulated to illustrate the movements of the bands in these materials. In Si the $<100>$ valleys are lowest in energy while the $<111>$ valleys are lowest in Ge and it can be seen that the pressure coefficients, relative to the valence band, are consistent with the Empirical Rule discussed earlier.

### 3.5. EFFECT OF UNIAXIAL STRESS ON BAND STRUCTURE

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 the pure dilatation of the crystal (which is one-third 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 valleys whose symmetry axes are parallel to the stress direction is lowered with respect to the energy of the equivalent valleys which are not
### TABLE 3.2

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s_{11} = 0.768 \times 10^{-6} \text{bar}^{-1}$</td>
<td>$s_{11} = 0.964 \times 10^{-6} \text{bar}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$s_{12} = -0.214 \times 10^{-6} \text{bar}^{-1}$</td>
<td>$s_{12} = -0.260 \times 10^{-6} \text{bar}^{-1}$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>8.0 eV</td>
<td>18.95 eV</td>
</tr>
<tr>
<td>$E_d$</td>
<td>-0.4 eV</td>
<td>-8.53 eV</td>
</tr>
<tr>
<td>$a$</td>
<td>1.095 eV</td>
<td>1.54 eV</td>
</tr>
<tr>
<td>$\frac{\delta E}{\delta P}$</td>
<td>$-3 \left( E_d \frac{1}{3} E_u \right) (s_{11} + 2s_{12})$</td>
<td>$-3a(s_{11} + 2s_{12})$</td>
</tr>
<tr>
<td></td>
<td>$-3 \times 2.27 \times 0.34 \times 10^{-6}$</td>
<td>$-3 \times (-2.21) \times 0.444 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$-2.31 \times 10^{-6} \text{eVbar}^{-1}$</td>
<td>$+2.95 \times 10^{-6} \text{eVbar}^{-1}$</td>
</tr>
<tr>
<td>$\frac{\delta E_v}{\delta P}$</td>
<td>$-3a(s_{11} + 2s_{12})$</td>
<td>$-3 \times 1.095 \times 0.34 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$-3 \times 1.54 \times 0.444 \times 10^{-6}$</td>
<td>$-2.05 \times 10^{-6} \text{eVbar}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$-1.12 \times 10^{-6} \text{eVbar}^{-1}$</td>
<td>$-1.12 \times 10^{-6} \text{eVbar}^{-1}$</td>
</tr>
</tbody>
</table>

\[
\frac{\delta E_{\delta}}{\delta P} = \left[ -2.31 - (-1.12) \right] \times 10^{-6} \]
\[
= -1.19 \times 10^{-6} \text{eVbar}^{-1}
\]

\[
\frac{\delta E_{\delta}}{\delta P} = \left[ 2.95 - (-2.05) \right] \times 10^{-6}
\]
\[
= +5.0 \times 10^{-6} \text{eVbar}^{-1}
\]
parallel to the direction of the applied stress.

In general, the shift of the conduction band edge, $\delta E_c$, is related to the six strain components, $\epsilon_j$, by

$$\delta E_c = \sum_{j=1}^{6} \epsilon_j$$

(3.10)

Since the strains are small, $\epsilon_1 \approx \epsilon_2$, the change in energy with strain may be described by a first order dependence, the $\delta E_j$ assumed independent of strain.

Using the definitions of $\delta_d$ and $\delta_u$ given earlier, from symmetry considerations (see Appendix B), the energy shift of valleys in the <100> directions due to a <100> stress is given by

$$\frac{\delta E_{<100>}}{\delta x_{<100>}} = \left( \epsilon_d - \frac{\epsilon_u}{3} \right) (s_{11} + 2s_{12}) \begin{bmatrix} \frac{1}{5} \delta_u (s_{11} - s_{12}) - [100][010][001] \\
- \frac{2}{5} \delta_u (s_{11} - s_{12}) - [100] \end{bmatrix} \right) (3.11)$$

Similarly, the shift of the <111> valleys due to a <111> stress, is

$$\frac{\delta E_{<111>}}{\delta x_{<111>}} = \left( \epsilon_d - \frac{\epsilon_u}{3} \right) (s_{11} + 2s_{12}) \begin{bmatrix} \frac{1}{3} \delta_u (s_{44} + s_{11}) - [111][111][111] \\
- \frac{1}{3} \delta_u (s_{44}) - [111] \end{bmatrix} \right) (3.12)$$

As stated earlier, <100> valleys under <111> stress, and <111>-<111> valleys under <100> stress, change only by the hydrostatic component, and the degeneracy is not lifted.

The degeneracy of the valence band at $k=0$ is also lifted by uniaxial stress, the heavy-hole band being raised in energy with respect to the light-hole band. Two more deformation potentials, $b$ and $d$, are used to describe this, the shift of the valence band with <100> stress being

$$\frac{\delta E_v}{\delta x_{<100>}} = -a(s_{11} + 2s_{12}) \begin{bmatrix} \frac{1}{5} b (s_{11} - s_{12}) - hh \\
- \frac{1}{5} b (s_{11} - s_{12}) - lh \end{bmatrix} \right) (3.13)$$
and with <111> stress,

\[
\frac{\delta E_v}{\delta x_{<111>}} = -a(s_{11} + 2s_{12}) \left\{ \begin{array}{c}
+ \frac{d}{2\sqrt{3}} s_{44} - hh \\
- \frac{d}{2\sqrt{3}} s_{44} - lh
\end{array} \right\} (3.14)
\]

Fig. 3.1 illustrates the movement of the various minima of the conduction band of GaAs, with respect to the centre of gravity of the valence band under <100> stress and <111> stress. In each case it can be seen that the dominant effect is the decrease in energy of the valley oriented along the stress direction.

Bhargava and Nathan (48) have shown that, at high stresses, the stress dependence of the upper valence band is non-linear. A quadratic dependence of energy on stress was obtained due to coupling between the top of the valence band and the third spin-orbit split-off band. In this case, equations (3.13) and (3.14) can be written

\[
\frac{\delta E_v}{\delta x_{<100>}} = -a(s_{11} + 2s_{12}) \left\{ \begin{array}{c}
+ b(s_{11} - s_{12}) \\
- b(s_{11} - s_{12})(1 - \frac{2b(s_{11} - s_{12})}{\Delta} x_{<100>})
\end{array} \right\} (3.15)
\]

and

\[
\frac{\delta E_v}{\delta x_{<111>}} = -a(s_{11} + 2s_{12}) \left\{ \begin{array}{c}
+ \frac{d}{2\sqrt{3}} s_{44} \\
- \frac{d}{2\sqrt{3}} s_{44} \left(1 - \frac{2s_{44}}{7\sqrt{3} \Delta} x_{<111>}\right)
\end{array} \right\} (3.16)
\]
FIGURE 3.1 Movement of GaAs conduction band minima relative to centre of gravity of valence band
4.1. HYDROSTATIC PRESSURE EQUIPMENT

4.1.1. Introduction

Truly hydrostatic pressure, which involves the compression of a fluid, is normally used only for pressures up to about 30kbar since most fluids freeze at or below this pressure at room temperature. To obtain pressures beyond this region, solid pressure-transmitting media can be used, such as pyropholite or epoxy resins. These systems produce non-hydrostatic stress below about 25kbar, but the medium then begins to flow and produces a good approximation to hydrostatic pressure allowing pressures greater than 100kbar to be obtained. (Recently, Piermarini et al. have obtained pressures of almost 100kbar at room temperature using a liquid medium of 4:1 methanol: ethanol). The apparatus used here was developed by the STL High Pressure Group for Hall effect and resistivity measurements and consists of a liquid-medium piston and cylinder device for pressures to 18 kbar and a solid-medium Bridgman anvil device which operates up to ~90 kbar.

4.1.2. Liquid-Medium Apparatus

A schematic diagram of the apparatus is shown in Fig. 4.1. The hardened tool steel thrust piston compresses the liquid, a 1:1 mixture of amyl alcohol and castor oil, in a cylinder of hot-work die steel, sealing being accomplished by a combination of neoprene O-rings and phosphor bronze rings. Load is applied to the top of the four-column die set with a hydraulic press which produces loads up to 200 tons. The thrust piston, which is 3.8 cm in diameter, is shown in Fig. 4.2. Leads to contact terminals at the end of the piston are passed out of the pressure chamber via hardened silver steel terminals ground into
Top of thrust piston

- Cu WOUND TOROID
- SCREW
- CONTACTS MANGANIN GAUGE WOUND ON PTFE FORMER
- 'O' RING
- PHOSPHOR BRONZE

Exploded view

- CERAMIC INSULATOR
- SILVER STEEL
- THRUST PISTON
- LEAD OUT HOLE

FIGURE 4.2 Detailed diagram of thrust piston
ceramic sleeves and thence through a hole in the piston. The pressure is monitored by a 100Ω manganin coil coupled to a standard bridge circuit.

The liquid mixture used is suitable for pressures up to 18 kbar, castor oil alone freezing at 12.5 kbar. Other serious limitations to the pressure are the extrusion of the phosphor bronze ring and also extrusion of the silver steel terminals down the holes.

The sample under observation is immersed in the liquid and its leads soldered to the terminals at the end of the piston. The piston is then carefully lowered into the cylinder. Measurements are made at 1 kbar intervals on increasing and decreasing pressure. After each pressure increment, 10 to 15 minutes are allowed to elapse before a reading is taken, in order to achieve thermal equilibrium.

4.1.3. Solid-Medium Apparatus

Fig. 4.3 is a schematic diagram of the apparatus which is an opposed Bridgman anvil device. The anvils, which are 3.8 cm in diameter with a 6° taper leading to 1.6 cm diameter flats, can be either high speed tool steel (10% Co) or tungsten carbide. Steel anvils are preferred for Hall measurements since tungsten carbide saturates magnetically at 8 kG, but for pressures greater than 70 kbar carbide anvils are used because of the higher compressibility of steel. Mild steel jackets of 10.2 cm diameter provide little support for the anvils, but act as cores for the field coils which consist of 600 turns of 24 s.w.g. Cu wire. Load is again applied by a 200 ton hydraulic press to the top of a mild steel, four-column die set, which is magnetically insulated from the press by syndanie pads. The load is measured by a strain gauge load-cell. Measurements can be made to low temperatures by using nitrogen gas to pump liquid nitrogen through copper coils surrounding the anvils.
FIGURE 4.3 Cross section of opposed anvil high pressure apparatus
4.1.4. Sample Preparation for Solid-Medium Apparatus

The sample is encapsulated in epoxy resin at the centre of an MgO loaded epoxy Bridgman ring, as shown in Fig. 4.4. The rings, with dimensions as shown in the diagram, are formed in a mould by curing a suspension of MgO in epoxy resin at 120°C for 24 hours. Grooves are cut to half the height of the ring to take sample leads and thermocouple if required. Epoxy resin is poured into the centre of the ring and allowed to flow into the grooves, care being taken to eliminate any air bubbles as these provide stress concentrations leading to possible fracture of the crystal. The ring is clamped between two sheets of Mylar and the encapsulated sample cured at 80°C for two hours and 120°C for about twenty-two hours. After curing, the ring is removed from the Mylar and both sides roughened on abrasive paper. A dispersion of jeweller’s rouge in methanol is painted on each side of the ring, which, after evaporation, provides a uniform coating of the high friction rouge to prevent slipping on the anvils. The ring is then situated centrally between the anvils, electrical leads being insulated from the anvils by sheets of 0.01 mm Mylar in which holes are cut to the size of the ring.

Application of the load to the ring causes the resin to flow and the MgO loaded resin gasket is extruded sideways and “locks on” to the anvil face. In this pressure region of deformation of the solid medium and formation of the gasket, the crystal is subjected to non-hydrostatic stresses, as discussed in the next section, but above 25 kbar the stress is approximately hydrostatic. Measurements are possible on loading only, since samples fracture on unloading. This is due to the different stress systems produced by friction on the loading and unloading cycles. The non-reversible gasket formation causes the sample to become subject to high shear stresses on unloading. (53)
FIGURE 4.4 Sample encapsulated in MgO loaded Bridgman ring

FIGURE 4.6 Ring loaded for calibration measurement
4.1.5. Calibration of Solid-Medium Apparatus

Various fixed points are obtained on the load/pressure calibration curve, by observing the large resistance changes due to known standard transitions of Bi I-II at 25.4 kbar\(^{(54)}\), V-VI at 76 kbar\(^{(55-56)}\) and II at 36 kbar\(^{(54)}\). Different values of load are required for the transitions with steel or carbide anvils due to the higher compressibility of steel. Calibration curves for the experiments described later are shown in Fig. 4.5.

The region below 25 kbar is non-hydrostatic as shown by the piezoresistance measurements of Pitt\(^{(51)}\) on <100> n-type Si. Under hydrostatic pressure the resistivity of n-Si should change slowly at a rate of -3.1 \(\times\) \(10^{-6}\)\(\text{bar}^{-1}\)\(^{(57)}\) as the effective mass in the <100> valleys changes. If any uniaxial components are present, larger changes usually result, due to splitting of the valleys and transfer of electrons to heavy (longitudinal) or light (transverse) mass valleys. Pitt's results indicate that, during initial compression, there is a compressive component along a radius of the sample to the centre of the ring, followed by a tensile component as the ring spreads out. At higher pressures, this is reduced as the gasket locks on to the anvil faces, and above 30 kbar the pressure is hydrostatic to within 2 kbar for 2mm diameter samples. The difference is larger for larger samples as a result of the differing compressibilities of sample and surrounding medium, as discussed by Lees and McCartney\(^{(57)}\) for a tetrahedral-anvil apparatus. The region below 25 kbar in the calibration curve is 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 kbar point on the calibration curve was checked as follows for
FIGURE 4.5  Calibration curves for solid-medium apparatus.
both steel and carbide anvils. A piece of 99.99% pure Bi was cut to fit the centre of a Bridgman ring. Contacts were made by 0.025 mm diameter Cu wires, flattened at the ends, and fixed in the grooves of the ring with MgO loaded epoxy resin, the Bi being held in position by two epoxy discs (see Fig. 4.6). The resistance of the Bi was monitored (by observing the potential difference across it due to a constant current) as load was applied to the samples. At ~18 tons (carbide anvils) and ~24 tons (steel anvils) the Bi underwent a very sharp resistance decrease, confirming the 25.4 kbar points in Fig. 4.5.

4.2. UNIAXIAL STRESS EQUIPMENT

4.2.1. Introduction

Under completely hydrostatic pressure, there is little possibility of sample breakage. However, with uniaxial stress this is normally the main problem. The crystal may be brittle, shattering under very small shear stresses 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, since the ends of the sample should be perfectly free to move. A good approximation may be obtained 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 kbar, tungsten carbide or sapphire anvils should be used (not steel due to its relatively higher compressibility), 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 pushrod (58–59); weights,
beam balance and pulling frame\(^{(60-61)}\), spring, lever and pulling frame\(^{(62-63)}\), and weights on a platform acting on a stylus\(^{(64)}\). The systems using levers have the disadvantage that, due to torque, unwanted shear stresses will be present and should be allowed for. The use of a stylus can also produce large shear stresses if there is a slight misalignment and weights mean the stress cannot be applied smoothly at a uniform rate.

The apparatus developed here, to be described, is of a simple basic 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, thus obviating the dangers and inconvenience of the use of compressed air. 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 to very low temperatures.

4.2.2. Apparatus

The apparatus, which is a piston and cylinder device, is shown in Fig. 4.7. 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 remove effects due to the clamped outer edge of the rubber sheet. 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
FIGURE 4.7 Uniaxial stress apparatus
piston in an unstrained state. In the initial development of the apparatus, the top of the piston was the same size as the internal diameter of the chamber and was itself provided with an O-ring round its perimeter instead of using a diaphragm. However this arrangement was unsatisfactory because of initial sticking of the O-ring on the chamber walls. In later stages the O-ring was simply removed and a diaphragm incorporated but the pressure obtained at the sample was less than expected due to edge effects.

The hollow tube and the outer tube in which it slides are of 1.3 mm stainless steel about 1 m long and their outer diameters are 2.2 cm and 2.8 cm respectively. Three teflon sleeves about 2 cm long are used as guides along the tube's length. 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. The length of the tubes also serves to minimise heat conduction when making measurements at low temperatures.

The piston is terminated in an anvil assembly as shown in Fig. 4.3. A tungsten carbide anvil, a cylinder of diameter and length 2mm, is embedded in stainless steel, which is insulated from the piston by paxolin as shown. The crystal is situated between this anvil and a similar anvil in an assembly which is completely of stainless steel, in the sample holder. The central hole of the sample holder has an anodised Al sheath to insulate it from the upper anvil assembly. The anvils were ground and then polished to an optical flat as described later on a 1µm diamond paste wheel.

Electrical connections are made to a screw in the upper anvil assembly which is in contact with the anvil but isolated from the piston tube by a paxolin sheath as shown. The circuit is completed
FIGURE 4.8 Lower part of uniaxial stress apparatus
to earth through the lower anvil which is in contact with the main body of the apparatus. Miniature co-axial leads are passed up through the piston tube and out of the apparatus at the top by means of Conhex, feed-through, air-tight connectors. The stainless steel outer tube may be by-passed as a path to earth by connecting the screen of the co-axial lead to a terminal screw on the brass block at the bottom of the piston, the gap between the piston and the outer tube being bridged by a copper spring connection.

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. Measurements at low temperatures may be made by immersing the sample holder in a Dewar containing appropriate liquids or freezing mixtures. 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. 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 connectors.

4.2.3. Operation of Apparatus and Calculation of Stress

A rotary vacuum pump is connected to the upper chamber of the apparatus by means of a system of valves as shown in Fig. 4.9. 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 kbar in 10 mins., and reduces the risk of crystal fracture. The lower part of the apparatus is maintained under vacuum by continuously evacuating with the pump while the stress is applied. Closing the needle valve allows a constant stress to be maintained and the stress may be reduced slowly by re-evacuating the upper
FIGURE 4.9 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 knowledge of the area of the top-plate of the piston, 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 included in the calculated force. This weight has been kept to a bare minimum while still having the required strength and is equal to 1.04 kg, which is equivalent to ~0.4 kbar on a 0.5 mm square sample.

Assuming no frictional losses, the stress, X, on the sample is given by

\[ X = \left[ \frac{2DA_1 \times 10^{-6}}{A_2 \times 1.0197} \right] + \left[ \frac{W \times 10^{-6}}{A_2 \times 1.0197} \right] \text{ kbar} \quad (4.1) \]

where \( I \) is the difference in the levels of the Hg column in cm, \( D \) is the density of Hg, viz. 13.6 g.cm\(^{-3}\), \( A_1 \), \( A_2 \) are the areas of the top-plate of the piston and the sample respectively in cm\(^2\), \( W \) is the weight of the piston in g and the factor \( \frac{10^{-6}}{1.0197} \) converts g cm\(^{-2}\) to kbar. With a top-plate 10 cm in diameter, the maximum stress obtainable on a 0.5 mm square sample, the size usually used, is ~30 kbar. However, for samples of different areas, the top-plate and the supporting ring may be replaced by different sizes to give the required available stress.

4.2.4. Anvil and Sample Preparation

After every few runs, or whenever the anvils become scratched or pitted, the anvils are re-polished to an optical flat. Stainless steel polishing discs with holes in the centre are placed over the anvils, the upper faces of the discs being flush with the anvils.
This combination is then polished, first on a 6μm diamond wheel and finally on a 1μm wheel. After several polishings the anvils may become domed and they are then skimmed flat by grinding with diamond paste on a piece of optically flat glass.

Before each run the anvils are cleaned with iso-propyl alcohol. Care being taken to exclude dust particles, pieces of <1μm thick gold foil (99.9999% pure gold) are then pressed on to each anvil, adherence being helped by spots of de-ionised water. Under load, the gold will flow minimising friction between sample and anvil in order to produce as pure a "uniaxial" stress as possible. The effect of any small imperfections in the anvils (which should be <1μm) should also be reduced by the gold. Pure gold is used because the presence of impurities would increase its yield stress, the effect being particularly noticeable at low temperatures. Piezoresistance measurements (see next section) at 77K using less pure gold (<96.5%) showed a much slower increase of resistivity with stress than those using pure gold, the latter agreeing well with the expected variation.

The samples used are cut from a slice having evaporated contacts (usually Ag–Sn) on the upper and lower surfaces. In order to obtain high stresses the samples should be accurately rectangular parallelepipeds. If any of the angles are more than a few degrees different from a right angle, apart from difficulty in knowing the exact value of the stress, parts of the sample will be subject to shear stresses leading to early breakage. Also, the area of the sample should be as small as is convenient both to reduce the load required for a certain stress and to increase the tolerance of any non-parallelism at the two anvils. Samples may be cut from the slice by cleaving, wire-sawing or diamond sawing. Careful cleaving may produce good samples from <100>-orientated slices since the
cleavage plane is at right-angles (±2°) to the surface of the slice but this method cannot be used for <111> samples since the cleavage plane is at approximately 55° to the surface. Samples are wire-sawn using a 0.12mm diameter stainless steel wire and a suspension of alumina in glycerol. Diamond sawing has been used very successfully to produce accurately cubic samples of Si which is much harder than GaAs.

The surface area of the sample is measured with a travelling microscope and, after cleaning in trichloroethylene, it is then placed on the lower anvil in the sample holder, care being taken not to break the surface of the gold. The assembly is then fixed in position at the bottom of the apparatus and the piston carefully lowered until the upper anvil is resting on the sample.

4.2.5. Calibration

In order to calibrate the stress in samples used piezoresistance measurements were made on Si dice having similar dimensions which could directly replace the samples to be investigated. The lowest conduction band edge in Si consists of 6 ellipsoidal valleys along the <100> directions (Δ). On application of a <100> stress, the two valleys with axes along the stress direction are lowered in energy with respect to the four "perpendicular" valleys, electrons transferring from the latter to the former. Since the mobility in the direction of the stress will now be determined by the longitudinal effective mass, \( m^\lambda \), which is greater than the transverse effective mass, \( m^\tau \), the resistivity measured in this direction will therefore be expected to increase with stress, although the stress dependence of the electron scattering is needed for detailed analysis. The piezoresistance coefficient, \( \pi_{11} \), was given by Smith\(^{(65)}\) as \(-102.2 \times 10^{-6} \text{bar}^{-1}\). However, the resistivity change with stress is only linear\(^{(66)}\) for small stresses (≤1 kbar) and so cannot be used directly to calibrate
the apparatus to high stresses.

The equivalent intervalley scattering in Si may be divided into scattering from one valley to the other valley in a parallel direction - g-scattering - and scattering from this valley to the four perpendicular valleys - f-scattering. High temperature phonons (mean $\theta \approx 600$ K) are believed to participate in f-scattering while a low temperature phonon ($\theta \approx 134$ K) causes g-scattering. When a high $<100>$ stress, $X$, causes a splitting of the valleys of a few $k_B T$, f-scattering will be completely eliminated and therefore the relaxation time, $\tau$, is dependent on stress. However at low temperatures ($<77$ K), even at zero stress, f-scattering is negligible and hence the relaxation time is now stress-independent. The resistivity, normalised to zero stress, $\rho / \rho_0$, may now be written (see Appendix C) as

$$\frac{\rho}{\rho_0} = \frac{(2K+1)(1+2e^{\frac{-\Delta E}{k_B T}})}{3(1+2e^{\frac{-\Delta E}{k_B T}})}$$

(4.2)

where $\Delta E$, the splitting of the valleys, is equal to $E_u (a_{11} - a_{12}) X$ from equation (3.11) and $K = \frac{\tau}{\tau + \frac{m_L}{m_t}}$ may be found from the equation

$$\frac{\rho_s}{\rho_0} = \frac{1}{3} (2K+1)$$

(4.3)

Here, $\rho_s$ is the saturation value of the resistivity when virtually all the electrons have transferred to the lower valleys, and the effective mass components are $m_L = 0.90 m_0$ and $m_t = 0.192 m_0$. Hence, the experimental resistivity versus stress curve may be compared to a theoretical curve obtained from equation (4.2).

The piezoresistance of several $<100>$ n-type Si samples was measured using a standard potentiometer system (see Section 4.3.3.). The slice, with $n = 1.5 \times 10^{16} \text{cm}^{-3}$, $\rho = 0.40 \text{cm}$, had diffused $n^+$ layers 2$\mu$m thick and evaporated Cr/Au ohmic contacts (Cr followed by about
7000 \, \text{Å} of Au) on each side. Cubic samples with sides of about 0.05 cm were diamond-sawn from the slice, having typical resistances of 8Ω.

The change in resistivity with stress at room temperature on increasing and decreasing stress is shown in Fig. 4.10. This result was very repeatable from sample to sample and, as can be seen, good agreement was obtained on decreasing the stress, indicating negligible frictional losses or damage to the sample. The results at 77K are shown in Fig. 4.11 compared with a curve obtained from equation (4.2), \( \rho / \rho^* \) is first obtained from the results and hence \( K \) from equation (4.3). It can then be seen that the rest of the curve between \( \rho^* \) and \( \rho_0 \) is fitted well by the theory for a value of \( E_u = 8.5 \, \text{eV} \), which is in good agreement with previous measurements (69). Good agreement was also obtained on unloading. The decrease in \( \rho / \rho^* \) beyond \( \rho_0 \) is probably due to the decrease in the effective mass in the <100> valleys as the direct band gap at \( A \) continues to decrease.

The above measurements indicate that a good approximation to uniaxial stress has been obtained in the region 0-7 kbar and the room temperature results provide evidence that this is also true to higher stresses. Measurements on bulk GaAs samples, in which the conductivity is controlled by deep-level impurities, to be described in Chapter 6, indicate that the stress on the crystal increases linearly with \( Z \) at the rate calculated from equation (4.1), up to about 15 kbar when the samples fractured.

4.3. MEASUREMENT PROCEDURES

4.3.1. Current/Voltage Measurements

The basic circuit used for the i/V measurements is shown in Fig. 4.12, although slight modifications were made for use with the hydrostatic pressure equipment and the uniaxial stress apparatus.
FIGURE 4.10 Normalised resistivity vs. <100> stress for n-type Si at room temperature.
FIGURE 4.11 Normalised resistivity vs $\langle 100 \rangle$ stress for n-type Si at 77K
FIGURE 4.12 Circuit diagram for i/V measurements
In the former case, a 0-250V Solartron power supply was used as the high tension supply to a mercury switched pulser, with an open-ended charge line of equivalent length 50 nsec determining the pulse length of 100 nsec. This pulse length was used at a repetition rate of 50 pps to avoid heating of the sample. A 15Ω delay line was incorporated between the pulser and sample to allow the sampled current and voltage pulses to arrive at the oscilloscope at the same time as the trigger pulse. 15Ω co-axial cable was preferred to 50Ω cable in order to reduce the possibility of avalanching at threshold. Screened cable was taken as close as possible to the sample when situated in the high-pressure apparatus. The voltage and current pulses were monitored at a point close to the sample, the latter being obtained from a Tektronix P6041/CT-2 5mV/mA current probe. The pulses were sampled by a Tektronix 564B storage sampling oscilloscope and the sampling point was chosen to be towards the end of the pulse, well away from any initial ringing caused by mis-matches. The i/V characteristic was then displayed on a Hewlett-Packard x-y plotter.

In the uniaxial stress equipment the 15Ω cable was taken as far as the lead-throughs near the top of the apparatus. Three miniature 50Ω co-axial cables connected in parallel were then passed down the inside of the stainless steel tube. This arrangement should provide a cable with an effective impedance close to 15Ω inside the apparatus where room is restricted. The current probe and voltage monitor were situated near the top of the apparatus.

4.3.2. Hall Measurements

Fig. 4.13 shows the basic circuit used for Hall coefficient and mobility measurements in conjunction with the hydrostatic pressure apparatus. A constant current is passed through the sample which is in the form of a Van der Pauw(71) clover-leaf with four contacts on
FIGURE 4.13 Circuit diagram for Hall measurements
the lobes. The Hall voltage, is measured in the presence of a magnetic field supplied by an electromagnet which had previously been calibrated for various current values. This measurement is then repeated with the field direction reversed.

The Hall constant, $R_H$, is given by

$$R_H = \frac{V_H d'}{B i}$$  \hspace{1cm} (4.4)$$

where $V_H$ is the Hall voltage, $d'$ is the sample thickness, $B$ is the magnetic field and $i$ is the sample current. The resistivity is obtained in the absence of the field for several sets of contacts and current directions.

4.3.3. Resistivity Measurements

Resistivity measurements were made in the uniaxial stress apparatus using a similar circuit to Fig. 4.13 without the magnetic field. In this case the microvoltmeter was replaced with a potentiometer measuring system.

The effect of the change in sample volume with pressure on the measured variation of threshold field, Hall coefficient and sample resistance has been considered. From the compression data of Hutson et al (72) the volume change is about 5% to 50 kbar. This results in a 1% error in threshold field measurements to 30 kbar and between 1% and 2% error in Hall and resistivity measurements to 50 kbar. For uniaxial stress measurements to 20 kbar the volume change is less than 1%.
CHAPTER 5
HYDROSTATIC PRESSURE MEASUREMENTS ON GALLIUM ARSENIDE

5.1. INTRODUCTION

As discussed earlier, the velocity-field characteristic is sensitively dependent on the band structure of the material and, in particular, on such parameters as the inter-valley energy difference, the effective mass and non-parabolicity of the central valley, and the inter-valley coupling constants. Therefore, measurements of the pre-threshold $1/V$ characteristic as the band structure is varied by the application of pressure may, through extrapolation back to atmospheric pressure, provide useful information on the normal band structure.

It is generally accepted that the microwave oscillations observed in GaAs\(^{(1)}\) are caused by the excitation of electrons, at high electric fields, from the central, low effective mass $\Gamma_{1c}$ minimum to high effective mass, $X_{1c}$ minima situated at the $100\theta$ zone edge. Under hydrostatic pressure, the sub-band gap, $\Delta E(\Gamma_{1c} - X_{1c})$, decreases at a rate of $\approx 11.5 \times 10^{-6}$ eV bar$^{-1}$ (16) and the high pressure measurements of Hutson et al\(^{(6)}\) and Wasse et al\(^{(73)}\) were used to provide confirmation that the Gunn oscillations were due to electron transfer to the higher valleys. They found that, as the sub-band energy gap decreased with pressure, the threshold field, $F_T$, for oscillations decreased rapidly from its atmospheric pressure value, the oscillations disappearing at the expected pressure, near 27 kbar. A similar effect was found in GaAs$_{1-x}$P$_x$ alloys\(^{(74)}\), where again the sub-band gap decreased with increasing $x$. The pressure data were fitted satisfactorily by the theory of Butcher and Fawcett\(^{(75)}\) obtained from calculated velocity-field curves for different values of $\Delta E$, assuming a displaced Maxwellian distribution and a pressure-independent effective mass. However, it has recently been predicted
(W. Fawcett, private communication) that, because of the increase in $\Gamma_{1c}$ effective mass with pressure, the threshold field might increase at low pressures in contrast to the previously published data. The predictions for GaAs$_{1-x}$P$_x$ alloys (76) did in fact show an initial increase in $F_T$ for low $x$ but this was not observed experimentally.

The effective mass in the central valley is strongly dependent on the direct energy gap, $E_g$, and hence pressure from equation (3.1). $E_g$ increases at a rate of about $11 \times 10^{-6}$ eV bar$^{-1}$, which corresponds to an effective mass increase of approximately 0.7% k bar$^{-1}$ (77). Thus the $\Gamma_{1c}$ mobility will decrease since it is proportional to $m^*^{-3/2}$ for polar optical mode scattering. This could result in an increase in $F_T$ since higher fields are then required to raise the electron temperature for transfer. There are, therefore, two main conflicting processes which could influence $F_T$: (a) the decrease in $\Gamma_{1c}$ mobility and (b) the decrease in $\Delta E$.

The high pressure threshold field measurements have been repeated using the more refined techniques and uniform epitaxial material which have been developed since the initial measurements. A careful study has been made on a number of diodes to observe whether an increase in $F_T$ takes place in the lower pressure range.

5.2. EXPERIMENTAL

Measurements of the variation of threshold field with pressure have been made, using both solid and liquid pressure-transmitting media. Samples were obtained from two different slices, both grown at STL by vapour epitaxy on $<100>$ orientation $n^+$ substrates (Se doped, thickness $\approx 70\mu$m). S268A had an active layer of thickness 129$\mu$m, $n \approx 10^{15}$ cm$^{-3}$ and resistivity $\approx 0.6\Omega$cm, while S358E had a thickness of 122$\mu$m, $n \approx 10^{15}$ cm$^{-3}$ and $\rho \approx 0.8\Omega$cm. Schottky barrier carrier
concentration profile measurements were made on adjacent samples and the uniformity was better than ±10%. Ag-Sn contacts were evaporated on to the slice and square dices of approximately 0.075 x 0.075 cm and 0.05 x 0.05 cm (typical resistances 1.5Ω and 4.25Ω) were sawn off. Au tapes (0.015 x 0.25 mm) were pressure welded to the Ag-Sn, and 0.15 mm diameter Cu wire welded to the gold.

Truly hydrostatic measurements to 15 kbar were made using the liquid-medium apparatus described in Section 4.1.2, measurements to 40 kbar being made with the solid-medium apparatus (Section 4.1.3.) Current-voltage characteristics were measured using the circuit shown in Fig. 4.12 (Section 4.3.1.) and recorded on an x-y plotter.

5.3. RESULTS

Fig. 5.1 shows the results obtained on two samples using the liquid hydrostatic pressure medium. There is no doubt that $F_T$ increases with pressure and that on decreasing the pressure $F_T$ decreased.

Fig. 5.2 is a plot of the very high pressure data to 40 kbar. Again for most samples (type 1) an increase in $F_T$ was observed at low pressures. The mean result is an increase in $F_T$ of 6-7% to 15 kbar. This agreement with the truly hydrostatic results indicates, as would be expected, that the pressure in the opposed-anvil apparatus approximates to hydrostatic pressure even below 25 kbar for small samples (<2mm) (51) as used in these measurements. At higher pressures $F_T$ dropped rapidly and passed through a minimum near 27 kbar at a value of 0.7-0.8 $F_T(0)$. Beyond this pressure, the threshold field increased again until it reached its original value, and subsequently the oscillations ceased. It can be seen that the scatter of data for the type 1 behaviour is considerable but there is no doubt about the
FIGURE 5.1 Liquid medium measurements of threshold field for two samples on increasing (□ ○) and decreasing (□ ○) pressure.
FIGURE 5.2 Solid medium measurements of threshold field compared with previous results (x, ref. 6, o, ref 73)
overall shape of the $F_i$/pressure results.

For other samples (type 2) the results showed, in contrast to type 1, a decrease in $F_i$ with pressure, even below 15 kbar. A further difference between the results for the two types of diodes can be seen from the variation of peak current, $i_p$, shown in Fig. 5.3. For type 1 diodes, $i_p$ decreases only by a few per cent to 10 kbar before decreasing rapidly beyond this pressure, while type 2 diodes show a rapid decrease in $i_p$ immediately on the application of pressure. The data presented in Figs. 5.2 and 5.3 are the means of eight runs for type 1 and two runs for type 2, the scatter being indicated by the error bars. No significant differences were observed between the two slices, S268A and S358E.

Fig. 5.4 is an experimental plot from the x-y recorder of $i/V$ plots at various pressures. The characteristic shape of $F_i$ versus pressure can be seen. The sharp increase at high pressures is due to the $F_{lc}$ and $X_{lc}$ minima being close enough to cause an appreciable thermal $X_{lc}$ population, and the oscillations cease when most of the electrons occupy the $X_{lc}$ minima. Such curves have also been previously observed by Wasse et al.\(^{16}\) and Hutson et al.\(^{17}\). The variation of low field resistivity with pressure is shown in Fig. 5.5. The low pressure region is in good agreement with the expected variation in mobility due to the effective mass increase in the $F_{lc}$ valley. At about 25 kbar the characteristic increase in resistivity occurs as transfer takes place and the resistivity tended to level off near 40 kbar at a ratio, $\rho(40)/\rho(0) \sim 20-30$, which is in reasonable agreement with the resistivity variations observed by Pitt and Lees\(^{16}\), indicating the presence of an impurity level $\sim 0.08$ eV below the $X_{lc}$ minima.

As one test of the quality of the samples used, an examination
FIGURE 5.3 Normalised peak current vs. pressure
FIGURE 5.4 Experimental i/v plots at various pressures
FIGURE 5.5 Normalised resistivity vs. pressure
was made of the shape of the i/V characteristic up to threshold. The results are illustrated in Fig. 5.6. Samples with type 1 pressure characteristics showed a linear variation of i against V, and the calculated $F_T$ was within ±10% of the theoretical value of $3.3kVcm^{-1}$. On reversal of the potential $F_T$ did not vary by more than 5%. All of the larger dices exhibited type 1 behaviour. All of the type 2 samples were smaller diodes and their i/V plots were non-linear. The difference in $F_T$ in the two directions for these samples was often greater than 20%, the forward direction ($n^+$ substrate positive) giving a lower $F_T$ than the reverse direction, typically 30% below the theoretical value. The effect is not simply a size effect since several of the smaller diodes had type 1 characteristics.

Because of uncertainties in the electrical cross-sectional area, $A$, of the diodes and the carrier concentration, an accurate value of the peak drift velocity, $v_p$, was difficult to obtain. Using the equation, $v_p = \frac{i}{A n_e}$, values between 1.3 and $2 \times 10^7$ cm$^{-1}$ were found, type 2 diodes tending to give values towards the lower end of the range.

The use of the pre-threshold i/V plot to indicate whether the devices are exhibiting low or high cathode fields has been discussed by Shaw et al.$^{78}$ and Solomon et al.$^{79}$ for GaAs. They found good linearity, prior to threshold, on sculptured samples with uniform fields, and also showed that the effect of a high cathode field, relative to that in the bulk, was to cause non-linearity and to reduce the threshold field and peak current. It is probable, therefore, that the onset of oscillations in the type 2 diodes is controlled by contact effects of the type observed by Wasse et al.$^{80}$ in similarly prepared samples. As a more stringent test that this was not the case in the type 1 diodes, measurements were made on the i/V
FIGURE 5.6 Two types of observed i/V characteristics (not to scale) A, forward; B, reverse.
characteristic down to temperatures \( \sim 100 \text{K} \). No asymmetry was observed, indicating that, if any barrier is present in these samples, its height must be less than 0.1 eV\(^{(81)}\).

5.4. CONTACT EFFECTS UNDER PRESSURE

The variation of threshold field with type 1 behaviour is therefore believed to reflect purely band structure effects in the bulk GaAs and this is discussed in the next section. From Fig. 5.2, however, it can be seen that the type 2 results are in good agreement with the previous data, except that the pressure at which \( F_T \) reaches a minimum is \( \sim 1 \text{kbar} \) higher than that observed by Wasse et al\(^{(73)}\). An investigation into the results of Hutson et al\(^{(6)}\) and Wasse et al\(^{(73)}\) shows that their samples also gave non-linear \( i/V \) characteristics below threshold, with \( F_T \) 25-30\% below the theoretical value, in agreement with our results for type 2 behaviour.

The pressure difference of the minimum in \( F_T \) can be explained from examination of the dimensions of the crystal used by Wasse et al\(^{(73)}\). This was the first single crystal measurement reported to such extreme pressures and the pressure distribution had not been fully characterised. A sample with a large length/thickness ratio immersed in epoxy resin, in the tetrahedral anvil apparatus used, will be subject to a greater stress than was originally appreciated. This is due to the build-up of stress along the length of the sample caused by the difference in compressibility of the surrounding medium\(^{(57)}\). J. Lees (private communication) has suggested that an underestimate of 3-4 kbar is of the correct order, for the crystal used in this early experiment.

A possible explanation of the decrease in \( F_T \) with pressure for samples in which the onset of oscillations is controlled by contact effects, can be obtained by considering the formation of ohmic
contacts with a metal on a semiconductor. This is shown schematically in Fig. 5.7. If a metal such as Ag is deposited on GaAs, a Schottky barrier is formed, since the work function of Ag is greater than that of GaAs (Fig. 5.7(a) and (b)). Electrons transfer from the semiconductor to the metal, the Fermi levels equalise, and the semiconductor becomes depleted near the surface. To produce ohmic contacts the semiconductor can be doped with a metal such as Sn, by alloying at a high temperature. The semiconductor becomes degenerate just below the surface and the Fermi level is above the bottom of the conduction band in this region (Fig. 5.7(c)). A reservoir of electrons is formed from which enough electrons can flow to the metal, until the Fermi levels are the same, without depleting the bulk of the semiconductor. Hence no barrier is formed, or it is sufficiently thin that electron tunnelling can easily occur, and the contact is ohmic (fig. 5.7(d)). However, Wasse et al\textsuperscript{(80)} have shown that barriers of varying height can still be present in diodes contacted by this method, and it is reasonable to assume that if the alloying is not uniform over the area of the slice, some sections may have a better electron reservoir than others. If this is the case, large diodes are more likely to include areas with a good reservoir than the small samples, whereas the latter may be either good or bad, in keeping with the observations.

A Schottky barrier at the cathode contact gives rise to a high cathode field. Shaw et al\textsuperscript{(78)} have shown that cathode fields in the range \(3.5-15 \text{ kV cm}^{-1}\) cause non-linearity in the \(i/V\) characteristic and reduce \(V_T^e\) and \(i_p\). Wasse et al\textsuperscript{(80)}, using diodes contacted by the same procedure as used in this investigation, have obtained barrier heights of 0.26-0.37 eV, which would produce cathode fields in the above range. Experiments on the change in barrier height with pressure
FIGURE 5.7 Schematic representation of formation of Schottky barrier and ohmic contact
in GaAs and GaSb\(^{82}\) show that the height increases with pressure, at a rate close to the movement of the lowest conduction band state, since this leads to an increase in \(\chi\) in Fig. 5.7. Under these circumstances, the depletion region will increase; if domains are nucleated in the high field region within the barrier, then the threshold field will decrease with increasing pressure as observed.

This interpretation is complicated by the fact that the barrier will filter out cool electrons from the metal\(^{83}\) and that this effect is dependent on pressure through changes in \(m^*\) as well as the barrier height, \(V_B\). Assuming thermal emission is the dominant conduction mechanism, we have from the Richardson equation for the current density, \(j\),

\[
j = \frac{4\pi e k_B^2 m^* T^2}{h^3} \exp\left(\frac{-eV_B}{k_B T}\right)
\]

(5.1)

The effective mass, which increases with pressure as discussed earlier, and the barrier height act in opposite ways, but, since \(V_B\) appears in the exponent, it has a much larger effect than \(m^*\). An exact analysis, however, requires a computer simulation of domain formation as a function of electrode filtering. Nevertheless, since it has been shown that the presence of a barrier decreases the measured threshold voltage, it appears that the increase in field at the cathode is the dominant effect or that the two are additive. Since the width of the barrier is only \(\approx 0.5\mu m\), the voltage across the bulk will hardly be affected in samples of the length (129\(\mu m\)) used. This is shown by a plot of the resistance at threshold against pressure, in which there is very good agreement between type 1 and 2 diodes.

The results of Shaw et al\(^{78}\) show that \(F_T\) decreases with increasing cathode field and, since this is proportional to the square root of barrier height, this agrees with the qualitative argument above. For a certain barrier height, the cathode field is proportional to \(n^4\)
(n = carrier concentration), and it should therefore increase, and hence \( F_T \) decrease, more quickly with pressure for a more highly doped sample. This is in fact borne out by comparing the carrier concentrations used by Wasse et al\(^{(73)}\) and Hutson et al\(^{(6)}\) with that used here. The former used \( n^{2} \times 10^{15} \text{cm}^{-3} \), and, if we include the calibration correction discussed earlier, their rate of change of \( F_T \) with pressure is not very different from the type 2 data. However, the data of Hutson et al\(^{(6)}\) using \( n^{2} \times 10^{16} \text{cm}^{-3} \), a carrier concentration an order of magnitude greater than that used in the present study, decreases more rapidly with pressure in qualitative agreement with the above model. This is another indication that the factor controlling \( F_T \) is the cathode field and not the width of the barrier, since the latter is inversely proportional to \( n^{1/2} \), and so increases less quickly for samples with higher \( n \).

On a qualitative basis, therefore, the observed behaviour of type 2 samples can be explained on this model of the formation of a barrier at the metal-semiconductor contact and it would seem that great care is necessary in the interpretation of high pressure high field results in which the effect of contacts may predominate. The results also indicate that any inhomogeneity in the effective doping below the contacts, arising for instance in the alloying process or during dicing, may result in an ohmic contact or barriers of varying heights, depending on the area of the diode used.

5.5. DISCUSSION OF TYPE 1 RESULTS

5.5.1. Low-field Mobility

From considerations given previously, the type 1 pressure variation is assumed to be due to band structure changes and the data will be compared in this section with theoretical variations in order
to obtain information about the band structure at atmospheric pressure. Any theory which explains the experimental results under normal conditions must also be consistent with the variation under pressure. Thus the pre-threshold i/V measurements provide three basic parameters whose pressure dependence must be fitted to theory - low-field mobility, threshold field for oscillations and the peak drift velocity.

The variation of low-field mobility with pressure for GaAs has been measured previously and agrees well with the expected theoretical variation. This, therefore, provides an indication of the reliability of the present results. The variation of threshold field and peak velocity will be compared with that obtained from velocity-field characteristics calculated using a Monte-Carlo procedure (see Section 2.4).

The low-field mobility is determined by the scattering mechanism in the central, \( \Gamma_{1c} \), valley and the effective mass of electrons in that valley. At room temperature polar optical mode scattering is dominant and the mobility, \( \mu \), is proportional to \( m^* \). The effective mass increases with pressure from \( k_p \) theory as given by equation (3.1) and hence the mobility decreases. The change in \( m^* \) with pressure has been measured directly to 15 kbar, using the magnetophonon effect (77), and the increase obtained of 0.7% kbar\(^{-1}\) was in good agreement with \( k_p \) theory. The Hall mobility measurements of Pitt and Lees (16) were also consistent with this rate of increase up to 25 kbar when transfer to the \( X_{1c} \) valleys begins to occur.

Since the carrier concentration in the \( \Gamma_{1c} \) valley is constant below 25 kbar, the resistivity, \( \rho \), is simply inversely proportional to \( \mu \). The variation of \( \rho \) with pressure is shown in Fig. 5.5 and is seen to be in good agreement with the expected variation.

5.5.2. Calculation of Velocity-Field Characteristics

Fawcett et al. (23) calculated the velocity-field characteristics of
GaAs using a Monte-Carlo method. For these calculations the $X_{1C}$ valleys were taken to be 0.36 eV above the $\Gamma_{1C}$ minimum and their effective masses assumed to be $0.35m_0$. A value of $0.067m_0$ was used for the effective mass at the bottom of the $\Gamma_{1C}$ valley and non-parabolicity was incorporated through the relation

$$\frac{\hbar^2 k^2}{2m^*} = E(1 + \alpha E)$$

(5.2)

where

$$\alpha = \frac{1}{E_g} \left(1 - \frac{m^*}{m_0}\right)^2$$

(5.3)

and $E_g$, the energy gap, is 1.52 eV at 0K. The scattering mechanisms considered were polar optical and acoustic in the central minimum, non-equivalent intervalley scattering between the $\Gamma_{1C}$ and $X_{1C}$ valleys, and polar optical, acoustic and equivalent intervalley scattering in the $X_{1C}$ valleys. Expressions for the scattering rates for these processes are given in reference (23) (also see Section 2.2).

The parameters required to determine the scattering rate in the $\Gamma_{1C}$ valley due to PO scattering are the polar phonon temperature, $\Theta$, of 410K, and the static and high frequency dielectric constants, $\varepsilon_0 = 12.53$ and $\varepsilon_\infty = 10.82$ respectively. For acoustic phonon scattering the acoustic deformation potential was taken as 7eV, the velocity of sound, $s = 5.22 \times 10^5$ cm s$^{-1}$ and the density of GaAs is 5.37 g cm$^{-3}$. In the $X_{1C}$ valleys, an acoustic deformation potential of 7eV was also used, and the coupling constant for scattering between the valleys was taken to be $1 \times 10^9$ eVcm$^{-1}$ ($\Theta = 347K$) by comparison with silicon.

As discussed in Section 2.2.3 the v/F characteristic is sensitively dependent on the value of the intervalley coupling constant and Fawcett et al (23) presented curves for $\Gamma_{TX}$ ranging from $2 \times 10^8$ to $2 \times 10^9$ eVcm$^{-1}$ ($\Theta = 347K$) (see Fig. 2.6). A value of
$1 \times 10^9 \text{eVcm}^{-1}$ gave best agreement with the available experimental data.

More recently, Fawcett and Herbert\(^{(26)}\) have calculated intervalley coupling constants using screened and unscreened pseudopotentials (see Section 2.2.3). The calculations show that scattering due to phonons other than the LO phonon is important, especially in the screened situation. The LO, TO and LA phonons have very similar energies and are therefore grouped together with the average temperature of 344K, while the TA phonon temperature is 113K. This low energy of the TA phonon means that it has a high contribution to the scattering even though its coupling constant may be low, since the phonon occupancy will be high and the scattering rate is also inversely proportional to the phonon energy (see equation (2.5)).

The velocity-field characteristic for GaAs was then re-calculated using an average phonon temperature of 344K for the LO, TO and LA phonons and including as a separate process scattering due to the TA phonons. Best agreement with experimental data was obtained with an unscreened coupling constant of $1.1 \times 10^9 \text{eVcm}^{-1}$ for the high energy phonon, since coupling to the TA phonons is relatively unimportant in this case, but again the screened effective value of $4.3 \times 10^8 \text{eVcm}^{-1}$ (effective phonon temperature = 344K) could not definitely be ruled out.

5.5.3. Velocity-Field Characteristics as a Function of Pressure

In collaboration with P J Vinson of Surrey University the calculations of the \(v-F\) characteristic as described above have been repeated for various pressures using the computer program developed by Dr W Fawcett for GaAs. The model of the band structure and scattering mechanisms is identical to that described by Fawcett et al\(^{(23)}\) and Fawcett and Herbert\(^{(26)}\). The direct band gap, \(E_g\), was assumed to increase at a rate of $10 \times 10^{-6} \text{eVbar}^{-1}$ and the pressure
The coefficient of the $\Gamma$-X sub-band gap was taken as $-11 \times 10^{-6}$ eV bar$^{-1}$.

The increase of the effective mass, $m^*$, with pressure was obtained from equation (3.1) with $E_p = 22.41$ eV and $\Delta = 0.305$ eV, using the pressure coefficient of the band gap as above. The non-parabolicity factor, $\xi$, having a value $0.573$ eV$^{-1}$ at atmospheric pressure, is also changed with the band gap from equation (5.3).

As in the calculations of Fawcett and Herbert$^{(26)}$ the calculations were performed including two separate processes for intervalley scattering. At atmospheric pressure the coupling constants calculated by Fawcett and Herbert$^{(26)}$, for both unscreened and screened scattering, were used. As discussed in Section 2.2.3 the coupling constants are assumed to decrease as the sub-band gap decreases with pressure. When the $\Gamma_{1c}$ and $X_{1c}$ valleys are at the same energy scattering will take place from the symmetry points and the group selection rules will then be applicable, i.e. scattering will be due to the LO phonon only. Therefore at the pressure required for this situation, viz. $32.7$ kbar on the basis of the above pressure coefficients, the coupling constant is assumed to be the screened value of $3.4 \times 10^8$ eV cm$^{-1}$ for $\theta = 346$ K for the LO phonon$^{(26)}$, coupling to the TO, LA and TA phonons being taken as zero. The coupling constant for each process has therefore been assumed to vary linearly with pressure between the atmospheric pressure values appropriate to $k \neq 0$ and the values for $k = 0$.

Velocity-field characteristics are built up from a series of values of the average electron velocity at certain field strengths. As can be seen from the typical set of points shown in Fig. 5.8 a certain amount of scatter is present, particularly at the onset of the NDM, which limits the accuracy of the value of the threshold field to about $\pm 5\%$. However, the peak velocity is a better defined value.
FIGURE 5.8 Typical points obtained from Monte-Carlo velocity-field calculations.
which can be more easily obtained from the v-F characteristic.

5.5.4. Comparison of Velocity-Field Characteristics with Experiment

The theoretical results will be discussed in terms of an "effective" coupling constant, except where necessary. This is obtained by combining the scattering rates due to the two separate scattering processes and subsequently calculating a pair of values of coupling constant and phonon temperature which in a single process would give the same total scattering rate.

From equations (2.5) and (2.6) the average scattering rate for scattering between valleys 1 and 2 is given by

\[ \lambda_{12} = k_1 \frac{Z_{12}}{\omega_{12}} \left( N_0 + \frac{1}{2} \right) \]

\[ = k_1 \frac{Z_{12}}{\omega_{12}} \frac{\exp \frac{\theta_{12}}{k_B T} + 1}{\exp \frac{\theta_{12}}{k_B T} - 1} \]  \hspace{1cm} (5.4)

Since \( \theta_{12} = k_B \theta_{12} \), where \( \theta_{12} \) is the characteristic phonon temperature, equation (5.4) can be written

\[ \lambda_{12} = k_1 \frac{Z_{12}}{\theta_{12}} \left( \exp \frac{\theta_{12}}{k_B T} + 1 \right) \frac{\exp \frac{\theta_{12}}{k_B T} - 1}{\exp \frac{\theta_{12}}{k_B T} + 1} \]  \hspace{1cm} (5.5)

The total scattering rate, \( \lambda_{12}^T \), is then obtained by adding the scattering rates due to the two separate processes. Hence the effective coupling constant, \( \Xi_{12}^T \), is calculated from

\[ \Xi_{12}^T = \left[ \lambda_{12}^T \frac{\theta_{12}^T}{\omega_{12}^T} \left( \exp \frac{\theta_{12}^T}{k_B T} - 1 \right) \right] \]  \hspace{1cm} (5.6)

where \( \theta_{12}^T \) is the equivalent phonon temperature, which may be chosen
to be any convenient value. To allow comparison with other data, $\theta_{12}^T$ has been taken here as the average of the LO, TO and LA phonons, i.e. 344K. For this phonon temperature, the values for the screened and unscreened coupling constants at atmospheric pressure give effective coupling constants of $4.32 \times 10^8 \text{eVcm}^{-1}$ and $1.11 \times 10^8 \text{eVcm}^{-1}$ respectively.

The results of a series of calculations are shown in Table 5.1.

Table 5.1

<table>
<thead>
<tr>
<th>P (kbar)</th>
<th>$\Delta E$ (eV)</th>
<th>$E_{TX}$ (eVcm$^{-1}$)</th>
<th>$F_T^0$ (kVcm$^{-1}$)</th>
<th>$v_p^0$ ($\times 10^3 \text{cms}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>1.7</td>
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<td>$8.77 \times 10^8$</td>
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<td>1.7</td>
</tr>
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<td>3.1</td>
<td>1.9</td>
</tr>
<tr>
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<td>$4.32 \times 10^8$</td>
<td>3.2</td>
<td>1.5</td>
</tr>
<tr>
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<td>0.25</td>
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<td>0.40</td>
<td>$4.32 \times 10^8$</td>
<td>3.3</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
<td>$3.78 \times 10^8$</td>
<td>3.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Values of threshold field and peak velocity were obtained at zero pressure and 10kbar pressure in order to compare with the experimentally observed variation, i.e. an increase in $F_T$ of about 6-7% and virtually no change in $v_p$. As can be seen, the variation of coupling constant discussed in the previous section, starting with either screened or unscreened values, leads to a decrease in $F_T$ and $v_p$ in disagreement with experiment. Keeping the coupling constant unchanged to 10kbar (a situation in disagreement with the theory) does lead to a slight increase in $F_T$ for the screened situation, but $v_p$ shows a large decrease. As discussed in Section 2.2.2 the variation of $\Delta E$ may be less important if its atmospheric pressure value is larger. However,
with \( \Delta E = 0.40 \text{eV} \), which is within the experimental determinations (see Section 10.2), \( T_p \) and \( v_p \) again decrease to 10 kbar.

It can therefore be seen that with the reasonable choice of parameters and the usual band structure model it is not possible to obtain the experimentally observed variation of both \( T_p \) and \( v_p \).

5.5.5. Influence of \( L_{1c} \) Minima.

Although the \( L_{1c} \) mobility decreases with pressure, it would appear that the decrease in \( \Delta E \) is the dominant parameter in the "2-level" situation. In order to try and reduce the influence of the decreasing sub-band gap, the possibility (discussed in detail later) was considered that the \( L_{1c} \) valleys and not the \( X_{1c} \) valleys are the next highest subsidiary minima. If the \( L_{1c} \) valleys are placed a few tens of meV below the \( X_{1c} \) valleys at atmospheric pressure, the positive pressure coefficient of the former would reduce the rate of decrease of \( \Delta E \) for the first few kbars, although at high pressures the situation would be as before, with the \( L_{1c} \) valleys having moved well out of the way (see, for example, Fig. 5.9). Depending on the relative coupling constants, electrons will be distributed at high electric fields between all three levels (\( \Gamma, L, X \)). As discussed in Section 2.3 coupling to the \( L_{1c} \) valleys might be expected to be weaker than that to the \( X_{1c} \) valleys and it is therefore possible that pressure could cause a transition from a "3-level" situation (as proposed for InP) to a "2-level" situation.

The \( L_{1c} \) valleys (4 in number) were therefore included in the computer program used earlier, with a pressure coefficient of \( 5 \times 10^{-6} \text{eVbar}^{-1} \) and the same effective mass and acoustic deformation potential as the \( X_{1c} \) valleys. The usual scattering processes within the \( L_{1c} \) valleys were considered as well as intervalley scattering between the \( L \) and \( X \) valleys with a coupling constant of
FIGURE 5.9 Possible variation of conduction band minima in GaAs with pressure.
$5 \times 10^8 \text{eVcm}^{-1}$ ($\theta=350\text{K}$). Initially, only one phonon was used for both $\Gamma$-$L$ and $\Gamma$-$X$ scattering and the $\Gamma$-$L$ coupling constant was assumed constant with pressure, since $\Delta E(\Gamma-L)$ decreases only slowly. Results for various positions of the valleys and different coupling constants are shown in Table 5.2.

*Table 5.2*

<table>
<thead>
<tr>
<th>$P$ (kbar)</th>
<th>$\Delta E(\Gamma-L)$ (eV)</th>
<th>$\Delta E(\Gamma-X)$ (eV)</th>
<th>$\xi_{\Gamma L}$ (eV cm$^{-1}$)</th>
<th>$\xi_{\Gamma X}$ (eV cm$^{-1}$)</th>
<th>$\xi_{LL}$ (eV cm$^{-1}$)</th>
<th>$E_{T'}$ (kV cm$^{-1}$)</th>
<th>$v_P$ (x10$^7$ cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>2.8</td>
<td>1.6</td>
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<td>3.1</td>
<td>1.75</td>
</tr>
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<td>$5 \times 10^8$</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
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<td>0.38</td>
<td>$8 \times 10^8$</td>
<td>$1 \times 10^9$</td>
<td>$5 \times 10^8$</td>
<td>3.4</td>
<td>1.9</td>
</tr>
<tr>
<td>10</td>
<td>0.28</td>
<td>0.27</td>
<td>$8 \times 10^8$</td>
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<td>$5 \times 10^8$</td>
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<td>1.6</td>
</tr>
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<td>0.36</td>
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</tr>
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<td>$5 \times 10^8$</td>
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<td>1.6</td>
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<tr>
<td>10</td>
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<td>0.29</td>
<td>$1.6 \times 10^8$</td>
<td>$1 \times 10^9$</td>
<td>$1.8 \times 10^8$</td>
<td>3.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Equivalent Phonon Temperature 350K

It can be seen that with the $L_{1c}$ valleys 0.05eV below the $X_{1c}$ valleys at 0.38eV, large $\Gamma$-$L$ coupling constants are required to obtain threshold fields near the experimental value of $3.3$ kV cm$^{-1}$. With pressure the peak velocity again drops rapidly as in the "2-level" case. However, if the $L_{1c}$ and $X_{1c}$ valleys are placed at 0.38eV and 0.40eV respectively above the $\Gamma_{1c}$ valley (not in disagreement with Pitt and...
Lees\(^{(16)}\) high pressure determination of \(\Delta E\) a large increase in \(F_T\) could be obtained with a virtually constant peak velocity. Empirically, it was found that a ratio of \(\Gamma-X\) to \(\Gamma-L\) coupling constants of about six is required. Although the increase in \(F_T\) is much larger than that observed experimentally, it would appear that, by a suitable choice of coupling constants, a variation of \(F_T\) and \(v_p\) much closer to experiment could be obtained than was possible when only the \(\Gamma\) and \(X\) valleys were considered. P J Vinson (private communication) has obtained closer agreement with the experimental results using coupling constants with a ratio of 4:1 and has extended the results to higher pressures. The \(\Gamma-L\) coupling constant used is of the same order as that determined directly for \(\Gamma-L\) transitions in GaSb\(^{(84)}\) \((3 \times 10^8 \text{eVcm}^{-1})\). This band structure model has also been shown to produce an atmospheric pressure velocity-field characteristic in reasonable agreement with that measured experimentally.
6.1. INTRODUCTION

The effect of uniaxial stress on the resistivity and threshold field of GaAs was first measured by Shyam, Allen and Pearson\(^{(85)}\) in 1966, results being quoted for stresses of up to 25 kbar. These measurements were repeated in 1970 by Harris, Moll and Pearson\(^{(64)}\) in the stress ranges 0-11 kbar for \(<100>\) samples and 0-19 kbar for \(<111>\) samples, significantly different results being obtained with little comment by the authors. No calibration measurements are given in either paper, although at the stress levels quoted the hardened steel anvils used will deform, complicating the applied stress. Also, the stylus type of apparatus used means that any slight misalignment will cause a large departure from uniaxial stress. The results are interpreted as providing evidence that the \(X_{1c}\) valleys are the next highest minima above the \(\Gamma_{1c}\) valley since larger changes are observed for \(<100>\) stress than \(<111>\) stress. However it is not clear how well the data support this interpretation since the rate of movement of an \(X_{1c}\) valley under \(<100>\) stress is larger than the rate of movement of an \(L_{1c}\) valley under \(<111>\) stress (see Fig. 3.1) and the latter may only produce large changes at the highest values of stress where the data are probably least reliable.

In view of the above uncertainties and in the light of the possibility (Chapter 5) that the \(L_{1c}\) valleys may be slightly below the \(X_{1c}\) valleys, a careful study has been made of a number of diodes under \(<100>\) and \(<111>\) stress. Uniaxial stress should allow a more direct determination of the positions of the higher-lying minima, particularly the \(L_{1c}\) minima, which are inaccessible to hydrostatic pressure.
6.2. SAMPLE DETAILS

The characteristics of the crystals used are given in Table 6.1.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Orientation</th>
<th>Type</th>
<th>n(x10$^{15}$ cm$^{-3}$)</th>
<th>thickness (µm)</th>
<th>ρ (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S268A</td>
<td>&lt;100&gt;</td>
<td>epitaxial</td>
<td>1.4</td>
<td>129</td>
<td>0.6</td>
</tr>
<tr>
<td>S268B</td>
<td>&lt;100&gt;</td>
<td>layer</td>
<td>0.8</td>
<td>124</td>
<td>1.04</td>
</tr>
<tr>
<td>S381E</td>
<td>&lt;100&gt;</td>
<td>on n$^+$</td>
<td>2.0</td>
<td>114</td>
<td>0.46</td>
</tr>
<tr>
<td>S273A</td>
<td>&lt;111&gt;</td>
<td>substrate</td>
<td>~20</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>G2-1397</td>
<td>&lt;111&gt;</td>
<td>bulk</td>
<td>2.0</td>
<td>500</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The epitaxial layers were all grown at STL by vapour epitaxy. The <111> epitaxial crystal was grown at the same time as some <100> samples. Impurities are incorporated at different rates depending on the growing face, higher carrier concentrations normally resulting for <111> samples. The bulk <111> crystal was obtained from Monsanto.

Each slice had evaporated Ag-Sn contacts on the upper and lower faces and dice of approximately 0.05 x 0.05 cm were either cleaved or wire-sawn off. The orientation of the crystals was checked by X-ray Laue photography.

i/V plots and low-field resistivity measurements were made using the circuits of Section 4.3 and uniaxial stress was applied with the apparatus described in Section 4.2.

6.3. RESULTS
6.3.1. <100> Stress

The i/V plot at atmospheric pressure was approximately linear up to threshold with good agreement in the forward and reverse directions.
It is therefore unlikely that the onset of oscillations is controlled by contact effects. However, the effect of any barrier that may be present would be expected to be small under uniaxial stress compared to hydrostatic pressure due to the much slower movement of the $F_{1c}$ minimum.

The variation of $F_T$ and low-field resistivity with $<100>$ stress are shown in Figs. 6.1 and 6.2. It can be seen that the results are in reasonable agreement with those of Harris et al\(^\text{(64)}\), both disagreeing markedly with the earlier results of Shyam et al\(^\text{(85)}\). Although the scatter in the threshold field data, indicated by the error bars, is considerable, there is no doubt about the overall shape of the curve. There is little change for the first kbar or so followed by a sharp decrease. At 5-6 kbar the threshold field goes through a minimum, $F_T$ increasing beyond this pressure until the oscillations ceased at about 9 kbar. The low field resistivity is obtained from the gradients of the $i/V$ plots and also from potentiometer measurements. This is constant until about 5-6 kbar when it increased rapidly up to the limit of measurement. The diodes fractured between 9 and 10 kbar. Some results were checked with decreasing pressure and no irreversible changes were observed indicating little structural damage.

The variation in low-field resistivity can be explained by the transfer of electrons to one of the $X_{1c}$ valleys as it moves towards the $F_{1c}$ minimum with stress (see Section 6.4.2). It would therefore be expected that larger changes in the attainable stress range would be observed if the experiment was performed at a higher temperature, since more transfer would then occur for a given value of stress. Stress was therefore applied with the sample holder well immersed in a beaker of boiling water and the results are shown in Fig. 6.3.
FIGURE 6.1 Normalised threshold field vs. $\langle 100 \rangle$ stress for GaAs
FIGURE 6.2 Normalised resistivity vs. \(\langle 100\rangle\) stress for GaAs
FIGURE 6.3 Normalised resistivity vs. ⟨100⟩ stress for GaAs at high temperature
Large changes were indeed observed, the resistivity increasing by about ten times by ~6.5 kbar, the highest stress obtained before the samples fractured. This variation in resistivity could not in fact be accounted for by the above theory. To ascertain whether this was a band structure effect a sample was stressed to 4 kbar at room temperature (with no change in resistivity) and then heated at constant stress. The results are shown in Fig. 6.4. It can be seen that the resistivity increases fairly linearly to about 340K mainly due to the decrease in mobility of the conduction electrons with temperature. Beyond this temperature the resistivity increased rapidly even when the temperature had virtually stopped rising at about 355K. On cooling the resistivity decreased slowly but did not return to its original value, an irreversible increase of about 65% having occurred. Examination of the sample under the microscope revealed no apparent change in appearance. It was therefore concluded that the results were not due to band structure changes but were probably due to some irreversible change such as the introduction of dislocations under the influence of temperature and stress. The lower breakage stress observed at this temperature may also be a consequence of this effect. The formation of dislocations has been observed during thermocompression bonding of GaAs diodes (86-87) and these results could indicate that uniaxial stress measurements at elevated temperatures will be extremely difficult. The results also show that bonding should be performed at the lowest temperature and stress possible, in agreement with the results of Hartnagel and Weiss (87), although the lower stresses used during bonding will permit higher temperatures than those obtained here.

6.3.2. <111> Stress

No measurements of the variation of threshold field with <111> stress were possible for the epitaxial samples due to the occurrence of avalanche breakdown at threshold.
FIGURE 6.4 Normalised resistivity vs. temperature for a GaAs sample under 4 kbar of stress
However, measurements were made on the bulk material and the results are shown in Fig. 6.5, the scatter in the data being indicated by the error bars. The $i/V$ plot at atmospheric pressure showed some curvature to threshold, although $F_T$ was within ±10% of the theoretical value of 3.3 kV cm$^{-1}$ and the curves were approximately symmetrical for both directions of applied voltage. Although this does not necessarily indicate the absence of a barrier, since the same barrier could be present at each contact of the bulk material, it is more likely that the curvature is due to a very inhomogeneous carrier concentration, leading to difficulties in interpretation of the results. $F_T$ decreased on application of stress down to a minimum value of $\sim 0.77 F_T(0)$ at $\sim 12$ kbar, beyond which an increase in $F_T$ was observed. The highest stress reached before fracture was $\sim 16$ kbar, at which stress the amplitude of the oscillations was very small.

The low-field resistivity obtained from the gradient of the $i/V$ plots is plotted against stress in Fig. 6.6. It can be seen that the resistivity increases immediately on the application of stress. This is probably due to the loss of electrons to a deep impurity level below the $T_{1c}$ minimum. This was confirmed by the measurement of the low-field resistivity for decreasing temperature for approximately zero stress. The reciprocal of the resistivity normalised to room temperature is plotted in Fig. 6.7 and it can be seen that the resistivity increases immediately with decreasing temperature, indicating the presence of a level deep in the forbidden gap. The mobility of electrons in the conduction band increases with decreasing temperature and therefore if the number of carriers was remaining constant the resistivity would decrease instead of increasing as observed.

The variation of low-field resistivity with stress for the
FIGURE 6.5 Normalised threshold field v.s. $\langle 111 \rangle$ stress for bulk GaAs samples
FIGURE 6.6 Normalised resistivity vs. $\langle 11 \rangle$ stress for bulk GaAs samples
FIGURE 6.7 Variation of resistivity and carrier concentration with temperature for bulk GaAs samples.
epitaxial samples, which do not exhibit carrier trap-out, is shown in Fig. 6,8. Samples broke at or below 12 kbar and the experimental points for one sample are shown in the figure together with a theoretical curve (see Section 6.4.3). This measurement was obtained using the potentiometer measuring circuit of Section 4.3.3. It can be seen that beyond ~5 kbar the resistivity begins to increase and the results showed a steady continuous increase in resistivity up to the point of fracture with no sudden discrete changes (which might indicate small pieces of the sample flaking off). These results are not in disagreement with the results of Harris et al.\textsuperscript{(64)} in the stress range under comparison. However, larger changes might have been expected at the higher stress levels quoted\textsuperscript{(64)} although, as noted earlier, it is in this region that the results will be least reliable. It should also be noted that in their previous paper\textsuperscript{(85)} oscillations were reportedly obtained up to 25 kbar of <100> stress, in gross disagreement with the later results and those of the previous section.

6.4. DISCUSSION OF LOW-FIELD RESISTIVITY RESULTS

6.4.1. Bulk <111> Samples

Most bulk GaAs has non-shallow impurity levels in the forbidden gap and the carrier concentration in these materials is therefore strongly dependent on temperature. Donor activation energies of the order of 0.2 eV have been reported\textsuperscript{(72)}. The variation of resistivity with temperature shown in Fig. 6.7 indicates the loss of carriers in the samples used here to an impurity level below the $T_{1c}$ minimum at atmospheric pressure.

At low temperatures, when $n \ll N_A^{-1} N_D$, equation (A.5) (see Appendix A) becomes

$$n = \frac{N_c}{g} \left[ \frac{N_D^{-1} N_A}{N_A} \right] \exp \frac{-\varepsilon_A}{k_B T}$$

(6.1)
FIGURE 6.8 Normalised resistivity vs. $\langle 111 \rangle$ stress for epitaxial GaAs sample.
and therefore the slope of a plot of $\log_n$ vs. $\frac{1}{T}$ yields the activation energy of the impurity. A plot of this form is also presented in Fig. 6.7 assuming a $T^{-1}$ mobility variation. The low temperature slope of this curve gives $E_A = 0.14 \pm 0.02$ eV. The slight curvature near room temperature is probably due to the onset of the "exhaustion" region, i.e. $n$ is approaching $N_D - N_A$.

Impurity levels are normally considered to be "associated" with a particular band state, i.e. the main contribution to the wave function of an electron in the field of an impurity centre comes from that state. Shallow hydrogenic levels have pressure coefficients similar to their associated band state and hence their activation energy is independent of pressure. Levels deep in the forbidden gap often remain fixed to the valence band with pressure. Camphausen et al. observed various pressure coefficients for levels at different positions in the band gap of Si, the deeper levels moving more like the valence band and the shallower levels having small pressure coefficients relative to the conduction band. Impurity levels have also been observed which are shallow or even degenerate with the bottom of the conduction band but which have pressure coefficients completely unlike that of the lowest conduction band state. These are assumed to be associated with higher-lying minima and, although they may be deep with respect to their associated state, have very similar pressure coefficients.

Impurity levels in the band gap of GaAs have been attributed to the $X_\Gamma$ levels. This was confirmed for a level $\sim 0.15$ eV below the $T_{1c}$ minimum by a study of the temperature dependence of the piezoresistance and the photoluminescence intensity, the latter indicating indirect transitions. If a similar level is present in the samples used here, the increase of resistivity with $<111>$ stress...
(Fig. 6.6) will therefore be due to the loss of electrons from the conduction band as the activation energy increases. Under <111> stress the activation energy will increase at a rate equal to one-third of the \( r-X \) hydrostatic pressure coefficient, assuming the level moves with the \( X_{1c} \) valleys. From equation (A.3) the carrier concentration is given by

\[
n = N_c \exp\left(\frac{E_F - E_c}{k_B T}\right)
\]

(6.2)

Assuming \( E_F \) is constant, the resistivity normalised to atmospheric pressure is given by

\[
\frac{\rho}{\rho_0} = \exp\left(-\frac{E_c - E_c(0)}{k_B T}\right)
\]

(6.3)

The gradient of Fig. 6.6 will therefore give the rate of movement of \( E_c \) away from the Fermi level. For \( n < N_D - N_A \), the Fermi level will be constant with respect to the impurity level and the gradient will then be the rate of change of activation energy. For stresses above 9-10 kbar \( d(E_c - E_D)/dX \) is found to be \( ~3.5(\pm1) \times 10^{-6} \text{ eVbar}^{-1} \), being approximately equal to \( 1/3[\Delta E(T_{1c} - X_{1c})/dP] \). (The error bars indicate the scatter in the data but the results for each individual run were linear above about 9 kbar). For lower stresses \( n < N_D - N_A \), as indicated by the \( \rho-T \) graph (Fig. 6.7) and the Fermi level may therefore be moving upwards towards the impurity level resulting in the curvature of Fig. 6.6. In the absence of information on \( N_D \) and \( N_A \) this cannot be put on a more quantitative basis. Similar curvature is noticeable in the low pressure region of the hydrostatic pressure measurements of Sladek\(^{93}\), the curvature being less pronounced in pressure measurements at lower temperatures.

The value of \( d(E_c - E_D)/dX \) obtained is in good agreement with that of \( 3.4 \times 10^{-6} \text{ eVbar}^{-1} \) obtained by Harris et al\(^{64}\). The resistivity measured by these authors, increased linearly on the application of stress. Their samples, however, had larger activation energies and
lower carrier concentrations ($\approx 10^{14}$ cm$^{-3}$) and the $\log_e n$ vs. $\frac{1}{T}$ graph showed no signs of saturating.

Harris et al$^{(64)}$ assumed that the impurity level remained fixed with respect to the valence band, but this will introduce little error since the movement of the $X_{1c}$ valleys and associated levels under $\langle 111 \rangle$ stress is small compared to the movement of the $\Gamma_{1c}$ minimum. However, if the level was associated with the valence band it would be expected to split into two states due to the splitting of the heavy and light hole valence bands. The movement of the upper state would be non-linear$^{(48)}$ resulting in a decreasing gradient, $d(E_{\text{c}} - E_{\text{p}})/dX$, with stress, contrary to observations. Similarly it is unlikely that the level is associated with the $L_{1c}$ valleys since again splitting would occur. Although the observations can be reasonably explained by assuming the level is associated with the $X_{1c}$ valleys, this cannot be regarded as conclusive since admixtures of wavefunctions from other states could possibly combine to give the observed variation.

Harris et al$^{(64)}$ assumed that the valence band and hence the impurity level did not move with stress and obtained a value of the deformation potential, $\varepsilon_d^0$, describing the movement of the $\Gamma_{1c}$ minimum, of 7.8 eV. In the present case the movement of the impurity level with the $X_{1c}$ valleys, although small, should be taken into account in the determination of $\varepsilon_d^0$. The rate of change of the activation energy may be written from equation (3.8)

\[
\frac{d(E_{\text{c}} - E_{\text{p}})}{dX} = -(s_{11} + 2s_{12})[\varepsilon_d^0 - (\varepsilon_d^X - \varepsilon_u^X)]
\]

(6.4)

where $\varepsilon_d^X$, $\varepsilon_u^X$ are the deformation potentials of the $\langle 100 \rangle$ minima and $\varepsilon_d^0$ is the deformation potential of the $\langle 000 \rangle$ minimum. Assuming the values of the elastic constants of GaAs to be$^{(46)}$ $s_{11} = 1.173 \times 10^{-6}$ bar$^{-1}$ and $s_{12} = 0.366 \times 10^{-6}$ bar$^{-1}$, the deformation potential ($\varepsilon_d^0 - \varepsilon_d^X - \varepsilon_u^X$), describing the rate of change of the ($\Gamma_{1c} - X_{1c}$) sub-band gap with

- 100 -
pressure, is found from the results of Fig. 6.6 to be \(-8(\pm 2)\) eV. From the pressure coefficient of the \(X_{1c}\) valleys relative to the valence band \((-1\times 10^{-6}\) eV bar\(^{-1}\)) and using equations (3.8) and (3.9) to give

\[
\frac{d(E_c^X - E_v)}{dP} = -3(s_{11} + 2s_{12}) \left( \frac{\xi_{d}^X - a}{\xi_{d}^X - a} \right) \quad (6.5)
\]

\((\xi_{d}^X - a)\) is found to be \(\approx 0.8\) eV. From equation (6.4) the value of \((\xi_{d}^X - a)\) is found to be \(-7(\pm 2)\) eV in agreement with the previous results. Since the movement of the valence band is expected to be small by comparison with Si and Ge\(^{47}\) the error introduced by the previous authors by assuming \(a=0\) will have little effect.

6.4.2. \langle 100\rangle Samples

Assuming the change in low-field resistivity with \(\langle 100\rangle\) stress (Fig. 6.2) is due to a redistribution of electrons between the \(\Gamma_{1c}\) and \(X_{1c}\) valleys, the resistivity, \(\rho\), can be written

\[
\rho = \frac{1}{e(n_1\mu_1 + n_2\mu_2)} \quad (6.6)
\]

where \(n_1\), \(\mu_1\), \(n_2\), \(\mu_2\) are the numbers and mobilities of the electrons in the lower and upper valleys respectively and the total number of electrons, \(n = n_1 + n_2\) is constant.

The resistivity at atmospheric pressure, \(\rho_0\), is given by

\[
\rho_0 = \frac{1}{e(n_1\mu_1)} \quad (6.7)
\]

and therefore

\[
\frac{\rho}{\rho_0} = \frac{(n_1 + n_2)\mu_1}{n_1\mu_1 + n_2\mu_2}
\]

\[= \frac{n_2}{n_1} \quad \frac{1 + \frac{n_2}{n_1}}{1 + \frac{n_2\mu_2}{n_1\mu_1}} \quad (6.8)
\]
Since \( n_2 \mu_2 / n_1 \mu_1 << 1 \), equation (6.8) becomes

\[
\frac{\rho}{\rho_0} = 1 + \frac{n_2}{n_1} \quad (6.9)
\]

If \( E_F \), the Fermi energy, is well below the conduction band, an exponential distribution of electrons exists as given by equation (3.4).

Hence, from equations (6.9) and (3.4) the normalised resistivity is given by

\[
\frac{\rho}{\rho_0} = 1 + \frac{N_2}{N_1} \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (6.10)
\]

The density-of-states ratio, \( N_2/N_1 \), for the \( X_{1c} \) valleys has been determined to be 45(15). \(<100>\) stress causes one \( X_{1c} \) valley to be lowered in energy with respect to the other two and therefore \( N_2/N_1 \) is reduced by a factor of three. From equation (6.10) and the results of Fig. 6.2 a variation of \( \Delta E \) with stress can be determined and is shown in Fig. 6.9 (for \( N_2/N_1 = 15 \)). Unfortunately, the scatter in the data is large, but a mean line through the points can be drawn with a gradient of \(-25(\pm10) \times 10^{-6} \text{eVbar}^{-1}\). The variation in resistivity with stress obtained from this line is shown in Fig. 6.2 and it can be seen that the results fit the expected variation reasonably well.

From equation (3.11) the variation of \( \Delta E \) with \( <100>\) stress, \( \xi \), can be written

\[
\frac{d\Delta E}{d\xi} = -(s_{11} + 2s_{12})(\frac{\xi}{d} + \frac{1}{3} \frac{\xi}{d} - \frac{2}{3} \frac{\xi}{d}) (s_{11} - s_{12}) \quad (6.11)
\]

For hydrostatic pressure, \( P \), the variation of \( \Delta E \) from equation (3.8) is

\[
\frac{d\Delta E}{dP} = -3(s_{11} + 2s_{12})(\frac{\xi}{d} + \frac{1}{3} \frac{\xi}{d} - \frac{2}{3} \frac{\xi}{d}) \quad (6.12)
\]

Equation (6.11) can therefore be written

\[
\frac{d\Delta E}{d\xi} = \frac{1}{3} \frac{d\Delta E}{dP} - \frac{2}{3} \frac{\xi}{d} (s_{11} - s_{12}) \quad (6.13)
\]
FIGURE 6.9 Variation of sub-band gap with stress for GaAs
From the hydrostatic pressure results of Chapter 5 and the measurements of Pitt and Lees\(^{(16)}\), \(\frac{d\Delta E}{dP}\) is taken as \(-11.5 \times 10^{-6}\ \text{eVbar}^{-1}\). Assuming the values \(s_{11} = 1.173 \times 10^{-6}\ \text{bar}^{-1}\) and \(s_{12} = -0.366 \times 10^{-6}\ \text{bar}^{-1}\) and using \(\frac{d\Delta E}{dP} = -25(\pm10) \times 10^{-6}\ \text{eVbar}^{-1}\), \(X_u^X\) is obtained from equation (6.13) as \(21(\pm9)\) eV, which is in agreement with the value of \(16.8\) eV obtained by Harris et al\(^{(64)}\). These authors assumed that \(\Delta E\) at atmospheric pressure was \(0.33\) eV but this may be determined as the intercept in Fig. 6.9. The present results give \(\Delta E\) at 1 bar as \(0.31(\pm0.07)\) eV.

Although the errors on the values of \(X_u^X\) and \(\Delta E\) are large, the considerations of Chapter 5 (and the results of reference \((16)\)) would indicate that the preferred values lie towards the upper limits.

The value of \(N_2/N_1\) used here was obtained from the results of Pitt and Lees\(^{(16)}\) from paired values of \(\Delta E\) and \(N_2/N_1\). These results could also be fitted with values of \(\Delta E = 0.40\) eV and \(N_2/N_1 = 85\), which would be more consistent with the calculations of Chapter 5. The uniaxial stress results have therefore been replotted in Fig. 6.9 for \(N_2/N_1 = 85/3 = 28.33\) which illustrates the dependence of the results on the density-of-states ratio. The value of \(\Delta E(\Gamma_{1c}^{X}-X_{1c}^{X})\) thus obtained is \(0.33(\pm0.07)\) eV.

Using the value of \((\Xi_{d}^{0}-\alpha)\) obtained as \(-7(\pm2)\) eV, \((\Xi_{d}^{X}-\alpha)\) may now be obtained from equations (6.11) or (6.12) as \(-5(\pm5)\) eV. This is in agreement with the value of \(-5.1\) eV \((\alpha=0)\) obtained by Harris et al\(^{(64)}\) although the errors are very large.

A possibility which must not be overlooked is that the increase of resistivity with stress may be due to the transfer of electrons to an impurity level lying below the \(X_{1c}\) minima and degenerate with the \(\Gamma_{1c}\) valley at atmospheric pressure. In this case, the number of electrons in the \(\Gamma_{1c}\) valley, \(n_r\), and the impurity level, \(n_c\), is given strictly by equations (A.1) and (A.4) but if the Fermi level is
sufficiently below the conduction band edge, $E_c$, and the impurity level energy, $E_D$, it may be approximated by

$$n_t = \frac{g N_t}{N_c} \exp \left( \frac{E_c - E_D}{k_B T} \right)$$

(6.14)

where $N_t$ is the impurity level density, $N_c$ is the density of states in the conduction band and $g$ is the degeneracy of the impurity level. $N_c$ is given by equation (A.2) as

$$N_c = 4.83 \times 10^{15} \left( \frac{m^*}{m_o} \right)^{3/2} \times 3/2$$

$$= 4.24 \times 10^{17} \text{cm}^{-3} \quad \text{for} \ m^* = 0.067 m_o \ \text{at} \ 295K$$

and is assumed to be independent of stress since the variation of $m^*$ is very small. $g$ is 3 for the $X_{1c}$ valleys, or 6 including spin degeneracy. From equations (6.9) and (6.14) a variation of $(E_c - E_D)$ with stress may be obtained if $N_t$ is known. Since $N_t$ may or may not be related to $N_o$, the number of donors, a family of curves may be obtained for different values of $g N_t$. Fig. 6.10 is plotted assuming $g N_t/N_c = 1/10 \left( N_t \approx 10^{16} \text{cm}^{-3} \right)$ which is not an unreasonable value for $N_t$. The intercept of this line at atmospheric pressure gives 0.19(±0.07)eV as the energy of the trap above the $X_{1c}$ valley. If the largest trap depth obtained by Vyas et al (52) of 0.14eV below the $X_{1c}$ valleys is added to this value, a similar value of $\Delta E$ is obtained as previously from Fig. 6.9. However it might be expected that the variation with stress of the trap depth would be non-linear (94), at low stress the rate of variation being less than that of the conduction band edge with which it is associated. This would tend to make $\Delta E$ smaller at atmospheric pressure, which is unlikely in the light of previous measurements and the considerations of Chapter 5. This fact, together with the threshold field measurements to be described in the next section would seem to make it more probable that the
FIGURE 6.10 Variation of trap depth with stress
electrons are transferring to the satellite valleys rather than impurity levels associated with them.

6.4.3. Epitaxial <111> Samples

The results of Fig. 6.8 can similarly be explained by the redistribution of electrons between the \( \Gamma_{1c} \) minimum and an \( L_{1c} \) valley which decreases in energy with stress. However, since the observed increase in resistivity is small, only \( \sim 5\% \), the effect of the change in effective mass on the resistivity must be considered. The rate of movement of the \( \Gamma_{1c} \) minimum with uniaxial stress is one-third the rate of movement caused by hydrostatic pressure and a simple extrapolation on this basis gives \( \frac{dm^*}{dx} \approx 0.2\% \text{ kbar}^{-1} \). However uniaxial stress also causes the heavy hole and light hole bands at the top of the valence band to split, the rate of increase of the direct energy gap, \( E_g \), with stress, \( x \), being given by

\[
\frac{dE_g}{dx} = \frac{1}{3} \frac{dE_g}{dp} + \frac{d}{2\sqrt{3} s_{44}}
\]  

(6.15)

where \( \frac{dE_g}{dp} \) is the rate of increase of \( E_g \) with hydrostatic pressure which is \( \sim 11 \times 10^{-6} \text{eV bar}^{-1} \). Taking values of \( d = -6.0 \text{ eV} \) \(^{63}\) and \( s_{44} = 1.584 \times 10^{-6} \text{ bar}^{-1} \) \(^{46}\) for GaAs, \( \frac{dE_g}{dx} \) is \( \sim 0.75 \times 10^{-6} \text{ eV bar}^{-1} \) which from equation (3.1) results in an effective mass increase of about \( 0.05\% \text{ kbar}^{-1} \), assuming the mass is determined by the direct gap to the upper valence band. This small increase is confirmed by the resistivity data in the 0 to 5 kbar range which is virtually constant. The measurements of Pollak and Cardona\(^ {63}\) also show that \( E_g \), and hence \( m^* \), change little from 0-10 kbar. Due to the quadratic dependence of \( E_g \) on \( x \) given by equation (3.16), \( E_g \) is virtually unchanged at 14 kbar.

An idea of the effective mass in the \( L_{1c} \) valleys may be obtained by comparison with Ge, using a similar technique to that used by Fawcett and Herbert\(^ {26}\) for InP. The transverse mass, \( m_t \), is
calculated from the energy gaps at the L point from

\[ \frac{m_0}{m_L} = 1 + \frac{p^2}{2E_2} \left( \frac{E_2'}{E_1'} - \frac{E_2'}{E_2} \right) \]  

(6.16)

where \( p^2 = 23 \text{ eV} \)\(^{(26)} \), \( E_2 \) is the \( (L_{1c}-L_{3y}) \) gap in GaAs of 3.05 eV\(^{(108)} \), \( E_1' \) and \( E_2' \) are the \( (L_{3c}-L_{3y}) \) gaps in Ge (5.4 eV) and GaAs (6.4 eV) respectively \(^{(95)} \). Equation (6.16) gives \( m_L = 0.135m_0 \). The longitudinal mass, \( m_L \), is more difficult to determine but an estimate may be made by assuming that the anisotropy factor is the same in GaAs as in Ge, i.e. 19.4\(^{(96)} \). This gives \( m_\parallel = 2.62m_0 \). The density-of-states effective mass in one \( L_{1c} \) valley is then obtained from

\[ m_{L*} = \left( m_\parallel \frac{m_L^2}{m_0} \right)^{1/3} = 0.4m_0 \]  

(6.17)

Hence, the density-of-states ratio is given by

\[ \frac{N_L}{N_\Gamma} = \left( \frac{0.4}{0.066} \right)^{3/2} = 15 \]

Using this value for \( N_L/N_\Gamma \) in equation (6.10) in conjunction with the results of Fig. 6.8, the variation of \( \Delta E(\Gamma_{1c}-L_{1c}) \) with <111> stress shown in Fig. 6.9 is obtained. The main source of error is the measurement of the sample size which would lead to a consistent overestimate or underestimate of the applied stress. The error lines have been drawn to take account of this and any error arising from the potentiometer measuring system. The results lie in a straight line, the gradient of which is \(-14.5(\pm 1.5) \times 10^{-6} \text{ eV bar}^{-1} \). The variation in resistivity with stress obtained from this line is shown in Fig. 6.8 and it can be seen that the results fit the expected variation very well.

From equation (3.12) the change in the sub-band gap to the \( L_{1c} \) valleys with <111> stress, \( X \), is given by

\[ \frac{d\Delta E(\Gamma_{1c}-L_{1c})}{dX} = -\left( s_{11} + 2s_{12} \right) \left( \varepsilon_{L_{1c}} \frac{1}{3} \eta_{d}^{3} u_{d}^{3} \varepsilon_{L_{1c}} \right) \frac{1}{3} \eta_{d}^{3} u_{d}^{3} \]  

(6.18)
For hydrostatic pressure the variation of \( \Delta E(L_{1c}^{L} - L_{1c}^{L}) \) is

\[
\frac{d\Delta E(L_{1c}^{L} - L_{1c}^{L})}{dP} = -3(s_{11}^{L} + 2s_{12}^{L})(\varepsilon_d L_{1c}^{L} E_{L_{1c}^{L}}^L o_{L_{1c}^{L}}^L)
\]

Equation (6.19) can therefore be written

\[
\frac{d\Delta E}{d\varepsilon} = \frac{1}{3} \frac{d\Delta E}{dP} - \frac{1}{3} \frac{L_{1c}^{L}}{E_{L_{1c}^{L}}^L}
\]

It is very difficult to measure \( (d\Delta E(L_{1c}^{L} - L_{1c}^{L}))/dP \) in GaAs because of the proximity of the \( X_{1c} \) valleys which decrease in energy with pressure. However, the pressure coefficient relative to the valence band of the \( L_{1c} \) minima in most of the III-V compounds is \( 5 \times 10^{-6} \text{ eVbar}^{-1} \) and it is reasonable to assume this value for GaAs. The pressure coefficient of the \( \Gamma_{1c} \) valley is \( 11 \times 10^{-6} \text{ eVbar}^{-1} \) relative to the valence band and so \( (d\Delta E(\Gamma_{1c}^{L} - L_{1c}^{L}))/dP \) would be expected to be \( -6 \times 10^{-6} \text{ eVbar}^{-1} \). Since most of the movement under uniaxial stress is due to the splitting of the \( L_{1c} \) valleys, the above assumptions will cause little error. Using \( \frac{d\Delta E}{d\varepsilon} = -14.5(\pm 1.5) \times 10^{-6} \text{ eVbar}^{-1} \), \( E_{L_{1c}^{L}}^L \) is obtained from equation (6.20) to be 22(\pm 3) eV, which is in agreement with the value of 18.95eV\(^7\) for the \( L_{1c} \) valleys in Ge. \( E_{\Gamma_{1c}^{L}}^L \) is obtained from equations (6.18) or (6.19) as \( -10(\pm 3) \text{ eV} \), being in good agreement with the Ge value of \( -10.07 \text{ eV}^{47} \).

The sub-band gap, \( \Delta E(\Gamma_{1c}^{L} - L_{1c}^{L}) \) is given by the intercept of Fig. 6.9 as 0.32(\pm 0.03) eV and from Chapter 5 it would seem that the upper limit is to be preferred. Within the experimental error of the low-field uniaxial stress measurements it would appear that the \( X_{1c} \) and \( L_{1c} \) minima are at approximately the same energy. The positions of these minima are discussed more fully in Section 10.2.

The possibility that the increase in resistivity may be due to the transfer of electrons to an impurity level associated with the \( L_{1c} \) minima may be considered in a similar manner to the \( <100> \) results. Thus the variation of \( (E_D^{L} - E_T^{L}) \) with \( <111> \) stress in Fig. 6.10 is
plotted assuming $gN_e/N_c = 1/10$. Again, assuming a reasonable trap
depth $\approx 0.13eV$ below the satellite valleys for $n = 10^{16} \text{ cm}^{-3}$ material, a similar value of $AE$ is obtained to that from Fig. 6.9.

6.5. DISCUSSION OF HIGH FIELD RESULTS

6.5.1. <100> Samples

The shape of the $F_x/\langle 100 \rangle$ stress curve of Fig. 6.1 is as might be expected from the decrease in $AE$, the threshold field going through a minimum as in the hydrostatic pressure measurements and the oscillations ceasing at high stresses. From the low-field resistivity measurements it can be seen that approximately 50% of the electrons have transferred to the satellite valleys at $\approx 9kbar$ when the oscillations ceased, which is in good agreement with the hydrostatic results. However the minimum in $F_x$ occurs at $\approx 6kbar$ and $AE$ at this pressure is $\approx 0.15eV$. This value is larger than that in the hydrostatic case although since the density-of-states ratio is smaller a smaller sub-band gap might have been expected. Indeed from Fig. 6.2 it can be seen that only about 5% of the electrons have transferred at this pressure. However the discussion in Chapter 5 of the variation of the high field properties with hydrostatic pressure indicates that qualitative deductions may not be very meaningful. In fact, the variation of coupling constant with only one $X_{1c}$ valley may be significantly different from that with all three valleys and also the absence of equivalent intervalley scattering in the former case will also be important. It is therefore possible that the variation of high field properties with uniaxial stress may be rather different from that with hydrostatic pressure and full Monte-Carlo calculations are now required for a detailed theoretical analysis. It may be that the uniaxial results provide a further different constraint on the value of the coupling constant at atmospheric
pressure. Certain modifications to the Monte-Carlo computer program will be required since the F-X scattering can no longer be considered to be isotropic.

There may be some significance in the fact that $F_T$ does not decrease very much for the first kbar or so. This was also observed by Harris et al.\(^{64}\) but it is more marked in the present results. It is possible that this is a result of the $X_{1c}$ valleys beginning to split. In fact the splitting is only $\sim k_B T$ after 1 kbar and so in this region the hot electrons may still be excited to all three valleys. However a similar result might be obtained if the $L_{1c}$ valleys were slightly below the $X_{1c}$ valleys at atmospheric pressure, since the experimental evidence for the position of the former is not conclusive (see Section 10.2). If this were the case $\Delta E$ would not begin to decrease rapidly until the $X_{1c}$ valley came below the $L_{1c}$ valleys. It is unlikely that Monte-Carlo calculations could differentiate between these two possibilities since the changes in $F_T$ in this region are so small.

6.5.2. $<111>$ Samples

The decrease in threshold field observed with $<111>$ stress in the bulk samples (Fig. 6.5) is much larger than would be expected at first sight from the decrease in $\Delta E$. Also, by comparison with the type 2 hydrostatic results, the increase in any barrier with stress would not be expected to produce such a large decrease in $F_T$. The decrease is probably due to a non-uniform carrier concentration or possibly an inhomogeneous loss of electrons across the slice to a non-uniform impurity level density.

However, it should be pointed out that the band structure at high $<111>$ stresses may correspond to an ideal 3-level oscillator situation with weak coupling to one $L_{1c}$ valley situated considerably below six other valleys ($L_{1c}$ and $X_{1c}$) with strong coupling. The threshold field
might now be much lower than in the normal situation by comparison with the InP 3-level oscillator calculations\(^{(11)}\). The large decrease in \(F_T\) in the first kbar or so for \(<111>\) stress compared to \(<100>\) stress may also be an indication that the \(\Gamma_{1c}\) valleys are below the \(X_{1c}\) valleys at atmospheric pressure. Again, Monte-Carlo calculations with the band structure model proposed in Chapter 5 are required for a better understanding of the variation of high-field properties with uniaxial stress.

The increase in \(F_T\) observed at high stresses may reflect a bulk property of the material. This rise is not due to the \(nZ\) product approaching its critical value since, from the low field results, \(nZ\) has only decreased to about \(3 \times 10^{13}\ \text{cm}^{-2}\) at 12-13 kbar. It is probable that the reason for this increase is the same as that for the increase observed with \(<100>\) stress. The minimum occurs at about 12 kbar and at this stress \(\Delta E\) is about 0.14 eV (from Fig. 6.9), approximately the same as the value of \(\Delta E\) at the minimum in the \(<100>\) measurements. Similarly, from Fig. 6.8, about 5% of the electrons have transferred to the \(\Gamma_{1c}\) valley at this stress. At \(\approx 16\) kbar, when the amplitude of the oscillations was very small, about 50% of the electrons would have transferred, in agreement with the \(<100>\) results.

6.6. CONCLUSIONS

From the series of uniaxial stress experiments described here several parameters of the band structure of GaAs have been determined. The energy gap to the next highest sets of subsidiary minima have been obtained as \(\Delta E(\Gamma_{1c}-\Gamma_{1c})=0.32(\pm 0.03)\text{eV}\) and \(\Delta E(\Gamma_{1c}-X_{1c})=0.33(\pm 0.07)\text{eV}\). By comparison with the hydrostatic pressure results of the previous chapter, these values are low and therefore the upper limits of the experimental error would be preferred. A possible reason for the low
values may be the presence of a stress gradient in the epitaxial layer. In the case of bulk samples such as those used for calibration this effect may be negligible but for epitaxial samples the layer is close to one anvil which could produce a larger effect. Recent theoretical work at the University of Surrey, incorporating stress gradients, indicates that the resistivity would start to increase at a lower stress and would increase at a slower rate than in the absence of a gradient. This would tend to depress the values of \( \Delta E \) obtained by extrapolation to atmospheric pressure. This may be overcome by using samples grown on semi-insulating substrates and applying stress to the ends of the layer.

Although the exact energies of the \( L_{1c} \) and \( X_{1c} \) valleys are somewhat uncertain, it would appear that both sets are at approximately the same energy with the \( L_{1c} \) valleys slightly below the \( X_{1c} \) valleys. In Chapter 10 this configuration will be shown not to be in contradiction with previous evidence for the positions of these minima.

The values of the deformation potentials of the \( <100> \) valleys obtained are \( \varepsilon_u^{X} = 21(\pm 9) \text{eV} \) and \( (\varepsilon_d^{X} - \alpha) = -5(\pm 5) \text{eV} \). These are in agreement with those of Harris et al.\(^{(64)} \) of \( \varepsilon_u = 16.8 \text{eV} \) and \( \varepsilon_d(\alpha=0) = -5.1 \text{eV} \) but are rather different to the values for the \( <100> \) valleys in Si\(^{(47)} \) \( \varepsilon_u = 8.0 \text{eV} \), \( (\varepsilon_d^{X} - \alpha) = -1.5 \text{eV} \) or Ge \( \varepsilon_u = 8.6 \text{eV} \), \( (\varepsilon_d^{X} - \alpha) = -2.7 \text{eV} \) (J. Lees, private communication). This may be due to the polar nature of GaAs or the fact that the three minima are at the zone edge (X-point) in GaAs while in Si and Ge they are some way in from the zone edge (\( \Delta \)) and are six in number.

For the \( <111> \) valleys, the values obtained are \( \varepsilon_u^{L} = 22(\pm 3) \text{eV} \) and \( (\varepsilon_d^{L} - \alpha) = -10(\pm 3) \text{eV} \). These are in good agreement with the values for the \( <111> \) valleys in Ge of \( \varepsilon_u = 16.95 \text{eV} \) and \( (\varepsilon_d^{X} - \alpha) = -10.07 \text{eV} \).\(^{(47)} \)

The \( <111> \) valleys in both GaAs and Ge are four in number and are
situated at the zone boundary. This very good agreement of the $<111>$ valley deformation potentials indicates that these valleys were probably being observed in the stress range up to 14 kbar. Therefore the $L_{1c}$ valleys must be reasonably close in energy to the $\Gamma_{1c}$ minimum at atmospheric pressure.
7.1. INTRODUCTION

Although there is some controversy about the positions of the higher-lying minima in GaAs and the results of the previous two chapters indicate that the $L_{1c}$ and $X_{1c}$ minima are at approximately the same energy at atmospheric pressure, there is no doubt that at high pressures (above 40 kbar) the $<100>$ valleys are the lowest set of minima in the conduction band. Because of their positive pressure coefficients, the $\Gamma_{1c}$ and $L_{1c}$ valleys will have crossed over the $X_{1c}$ valleys and moved well away at high pressures (see Fig. 5.9). At pressures of 35 to 40 kbar, Pitt and Lees\(^{(16)}\) observed a saturation in the resistivity as the electrons transferred from the $\Gamma_{1c}$ valley to the $X_{1c}$ valleys. Under these conditions, measurements may be made of the properties of the electrons in the $X_{1c}$ valleys which are inaccessible under normal conditions. An attempt has been made here to perform velocity-field measurements as a function of temperature. These results have relevance to the situation existing at high fields in the Gunn effect where the electrons transfer to the subsidiary minima. Even if the $L_{1c}$ minima are slightly below the $X_{1c}$ minima at atmospheric pressure, at high fields electrons will probably be excited to both sets of minima, especially if the $\Gamma-X$ coupling constant is large.

7.2. RESULTS

Several of the high pressure runs of Chapter 5 were continued beyond the cross-over point of the $\Gamma_{1c}$ and $X_{1c}$ minima. Some samples exhibited large resistivity ratios, probably indicating carrier trap-out
to deep impurity levels below the $X_{1c}$ minima by comparison with the results of Pitt and Lees\textsuperscript{(16)}, and leading to difficulty in interpretation of the results in the absence of Hall measurements. One sample had a resistivity ratio at saturation of $\frac{\rho(40)}{\rho(0)}=20$, indicating little or no carrier loss on transfer. $i/V$ plots were made on this sample at a constant pressure of 50 kbar. The temperature was decreased using the modification of the solid-medium apparatus described by Vyas et al\textsuperscript{(52)}, and $i/V$ plots were obtained for various temperatures down to 100K, the results being shown in Fig. 7.1.

### 7.3. ANALYSIS AND DISCUSSION

From the results of Vyas et al\textsuperscript{(52)}, the mobility in the $X_{1c}$ valleys would be expected to increase as the temperature is lowered. The observed increase in resistivity is due to the loss of electrons to an impurity level situated below the $X_{1c}$ valleys. A variation of carrier concentration with temperature was obtained by assuming a mobility variation as sample 4LE149 of reference (52), a sample having a similar room temperature carrier concentration. The low temperature slope of a plot of $\log{\rho}$ against $\frac{1}{T}$ indicated an impurity level activation energy of approximately 0.06eV, in agreement with the shallower level observed previously. The values of $n$ thus obtained were used to calculate the drift velocity, $v_d = \frac{j}{ne}$, which is plotted against electric field for several temperatures in Fig. 7.2.

The experimental curves are seen to be in reasonable agreement with the theoretical calculations of Ruch and Fawcett\textsuperscript{(97)} obtained using a Monte-Carlo method. The saturation of the drift velocity, which is possibly more pronounced in the theoretical curves since they are incorrectly shown not passing through the origin, is not observed experimentally until temperatures of 120K for the range of electric
FIGURE 7.1  i-V plots at 50 kbar for various temperatures.
fields below 8.5 kV cm\(^{-1}\). The values of the drift velocity observed tend to be lower than those predicted theoretically, the discrepancy probably being attributable in part to the assumption of zero carrier loss on transfer, i.e. the room temperature electron concentration transferred to the X\(_{1c}\) valleys may have been over-estimated. It should also be noted that absolute agreement would probably not be expected since two slightly different situations are being compared. The calculated curves were obtained for GaAs at atmospheric pressure and therefore the \(\Gamma_{1c}\) valley was included. Hence the curves are only presented for fields in excess of 3 kV cm\(^{-1}\) since electrons are not present in the satellite valleys for lower fields. The accuracy of the calculations would be expected to be low in this region due to the relatively small number of electrons transferred. At fields \(>9\) kV cm\(^{-1}\) about 60\% of the electrons have transferred in the model used. \(\Gamma-X\) scattering will be present which would tend to reduce the X\(_{1c}\) mobility compared to the situation at high pressures where the \(\Gamma_{1c}\) valley has moved well away in energy. However the predicted curves are not lower than the experimental results which may indicate that equivalent intervalley scattering is dominant in the X\(_{1c}\) valleys at atmospheric pressure, as observed by Vyas et al\(^{52}\) at high pressures. The situation is further complicated by the recent calculations of Neumann et al\(^{98}\) which indicate that the X\(_{1c}\) valleys may be in from the zone edge \((k \approx 0.94k_b)\) at low temperatures. The additional scattering between the extra minima may cause a reduction in mobility. This was not taken into account in the theoretical curves presented here.

The i/V plots of Fig. 7.1 were reversible with temperature as confirmed by allowing the sample to heat up to room temperature and then re-cooling to about 120 K. As the sample was allowed to heat up for a second time a region of negative differential mobility (NDM) was
observed below 250K as shown in Fig. 7.3. During this observation the pressure had been allowed to increase by several kilobars. On re-cooling, the sample fractured preventing confirmation of the result. An attempt was made to explain this result in terms of a superimposed uniaxial stress and transfer of electrons between strain-split <100> valleys. Certainly it is possible that expansion during heating, especially since the pressure was not kept constant, could result in a uniaxial component appearing. However it might be expected to be perpendicular to the plane of the sample, i.e. in the <100> direction and parallel to the direction of the current. In this case, electrons would occupy the longitudinal, heavy mass valley and transfer with increasing field to the transverse, light mass valleys. Although this would not be expected to produce a NDM, it may be possible that the equivalent intervalley scattering between the higher $X_{1c}$ valleys could cause a sufficient reduction in mobility to counteract the lighter effective mass. The stress system in this situation is, however, very complex and it is conceivable that a compressive stress along a radius of the ring could occur, producing a situation more favourable for NDM. Another possible explanation for the effect could be transfer to other higher-lying minima, e.g. $X_{3c}$, although this is unlikely since the electrons in the $X_{1c}$ valleys would not be expected to be significantly heated at the values of electric field used here.

Further attempts were made to repeat the observations by cooling and re-heating samples at various rates at high pressure, without controlling the load. No indications of NDM were observed and the result is therefore included without further speculation, for the sake of completeness and as stimulation for possible further research.
FIGURE 7.3 Observation of NDM at 50 kbar in GaAs.
CHAPTER 8

HYDROSTATIC PRESSURE MEASUREMENTS ON INDIUM PHOSPHIDE

8.1. INTRODUCTION

The conduction band structure of InP shown in Fig. 2.7 was determined from high pressure Hall effect measurements \(^{(29-30)}\) and photoemission data \(^{(39-100)}\). The central \( \Gamma_{1c} \) minimum has an effective mass of \( 0.078m_0 \) \(^{(101)}\) and, under hydrostatic pressure, moves away from the valence band at a rate of \( 9.5 \times 10^{-6} \text{eVbar}^{-1} \). Pitt \(^{(30)}\) found that the Hall data could be fitted assuming effective masses of \( 0.4m_0 \) and \( 0.5m_0 \) for the \( L_{1c} \) and \( X_{1c} \) states respectively and pressure coefficients relative to the valence band of \( +2-3 \times 10^{-6} \text{eVbar}^{-1} \) and \( -2 \times 10^{-6} \text{eVbar}^{-1} \) respectively.

Pitt and Vyas \(^{(102)}\) have recently reported the first measurements of the pressure variation of the threshold field in InP. They obtained two types of variation - one with no change to 40 kbar followed by a large increase (type 1), and also a decrease of about 20% to 20 kbar followed by a rapid increase (type 2). By comparison with the explanation previously proposed for GaAs \(^{(103)}\), (section 5.4), they attributed the type 2 variation to samples having Schottky barriers at the contact and concluded that the true variation of \( F_T \) with pressure in InP was given by the type 1 data. The type 1 \( i/V \) plots had the same characteristics as the GaAs type 1 curves while the type 2 plots were very non-linear and often showed a current saturation without oscillations, the threshold field being taken as the 'knee' in the curve. In order to substantiate the theory that the type 1 data is due to the variation in the bulk properties, the measurements described here have been made using samples with re-grown \( n^+ \) contact layers which should therefore have ohmic contacts. The properties of contacts
8.1. EXPERIMENTAL

The experimental procedure and sample preparation is the same as for GaAs (Section 5.2). The InP\(^+\) crystal (CV 338 supplied by RRE) was grown on an \(n^+ (10^{16} \text{ cm}^{-3})\) substrate of thickness \(\sim \text{320} \mu\text{m}\), the active layer having thickness \(15-18 \mu\text{m}\) and carrier concentration varying from \(2 \times 10^{15} \text{ cm}^{-3}\) at the substrate interface to \(7 \times 10^{14} \text{ cm}^{-3}\) at the cathode. A \(3 \mu\text{m} n^+\) contact layer (\(10^{17} \text{ cm}^{-3}\)) was re-grown on the active layer and Ag-Sn contacts evaporated on each side. 0.05 x 0.05 cm square dices were sawn off the slice, the samples having resistances of approximately 3\(\Omega\).

8.3. RESULTS

The \(i/V\) characteristics at atmospheric pressure was similar to those designated type 1 by Pitt and Vyas\(^{(102)}\), i.e. approximately linear up to threshold with a definite current drop-back with oscillations at \(F_T\) and good agreement for both directions of applied voltage. Allowing for the voltage drop across the relatively resistive substrate (\(R_s \sim 20\)) the threshold field across the active layer was within 15\% of \(10\text{kVcm}^{-1}\) (on the low side) in agreement with the observations of Pitt and Vyas\(^{(102)}\). Data supplied by RRE showed that a sample from part of the slice having a \(2\mu\text{m} 3 \times 10^{15} \text{ cm}^{-3}\) contact layer and Au-Ge contacts had a type 2 characteristic. The curve showed a current saturation, occurring at about \(5\text{kVcm}^{-1}\).

The variation of threshold field with pressure is shown in Fig. 8.1, normalised to atmospheric pressure. The data are the means of three...
runs, the scatter being indicated by the error bars. It can be seen that there is little or no change to about 20 kbar but beyond this pressure \( P \) increases rapidly. The variation in low-field resistivity with pressure is shown in Fig. 8.2. Also included in this data is a potentiometer measurement of the low-field resistivity. The region below 20 kbar is in good agreement with the measurements of Pitt\(^{(29)}\), the increase in resistivity being well explained by the increase in the \( \Gamma_{1c} \) effective mass from \( k \cdot p \) theory. \( \frac{\Delta m^*}{\Delta P} \) has been measured as \( \approx 0.02 \) kbar\(^{-1} \) \((77)\) giving a resistivity increase of \( \approx 0.02 \) kbar\(^{-1} \) assuming \( \mu = m^* \nu^{-3/2} \) for polar optical scattering). Beyond 20 kbar the large increase in resistivity is probably due to the loss of electrons to impurity levels which are degenerate with the \( \Gamma_{1c} \) minimum at atmospheric pressure but emerge into the forbidden gap as the pressure is increased.

8.4. DISCUSSION

Assuming the large increase in resistivity is due to the loss of electrons to an impurity level, the pressure coefficient of the level may be obtained from the gradient of the \( \log_{e} \rho \) vs. \( P \) curve. If the Fermi level is sufficiently below the conduction band edge, the ratio of electrons in traps, \( n_T \), to those in the \( \Gamma_{1c} \) valley, \( n_{\Gamma} \), is given by equation (6.14) as

\[
\frac{n_T}{n_{\Gamma}} = \frac{gN_T}{N_c} \exp \left( \frac{E_C - E_D}{k_B T} \right) \tag{8.1}
\]

This may be written

\[
k_B T \log_{e} n_T = k_B T \log_{e} \frac{gN_T}{N_c} + (E_C - E_D) \tag{8.2}
\]

in which the final term is proportional to pressure. Since \( n_T/n_{\Gamma} = \rho/\rho_o - 1 \), ignoring any change of mobility with pressure, the gradient of \( \log_{e} \rho \) vs. \( P \) yields \( (1/k_B T)(d(E_C - E_D)/dP) \). From Fig. 8.2
FIGURE 8.2 Normalised resistivity vs. pressure for InP
\( \frac{d(E_c - E_p)}{dP} \) is obtained as \( 11(\pm 4) \times 10^{-6} \text{eVbar}^{-1} \). Taking the pressure coefficient of the \( \Gamma_{1c} \) valley as \( 9.5 \times 10^{-6} \text{eVbar}^{-1} \), the impurity level would appear to move at a rate of about \( -2(\pm 4) \times 10^{-6} \text{eVbar}^{-1} \). From the similarity in pressure coefficients the impurity level is probably associated with the \( X_{1c} \) valleys although neither the \( I_{1c} \) valleys nor the valence band can be completely ruled out (see Section 9.4.1). In the absence of Hall measurements, little more information can be deduced about the impurity level. However, assuming that at 25 kbar when trap-out begins the level is slightly above the conduction band edge, the position of the level at atmospheric pressure is approximately 0.5 eV below the \( X_{1c} \) valleys. Similar non-hydrogenic impurities observed in InAs are discussed further in the next chapter.

The threshold field/pressure variations obtained here are in good agreement with the type 1 data of Pitt and Vyas\(^{102}\) up to 20 kbar, indicating that this is a measurement of the bulk properties of InP. A small increase may be present but it is difficult to be sure of this due to the scatter and experimental error. There is certainly no decrease in \( F_T \), which is therefore attributed to the presence of Schottky barriers at the contacts. These results indicate that the decrease in threshold field observed by Pitt and Vyas\(^{102}\) in type 2 samples was indeed a contact effect. This therefore substantiates the proposal (Section 5.4) that the behaviour of type 2 GaAs samples was due to a metal-semiconductor barrier.

The large increase in \( F_T \) observed here beyond 20 kbar may be due to the \( nZ \) product approaching its critical value as the carrier concentration decreases due to trap-out. This critical value, \( (nZ)_{\text{crit}} \), below which a space charge region cannot stabilise in a time less than the transit time, is given by the Kroemer\(^{5}\) criterion as

\[
(nZ)_{\text{crit}} = nZ < \frac{e_r e_s v_d}{4\pi e |\mu_d|} \tag{8.3}
\]
where $\mu_d$ is the differential mobility in the NDM region of the $v$-$F$
characteristic, $\epsilon_r$ is the relative permittivity of the semiconductor and
$\epsilon_s$ is the free space permittivity. In GaAs, $(nZ)^{\text{crit}}$ is $\approx 5 \times 10^{11} \text{cm}^{-2}$
and it has been shown that for $nZ < 10^{12} \text{cm}^{-2}$, $F_T$ increases rapidly.$^{(104)}$
For the InP used here $nZ = 10^{12} \text{cm}^{-2}$ at atmospheric pressure and therefore,
if a similar value of $(nZ)^{\text{crit}}$ holds for InP as for GaAs, only a small
decrease in $n$ is required for $nZ$ to approach the critical value. At
about 33 kbar, when the oscillations ceased, the value of $nZ$ was
approximately $5 \times 10^{11} \text{cm}^{-2}$.

Preliminary calculations have been performed by P J Vinson and
W Fawcett (private communication) on the variation of $F_T$ with pressure
in InP, using the coupling constants and band structure model
described by Fawcett and Herbert.$^{(26)}$ The coupling constants were
assumed independent of pressure using screened effective values of
$1 \times 10^9 \text{eVcm}^{-1}$ ($\Theta = 344 K$) or unscreened values of $2.7 \times 10^9 \text{eVcm}^{-1}$ ($344 K$).
With either value, the calculated variation of $F_T$ was approximately
constant to 40 kbar in good agreement with the experimental results.
It would seem therefore, that a two-level model with strong coupling
between the $P_{1c}$ and $L_{1c}$ valleys, is appropriate for InP (see Section 2.3).
CHAPTER 9

HYDROSTATIC PRESSURE MEASUREMENTS ON INDIUM ARSENIDE

9.1. INTRODUCTION

Under normal conditions InAs exhibits carrier multiplication under the influence of electric fields of about 1kVcm$^{-1}$ (105). This is because the direct energy gap, $E_g$, of 0.36eV at 300K (106) is much smaller than the sub-band gap to the next highest subsidiary minima, assumed to be of L$_{1c}$ symmetry. Therefore, impact ionisation of electron-hole pairs across the band gap is the dominant effect at atmospheric pressure, precluding the observation of electron transfer to the L$_{1c}$ valleys and the Gunn effect.

The conduction band structure of InAs is somewhat uncertain, experimental results for the $\Gamma_{1c}$-$L_{1c}$ sub-band gap including values of 0.70(±0.02)eV (107) and 0.86(±0.05)eV (9) while theoretical estimates are even more varied, lying between 0.89eV and 1.54eV (108-110). The $\Gamma_{1c}$ minimum, which has an effective mass of 0.022m$_o$ (111) and is normally occupied by the conduction electrons, moves away from the valence band under hydrostatic pressure at a rate of 10.0(±0.4) x 10$^{-6}$eVbar$^{-1}$ (112), while the $L_{1c}$ minima are expected to have a pressure coefficient of 6.0(±1.5) x 10$^{-6}$eVbar$^{-1}$ from theoretical results of Camphausen et al (41).

Therefore, under pressure, $\Delta E(\Gamma_{1c}-L_{1c})$ decreases with respect to $E_g$ and so the band structure becomes more favourable for the observation of the Gunn effect. From measurements on In$_{1-x}$Al$_x$As alloys the X$_{1c}$ valleys have been estimated to be 1.46eV above the $\Gamma_{1c}$ minimum (113) and, having a pressure coefficient of -0.1(±1.5) x 10$^{-6}$eVbar$^{-1}$ (41), would not be expected to affect the high field transport in the pressure range considered, unless the coupling to the L$_{1c}$ valleys is very weak.
Smith and Camphausen (9) observed the Gunn effect at 16 kbar at electric fields much higher than the impact ionisation field. They measured the variation of the threshold field for oscillations, $F_T$, with pressure and found that it decreased from $\approx 3.3\text{kVcm}^{-1}$ to $\approx 2\text{kVcm}^{-1}$ at 27 kbar. However, up to 25(±1) kbar, carrier multiplication was present below $F_T$. Monte-Carlo calculations (114) have shown that in InSb the effect of impact ionisation is to modify the $v/F$ curve, decreasing the NDM and increasing $F_T$. Since the amount of carrier multiplication decreases with pressure (generation rate for a given field decreases with pressure) the $F_T$/pressure curve of Smith and Camphausen (9) could be a consequence of this. The gradient of their curve, $dF_T/dP$, is a decreasing function of pressure until, at 25(±1) kbar, it is virtually zero, in agreement with the above considerations. It is unlikely that the decrease in $F_T$ is a contact effect. Apart from the difficulty in making Schottky barriers to narrow-gap semiconductors, such a large decrease would not be expected from comparison with the type 2 results for GaAs.

In the light of the new data on GaAs (103) and InP (102), measurements have been made on InAs (115) to higher pressures than previously in order to eliminate the complications of impact ionisation below the Gunn effect threshold. W Fawcett (private communication) has suggested that a small change in $F_T$ might also be expected in InAs.

9.2. EXPERIMENTAL

The InAs crystals were cut from a nominally undoped polycrystalline slice having $n=2.7 - 3.5 \times 10^{16}\text{ cm}^{-3}$, $\rho=0.011 - 0.007\Omega\text{cm}$, $\mu=20,750 - 24,850\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The slice included several large areas of single crystal so diodes were selected not to include grain boundaries. Part of the slice was polished to a thickness of 60µm and diodes of
approximate dimensions 100-200μm wide and 0.5-1mm long cleaved from it. After degreasing in trichloroethylene, ohmic contacts were made by indium soldering a 0.15mm diameter Cu wire to each end (see Fig. 9.1). (Ohmic contacts are easily made to n-type InAs, probably due to its electron affinity being larger than the work function of most metals). Resistances of the diodes were in the range 2.5-11Ω.

Clover-leaf shaped samples were also prepared for Hall measurements. These were 2mm in diameter and were cut using an ultrasonic drill from part of the slice which had been polished to a thickness of 0.027cm. After degreasing, four ohmic Sn contacts were alloyed to the samples and Au tapes (0.015 x 0.25 mm) and Cu wires pressure welded to the contacts.

High pressure was applied using the solid-medium apparatus described in Section 4.1.3. I/V characteristics were measured using the circuit of Fig. 4.12 (Section 4.3.1) and Hall measurements were made with the techniques of Section 4.3.2.

9.3. RESULTS

The I/V plot at atmospheric pressure was approximately linear up to the onset of impact ionisation, which was marked by a large increase in the current, and was symmetrical for the two directions of applied voltage, indicating reasonable field uniformity and the absence of contact effects. Because of the uncertainty in the electrical length of the diodes, the onset of impact ionisation was taken to occur at 1kV cm⁻¹ and the length determined from the measured avalanche voltage, V_a. This, therefore, gives a lower limit for the length since breakdown must occur at or below 1kV cm⁻¹. The results are shown in Table 9.1. For most diodes, it can be seen that the electrical length lies between the measured z₁ (sample length) and z₂ (distance between
contacts) as expected (see Fig. 9.1). For two diodes (2 and 4) however, this value is rather close to the value of $L_z$, possibly indicating the existence of a high field region.

**TABLE 9.1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R$ (Ω)</th>
<th>$L_1$ (cm)</th>
<th>$L_2$ (cm)</th>
<th>$V_a$ (V)</th>
<th>Electrical length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.5</td>
<td>0.116</td>
<td>0.042</td>
<td>68</td>
<td>0.068</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.110</td>
<td>0.052</td>
<td>54</td>
<td>0.054</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.090</td>
<td>0.020</td>
<td>44.5</td>
<td>0.0445</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.108</td>
<td>0.056</td>
<td>61.5</td>
<td>0.0615</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>0.050</td>
<td>0.024</td>
<td>41</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Under pressure, $V_a$ increased until at ~33 kbar violent oscillations were observed with a definite current drop-back. These oscillations were similar to those observed in GaAs and InP and are interpreted as Gunn oscillations. This threshold voltage, $V_T$, also increased with pressure until oscillations ceased at about 48 kbar. Beyond this pressure the $i/V$ curves showed a current saturation as previously observed in GaAs and InP. An experimental plot from the x-y recorder is shown in Fig. 9.2.

The field for the onset of the instability (either impact ionisation or Gunn oscillations) is plotted against pressure in Fig. 9.3 normalised to atmospheric pressure. The variation of the resistivity and Hall coefficient with pressure obtained from measurements on the clover-leaf samples is shown in Figs. 9.4 and 9.5. The resistivity increased slowly at first due to the increase in the $m_{\text{ec}}$ effective mass, until at about 25 kbar it increased rapidly before undergoing the zincblende to rock-salt phase transformation at about 69 kbar. The
FIGURE 9.1 InAs sample configuration

FIGURE 9.2 Typical experimental I/V plots to 50 kbar
FIGURE 9.3 Normalised threshold field for avalanche breakdown and Gunn effect vs. pressure for InAs samples: - o, 1; +, 2; □, 3; △, 4; x, 5.
FIGURE 9.4 Normalised resistivity vs pressure for InAs.
FIGURE 9.5 Normalised Hall constant vs pressure for InAs.
Hall coefficient remained constant to about 25 kbar when it also increased rapidly before turning over prior to the transition. At the transition the resistivity dropped by seven orders of magnitude, as the conduction became metallic.

9.4. ANALYSIS OF DATA

9.4.1. Hall Data

The Hall constant, $R_H$, is given by

$$R_H = \frac{r}{n_e e}$$

(9.1)

where $r$ is the scattering constant (assumed to be 1.1 and independent of pressure) and $n_e$ is the carrier concentration. The measured variation of $R_H$ with pressure (Fig. 9.5) indicates that the carrier concentration in the $\Gamma_{1c}$ valley begins to decrease rapidly at pressures above 25 kbar. On the basis of the expected pressure coefficients there should be no carrier transfer to the higher-lying valleys in the pressure range considered. It is therefore expected that the decrease in carrier concentration is due to the loss of electrons to impurity levels which are degenerate with the $\Gamma_{1c}$ valley at atmospheric pressure and emerge into the forbidden gap as the pressure increases. The data can therefore be analysed by using Fermi-Dirac statistics in a one-carrier situation. The number of carriers on impurity level sites, $n_t$, is known from the value of the Hall constant and the charge balance equation,

$$N_D - N_A = n_T + n_t$$

(9.2)

From equation (A.4) $n_t$ is given by

$$n_t = \frac{N_t}{1 + \frac{1}{g} \exp \frac{E_D - E_F}{k_B T}}$$

(9.3)

where $N_t$, the impurity density, may or may not be related to $N_D$. From
the known variation of \( n_c \) with pressure, and treating \( N_c \) as an adjustable parameter, a variation of \( E_D - E_F \) with pressure can be obtained (the \( X_{1c} \) state is triply degenerate at the zone boundary and therefore \( g \) is assumed to be 6 including spin degeneracy if the impurity level is associated with this state. The \( L_{1c} \) state is four-fold degenerate).

The position of the Fermi level is calculated from equation (A.1). \( N_c \), which is given by equation (A.2), increases with pressure since \( m^* \) is dependent on \( E_g \) from equation (3.1) with \( \Delta = 0.43\text{eV} \) and \( E_F = 20\text{eV} \), which is assumed to be constant with pressure. The effective mass is taken to be \( 0.022m_0 \) at atmospheric pressure. This equation, which gives the dependence of \( m^* \) at the bottom of the conduction band on pressure, is only valid if the InAs is non-degenerate at atmospheric pressure. The position of the Fermi level in the samples used here is found as follows:

\[
F = \frac{N}{N_c} = \frac{3.5 \times 10^{16}}{7.89 \times 10^{16}} = 0.44
\]

From tables (117),

\[
\frac{E_F - E_C}{k_B T} = -0.65
\]

\[
F_C - E_F = 0.016\text{eV}
\]

i.e. the Fermi level is 0.016eV below the conduction band edge at atmospheric pressure and room temperature. (In fact InAs does not become degenerate until \( n = 6 \times 10^{16} \text{cm}^{-3} \)). Demchuk et al (118) measured the variation of \( m^* \) with pressure for InAs samples having \( n \) between 3.5 and \( 6 \times 10^{16} \text{cm}^{-3} \), and found it agreed well with that calculated using Kane's (21) formula for \( k = 0 \). (\( k = (3\pi^2n)^{1/3} \) gives \( k = 10^6 \text{cm}^{-1} \) for \( n = 3.5 \times 10^{16} \text{cm}^{-3} \) and since \( k \) at the zone boundary is \( \approx 10^8 \text{cm}^{-1} \), \( k/k_{zb} = 0 \)).
Thus, we obtain values of $m^*$, $N_c$ and hence $\epsilon_A$ for various pressures (see Table 9.2 which is an example for $N_e = 7 \times 10^{16} \text{ cm}^{-3}$, $g=6$).

### Table 9.2

<table>
<thead>
<tr>
<th>$P$ (kbar)</th>
<th>$R_H/R_H(0)$</th>
<th>$m^*/m_0$</th>
<th>$N_c \times 10^{17} \text{ cm}^{-3}$</th>
<th>$E_{c-E_F}$ (eV)</th>
<th>$E_{D-E_F}$ (eV)</th>
<th>$\epsilon_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1</td>
<td>0.034</td>
<td>1.52</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>0.037</td>
<td>1.73</td>
<td>0.04</td>
<td>0.121</td>
<td>-0.081</td>
</tr>
<tr>
<td>35</td>
<td>1.65</td>
<td>0.039</td>
<td>1.87</td>
<td>0.05</td>
<td>0.080</td>
<td>-0.030</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
<td>0.041</td>
<td>2.01</td>
<td>0.08</td>
<td>0.055</td>
<td>0.025</td>
</tr>
<tr>
<td>45</td>
<td>50</td>
<td>0.043</td>
<td>2.16</td>
<td>0.14</td>
<td>0.046</td>
<td>0.094</td>
</tr>
<tr>
<td>50</td>
<td>600</td>
<td>0.045</td>
<td>2.31</td>
<td>0.21</td>
<td>0.045</td>
<td>0.162</td>
</tr>
</tbody>
</table>

A family of curves for various values of $N_e$ is shown in Fig. 9.6. For $N_e > 5 \times 10^{16} \text{ cm}^{-3}$ the results lie in a straight line within experimental error, the gradient of the curves being independent of $N_e$ and equal to $12(\pm 2) \times 10^{-6} \text{ eV bar}^{-1}$. This indicates that the impurity level is either associated with the $X_{1c}$ valleys or the valence band from the similarity in pressure coefficients. We cannot differentiate between the various values of $N_e$, since this may or may not be related to $N_D$, but the absence of carrier loss to this level in samples with $n < 10^{18} \text{ cm}^{-3}$ (91) and similar measurements in InSb (119) may indicate that the lower ranges of impurity level density are to be preferred. The movements of the $X_{1c}$ minimum and an impurity level assuming $N_e = 7 \times 10^{16} \text{ cm}^{-3}$ are shown in Fig. 9.7. By linear extrapolation, and assuming $N_e < 10^{18} \text{ cm}^{-3}$, a level $0.8(\pm 0.1)$ eV above the valence band at atmospheric pressure is obtained which is in reasonable agreement with the value of $0.71(\pm 0.03)$ eV obtained by Pitt and Vyas (91). However, in
FIGURE 9.6. Impurity level activation energy vs. pressure.
FIGURE 9.7 Movement of $T_{ic}$ valley and impurity level under pressure
their analysis, these authors assumed \( N_t = N_D \) and \( N_A \) to be small.

The Hall mobility, \( \mu_H \), is given by

\[
\mu_H = \frac{R_H}{\rho}
\]  

(9.4)

and its variation with pressure is shown in Fig. 9.8.

It can be seen that below 25 kbar, \( \mu_p \) decreases in agreement with the variation of \( m^* \) discussed above, assuming \( \mu_H \propto m^*^{-3/2} \) for polar optical scattering. The sharper decrease at 25 kbar corresponds to the region in which electrons are beginning to trap-out to the impurity level. Although the errors are large, since in this region \( R_H \) and \( \rho \) are increasing rapidly, \( \mu_H \) does appear to be lower than expected from the effective mass variation. At 42 kbar, \( n \) has decreased to 1/10 of its original value and so an extra \( 10^{16} \text{cm}^{-3} \) or so scattering centres have been created. Therefore, the observed decrease of \( \mu_H \) by a factor of two from its expected value may be a consequence of this. This would indicate that the impurity level is due to an acceptor impurity since it must become charged on receiving an electron. Therefore, the impurity is probably not associated with the donor impurity which gives rise to the extrinsic carrier concentration. Yonczykowski et al.\(^{120}\) observed a mobility increase with pressure in InSb and attributed this to a decrease in the number of scattering centres; therefore their impurity was probably a donor.

At 42 kbar, the majority of the electrons have been lost to the impurity level and so \( \mu_H \) is fairly constant to 55 kbar. The reason for the sharp drop at this pressure, and the continuing increase in resistivity with no further decrease in \( n \), is not clear but may be due to the nearness of the phase transition.

Taking the pressure coefficient of the \( \Gamma_{1c} \) valley to be \( 10 \times 10^{-6} \text{eVbar}^{-1} \) indicates that the impurity level approaches the
FIGURE 9.8 Normalised Hall mobility vs. pressure for InAs

\[ \frac{\mu_H}{\mu_H(0)} \]

PRESSURE (kbar)

\[ \mu_H \propto m^\frac{3}{2} \]
valence band at $2(\pm 2) \times 10^{-6} \text{eVbar}^{-1}$. From measurements on deep levels in Si$^{(89)}$ it was concluded that the further away from a particular band edge an impurity level lies, the less likely it is to have a similar pressure coefficient, whereas shallow hydrogenic levels tend to move with their associated band state. The level observed here is effectively a deep acceptor $\sim 0.8\text{eV}$ above the valence band which, since the band gap of InAs is only $0.36\text{eV}$, lies in the conduction band. The level appears to have a pressure coefficient similar to that of the valence band when it emerges into the band gap and therefore may be considered to be associated with this state. (The assumption of $g=6$ for the impurity degeneracy factor will have little effect on the calculations, being approximately equivalent to using a different value of $N_t$). From Fig. 9.7 there may be a slight curvature in the slope of $E_D$ as it crosses the $\Gamma_{1c}$ minimum. This could indicate a change in the pressure coefficient of the impurity level due to an increasing admixture of $\Gamma_{1c}$ wavefunctions as observed by Paul$^{(121)}$ in GaSb but measurements of $\varepsilon_A$ below 30 kbar are required to substantiate this. In this case the position of the impurity level at atmospheric pressure is somewhat uncertain, any curvature tending to reduce the value of $E_D$. Recently, higher-lying levels have been observed in CdTe$^{(90)}$ and InAs$^{(91)}$ with positive pressure coefficients which were assumed to be associated with the $L_{1c}$ satellite valleys. It is therefore also possible that the level observed here may be associated with the $X_{1c}$ valleys from the similarity in pressure coefficients.

9.4.2. High Field Data

From Fig. 9.3 it can be seen that up to about 25 kbar $V_a$ increases approximately proportional to $m^*$. The fact that $V_a$ drops below the line of proportionality in the region 15 to 25 kbar may be due to the difficulties of calibration in this region and the presence of non-
hydrostatic stresses (see Section 4.1.5). Above 25 kbar \( V_a \) increases at different rates for the various diodes. For two samples (1 and 5) there is no significant change in the gradient. For the other diodes, \( V_a \) increases more rapidly. This corresponds to the region in which \( \mu_H \) is decreasing below its expected value, possible due to the loss of electrons to the impurity level causing an increase in scattering centres. If the impurity level density varies across the slice, the pressure at which electrons begin to appreciably trap out will also vary and so the various rates of increase of \( V_a \) may be attributable to this. Presumably, for samples 1 and 5, \( \mu_H \) does not drop below its expected value until much higher pressures, as observed by Pitt and Vyas (91). This is substantiated by the fact that the resistivity of samples 1 and 5 is approximately proportional to \( m^*^{3/2} \) until about 35 kbar, indicating no significant loss of electrons below this pressure.

At 34(\pm 2) kbar Gunn oscillations were observed. For samples 1 and 5 \( V_T \) continued to increase linearly like \( V_a \). For diode 3 there was also no significant change in the gradient. However, sample 2 did not exhibit oscillations until much higher fields were applied and impact ionisation continued to occur below \( V_T \). Also, diode 4 did not exhibit the Gunn effect even at higher fields, but exhibited stronger impact ionisation at these fields until destructive avalanche breakdown occurred. These observations could possibly be explained by the existence of a high field region near the anode. The impact ionisation could occur in this region, preventing the rest of the sample from reaching the Gunn effect threshold until much higher fields are applied. \( V_T \) for diode 2 then increased at a slightly slower rate than \( V_a \), which may be due to the effect of the avalanching occurring before the Gunn oscillations.
It would seem, therefore, that the most reliable results are those for diodes 1 and 5, in which the field for the onset of impact ionisation or Gunn oscillations increases approximately linearly over the whole pressure range to about 42 kbar.

The underlying mechanism for both avalanche breakdown and electron transfer to the higher-lying valleys is the same, i.e. the ineffectiveness at high electric fields of the polar phonon scattering mechanism in removing energy from the electrons, and it is therefore reasonable to expect a continuous variation of the threshold field for both processes over most of the pressure range. As discussed in Section 2.2.1, at energies greater than the polar phonon energy the scattering rate decreases with energy, and for a parabolic band this causes the electron temperature to "run away" at a critical field, $F_c$, given by equation (2.1). If this holds for InAs, then at $F_c$ either impact ionisation or the Gunn effect will occur, depending on the relative energy gaps. $F_c$ should be proportional to the effective mass which increases with pressure as discussed in Section 9.4.1. This may give a qualitative idea of the situation but is unlikely to give any quantitative agreement. In InAs the conduction band is strongly non-parabolic and so the effective mass is dependent on electron energy as given by equation (2.3). This leads to a much slower variation of electron temperature with field than the parabolic case (See Section 2.2.1). This discussion has also neglected any effect of decreasing the sub-band gap, $\Delta E(L_{1c} - L_{1c})$. However, this is reasonable since $\Delta E$ is large and the relative change is small and recent measurements of $F_c$ in InP (102) indicate that, to first order, the threshold field is unaffected by changes in the sub-band gap, if this is large. Also, the possibility of variations in coupling constants with pressure means that Monte-Carlo calculations are required and these are discussed in Section 9.5.
The best of the present measurements of the variation of the Gunn threshold field are compared with the previous results of Smith and Camphausen (9) in Fig. 9.9. It is likely that the earlier results were affected by the presence of carrier multiplication and that the true pressure variation of $F_T$ for InAs without the complicating effects of carrier multiplication is given by the present curve in the region 33 to 42 kbar. The highest pressure at which impact ionisation was observed before Gunn oscillations in the present measurements was 32 (±2) kbar, which is slightly higher than that observed previously. It is possible that although the band structure may be favourable for Gunn oscillations at lower pressures, the initial observation was complicated by the occurrence of impact ionisation within the high-field domains. Also, $F_T$ as observed by Smith and Camphausen, is still decreasing slightly at 25 kbar and it is possible that a small amount of carrier multiplication occurred undetected below $F_T$. From Kane's(21) theory, it is expected that the threshold energy for impact ionisation will be about $1.2 \times E_g$, which must be equal to $AE$ at 32 (±2) kbar, assuming this to be the pressure at which the threshold energies for impact ionisation and the Gunn effect are the same. On the basis of the expected pressure coefficients, $AE$ at atmospheric pressure is 0.94(±0.07)eV which agrees with Smith and Camphausen's value of 0.86(±0.05)eV. 1.6(±0.2)kVcm$^{-1}$ is obtained for the value of the threshold field at 33 kbar, which is slightly smaller than that observed by Smith and Camphausen at 27 kbar, but their measurements ignored any inductive component which was probably large due to the short sampling time used. There could, therefore, be agreement within the measuring error, taking account of the pressure difference between the two results. Theoretical analysis tends to indicate slightly higher ($\Gamma_{1c}-\Gamma_{1c}$) gaps at 0K, e.g. Higginbotham et al(110) obtain a result
FIGURE 9.9. Threshold field vs. pressure results compared with previous measurements.
near 1.1 eV. This can be reconciled with our data at 300K, taking a reasonable temperature coefficient for the sub-band gap of about $-2 \times 10^{-4} \text{ eV K}^{-1}$.

Beyond 42 kbar, $V_T$ increased sharply until the oscillations ceased at about 48 kbar. A similar increase before oscillations ceased, observed in GaAs$^{(103)}$ and InP$^{(102)}$ was due to the thermal occupation of the higher valleys at small values of $\Delta E$. Assuming this occurs at $\Delta E=0.1 \text{ eV}, \Delta E(T_1c - 1_1c)$ in InAs would have to be about 0.3 eV at atmospheric pressure, which is very unlikely. The rise in $V_T$ observed here is interpreted as being due to the $nZ$ product approaching its critical value as electrons are lost to the impurity level, as discussed previously for InP (section 8.4). For these samples the $(nZ)_\text{crit}$ value is modified for thin diodes and by the surrounding dielectric, epoxy resin ($\varepsilon_r \approx 2.5$) to

$$(nZ)_\text{crit} = (nZ)_1 \left[ 1 + \frac{\varepsilon_r d'}{\varepsilon_r d} \right]$$

(9.5)

where $(nZ)_1$ is the critical value of the one-dimensional $nZ$ product

$= 5 \times 10^{11} \text{ cm}^{-2}$ for GaAs, $Z$ is the length, $d'$ is the thickness and $\varepsilon_r$ is the relative permittivity of the semiconductor $= 12.5$ for InAs.

Assuming $(nZ)_1$ to be the same for InAs as for GaAs, $(nZ)_\text{crit} = 1 - 2 \times 10^{12} \text{ cm}^{-2}$ for these diodes. At 48 kbar, $n$ is about $10^{14} \text{ cm}^{-3}$, and since $Z$ is 0.04 - 0.07 cm, $nZ$ is $4 - 7 \times 10^{12} \text{ cm}^{-2}$. That this is slightly higher than the calculated value of $(nZ)_\text{crit}$ may be due to the domain velocity in InAs being higher than that in GaAs, assuming the magnitude of the NDM to be of the same order in the two materials. Porowski et al$^{(119)}$ also used the loss of carriers to impurity levels to explain the rise in $R_T$ they observed in InSb (curve C, Fig. 10.1), and showed that this did not occur when the carrier concentration was artificially kept constant by illumination of the diode under test (curve D, Fig. 10.1).
9.5. MONTE-CARLO CALCULATIONS OF VELOCITY-FIELD CHARACTERISTICS

Velocity-field characteristics for InAs have been calculated with the Monte-Carlo method used for GaAs in Section 5.5. Calculations have been performed in the pressure range above 32 kbar in which impact ionisation is eliminated.

9.5.1. Band Structure Model for Monte-Carlo Calculations

The next highest subsidiary minima above the \( \Gamma_{lc} \) minimum are assumed to be of \( L_{lc} \) symmetry, \( \Delta E(\Gamma_{lc} - L_{lc}) \) being taken as 0.85 eV\(^{(9)}\) with a pressure coefficient of \(-5 \times 10^{-6}\) eV bar\(^{-1}\). For some calculations, the \( X_{lc} \) valleys were included at 1.46 eV\(^{(113)}\) above the \( \Gamma_{lc} \) valley, the pressure coefficient of \( \Delta E(\Gamma_{lc} - X_{lc}) \) being \(-11 \times 10^{-6}\) eV bar\(^{-1}\). The effective mass at the bottom of the \( \Gamma_{lc} \) valley is 0.022 m\(_o\)\(^{(111)}\), non-parabolicity being incorporated through equation (5.2), while m\(^*\) of the satellite valleys is assumed to be 0.4 m\(_o\). The direct band gap is 0.36 eV\(^{(106)}\) at 300 K and has a pressure coefficient of \(10 \times 10^{-6}\) eV bar\(^{-1}\)\(^{(112)}\). The increase in the effective mass of the \( \Gamma_{lc} \) valley was obtained from equation (3.1) with \( E_p = 20\) eV and \( \Delta = 0.43\) eV\(^{(43)}\), and \( \alpha \), the non-parabolicity factor, is also changed with pressure, from equation (5.3), its atmospheric pressure value being 2.657 eV\(^{-1}\).

The scattering processes included are identical to those used for GaAs as described earlier. For PO scattering in the \( \Gamma_{lc} \) valley, the polar phonon temperature of 337 K\(^{(123)}\) is used and the values of the dielectric constants are \( \varepsilon_o = 14.55 \) and \( \varepsilon_\infty = 12.25\)\(^{(123)}\). For acoustic phonon scattering the acoustic deformation potential was taken as 7 eV in the \( \Gamma_{lc} \) valley and 10 eV in the \( L_{lc} \) and \( X_{lc} \) valleys by comparison with InSb\(^{(124)}\). The velocity of sound, \( v = 4.0 \times 10^3\) cm s\(^{-1}\) and the density of InAs is 5.66 g cm\(^{-3}\)\(^{(88)}\).
9.5.2. Choice of Coupling Constants and Phonon Temperatures

The values of the phonon temperatures at the L and X points were those given by Stierwalt and Potter (125). At atmospheric pressure the LO, TO and TA phonons are averaged for Γ-L and Γ-X to one high energy phonon. At high pressures when the \( T_{1c} \) and satellite valleys are at the same energy, the intervalley selection rules (22) apply strictly and only the LO and LA phonons cause Γ-L scattering while only the LA phonon participates in Γ-X scattering. The sets of phonons which are averaged are therefore different at atmospheric and high pressures and to try to take account of this the values of the phonons in the pressure region of interest, near 40 kbar, are obtained by linearly interpolating between the two extremes. The values used are, for Γ-L 252 K and 132 K, and for Γ-X 235 K and 187 K. These values are assumed to be constant over the small pressure range involved. This method therefore will not give absolute values of phonon temperatures but when combined with empirically chosen values of coupling constants should give a reasonable estimate of the scattering rate. For the Γ-L scattering \( 1 \times 10^8 \text{ eVcm}^{-1} \) is used for the low energy phonon and values between 1 and \( 3 \times 10^8 \text{ eVcm}^{-1} \) for the high energy process. For Γ-X, values of \( 3 \times 10^8 \) and \( 1 \times 10^9 \text{ eVcm}^{-1} \) are used, respectively, to give stronger Γ-X scattering. The phonon temperatures for L-L, L-X, and X-X scattering were obtained from a Brillouin zone construction which showed that L-L was the same as Γ-X and L-X the same as Γ-L. One phonon only was used for each of these processes, being the average of the high and low energy atmospheric pressure phonons mentioned earlier. By comparison with Ge and Si, the L-L coupling was taken as \( 1.5 \times 10^8 \text{ eVcm}^{-1} \) (205 K), L-X, \( 5 \times 10^8 \text{ eVcm}^{-1} \) (187 K) and X-X, \( 1 \times 10^9 \text{ eVcm}^{-1} \) (196 K) and these values were assumed to remain constant with pressure.
9.5.3. Calculated Velocity-Field Characteristics

Calculations were made initially for pressures of 33 kbar, corresponding to the beginning of the range of observation of Gunn oscillations. The threshold fields at this pressure were between 2.2 and 2.4 kVcm\(^{-1}\) for weak and strong \(\Gamma\)-\(L\) coupling respectively (see Table 9.3). These values are rather high compared to the experimental values. Including the \(X_{1c}\) valleys with \(\Delta E(\Gamma_{1c}-X_{1c}) = 1.46\) eV\(^{(113)}\) at 0 kbar had no effect since transfer to the \(X_{1c}\) valleys was negligible at 33 kbar. Reducing the energy of the \(X_{1c}\) valleys to 0.2 eV above that of the \(L_{1c}\) valleys at 33 kbar (\(\Delta E(\Gamma_{1c}-X_{1c}) = 1.25\) eV at 0 kbar) produced a slightly lower threshold field of 2 kVcm\(^{-1}\) with certain values of the \(\Gamma\)-\(L\) coupling constant.

### Table 9.3

<table>
<thead>
<tr>
<th>(P) (kbar)</th>
<th>(\Delta E(\Gamma-L)) (eV)</th>
<th>(\Delta E(\Gamma-X)) (eV)</th>
<th>(E_{\Gamma-L}) (kVcm(^{-1}))</th>
<th>(E_{\Gamma-X}) (kVcm(^{-1}))</th>
<th>(F_T) (kVcm(^{-1}))</th>
<th>(v_p) (x10(^7) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>0.685</td>
<td>-</td>
<td>4.7x10(^8)</td>
<td>2.4</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.66</td>
<td>-</td>
<td>4.7x10(^8)</td>
<td>2.4</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.66</td>
<td>1.04</td>
<td>3.7x10(^8)</td>
<td>1.5x10(^9)</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>33</td>
<td>0.685</td>
<td>0.885</td>
<td>4.7x10(^8)</td>
<td>1.5x10(^9)</td>
<td>2.2</td>
<td>2.8</td>
</tr>
<tr>
<td>33</td>
<td>0.685</td>
<td>0.885</td>
<td>2.8x10(^8)</td>
<td>1.5x10(^9)</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>33, 38</td>
<td>0.685</td>
<td>0.885</td>
<td>3.2x10(^8)</td>
<td>1.5x10(^9)</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>40, 42</td>
<td>0.65</td>
<td>0.81</td>
<td>3.2x10(^8)</td>
<td>1.5x10(^9)</td>
<td>2.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Equivalent phonon temperature 344K.

The clearest increase in \(F_T\) with pressure was obtained with an effective \(\Gamma\)-\(L\) coupling constant of 3.2 x 10\(^8\) eVcm\(^{-1}\) (\(\theta = 344\)K) for a
2-level model (*) and the curves for pressures of 33 and 40 kbar are shown in Fig. 9.10. However, an increase could also be obtained with a 3-level model (†) as can be seen from the table.

9.5.4. Conclusions

The increase of about 10% in \( F_T \) from 33 to 40 kbar obtained from the Monte-Carlo calculations agrees well with that observed experimentally. Also there is virtually no change in the peak velocity in agreement with the measured i-V curves when allowance is made for the loss of electrons to an impurity level. This variation is obtained with the normal band structure model for InAs involving transfer between the \( \Gamma_{1c} \) and \( L_{1c} \) valleys only. The absolute value of the threshold field is higher than that observed experimentally, but this may be due to the difficulties in obtaining the electrical length discussed earlier. Indeed, the sample configuration used was not ideal for electric field measurements with the badly defined contact regions. With the arrangement used, the field may have been higher near the contacts than in the bulk. However the trend of the variation with pressure would be expected to be valid, particularly since the low-field resistivity varies as expected. Although inhomogeneities in the carrier concentration will tend to reduce both \( v_a \) and \( v_T \), it is not clear that they will do so to the same extent, thus affecting the calculation of the electrical length.

Slightly lower values of \( F_T \) could be obtained in calculations involving the \( X_{1c} \) valleys about 0.2eV above the \( L_{1c} \) valleys at 33 kbar. A similar increase in \( F_T \) with pressure to 40 kbar was obtained as in the 2-level case. Although the energy of the \( X_{1c} \) valleys is not well-known it would seem that there is little justification for their inclusion at this stage.

It would appear that a gradual increase in \( F_T \) with pressure is
FIGURE 9.10 Calculated $v$-$F$ curves for InAs (T-L coupling constant $= 3.2 \times 10^8$ eV cm$^{-1}$)
obtained in InAs above about 30 kbar. The results of Smith and Camphausen\textsuperscript{(9)} are not contradicted by these conclusions since they were over a lower pressure range, but these earlier results should be interpreted as the variation of $F_T$ in the presence of carrier multiplication. Another justification for the present results can be obtained from consideration of InAs$_{1-x}$P$_x$ alloys. From Fig. 9.11 it can be seen that increasing $x$ is approximately equivalent to the effect of pressure. M Young (private communication) has measured $F_T$ for $x$ decreasing from 1. He obtains a gradual decrease from $\sim$9 kV cm$^{-1}$ for InP to values of the order of 2-3 kV cm$^{-1}$ for $x \approx 0.3$. At this alloy composition, avalanche breakdown began to occur before Gunn oscillations.
FIGURE 9.11 Comparison of effects of pressure and alloying.
10.1. INTRODUCTION

The conduction band structure of the III-V semiconductors is characterised by various minima situated along symmetry directions and separated from each other by differing amounts of energy and momentum. The main effect of pressure on these semiconductors is to cause the minima to move with respect to one another. Observation of the variation of certain properties of the materials with pressure can therefore give information on the band structure, by extrapolation back to atmospheric pressure. This method has been used to investigate the band structures of many semiconductors, e.g. InP\textsuperscript{(29-30)}.

Under normal conditions in n-type semiconductors, the electrons occupy the minimum lying lowest in energy. If the minima are close enough in energy and high enough pressures can be applied, direct observation of electron transfer as the minima approach and cross over can be obtained by means of low-field resistivity and Hall effect measurements. This is not always possible as, for example, in InAs, where a phase change occurs before electron transfer can take place. The combination of pressure with high field measurements can allow the effects of inaccessible higher-lying minima to be observed and may also lead to constraints on parameters such as the intervalley coupling constants which are important in high field calculations for Gunn effect devices.

The III-V compounds, apart from alloys (see later) which exhibit the Gunn effect are GaAs, InP, InAs and InSb, the latter two only under the influence of pressure. As can be seen in Fig. 10.1, the early pressure measurements on GaAs\textsuperscript{(73)} (curve E), InAs\textsuperscript{(9)}
FIGURE 10.1 Threshold field vs. sub-band energy gap for the III–V compounds which exhibit the Gunn effect
(curve B) and InSb\(^{(119)}\) indicated that the threshold field decreased with pressure and this was interpreted as being principally due to the decreasing sub-band gap. However, the measurements reported here on GaAs\(^{(103)}\) (curve F), InP (Chapter 8 and reference (102)) and InAs\(^{(115)}\) (curve A) (see Fig. 10.1) show that pressure can initially cause small increases in threshold field. In order to interpret the measurements, therefore, and before any detailed comparison can be made, extensive calculations are required to determine the relative effects of changes in the effective mass, non-parabolicity, sub-band gap and coupling constants with pressure. One interesting recent result involves the effect of hydrostatic pressure on GaAs p→+v diodes\(^{(126)}\). In an attempt to investigate the origin of the controversial sub-linearity in the i-V characteristic of these diodes, the authors observed that the voltage for the onset of the sub-linearity increased by a few per cent to 18 kbar. Since no decrease was observed, it was stated that an explanation of the sub-linearity in terms of intervalley transfer in the GaAs could be eliminated by comparison with the results of Hutson et al\(^{(6)}\). However the observed increase is in agreement with the later results reported here although this does not necessarily confirm the intervalley transfer explanation.

10.2. GALLIUM ARSENIDE

Much information on the band structure of GaAs has been obtained from pressure experiments. For instance, the pressure dependence of the optical absorption edge indicated that the lowest band minimum was of \( \Gamma \) symmetry by comparison with Paul's\(^{(38)}\) Empirical Rule. That this valley is a single, spherical (000) valley was confirmed by the small piezoresistance coefficient for pure material which is virtually
independent of orientation. Evidence for subsidiary minima of 
<100> symmetry was obtained from a change in the pressure dependence 
of the absorption edge at high pressures. High pressure Hall and 
resistivity measurements led to a more accurate determination of 
$\Delta E(\Gamma_{1c} - X_{1c})$. However, the evidence that the $X_{1c}$ valleys are the next 
highest subsidiary minima is still not conclusive.

The combination of high field/pressure measurements with uniaxial 
stress techniques allows other parts of the conduction band to be 
investigated which are normally inaccessible. It has been seen in 
Chapter 5 that a much better fit to the high field hydrostatic pressure 
results for GaAs is possible if the $L_{1c}$ minima are slightly below the 
$X_{1c}$ minima at atmospheric pressure. The uniaxial stress measurements 
of Chapter 6 indicate that both sets of subsidiary valleys are at 
approximately the same energy. The previous evidence that the $X_{1c}$ 
valleys are the lowest will now be reviewed and the presence of the 
$L_{1c}$ valleys compared with other existing experimental data.

Several different types of measurement indicate that a set of 
subsidiary minima exist in GaAs between 0.33 and 0.43 eV above the 
central valley at 300 K. Little indication of the symmetry of these 
subsidiary minima can be obtained from theoretical band structure 
calculations which are inconsistent with each other. For instance, 
from pseudopotential calculations Cohen and Bergstresser\textsuperscript{(95)} obtain 
the $\Gamma$-$L$ separation as 0.3eV and $\Gamma$-$X$ as 0.4eV, while with a different 
form of pseudopotential Jones and Lettington\textsuperscript{(127)} obtain values of 
0.8 and 0.4 eV respectively. The $k.p$ calculation of Pollak et al\textsuperscript{(128)} 
places the $X_{1c}$ and $L_{1c}$ minima at approximately the same energy while 
Collins et al\textsuperscript{(129)} and van Vechten\textsuperscript{(108)} find the $L_{1c}$ minima to be 
0.44 to 0.48 eV below the $X_{1c}$ minima.

Much of the experimental evidence for the assignment of $X_{1c}$
symmetry to the lowest subsidiary valleys is from high pressure measurements. The proposal that the subsidiary minima lay along <100> directions was first put forward by Ehrenreich$^{(18)}$ from an analysis of high pressure resistivity measurements. The high pressure, threshold field measurements of Hutson et al.$^{(6)}$ were also used to substantiate the proposal since the threshold field decreased on the application of pressure. It has been seen in Chapter 5 that this interpretation is not necessarily correct. Indeed, even if the $X_{1c}$ valleys are lowest at some elevated pressure it should not be concluded that this is true at atmospheric pressure, since similar results would be obtained if the $L_{1c}$ valleys were slightly below the $X_{1c}$ valleys at 1 bar (see Fig. 5.9). High field uniaxial stress measurements$^{(64)}$ have also been used to identify the next highest minima. However, one $L_{1c}$ minimum under <111> stress would be expected to decrease in energy at a slower rate than a <100> minimum with <100> stress (see Fig. 3.1) and therefore again if the $L_{1c}$ valleys and the $X_{1c}$ valleys are in close proximity at atmospheric pressure, these results must be interpreted very carefully.

Optical techniques have also been used to obtain information on the subsidiary minima. Balslev$^{(130)}$ measured the infrared absorption due to free carriers in n-type GaAs and showed, by the use of uniaxial stress, that the absorption was due to transitions to minima along the <100> directions. However, transitions to <111> minima would be expected to be very weak, and it has been shown that the $L_{1c}$ minima in GaSb, which are 0.08eV above the $\Gamma_{1c}$ minimum, do not contribute to infrared absorption$^{(131)}$. Balslev obtained a value of 0.43(±0.015)eV for the sub-band gap to the $X_{1c}$ valleys at 80K. Onton et al.$^{(132)}$ used a similar method and obtained a value of 0.483(±0.015)eV at 2K. They estimated that $\Gamma$-$L$ transitions were at least 5 to 10 times weaker than
the corresponding $\Gamma-X$ transitions. James and Moll\textsuperscript{(133)} have performed photoemission measurements on GaAs. The energy distribution of the emitted electrons showed two large peaks which were attributed to the $\Gamma_{1c}$ and $X_{1c}$ valleys from previous evidence. They obtained $\Delta E$ as 0.33eV at 300K and 0.35eV at 77K which are considerably lower than other data. James et al\textsuperscript{(134)} also observed a very small shoulder on the high energy side of the $X_{1c}$ peak which was attributed to $L_{1c}$ minima by comparison with earlier indirect evidence. The $(X_{1c}-L_{1c})$ gap was estimated to be 0.09(±0.02)eV. However, there is no direct evidence as to which valleys give rise to which peaks, and it would be very difficult with this type of measurement to resolve two sets of minima at approximately the same energy.

Pitt\textsuperscript{(30)} has reviewed determinations of $\Delta E$ and showed that its value tends to increase as the temperature is decreased. The results could be fitted approximately by a linear variation of $2.4 \times 10^{-4}$ eV K$^{-1}$ although the variation would be expected to be non-linear below 100K. Most measurements at 300K give values around 0.38eV. From high pressure Hall and resistivity measurements Pitt and Lees\textsuperscript{(16)} obtained 0.38(±0.02)eV. As discussed earlier, extrapolation of hydrostatic pressure data to atmospheric pressure must yield the $(\Gamma_{1c}-X_{1c})$ gap but gives no indication of the position of the $L_{1c}$ minima due to their positive pressure coefficient. From an analysis of high temperature Hall data values of 0.36eV\textsuperscript{(18)} and 0.38(±0.05)eV\textsuperscript{(135)} were obtained.

As can be seen from the above, and was pointed out by Fawcett et al\textsuperscript{(23)}, it is not conclusive that the lowest subsidiary minima lie along $<100>$ directions. A different ordering of these minima would not necessarily conflict with data on GaAs$_{1-x}$P$_x$ alloys\textsuperscript{(18)}. 

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In GaP the $X_{1c}$ valleys are the lowest and the cross-over from the
direct gap in GaAs to the indirect gap occurs at about $x = 0.5^{(136)}$.
The difficulty in extrapolating to find the position of the $X_{1c}$
minima in GaAs lies in the largely unknown bowing (non-linear energy
variation with alloy composition) across the alloy system. By means
of high pressure Hall measurements, Pitt and Stewart$^{(136)}$ have
recently extended the range of determination of the energy of the
$X_{1c}$ minima below the cross-over composition to $x \geq 0.3$. The best
fit to both sets of data indicates $\Delta E(T_{1c} - X_{1c})$ in GaAs as approximately
0.4eV at 300K. Onton and Foster$^{(137)}$, however, at 6K find marked
bowing of the $X_{1c}$ minima in the indirect range and obtain agreement
with the value of 0.48eV$^{(132)}$ for $\Delta E$ at $x = 0$. Pitt et al$^{(138)}$
estimated that in GaP the $L_{1c}$ minima lie approximately 0.2eV above
the $X_{1c}$ minima. Therefore, if the $L_{1c}$ minima in GaAs are slightly
below the $X_{1c}$ minima, they would be expected to cross over in the
region $x \lesssim 0.2$, assuming reasonable bowing. The data on GaAs$_{1-x}$P$_x$
alloys therefore gives no evidence for the position of the $L_{1c}$ valleys.
Information on this could be obtained from uniaxial stress measurements
on alloys of different compositions, in order to follow the movement
of the $L_{1c}$ and $X_{1c}$ valleys across the alloy range. Recent
measurements$^{(139)}$ on the variation of the $L_{1c}$ minima in GaAs$_x$Sb$_{1-x}$
alloys indicate that the $L_{1c}$ minima in GaAs are in the energy range
under consideration. The difficulty again lies in the amount of
bowing to be used in the extrapolation since the data are only
obtained for $x \leq 0.36$. The authors fit the results to a bowing
parameter of 0.96 assuming a value of $\Delta E(T_{1c} - L_{1c})$ in GaAs of ~0.48eV.
However, if the theoretical bowing parameter of 0.84$^{(140)}$ is used,
which also fits the data within experimental error, $\Delta E$ is obtained
as ~0.4eV in agreement with the measurements reported here.
The picture of the conduction band structure of GaAs obtained from the series of measurements described in Chapters 5 and 6 is therefore of the $X_{1c}$ valleys at about 0.4 eV above the $\Gamma_{1c}$ valley, with the $L_{1c}$ valleys slightly below ($\sim k_B T$) the $X_{1c}$ valleys. Thus it is likely that all three sets of minima are involved in the conduction process at high fields. This is different to the "3-level" model proposed for InP\(^{(11)}\) due to the closeness of the two sets of subsidiary minima. As pointed out by Pitt and Lees\(^{(16)}\) the total density-of-states effective mass of the subsidiary minima is normally taken as $1.2m_0$ in high field calculations, rather than the high pressure experimental value of $0.85 m_0$ and the former value could therefore be nearer the correct value.

Values have also been obtained for the deformation potentials of the conduction band minima. Since the relative change in energy of two bands is normally observed, unequivocal determination of the deformation potentials is difficult and the hydrostatic deformation potential of the valence band, $a$, must be included. For the $\Gamma_{1c}$ valley, $(\tilde{\varepsilon}_u^0 - a)$ was found to be $-7(\pm 2)eV$. For the $X_{1c}$ valleys, values of $\tilde{\varepsilon}_u^X = 21(\pm 9)eV$ and $(\tilde{\varepsilon}_d^X - a) = -5(\pm 5)eV$ were obtained while $\tilde{\varepsilon}_u^L = 22(\pm 3)eV$ and $(\tilde{\varepsilon}_d^L - a) = -10(\pm 3)eV$ were the values for the $L_{1c}$ valleys. The good agreement of the deformation potentials for the $L_{1c}$ valleys with those obtained in Ge, discussed in Section 6.6, is good evidence for the observation of these valleys and indicates that they are reasonably close to the $\Gamma_{1c}$ minimum in energy at atmospheric pressure.

10.3. INDIUM PHOSPHIDE

Interest in InP as an alternative material to GaAs for microwave oscillators increased following a proposal in 1970 by Hilsum and Rees\(^{(11)}\)
that a system involving three sets of conduction band valleys would have several advantages over one with only two sets (see Section 2.3). InP was subsequently shown to have the required band structure (see Fig. 2.7), i.e. $L_{1c}$ valleys below the $X_{1c}$ valleys, by means of high pressure Hall and resistivity measurements\(^{(29)}\). To operate as a "3-level oscillator" the coupling constant to the $L_{1c}$ valleys needed to be significantly lower than that to the $X_{1c}$ valleys, situated about 0.3eV higher in energy. However, it now seems more likely, from calculations with high $\Gamma$-$L$ coupling constants\(^{(26)(141)}\)
($E_{\Gamma L} \approx 1 \times 10^9$ eVcm$^{-1}$) and high field experiments on samples with well-characterised uniform fields\(^{(35)}\), that InP is operating as a 2-level $\Gamma$-$L$ oscillator. InP has recently been shown to have a large peak-to-valley ratio (approaching 4:1), the $\nu$-$F$ curve\(^{(142)}\) being in good agreement with the 2-level calculations\(^{(26)}\). Higher efficiencies should therefore be possible than for GaAs but initial results from devices were very sensitive to the contact properties\(^{(83)}\). It now appears that certain types of barrier cathode contacts are necessary to realise the full device potential of InP oscillators by reducing the cathode "dead-space" in which electrons are accelerated to their transfer velocity.

The threshold field/pressure measurements on GaAs (Chapter 5) and InP (Chapter 8 and reference (102)) have emphasized the importance of contacts in high field measurements. Large variations in behaviour under pressure have been observed between samples with or without barriers at the contacts. Care must be taken to ascertain that the contacts are ohmic in order to avoid wrongly interpreting contact effects as bulk properties of the semiconductor. A decrease in threshold field with pressure due to increasing barrier height at the contact has been observed in both GaAs and InP\(^{(102)}\). In the absence
of a barrier no decrease occurred. This latter behaviour in InP is consistent with the 2-level model. However, an extensive series of calculations with varying coupling constants are required to fit the data to a theoretical band-structure model. Unfortunately, calculations involving the unscreened coupling constants preferred by Fawcett and co-workers\(^{(26)(141)}\) require unmanageably large amounts of computer time for a series of parameters chosen on a trial-and-error basis.

10.4. INDIUM ARSENIDE

The band structure of InAs has been discussed in Section 9.1. The positions of the higher-lying valleys cannot be determined by high pressure Hall and resistivity measurements since a phase transition occurs at 69 kbar, before any transfer can take place. The absence of any observed transfer in the pressure range below 69 kbar can only place lower limits on the sub-band gap, viz. \(\Delta E(\Gamma_{1\text{c}}-L_{1\text{c}}) \geq 0.40 \text{eV}\) and \(\Delta E(\Gamma_{1\text{c}}-X_{1\text{c}}) \geq 0.75 \text{eV}\)\(^{(91)}\). The next highest subsidiary minima were determined to be \(0.86(\pm 0.05) \text{eV}\) above the \(\Gamma_{1\text{c}}\) minimum by high field/high pressure measurements\(^{(9)}\) and were assigned \(L_{1\text{c}}\) symmetry from consideration of the \(\text{In}_{1-x}\text{Al}_x\text{As}\) alloy system. The repeat of these measurements to higher pressure reported here produces a result of \(\Delta E(\Gamma_{1\text{c}}-L_{1\text{c}}) = 0.94(\pm 0.07) \text{eV}\) in reasonable agreement with the earlier results. Extrapolation of optical results from the \(\text{In}_{1-x}\text{Al}_x\text{As}\) system also led to the only experimental determination of the \(\Gamma_{1\text{c}}-X_{1\text{c}}\) sub-band gap, i.e. \(1.46 \text{eV}\)\(^{(113)}\). An extension of the high field results to still higher pressures and comparison with an extensive series of Monte-Carlo calculations would be needed to obtain more information about the band structure. The present limited calculations fit the observed pressure variation with a 2-level model and a \(\Gamma\)-\(L\) coupling.
constant of $3.2 \times 10^8 \text{eVcm}^{-1}$ ($\theta = 344^\circ \text{K}$). Inclusion of the $X_{1c}$ valleys at 1.25eV above the $\Gamma_{1c}$ valley at atmospheric pressure and with a high $\Gamma$-$X$ coupling constant of $1.5 \times 10^7 \text{eVcm}^{-1}$ reduces the threshold field at 33 kbar slightly nearer the experimental value, but there would seem little justification for their inclusion at this stage.

In 1966 Allen et al. reported the observation of microwave oscillations in InAs under 14 kbar of $<111>$ uniaxial stress. This however would require an abnormally large value of the shear deformation potential, $\Sigma_u$, and Smith and Camphausen suggested that the oscillations may have been due to transfer to impurity levels below the $<111>$ minima although the scattering rate would have to be very high. Pitt and Vyas have suggested that non-uniaxial components of stress may have been present. This would seem to agree with the observation of Smith and Camphausen that under uniaxial stress InAs crystals break at or below 7 kbar, whereas Allen et al. reported 14 kbar. It would obviously be desirable to repeat the uniaxial stress measurements on InAs using the apparatus developed here, but a modification will be necessary to give a low input impedance in order to make high field measurements on the very low resistance samples available.

### 10.5. III-V SEMICONDUCTOR ALLOYS

As discussed in Section 2.3, the band structure of a semiconductor can be varied, in an analogous way to the application of pressure, by alloying with another suitable semiconductor. In this way, a semiconductor can be "engineered" to produce certain desired properties, e.g. for Gunn effect material, a low threshold field, high peak-to-valley ratio and efficiency. Several mixed crystal systems based on the III-V semiconductors have received attention, two of the
most important being Ga\textsubscript{\(x\)}In\textsubscript{\(1-x\)}Sb and InAs\textsubscript{\(1-x\)}P\textsubscript{x}.

Oscillations have been observed in Ga\textsubscript{\(x\)}In\textsubscript{\(1-x\)}Sb in the composition range 0.3\(<x<0.85\)\textsuperscript{(144-146)}. The threshold field was much lower than that in GaAs, values reported lying between 400 and 900 V cm\(^{-1}\) with peak-to-valley ratios in excess of 2:1. This is a particularly interesting alloy system for comparison with pressure measurements and theoretical calculations since the sub-band gap, \(\Delta E(\Gamma-L)\), decreases markedly from about 0.6 eV in InSb to 0.08 eV in GaSb (see Fig. 2.9), while the \(\Gamma\) effective mass increases from 0.014\(m_0\) to 0.047\(m_0\).

Unfortunately, uncertainties in sample length and effects of the contacts prevented any observation of a systematic trend in \(F_T\) with composition. Monte-Carlo calculations on the velocity-field characteristic in Ga\textsubscript{\(x\)}In\textsubscript{\(1-x\)}Sb have been performed\textsuperscript{(147)} using a 2-level \(\Gamma-L\) model. The coupling constant used was 3 \times 10\(^8\) eV cm\(^{-1}\) determined for GaSb\textsuperscript{(84)} rather than the value of 1 \times 10\(^8\) eV cm\(^{-1}\) assumed by Hilsum and Rees\textsuperscript{(11)} in their three-level calculation. The threshold field was shown to increase from 600 V cm\(^{-1}\) at \(x = 0.3\) to 700 V cm\(^{-1}\) at \(x = 0.6\) and then remain approximately constant to \(x = 0.9\) when the NDM disappeared. Thus, \(F_T\) has increased by about 20\%, even though \(\Delta E\) has decreased from about 0.6 eV to 0.25 eV, due presumably to the large increase in \(m^*\) from 0.018\(m_0\) to 0.025\(m_0\). Little further increase is observed beyond \(x = 0.6\), since the small \(\Delta E\) will probably be dominating the increase in \(m^*\). This is in qualitative agreement with the \(F_T\) versus pressure (sub-band gap) results reported here for GaAs, InAs and InP. For GaAs, \(F_T\) increases until \(\Delta E \approx 0.2\) eV when the decrease in \(\Delta E\) begins to dominate, the increase in \(m^*\) in this case being smaller than for Ga\textsubscript{\(x\)}In\textsubscript{\(1-x\)}Sb. In InAs, the increase in \(m^*\) is large and decrease in \(\Delta E\) is small and an increase in \(F_T\) is observed. It would appear, therefore, that the exact value of \(\Delta E\) is
not so important in determining the threshold field as long as it is large (see Section 2.2.2).

\[ F_T \] in InSb has been shown to decrease with pressure (see Fig. 10.1) which is in disagreement with the results for the other III-V compounds. This decrease may be explained partly by a similar argument to that used in Chapter 9 for InAs since impact ionisation was observed before the Gunn effect below 9 kbar, although \( F_T \) does still appear to be decreasing slightly beyond this pressure to 13 kbar. From 0 to 13 kbar \( \Delta E \) will only have decreased by 0.13eV while the effective mass has approximately doubled to about 0.028m. This would seem to make a decrease in \( F_T \) unlikely, in the absence of carrier multiplication, by comparison with the calculations for the alloy system, in the range 0.3<x<0.6.

InAs\(_{1-x}\)P\(_x\) alloys have received attention since a suggestion by Fawcett et al\(^{(148)}\) that high drift velocities required for microwave FET’s should be obtainable due to the large sub-band gap. However, more recent determinations of the energies of the subsidiary minima show that the advantage is less significant. It can be seen from Fig. 9.11 that the effect of increasing x is equivalent to the application of pressure to InAs. M Young (private communication) has observed oscillations in alloys with x>0.3 which is in good agreement with the pressure measurements.

10.6. CONCLUSION

From the preceding sections, it can be seen that a great deal of information about the band structure of semiconductors has been obtained from high pressure and uniaxial stress experiments. However, it is often difficult to draw firm conclusions from a series of observations due to the complexity of the situation. For instance,
a detailed theory of high field transport in many-valley semiconductors is exceedingly complicated with many adjustable parameters, but comparison with such a theory may be necessary to interpret the observations. As the amount of experimental data builds up, however, the constraints on the band structure parameters become tighter and it would appear that fairly firm trends are now being established.
APPENDIX A

INFLUENCE OF IMPURITY LEVELS ON
THE DISTRIBUTION OF ELECTRONS

The number of electrons in the conduction band may be written

\[ n = N_c F_{\frac{1}{2}} \left( \frac{E_F - E_C}{k_B T} \right) \]  \hspace{1cm} (A.1)

where \( F_{\frac{1}{2}} \) is a Fermi-Dirac integral (117) given by

\[ F_{\frac{1}{2}}(n) = \frac{2}{\pi^2} \int_0^\infty \frac{\phi^2 d\phi}{1 + \exp(\phi - n)} \]

where \( \phi = \frac{E - E_C}{k_B T} \) and \( n = \frac{E_F - E_C}{k_B T} \). \( N_c \) is the density of states in the conduction band given by

\[ N_c = 2 \left( \frac{2\pi m^* k_B T}{\hbar^2} \right)^{3/2} = 4.83 \times 10^{15} \left( \frac{m^*}{m} \right)^{3/2} T^{3/2} \] \hspace{1cm} (A.2)

and \( E_C \) and \( E_F \) are the energies of the conduction band edge and the Fermi level, respectively. When \( n \ll N_c \), equation (A.1) is approximated by

\[ n = N_c \exp \left( \frac{E_F - E_C}{k_B T} \right) \] \hspace{1cm} (A.3)

for the special case of Boltzmann statistics.

If a donor impurity of density, \( N_D \), gives rise to levels below \( E_C \), the electrons will be distributed between the conduction band and the level. The number of electrons occupying the impurity level, \( n_d \), is given by Fermi-Dirac statistics as

\[ n_d = \frac{N_D}{1 + \frac{1}{g} \exp \left( \frac{E_D - E_F}{k_B T} \right)} \] \hspace{1cm} (A.4)

where \( g \) is the degeneracy of the level and \( E_D \) is its energy, i.e.
$E_D = E_c - \varepsilon_A$, where $\varepsilon_A$ is the activation energy.

The electrons in the conduction band and those on impurity sites must have come from $N_D$ and thus

$$n + n_d = N_D$$

Therefore,

$$n = N_D - n_d = \frac{N_D}{1 + \exp\left(\frac{E_F - E_D}{k_B T}\right)}$$

Most semiconductors also contain a number of acceptor impurities, $N_A$, which become negative by receiving an electron. If $N_D >> N_A$, the acceptors will be "compensated" by electrons from $N_D$ and therefore,

$$n + N_A = N_D - n_d = \frac{N_D}{1 + \exp\left(\frac{E_F - E_D}{k_B T}\right)}$$

This may be written

$$g(n+N_A) \exp\left(\frac{E_F - E_D}{k_B T}\right) = N_D - N_A - n$$

and hence,

$$\frac{n + N_A}{N_D - N_A - n} = \frac{1}{g} \exp\left(\frac{E_c - \varepsilon_A - E_F}{k_B T}\right)$$

If $n << N_c$, then

$$\exp\left(\frac{E_F - E_c}{k_B T}\right) = \frac{n}{N_c}$$

and therefore

$$\frac{n(n+N_A)}{N_D - N_A - n} = \frac{N_c}{g} \exp\left(\frac{-\varepsilon_A}{k_B T}\right)$$

(A.5)
APPENDIX B

DEFORMATION POTENTIAL THEORY

The shift of the conduction band edge for a general deformation of the lattice given by equation (3.10) may be written as

\[ \delta E_c = \sum_{i=1}^{6} \delta \varepsilon_i (\varepsilon_{1} + \varepsilon_{2} + \varepsilon_{3} + \varepsilon_{4} + \varepsilon_{5} + \varepsilon_{6}) \]  

(B.1)

where the strain components \( \varepsilon_i \) are expressed in terms of the elements of the general strain tensor as

\[ \varepsilon_1 = \varepsilon_{xx}, \quad \varepsilon_2 = \varepsilon_{yy}, \quad \varepsilon_3 = \varepsilon_{zz}, \]

\[ \varepsilon_4 = \varepsilon_{xy} + \varepsilon_{yx}, \quad \varepsilon_5 = \varepsilon_{xz} + \varepsilon_{zx}, \quad \varepsilon_6 = \varepsilon_{yz} + \varepsilon_{zy} \]

and the deformation potential constants are \( E_1 = \frac{\partial E}{\partial \varepsilon_{xx}}, \quad E_2 = \frac{\partial E}{\partial \varepsilon_{yy}}, \ldots, \quad E_4 = \frac{\partial E}{\partial \varepsilon_{xy}}, \ldots \), referred to the crystal axes.

(a) For a <111> valley, \( \varepsilon_1 = \varepsilon_2 = \varepsilon_3 \) and \( \varepsilon_4 = \varepsilon_5 = \varepsilon_6 \) from symmetry and therefore

\[ \delta E_c = \varepsilon_1 (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) + \varepsilon_4 (\varepsilon_4 + \varepsilon_5 + \varepsilon_6) \]  

(B.2)

Transforming from the crystal axes to a rectangular co-ordinate system with the z-axis along the <111> direction (e.g. [112] [110] [111]) using the equation

\[ \varepsilon_{ij} = a_{ki} a_{lj} \varepsilon_{kl} \]  

(B.3)

and the transformation cosines

\[ a_{ki} a_{lj} = \begin{pmatrix} \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix} \]

we obtain in terms of strain components and deformation potentials with respect to the co-ordinate system of the valley, \( \varepsilon_{kl} \) and \( \varepsilon^1 \),

\[ \delta E_c = \varepsilon_1 (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) + \varepsilon_4 (\varepsilon_1 + \varepsilon_2 - 2\varepsilon_3) \]

(B.4)
By definition (44), for cubic crystals with valleys along the symmetry axes,

\[ E_d = \frac{1}{4} \left( \frac{\partial E}{\partial e_{xx}} + \frac{\partial E}{\partial e_{yy}} \right) = \frac{1}{4} (E_1 + E_2) \]

and \[ E_u = \frac{1}{4} \left( -\frac{\partial E}{\partial e_{xx}} - \frac{\partial E}{\partial e_{yy}} + 2 \frac{\partial E}{\partial e_{zz}} \right) = \frac{1}{4} (-E_1 + E_2 + 2E_3) \]  

From equation (B.4),
\[ E_1 = E_2 = E_4 \quad \text{and} \quad E_3 = E_1 + 2E_4 \]

Hence from equations (B.5)
\[ E_d = E_4 \quad \text{and} \quad E_u = 3E_4 \]

Therefore equation (B.2) may be written
\[ \delta E_c = (E_4 + \frac{1}{3} E_u) (E_1 + E_2 + E_3) + \frac{1}{3} E_u (E_4 + E_5 + E_6) \]  

(B.6)

For a cubic crystal the strain components may be written in terms of the stress components, \( \sigma \), and elastic compliances as
\[ \begin{align*}
E_1 &= s_{11} \sigma_1 + s_{12} \sigma_2 + s_{13} \sigma_3 \\
E_2 &= s_{21} \sigma_1 + s_{22} \sigma_2 + s_{23} \sigma_3 \\
E_3 &= s_{31} \sigma_1 + s_{32} \sigma_2 + s_{33} \sigma_3 \\
E_4 &= s_{44} \sigma_4 \\
E_5 &= s_{45} \sigma_5 \\
E_6 &= s_{46} \sigma_6 
\end{align*} \]  

(B.7)

For a <111> compressive stress, \(-X\),
\[ \sigma_1 = \sigma_2 = \sigma_3 = \sigma_4 = \sigma_5 = \sigma_6 = -\frac{X}{3} \]

Therefore, \( \epsilon_1 = \epsilon_2 = \epsilon_3 = -\frac{X}{3} (s_{11} + 2s_{12}) \)
\[ \epsilon_4 = \epsilon_5 = \epsilon_6 = -\frac{X}{3} s_{44} \]

Hence equation (B.6) becomes
\[ \delta E_c = - (E_4 + \frac{1}{3} E_u) (s_{11} + 2s_{12}) \frac{X}{3} s_{44} \]  

(B.8)

Here, \( E_d + \frac{1}{3} E_u \) is the deformation potential for pure dilatation,
i.e. \( \frac{1}{3}(\varepsilon_1^1 + \varepsilon_2^1 + \varepsilon_3^1) \) and \( E_u \) is the deformation potential for pure shear. The equations for the other <111> valleys may be found similarly.

(b) For a <100> valley, \( E_1 = E_3 \) and \( E_4 = E_5 = E_6 = 0 \) from symmetry and therefore

\[
\delta E_c = \varepsilon_1 E_1 + \varepsilon_2 (\varepsilon_2^1 + \varepsilon_3^1) \quad \text{(B.9)}
\]

Transforming to a rectangular co-ordinate system of the <100> valley (e.g. \([001][100][010]\)) equation (B.3) gives, with the transformation cosines

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
\begin{align*}
\delta E_c &= \varepsilon_1 E_1 + \varepsilon_2 (\varepsilon_2^1 + \varepsilon_3^1) \\
&= \frac{1}{3} \varepsilon_1^1 + \varepsilon_2 (\varepsilon_2^1 + \varepsilon_3^1) \\
&\text{(B.10)}
\end{align*}
\]

Therefore, \( \varepsilon_1^1 = \varepsilon_1 \) and \( \varepsilon_2^1 = \varepsilon_3^1 = \varepsilon_2 \)

and from equations (B.5)

\[
E_d = \frac{1}{3} (E_1 + E_2) \quad \text{and} \quad E_u = \frac{1}{3} (E_2 - E_1)
\]

Equation (B.9) may then be written

\[
\begin{align*}
\delta E_c &= (E_d - E_u) \varepsilon_1 + (E_d + E_u) (\varepsilon_2^1 + \varepsilon_3^1) \\
&= (E_d + E_u) (\varepsilon_2^1 + \varepsilon_3^1) + \frac{2}{3} E_u (\varepsilon_2^1 + \varepsilon_3^1) \varepsilon_1 \\
&\text{(B.11)}
\end{align*}
\]

For a <100> stress, \( \sigma_3 = -X, \sigma_1 = \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0 \).

Therefore, \( \varepsilon_1 = -s_1^2 X \) and \( \varepsilon_3 = -s_1^1 X \) and equation (B.11) becomes

\[
\delta E_c = -\frac{1}{3} (E_d + E_u) (s_1^2 + 2s_1^1) X - \frac{2}{3} E_u (s_1^1 - s_1^2) X \\
\text{(B.12)}
\]

It should be noted that for a <111> stress the second term of equation (B.11) is zero and similarly for a <100> stress the second term of equation (B.6) is zero.
APPENDIX C

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

\[ \sigma_0 = n_x^0 \mu_x^0 + 2n_t^0 \mu_t^0 \]  \hspace{1cm} (C.1)

where \( n_x^0 \), \( \mu_x^0 \) and \( n_t^0 \), \( \mu_t^0 \) 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

\[ \frac{\rho_s}{\rho_0} = \frac{\sigma_0}{\sigma_1} = \frac{n_x^0 \mu_x^0 + 2n_t^0 \mu_t^0}{n_x^1 \mu_x^1 + 2n_t^1 \mu_t^1} \]  \hspace{1cm} (C.2)

At 77K, since f-scattering is negligible, \( \mu_x^0 = \mu_x^1 \) and \( \mu_t^0 = \mu_t^1 \), assuming no significant distortion of the ellipsoids. Hence,

\[ \frac{\rho_s}{\rho_0} = \frac{n_x^0 + 2n_t^0}{n_x^1 + 2n_t^1} \]  \hspace{1cm} (C.3)

where \( K = \frac{\mu_x^0}{\mu_t^0} = \frac{\mu_x^1}{\mu_t^1} \) is the mobility anisotropy factor.

Since \( n_t^0 = n_x^0 \), equation (C.3) may be written

\[ \frac{\rho_s}{\rho_0} = \frac{n_x^0 (2K+1)}{n_x^1 + 2n_t^1} \]  \hspace{1cm} (C.4)

Now, the total number of electrons is given by

\[ N = n_x^1 + 2n_t^1 = 3n_x^0 \]  \hspace{1cm} (C.5)

Therefore,

\[ \frac{3n_x^0}{n_x^1} = 1 + \frac{2n_t^1}{n_x^1} \]  \hspace{1cm} (C.6)

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

$$\frac{n_t^s}{n_x^s} = \exp \frac{-\Delta E}{k_B T}$$

(C.7)

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

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

(C.8)

and equation (C.4) becomes

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

(C.9)

From equation (3.11),

$$\Delta E = \varepsilon_u (q_{11} - q_{12}) X$$

(C.10)

Therefore, if $K$ is known, a variation of $\rho_s$ with stress, $X$, may be fitted to equation (C.9) and a value of $\varepsilon_u$ 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, $n_x^s = N$ and $n_t^s = 0$.

Therefore from equation (C.2)

$$\frac{\rho_{sat}}{\rho_o} = \frac{(\mu_x^o + 2\mu_t^o) N}{N m_x^s} = \frac{1 + 2K}{3}$$

(C.11)

Thus, the value of $K$ can be found from the saturation value of resistivity and inserted into equation (C.9).

The anisotropy factor, $K$, will vary from sample to sample since it is given by

$$K = \frac{\mu_L}{\mu_L} = \frac{\mu_t}{\mu_L} \frac{n_t^s}{n_x^s}$$

(C.12)
where $\tau_e$, $\tau_\perp$ and $m_e$, $m_\perp$ are the relaxation times and effective mass components respectively. $\tau_e/\tau_\perp$ will depend on the relative strengths of the various scattering mechanisms.
ACKNOWLEDGMENTS

The work reported in this thesis was carried out in the Department of Physics at the University of Surrey and in the High Pressure Laboratory at Standard Telecommunication Laboratories Limited (STL), Harlow, Essex. Support was provided by the Science Research Council in the form of a CAPS studentship with STL.

Thanks are particularly due to Dr A R Adams*, under whose supervision the work was performed, for his continual interest and advice. Special thanks are also due to Dr G D Pitt+ for his help and encouragement and to Dr J Froom†, Dr J Lees† and Dr K W H Foulds*.

The computer calculations were performed in collaboration with Mr P J Vinson* and Dr W Fawcett (RRE, Malvern), whose valuable discussions are gratefully acknowledged.

The following should also be acknowledged for technical assistance and sample preparation:— Messrs. M K R Vyas†, J Mun†, B E Barry†, J Rainer†, B J Gunney*, F Bristowe* and Mrs V Stannard*.

Thanks also to Mrs J Docwra (SERL) for her careful typing and, especially, to my wife for her help.

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